Volume I



STRUCTURAL INVESTIGATION OF SOME MOLECULAR COMPLEXES, AND THEIR RELATED COMPOUNDS.

A thesis submitted for the degree of

Doctor of Philosophy.

by

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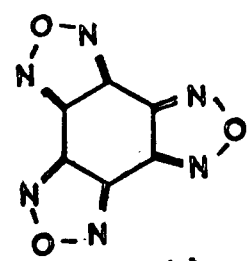
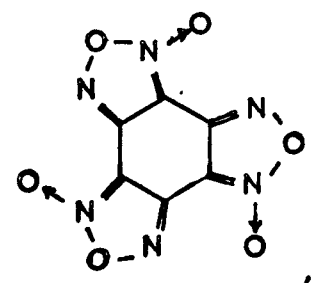
INTRODUCTION

During an investigation into molecular complexes, the π-acceptor benzotrifurazan(I) was prepared by the reduction of benzotrifuroxan(II).



(I)



(II)

Among the reagents that will reduce furoxans to furazans are various compounds of trivalent phosphorus. It was found that trialkyl phosphites reduce benzotrifuroxan(II) in good yield, the product being a 1:1 molecular complex of benzotrifurazan(I) with the corresponding trialkyl phosphate ester.

There was some spectroscopic evidence to suggest that the molecules of this complex were associated through an interaction which involved the phosphoryl (P=O) bond of the ester. In the absence of hydrogen bonding there was no precedent for such an interaction, and it was decided to examine the complex by X-ray crystallography.

The X-ray structure analysis proved difficult, and in an attempt to prepare a different derivative, benzotrifuroxan was reduced by triphenyl phosphine.

The reaction was strikingly different, and produced no benzotrifurazan. The product was a mixture of triphenyl phosphine oxide and a large number of coloured compounds. Five of these: a red, a light green, a yellow, a blue and a darker green compound (Plate 1) were obtained in small quantities as crystalline solids. Chemical analysis and spectroscopic measurements revealed little of their identity.

The differences in the two reductions were curious, and the colours of the five derivatives beautiful. As only small quantities of the coloured compounds were available it was decided to attempt to analyse them by X-ray crystallography, to try to explain the differences in the two reactions and to see if the structures of these coloured compounds cast any light upon the nature of the complex.

In this thesis, the X-ray crystal analysis is described* for the red, light green, yellow and blue compounds and for the phosphate ester complex. The chemical mechanisms of the reduction of benzotrifuroxan by trialkyl phosphites and triphenyl phosphine is discussed. The structures of benzotrifurazan and the coloured compounds are compared and an attempt is made to discover the cause for the various colours of the phosphine derivatives.

*The structure of the dark green compound was determined by Miss J. M. Evans.

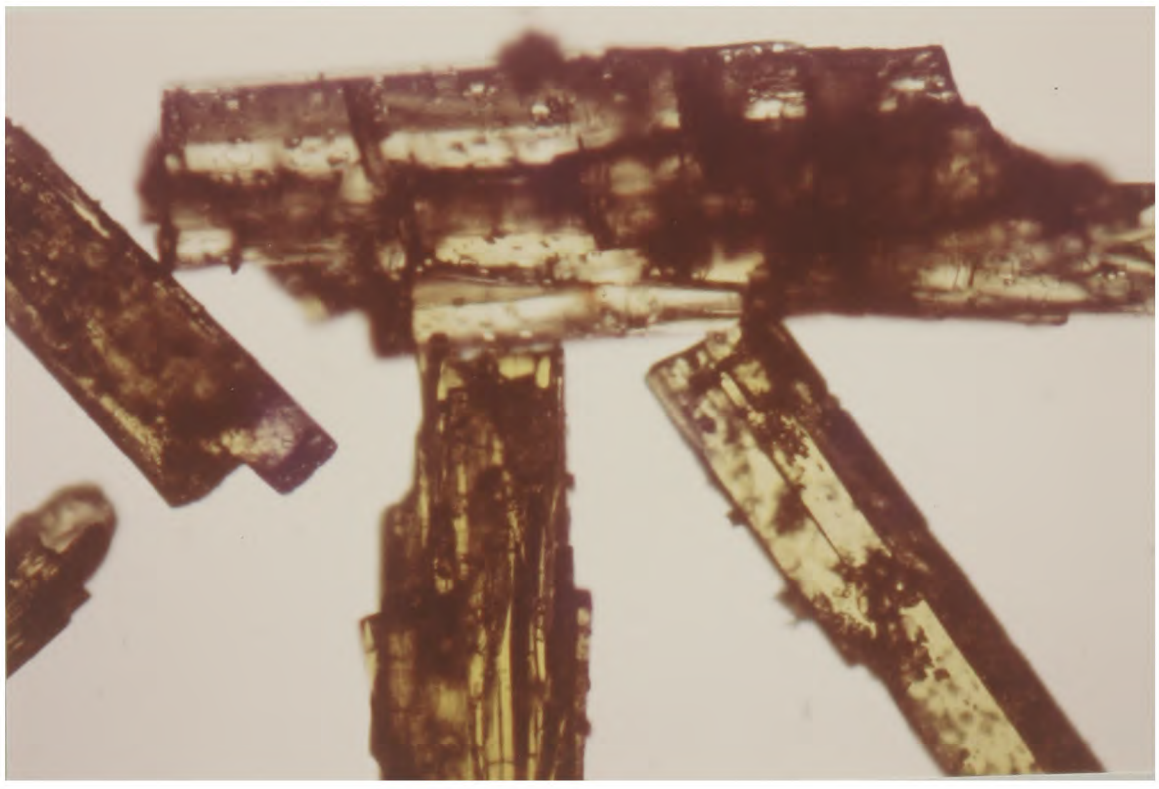
CHAPTER 1

The Coloured Compounds

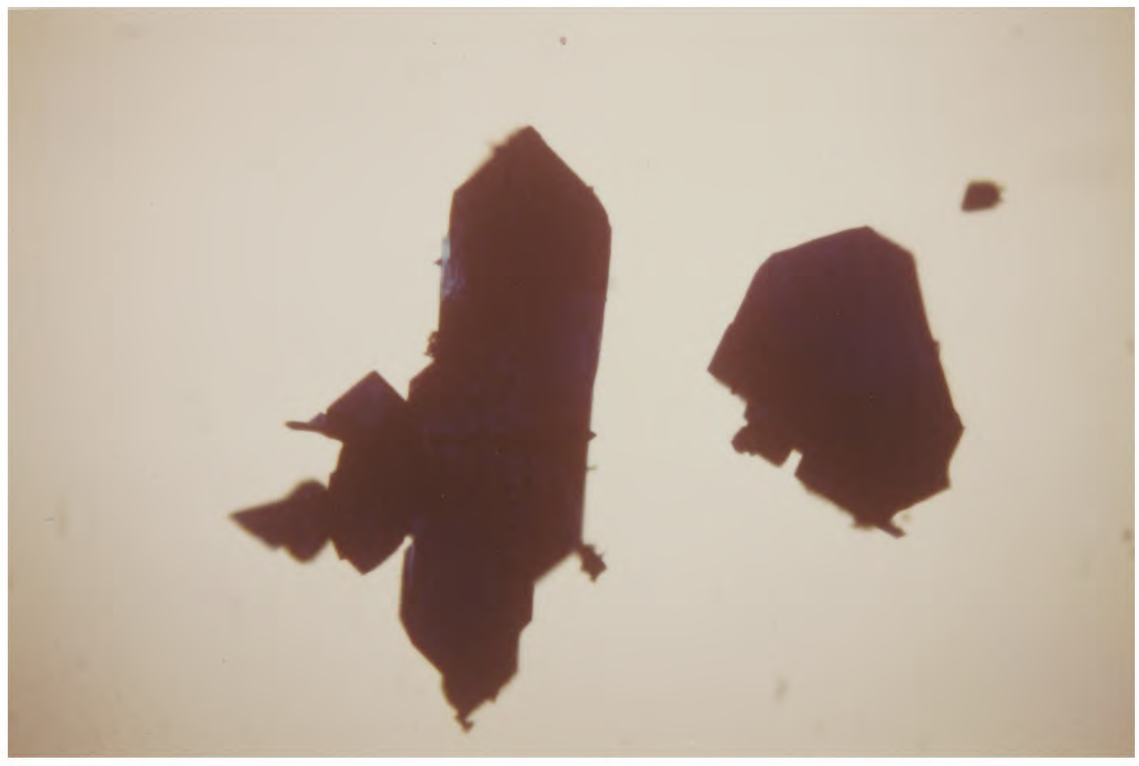
PLATE 1



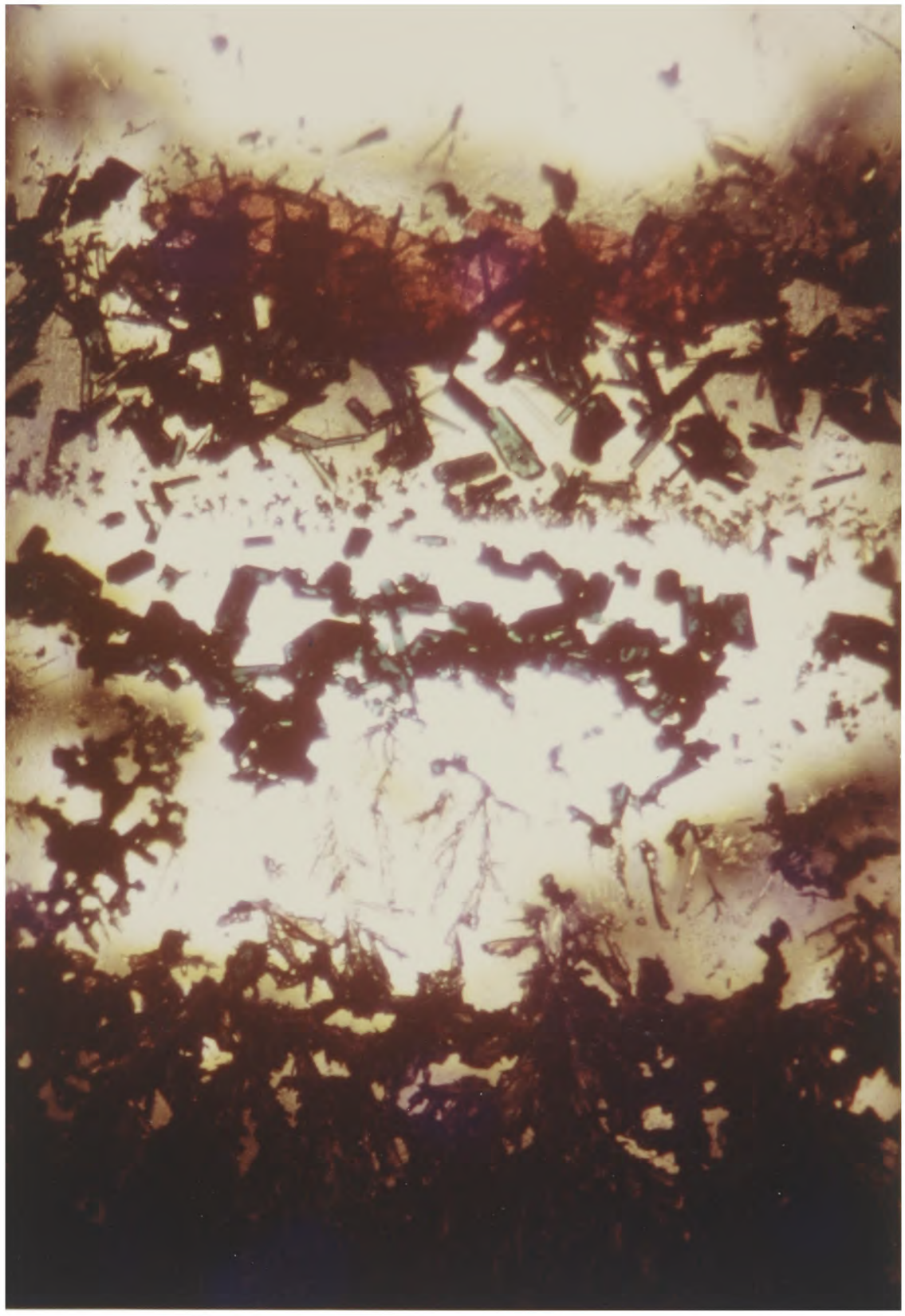
a. The red compound (x200)



b. The yellow compound ×200



c. The blue compound ×200



d. Impure sample of the light green compound. x150

INTRODUCTION

The nature of the problem

The coloured compounds were isolated[1] from the reduction of benzotrifuroxan by triphenyl phosphine in benzene or toluene solutions. The reaction was run many times with 1, 2, or sometimes 5g. quantities of benzotrifuroxan, but the products were contaminated with triphenyl phosphine oxide and were difficult to purify. The coloured derivatives, therefore, were seldom obtained in quantities greater than 60 mg. though the yields were probably higher.

When the compounds were chemically analysed, they left residues after combustion and the analysis figures are unreliable (p.156). Spectroscopic analysis was equally unsatisfacory[1]. The NMR spectra indicated little else but the presence of phenyl protons, the IR absorption spectra were complex and since the absorption maxima in the IR spectrum of the parent compound, benzotrifuroxan, have not yet been assigned, the interpretation of the spectra of the coloured compounds was impracticable. The compounds decomposed in the inlet to the mass spectrograph and, after one compound had explosively disintegrated in the spectrograph chamber, mass spectroscopy was discontinued.

It was presumed that all the compounds contained phosphorus atoms and as all were obtained as well-formed, high melting point, crystals (plate 1) it was thought that X-ray crystal analysis was the most

promising technique for determining their molecular structure and formulae.

X-ray data collection

With the exception of the red compound, the crystals in the various samples were smaller than the optimum size for X-ray structure analysis[2]. Though they produced good diffraction pattern without much thermal diffuse scatter or marked falling off of intensity with increasing Bragg angle, these patterns were faint and for each equi-inclination Weissenberg layer exposure times of the order of a week were necessary for multiple film intensity data photographs. For layers where the equi-inclination angle (μ) was greater than 10° the exposure time was reduced by photographing the crystal with unfiltered radiation. Unwanted diffraction spectra were eliminated by a careful setting of the layer line screen on the camera.

A lead glass tube was used as a collimator for the X-ray beam (a selection of such tubing with bores ranging from the microscopic to $\approx$2 mm. is available in this laboratory). For each crystal that was studied, a collimating system was constructed so that the sample was totally irradiated by a beam that emerged from the colimator no more than 3 mm. from the crystal, and such that the X-ray beam so diverged that the resulting diffraction spectra on the contracted side of the Weissenberg photographs did not significantly alter in shape throughout a range of (μ) of 0° - 40°.

The intensity data was measured (by a visual comparison with a strip of standard intensities) on the contracted side of the films only and no spot shape correction was applied when the data was reduced.

Refinement

The programme that is available for the method of least squares allows for refinement of parameters both by a full matrix and by a block diagonal approximation to the full matrix. The block diagonal approximation places no restriction on the order of the blocks so that all parameters for which siginificant interactions are expected can be included in the same block. By this means the advantages of the reliable convergence of a full matrix method are combined with the increased computational speed of the block diagonal approximation.

The programme contained the restriction that only a total of 180 refinement parameters were allowed in any one calculation; this restriction has now been altered[3] to 400 parameters.

For initial refinement of trial structures the observations were given unit weight, but once it was clear that a trial structure was essentially correct a weight (w) was applied to each observation where:

$$w = \frac{1}{(1+[(|F_o| - P_2)/P_3]^2)^{\frac{1}{2}}} \qquad \ldots.(1)$$

F_o is the absolute value of the observation, and P_2, P_3 are empirical parameters. P_2 was chosen so that $w \approx 1$ over a range of F_o that coincided with the most densely populated range over all observations. P_3 was chosen so that (w) decreased in approximately the same manner as the number of observations of F_o in the various ranges decreased, (figure 1). For a structure where the crystal analysis was already completed, a series of refinements were calculated with a weight (w) for P_2 constant and P_3 varying between $^1/_3P_2$ to $2P_2$. For this range of P_3, the function,

$$\sum_N w(||F_o| - |F_c||)/N \qquad \text{(N observations)}$$

was invariant for any reasonable sample of the observations.

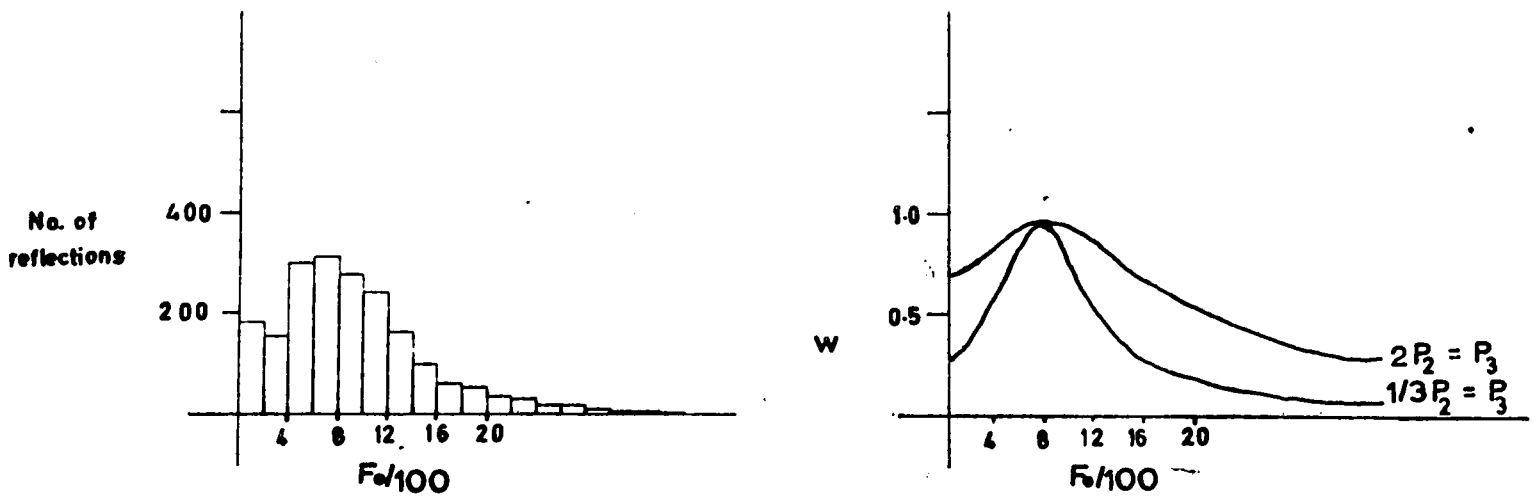


Figure 1

Data correction

The data was measured systematically along the loom lines of the Weissenberg photographs, and observations were included that could not be accurately estimated. These reflections included those that appeared only once at the edges of the films, those in the region of the direct beam back stop and many that were too weak to be observed. The unobserved reflections were assigned a median value between the lowest measurable intensity and zero, and their calculated values were used as a check of the trial structure in the early stages of the analysis and of the indexing of the data at a later stage.

In several of the analyses intensity data collected by rotation about one axis* only was used and at an advanced stage in the least squares refinement, it was necessary to inspect the data.

All observations where F_o and F_c were seen to be in bad agreement were investigated for error and the reflections that could not be accurately measured were removed. In cases where the visual estimation was suspect, it was checked by measuring first a similar observation (a reflection of equivalent intensity and measured on the same occasion as the suspect but where F_o and F_c were in reasonable agreement) to

*The individual Weissenberg layer scale factors were roughly determined from limited second axis data, and the scale factors were refined during the least squares process.

determine the probable deviation in a correct estimate and then by re-measuring the suspect. If the check discovered an error greater than the estimated deviation, then the suspected observation was corrected by this error.

Estimated standard deviations

The e.s.d.'s of the bond lengths and angles were calculated according to the formulae of Cruickshank[4] and Darlow[5]:

$$\sigma^2(l) = (\sigma^2(x_1) + \sigma^2(x_2))\mathrm{Cos}^2(\alpha) + \text{Similar terms in } (y),\ (z).$$

Where $\sigma^2(l)$ is the e.s.d. of the length between atoms 1 , 2 which have co-ordinates (x_1, y_1, z_1) , (x_2, y_2, z_2).

$$\sigma^2(\theta) = (1/l_1 l_3)\,\mathrm{Sin}^2(\theta)\ (A_3^2\sigma^2(x_1) + (A_1 + A_3)^2\sigma^2(x_2) + A_1^2\sigma^2(x_3) + \ldots \text{Similar terms in } (y)\ ,\ (z).$$

Where $\sigma^2(\theta)$ is the e.s.d. of the angle at atom (2) in the atom (1) - (2) - (3) triplet.

$$A_1 = l_1(\cos(\alpha_1) - \mathrm{Cos}(\theta)\ \mathrm{Cos}(\alpha_3))\ ;\quad A_3 = l\ (\mathrm{Cos}(\alpha_3) - \mathrm{Cos}\ (\theta)\mathrm{Cos}(\alpha_1)).$$

Where (l_1) is the length atom (1) - (2) and (l_3) the length for atom (2) - (3) . Cos (α_1) is the direction cosine for (l_1) to axis $(\underline{x})$.

The Programme that was written to perform the calculation treated the ellipsoid of deviation for any atom as a sphere with a radius the average of the deviations in the positional parameters. For the

coloured compounds this appears to be a good approximation (p.195 ff.)

Structural diagrams

The skeletal diagrams were drawn for projections down the principal axes of the crystal lattices. A programme was written which orthogonalised the co-ordinates of the atoms with respect to an axis of projection, (Z'), and then plotted the co-ordinates (x', y') on an x, y graph plotter linked on-line to the computer. The programme and a typical plot is given in Appendix II.

Table 1 (P - P vectors , relative to an origin height of 500, in the Patterson functions of the coloured compounds)

	Vector	x/a	y/b	z/c	Peak Height
Red compound	$2(\underline{X})$	0.57032	0.02322	0.36088	80
Light green compound	$2(\underline{X})$	0.31940	0.76110	0.23354	43
	$\frac{1}{2}+2x,\frac{1}{2}+2y,\frac{1}{2}$	0.81940	0.26110	0.5	90
	$\frac{1}{2},\frac{1}{2},\frac{1}{2}-2z$	0.5	0.5	0.26454	93
Yellow compound	$2(\underline{X}_1-\underline{X}_2)$	0.13461	0.48789	0.19832	80
	$2(\underline{X}_2-\underline{X}_3)$	-0.03513	-0.48588	0.07640	82
	$2(\underline{X}_1-\underline{X}_3)$	0.09948	0.00201	0.27472	80
	$2(\underline{X}_1+\underline{X}_2)$	0.90613	0.10145	0.60690	80
	$2(\underline{X}_2+\underline{X}_3)$	0.80665	0.09904	0.33218	84
	$2(\underline{X}_1+\underline{X}_3)$	0.94126	0.58733	0.53050	85
	$(\underline{X}_1)$	0.04074	0.58934	0.80522	37
	$(\underline{X}_2)$	0.77152	-0.38644	0.40858	38
	$(\underline{X}_3)$	0.84178	0.58532	0.25578	40
Blue compound	$(\underline{X}_1-\underline{X}_2)$	-0.30905	0.34332	-0.56060	60
	$0,\frac{1}{2},-2z_1$	0.0	0.5	-0.05210	111
	$0,\frac{1}{2},-2z_2$	0.0	0.5	0.06890	115
	$x_1-x_2,\frac{1}{2}+y_1-y_2,z_1+z_2$	-0.30905	0.84332	0.50840	80

RED COMPOUND

Crystal data*: Triclinic; $\underline{a}$ = 9.615 ± 0.001, $\underline{b}$ = 10.828 ± 0.006, $\underline{c}$ = 11.226 ± 0.007Å; $\underline{\alpha}$ = 81.82° ± 0.02, $\underline{\beta}$ = 97.72° ± 0.02, $\underline{\gamma}$ = 99.67° ± 0.01; M.pt. = 168°C; Space group $P\bar{1}$; Cu-K_α radiation, μ = 15.44 cm.$^{-1}$; D_m = 1.477 g.cm.$^{-3}$ (by flotation) which gave an estimated molecular weight of 503 and two molecules to the unit cell. From the structure analysis, the formula is $C_{24}H_{17}N_6O_5P$; M = 502; Z = 2.007. 3670 independent reflections were used in the initial calculations. 217 reflections were removed when the data measurement was checked.

There was only one crystal among the samples of the red compound that was suitable in size and shape for X-ray photography. This crystal was an irregular lump (6 x 3 x 3 mm.) with no obvious crystal faces; it possessed, however, distinct cleavage planes and it was cut into a 'cube' of side .5 mm.

Survey X-ray photography, zero layer single film Weissenberg photographs for three axes and two-axis, three-dimensional intensity data photographs were all collected with the same crystal.

The data was reduced for Lorentz and polarisation factors, but no spot shape or absorption corrections were applied.

*A paper was published[6] with incorrect cell dimensions; these have been corrected.

The correlation between equivalent reflections in the two-axis data was poor* and remeasurement of reflections badly in agreement caused little improvement. (This phenomenon has been observed[7] frequently in this laboratory with X-ray diffraction data from crystals that contain organic planar molecules.) The data from the two axes were not combined and only that collected with rotation about axis a (the first to be photographed) were used for the structure analysis.

An overall temperature factor (B) of 5.5 was calculated from a Wilson's plot.

Three three-dimensional Patterson functions were calculated, with data; unsharpened, sharpened to 'point atoms at rest' for (B = 3) and (B = 5.5). The third function (B = 5.5) was seriously over-sharpened and uninterpretable, the first was diffuse, but in the second function (B = 3) there was only one peak significantly larger than the others (Table 1) and this, it was assumed, represent a P-P vector in spacegroup $P\bar{1}$ with one phosphorus atom to the asymmetric unit. It was found in this and in subsequent analyses that an empirical value of ≈ 3 for (B) gave the most interpretable Patterson function.

The positions of the phosphorus atom, three phenyl groups attached to it and one atom, which with three phenyl carbon atoms made a tetrahedron around the phosphorus atom were established from the second Patterson function (B = 3) by inspection and vector superposition.

* Even after the cell dimensions had been corrected.

An F_o synthesis,phased on these established atomic positions, confirmed the positions and revealed the presence of a second molecule with a peculiar shape (figure 2a). Another F_o synthesis phased on all the atomic positions that had been determined (light atoms were treated as carbon atoms) confirmed their positions and indicated four more atoms, (figure 2b).

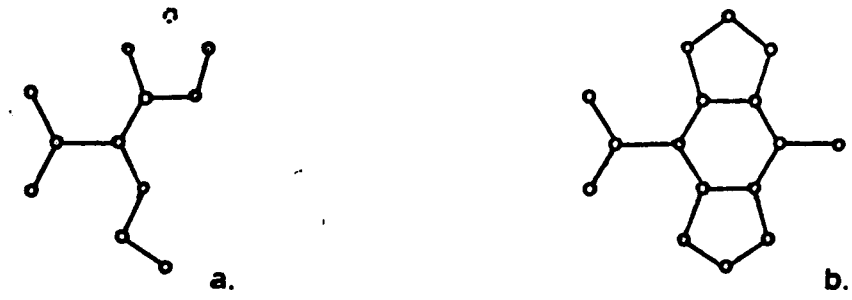


Figure 2

A difference Fourier synthesis phased on all atoms showed that there were no more to be located, while from the residual electron density at atomic sites and with chemical knowledge, the structural formula given in figure 3 was suggested.

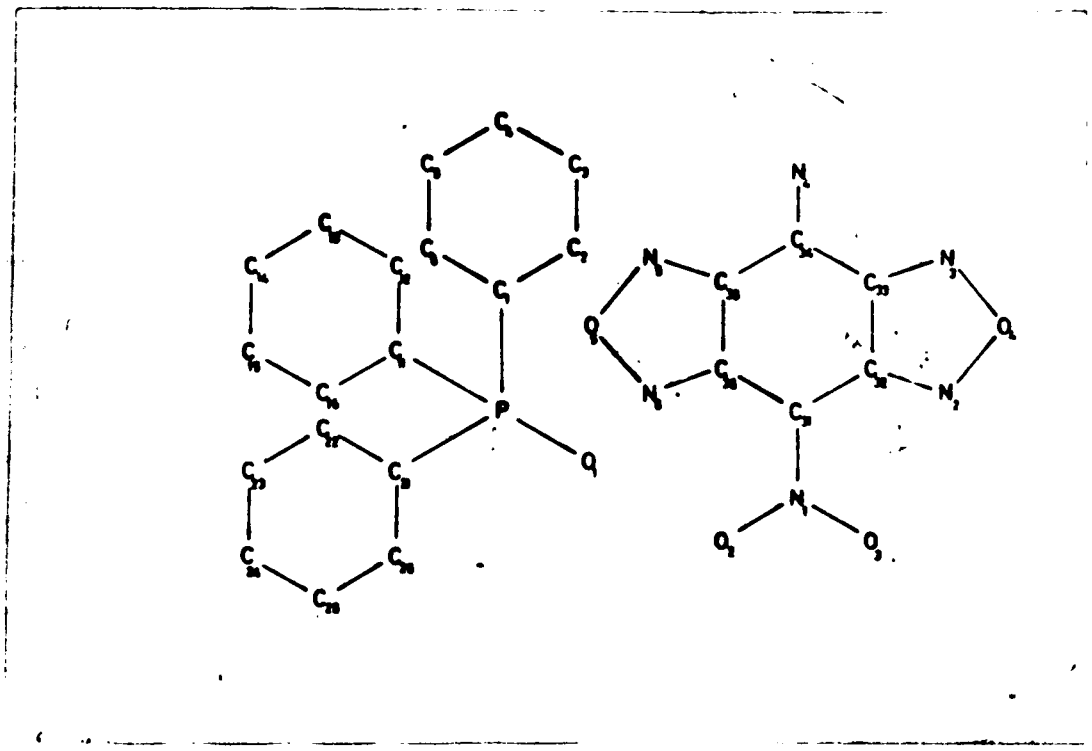


Figure 3

The trial structure with individual isotropic temperature factors was refined by a method of least squares that used a block diagonal approximation to the full matrix (p. s). Three blocks were used, one for the overall scale factor and temperature factors, and one each for the positional parameters of the benzotrifuroxan and triphenyl phosphine fragments.

Three rounds of refinement were calculated with unit weights, and two rounds with weight (w), for each observation, where (w) is given in Equation (1) and $P_2 = P_3$.

After five rounds the reliability factor R was 15.9%. A difference fourier synthesis was calculated and contained no remarkable features. The data measurement was checked and after three more rounds with the weighting parameters unchanged, the R factor was 12.4%.

The structure is shown in figures I, II, the projection onto the least squares best plane of the benzotrifuroxan fragment in figure III and the bond lengths and angles in figures IV, V. (For full tables of co-ordinates, bond lengths and angles and e.s.d.'s, see page 196).

The packing of the molecules form essentially a 'layer structure' the phosphorus atoms lie almost in the plane of the ac face of the crystal and layers of molecules of the triphenyl phosphine residue stack up the b axis alternately with layers of the benzotrifuroxan fragment, (fig. II). Within a layer of the benzotrifuroxan

fragments, the molecules pack together in pairs with a planar separation of 3.2 Å (fig. 4) and phenyl groups , attached to phosphorus atoms, protrude into gaps in the layers between the pairs.

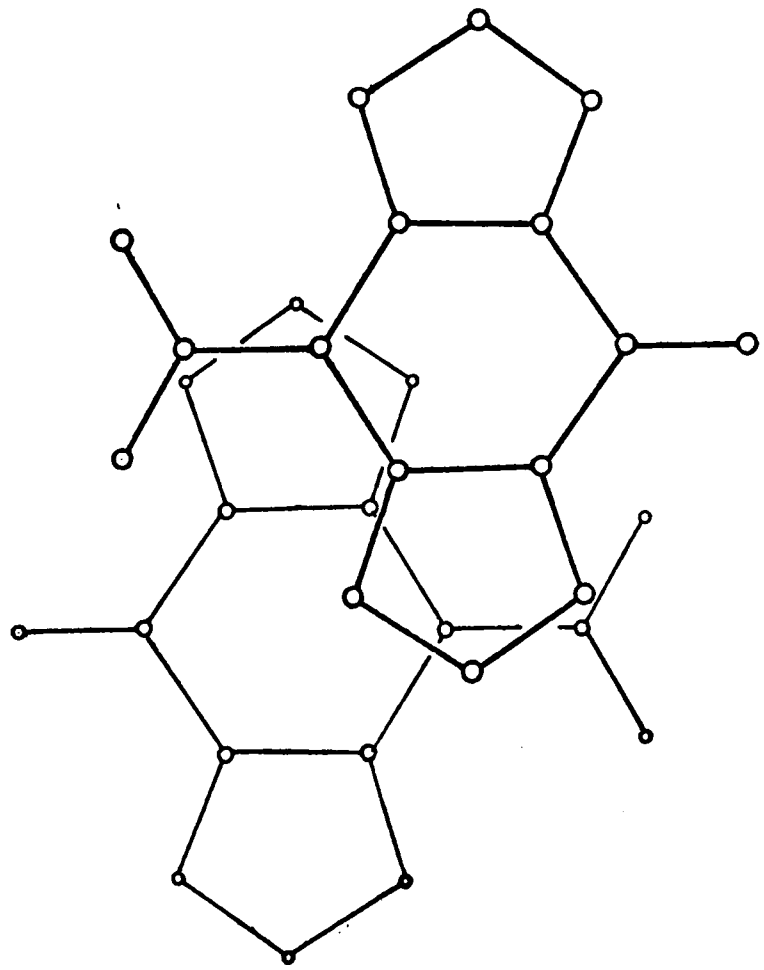


Figure 4

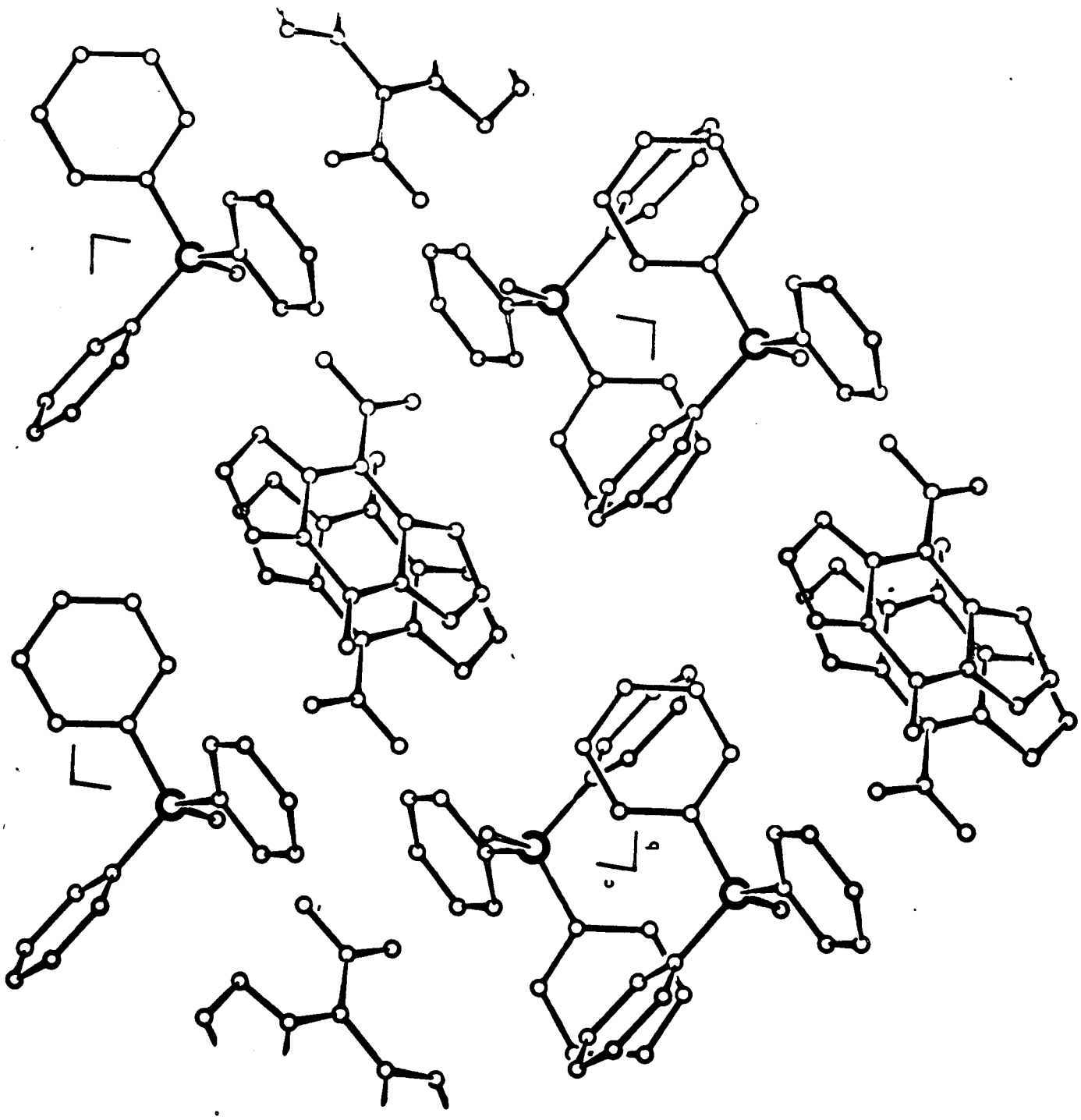


Figure I Red Compound Projection (1 0 0)

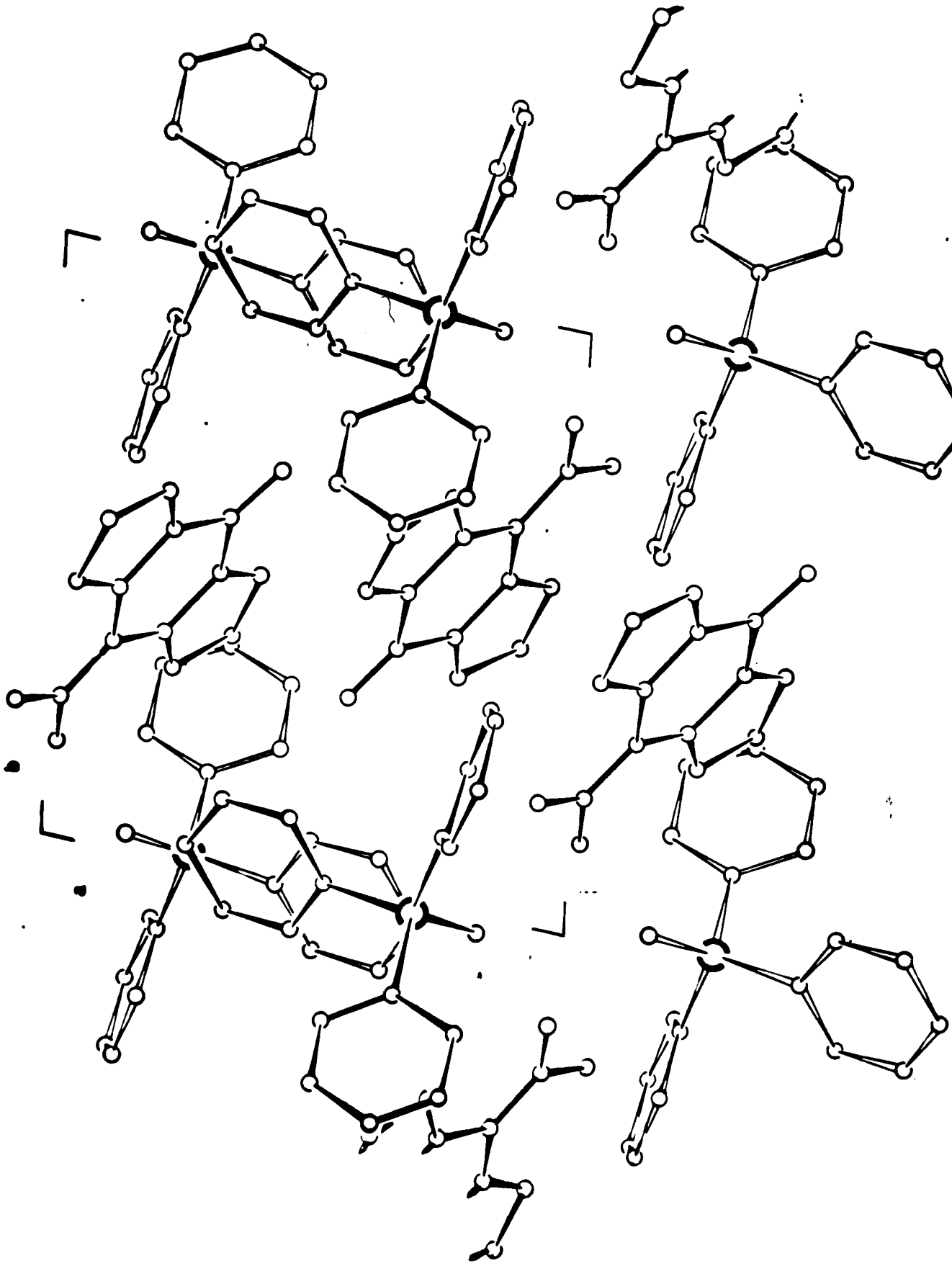


Figure II Red Compound Projection (0 0 1)

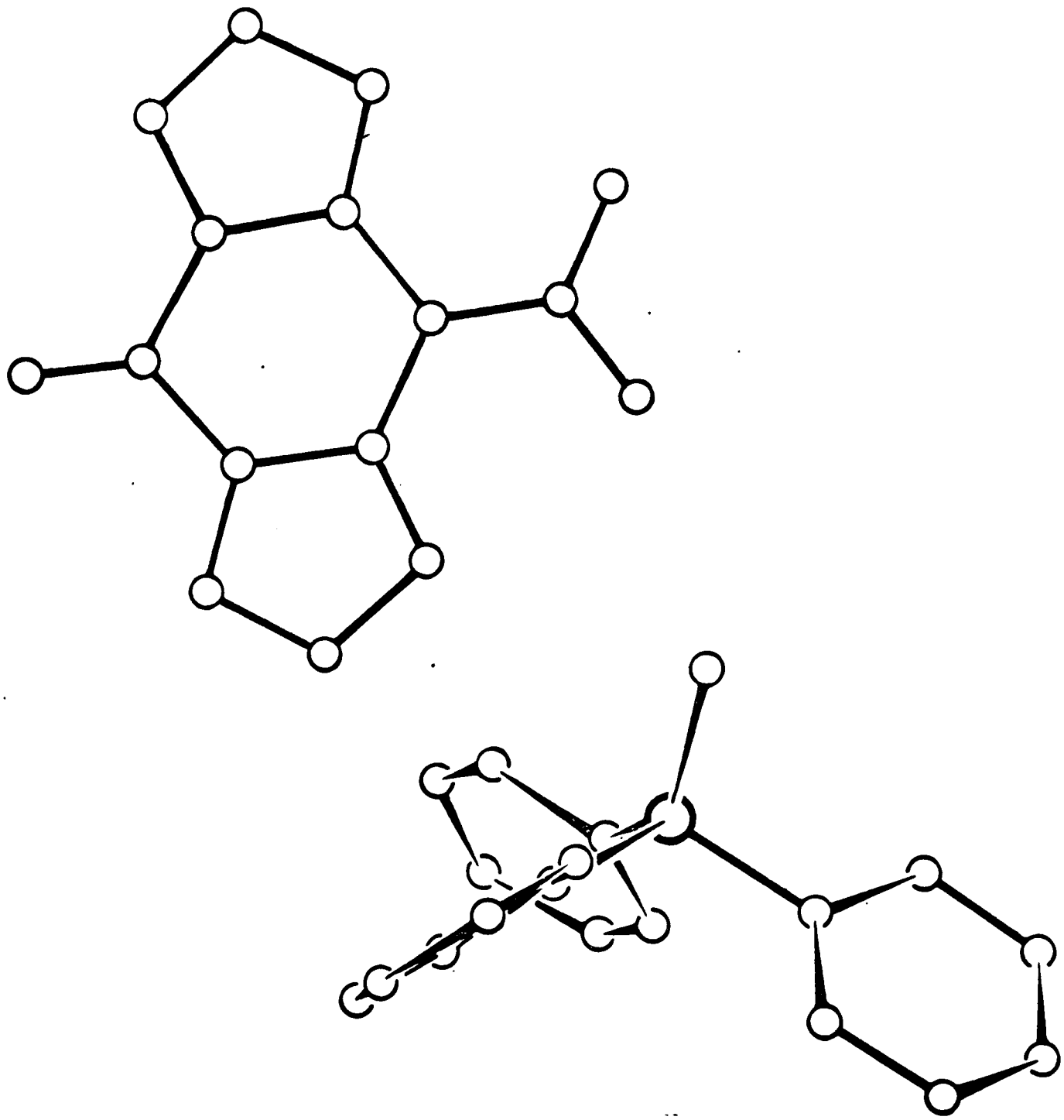


Figure III Red Compound

Projection onto the least squares best plane of the difurazan molecule

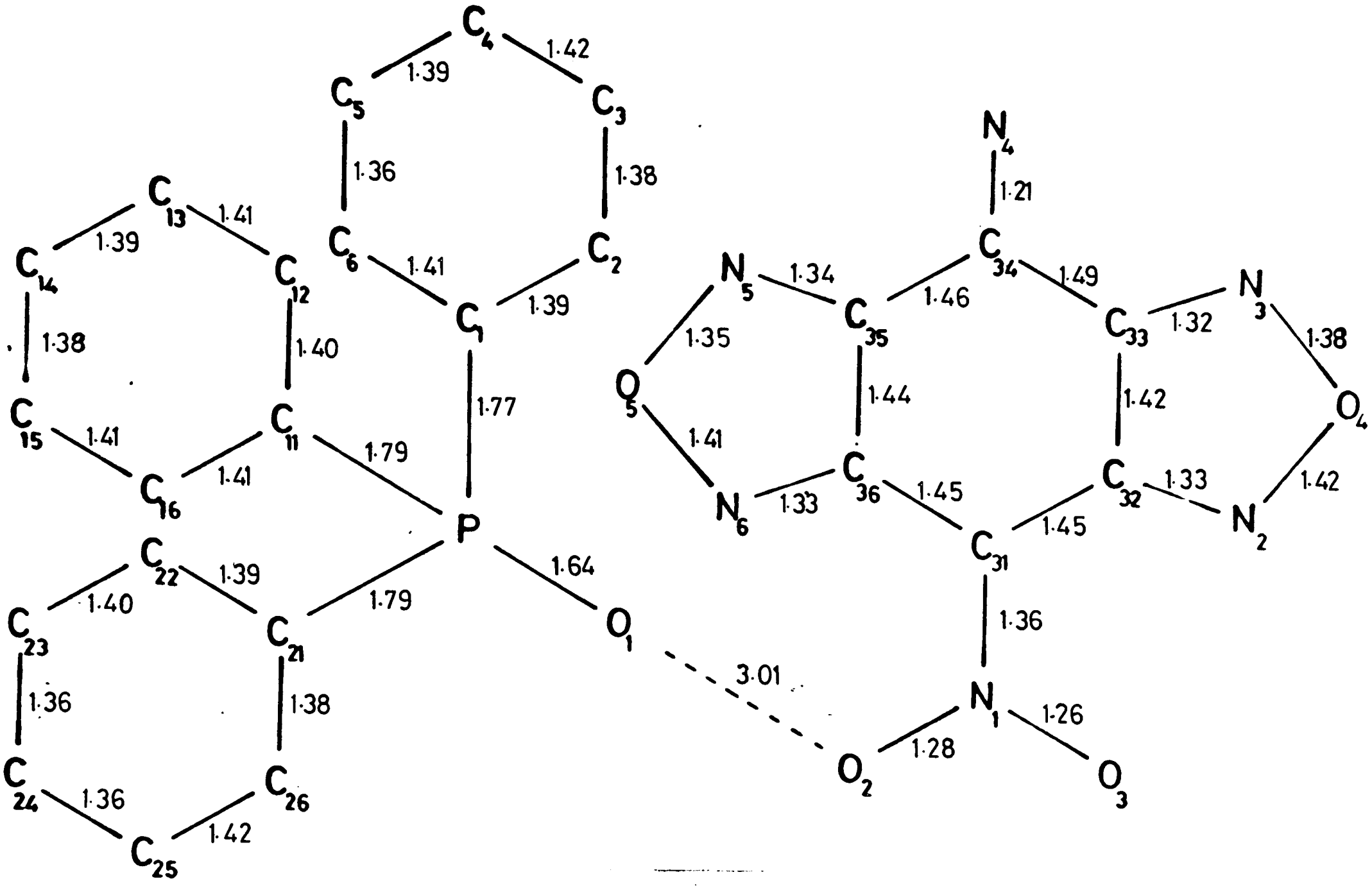


Figure IV Red Compound Interatomic distances. (Å)

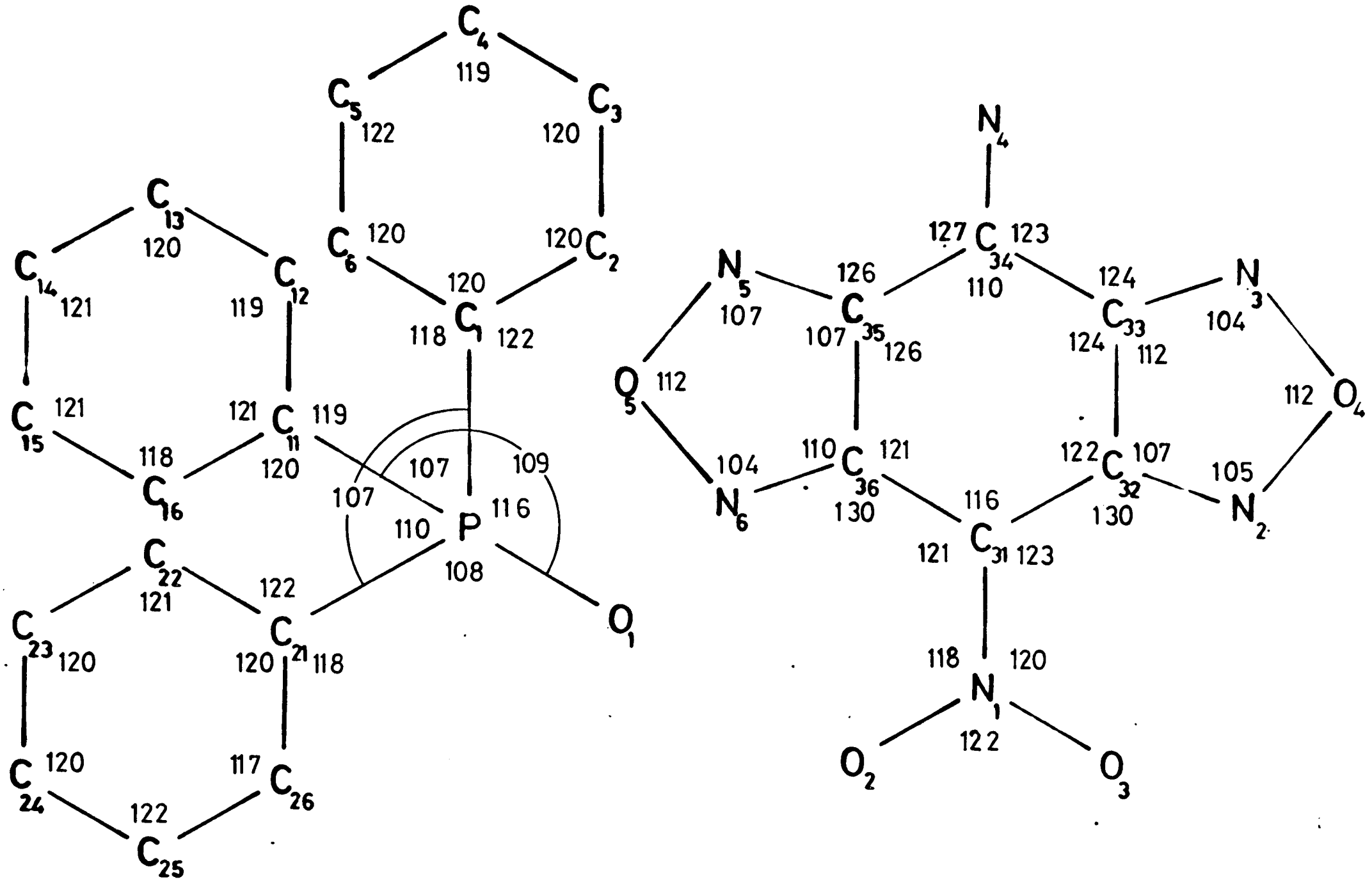


Figure V Red Compound Bond angles.

LIGHT GREEN COMPOUND

Crystal data: Monoclinic needles; a = 8.57 ± 0.01, b = 12.12 ± 0.01, c = 21.07 ± 0.01Å; γ = 95.08° ± 0.02; Space group $P2_1/n$; Cu-K_α radiation, μ = 14.66 $cm.^{-1}$; M.pt. = 268°C; D_m = 1.423 $g.\ cm.^{-3}$ (by flotation) which gave an estimated molecular weight of 467.0 and four molecules to the unit cell. From the structure analysis the formula is $C_{24}H_{15}N_6O_3P$; M = 466.4; Z = 4.005. 3086 independent reflections were used in the initial calculations; 299 reflections were removed when the data measurement was checked.

A mass spectroscopic molecular weight (466, 467) was available[1] for the compound. The formula that fits this weight most closely is $C_{24}H_{15}N_6O_3P$ and the molecular formula (figure 5) was proposed.

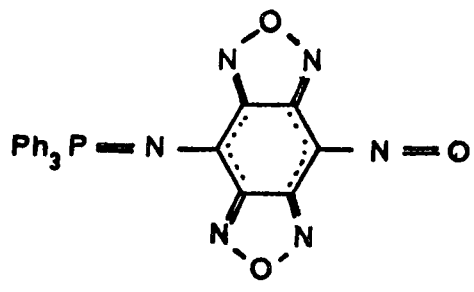


Figure 5

The sample of the light green compound contained no well-formed crystals that were suitable for X-ray photography. Since compounds containing nitrosos groups tend to be unstable and as this sample had been prepared a year previously a fresh batch of crystals was prepared. Two suitable crystals were grown after seven recrystallisations from 1:10 $MeOH/CHCl_3$.

Complete three-dimensional intensity data were collected with rotation about the needle axis (a) of the crystal. The Weissenberg photographs were indexed for space group $P2_1/n$ rather than the space group with the orthodox axial glide, as $P2_1/n$ contained the monoclinic angle (γ) nearest to 90°.

The data were reduced for Lorentz and polarisation factors, but no spot shape or absorption corrections were applied.

A three-dimensional Patterson function sharpened to 'point atoms at rest'; (B = 3) was calculated. For one phosphorus atom to the asymmetric unit (at x, y, z) in space group $P2_1/n$ the P-P vectors expected in the Patterson functions will be found at:

2x,	2y,	2z	Multiplicity 1
1/2+2x,	1/2+2y,	1/2	Multiplicity 2
1/2,	1/2,	1/2-2z	Multiplicity 2

A set of peaks was discovered in the Patterson function which in position and multiplicity was consistent with these vectors (table 1).

A three-dimensional F_o synthesis was calculated phased on the position of the phosphorus atom. This contained $\approx$ 100 significant peaks from which 33 were selected to represent atoms by consideration of peak shape and position and by comparison of the F_o synthesis with the Patterson function.

A difference Fourier was calculated phased on the positions of the 34 atoms (light atoms treated as carbon atoms) which confirmed the positions and by the residual electron density at atomic sites

indicated the hetero-atoms. The molecular formula (figure 6) was proposed.

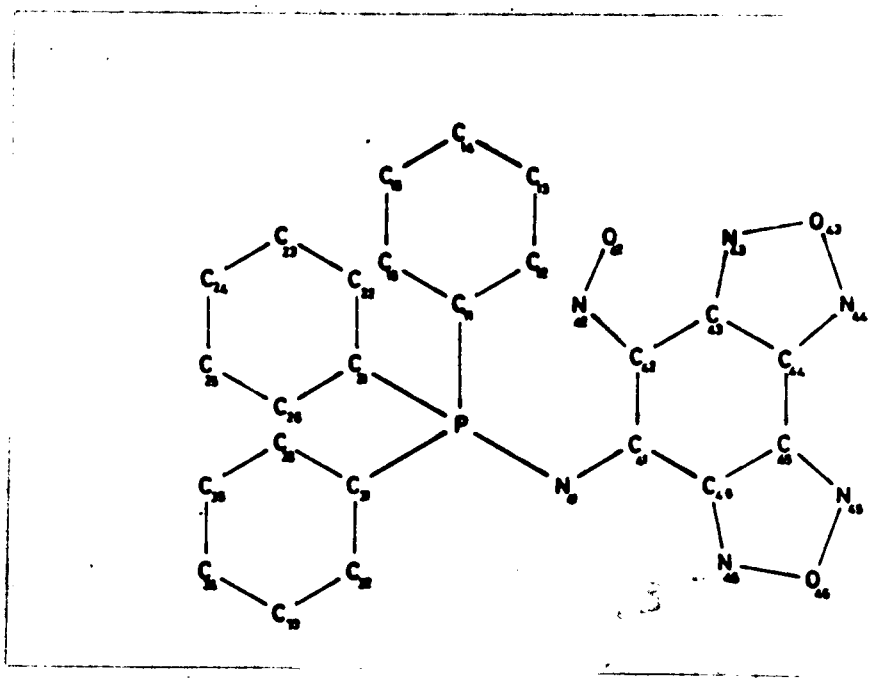


Figure 6

The trial structure with individual isotropic temperature factors was refined by least squares with a block diagonal approximation to the full matrix. The refinement parameters were divided into three blocks, one for the overall scalefactor and temperature factors and one each for the positional parameters of the triphenyl phosphine and benzotrifuroxan fragments.

Four rounds of refinement were calculated with unit weights and three rounds with a weight (w) for each intensity observation where: (w) is given by Equation (1) and $P_2 = P_3$.

After seven rounds of refinement, the reliability index (R) was

16%. A difference Fourier synthesis showed no remarkable features. The data measurement was checked and after two more rounds of refinement with the weighting parameters unchanged the R factor was 11.6%.

The structure is shown in figures VI, VII, the projection onto the least squares best plane of the benzotrifuroxan residue in figure VIII, and the bond lengths and angles in figures IX, X. (For full details of co-ordinates, bond lengths and angles, and e.s.d.'s, see p.202).

In one molecule of the compound, the atoms of the heterocyclic rings, one phenyl group and the phosphorus atom all lie in a plane (figure VIII) and the molecules pack together in the crystal to form a 'layer structure' based on this plane (figure VI).

The two phenyl groups that do not lie in the plane project on either side of it, fit into gaps in adjacent layers and form in themselves layers transverse to the planes of the hetero-atoms (figure VI).

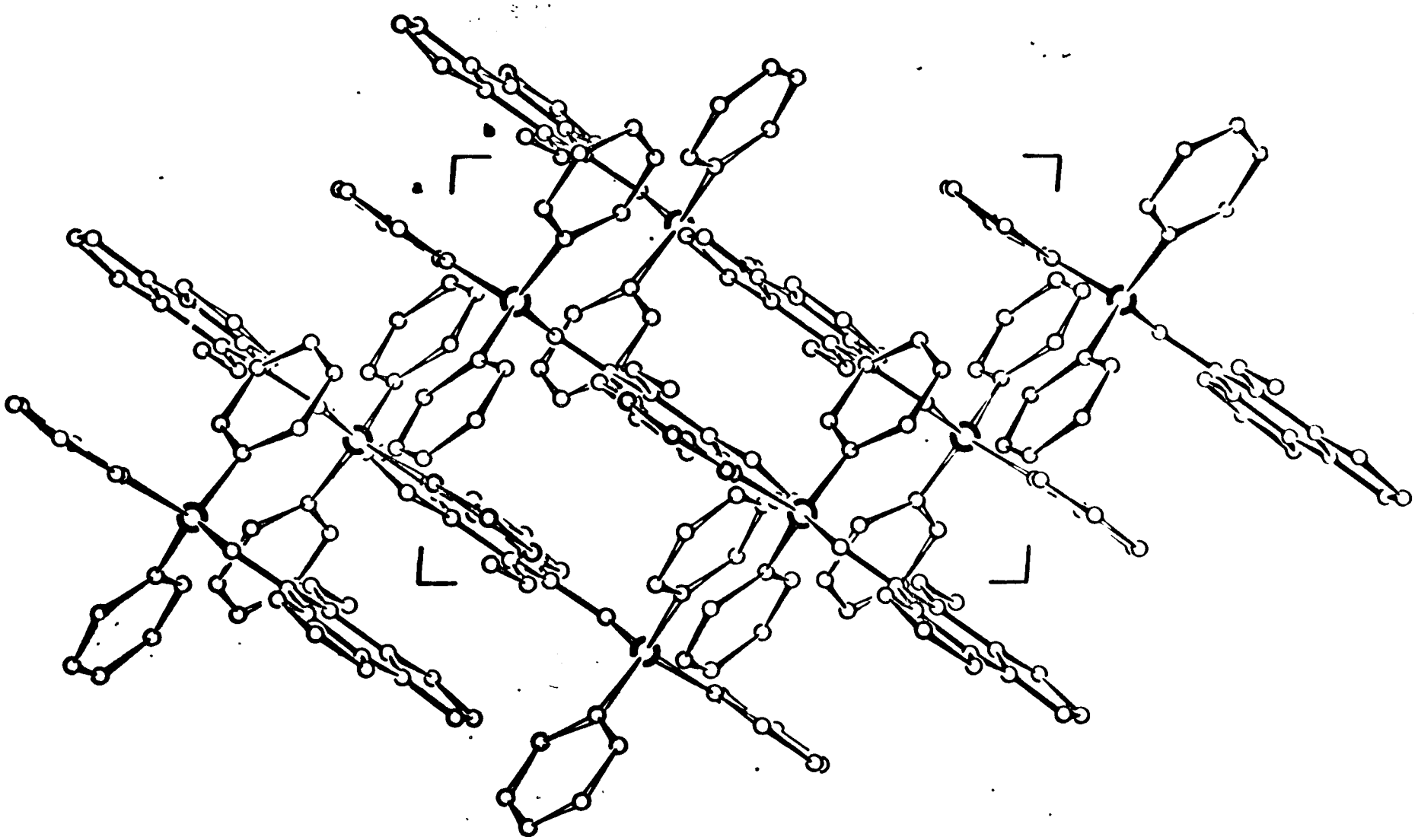


Figure VI Light Green Compound Projection (0 0 1)

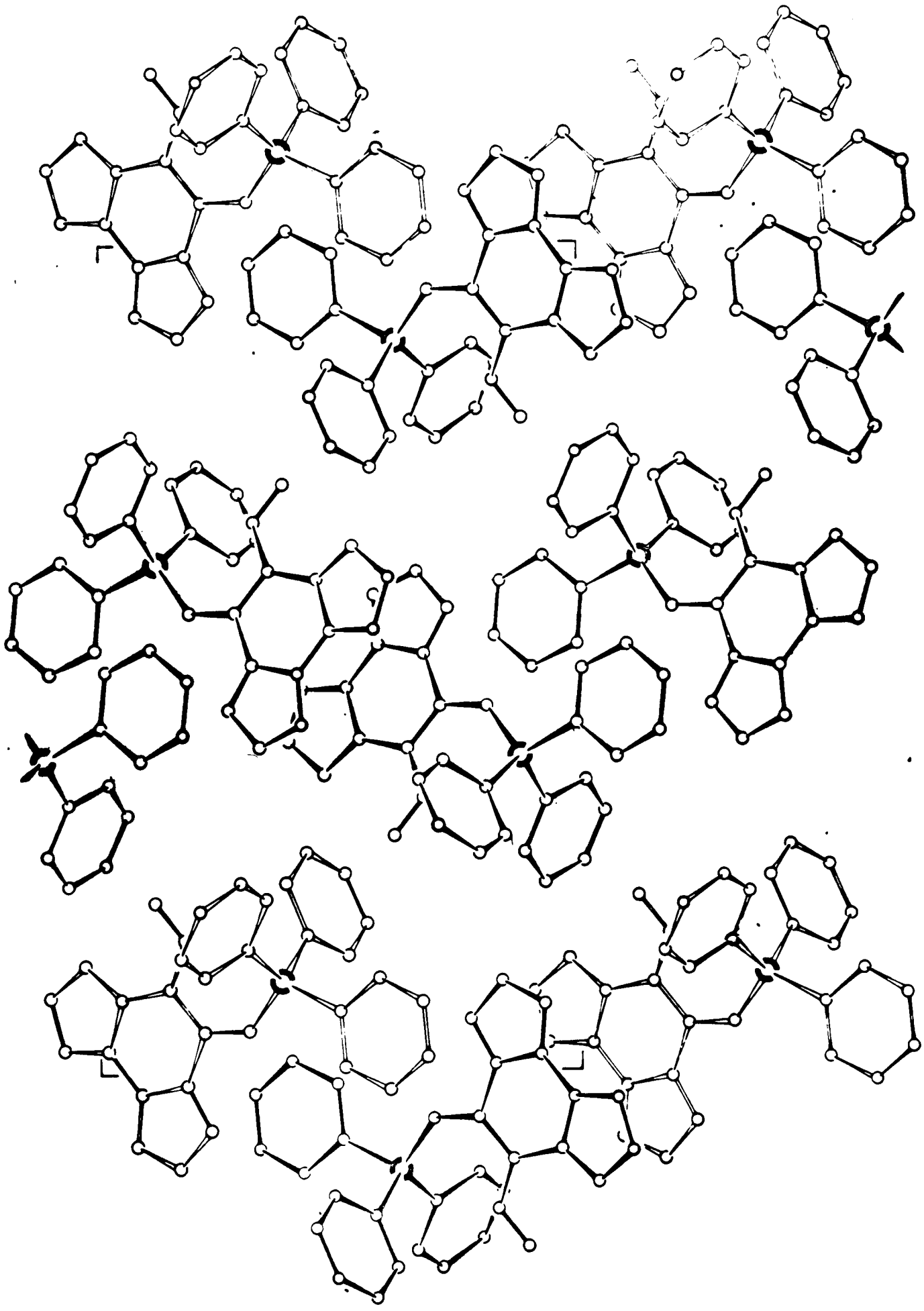


Figure VII Light Green Compound Projection (1 0 0)

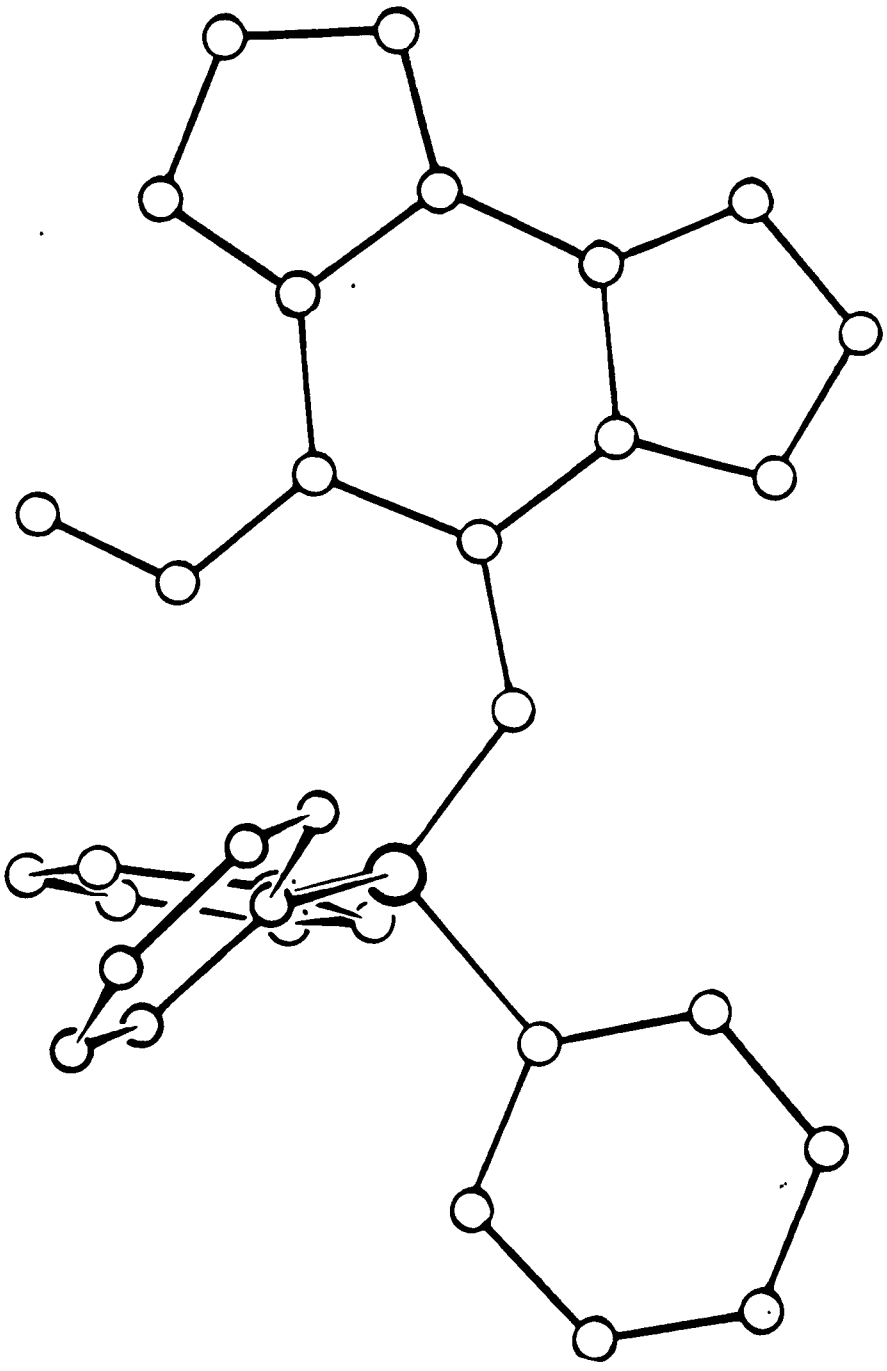


Figure VIII Light Green Compound

Projection onto the least squares best plane of the benzotrifuroxan residue

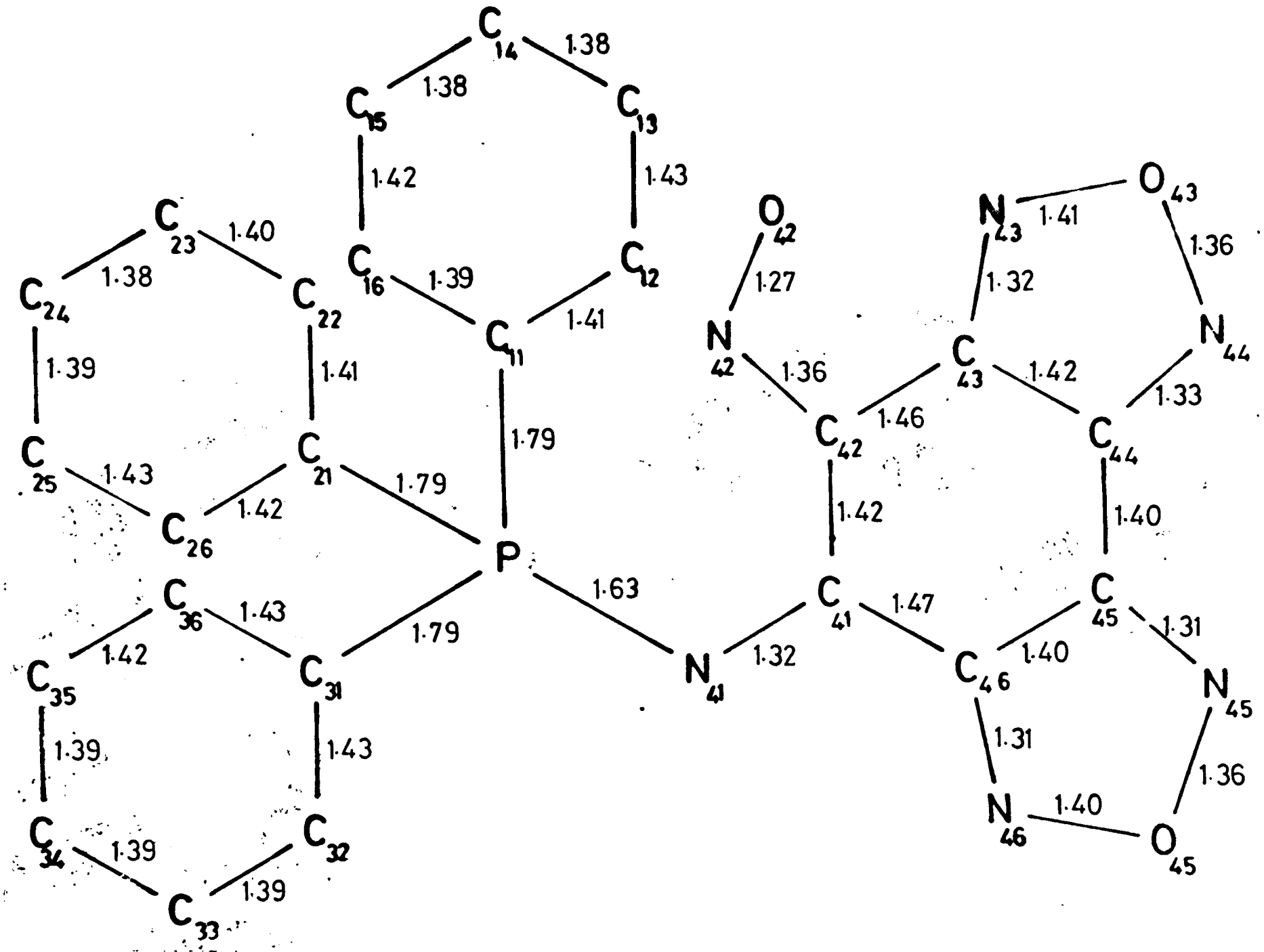


Figure IX Light Green Compound Interatomic distances (Å)

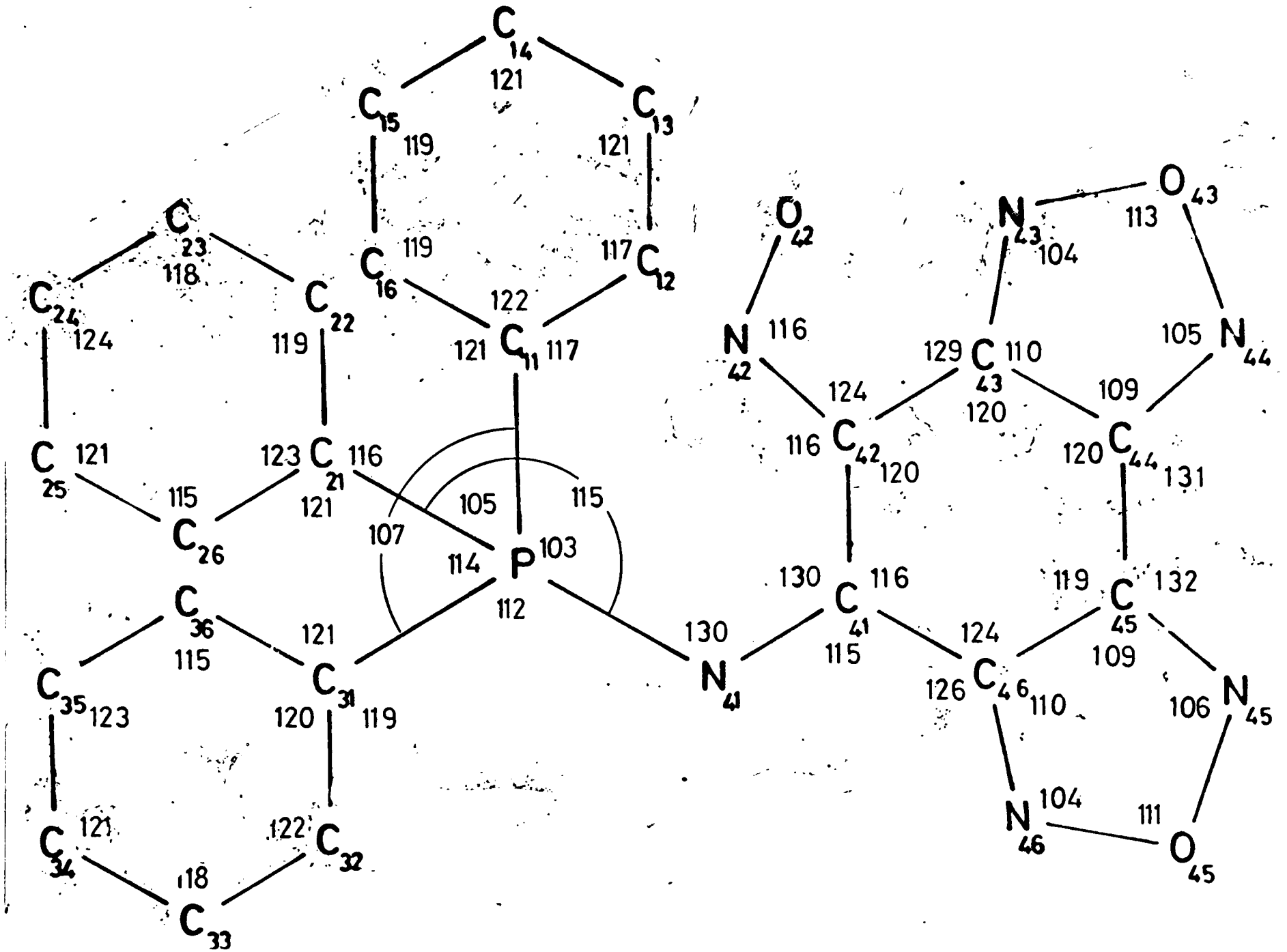


Figure X Light Green Compound Bond angles

YELLOW COMPOUND

Crystal data: Triclinic needles; $\underline{a}$ = 8.864 ± 0.001, $\underline{b}$ = 13.502 ± 0.008, $\underline{c}$ = 25.534 ± 0.005Å; $\underline{\alpha}$ = 97.92°, $\underline{\beta}$ = 99.13°, $\underline{\gamma}$ = 111.47° ± 0.01; Cu-K_α radiation; μ = 11.28 cm.$^{-1}$; M.pt. < 330°C; D_m = 1.2975 g.cm.$^{-3}$ (by flotation); D_c for $2(C_{60}H_{45}N_6O_6P_3)$, $-CH_3C_6H_5$, 1.30049 g.cm.$^{-3}$; Space group $P\bar{1}$; 6218 independent reflections were used in the initial calculations. 610 reflections were removed when the data measurement was checked.

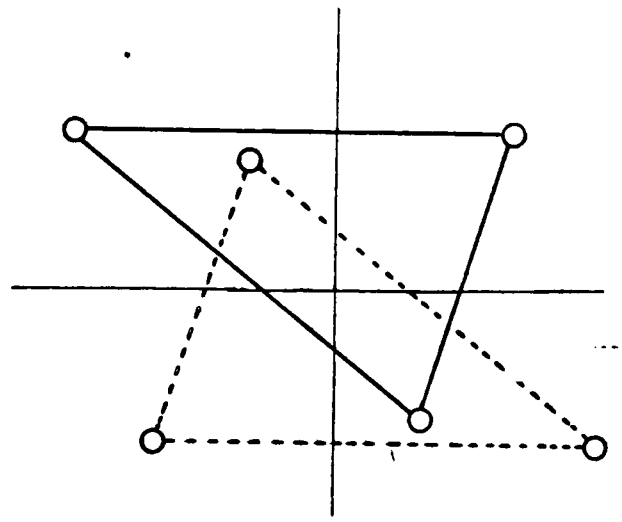
Crystals of the yellow compound are deposited[1] as small needles from the reaction of benzotrifuroxan with triphenyl phosphine in benzene solution. They are insoluble in most common solvents, though sparingly soluble in dimethyl sulphoxide and triethyl phosphate, and do not recrystallise satisfactorily. When benzene is replaced by toluene as the solvent for the reduction of benzotrifuroxan, some of the crystals that separate are just large enough for X-ray photography.

An integrated NMR spectrum of a sample of the compound (from toluene solution) indicated[8] the presence of three methyl protons to about 100 phenyl protons which suggested a clathrate solvent molecule in the crystal lattice (no methyl protons were seen in the NMR of a sample from the benzene solution).

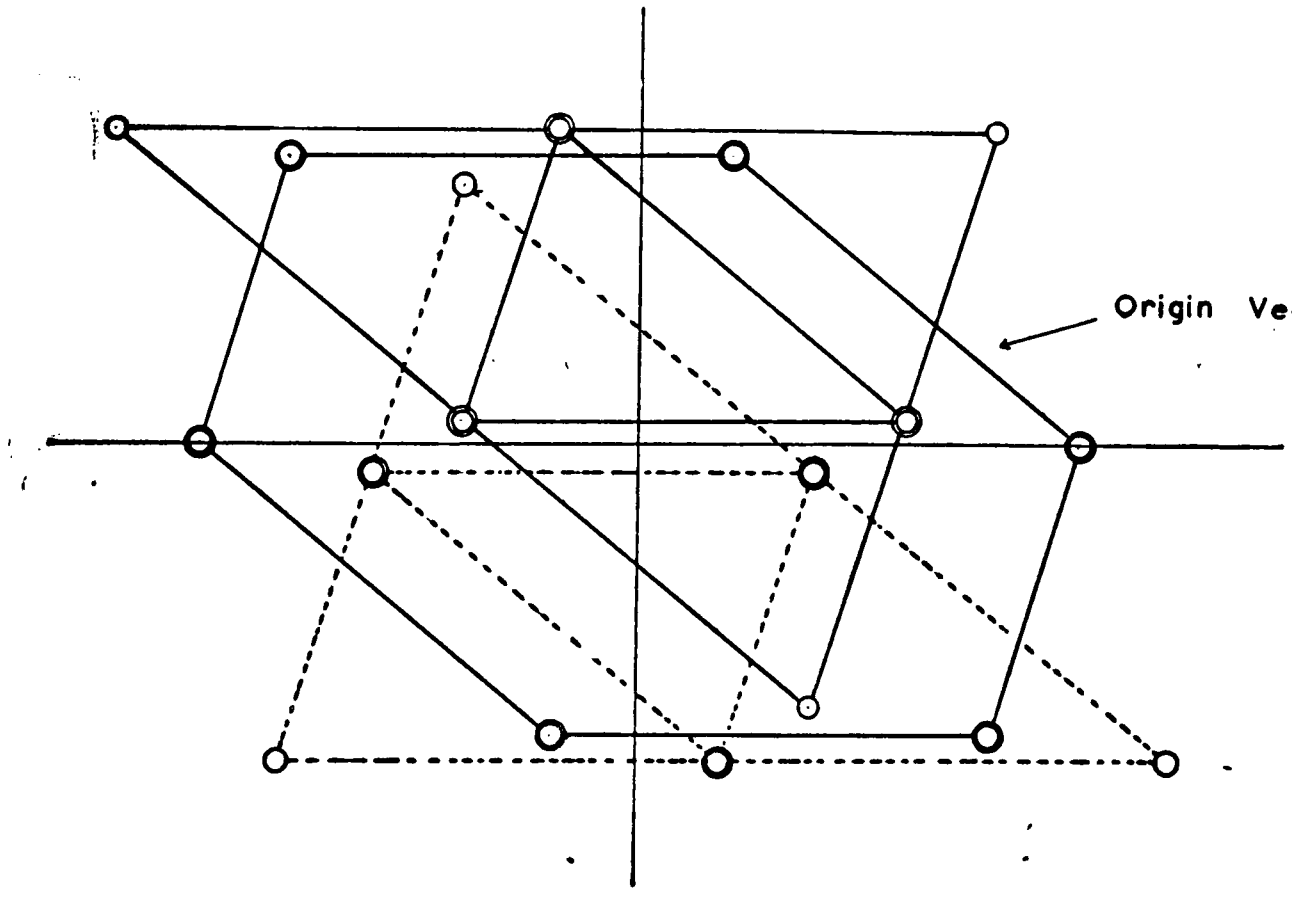
Three dimensional intensity data were collected with rotation about the $\underline{a}$ axis and the data were reduced for Lorentz and polarisation factors.

From a consideration of the calculated molecular weight (1083) and assuming that the majority of the weight was concentrated in triphenylphosphine fragments (262) it was thought that the crystal contained three phosphorus atoms in the asymmetric unit.

If three atoms are arranged as in figure 7a, then the resulting vector pattern in a Patterson function is given in figure 7b.



a.



b.

Figure 7.

Formally, if three independent atoms in space group $P\bar{1}$ are placed at:

$$x_1, y_1, z_1, \qquad x_2, y_2, z_2, \qquad x_3, y_3, z_3,$$

the vectors between them are:

$$\pm \begin{vmatrix} x_1 - x_2, & y_1 - y_2, & z_1 - z_2 \\ x_1 - x_3, & y_1 - y_3, & z_1 - z_3 \\ 2x_1, & 2y_1, & 2z_1 \\ x_1 + x_2, & y_1 + y_2, & z_1 + z_2 \\ x_1 + x_3, & y_1 + y_3, & z_1 + z_3 \end{vmatrix}$$

$$\pm \begin{vmatrix} x_2 - x_1, & y_2 - y_1, & z_2 - z_1 \\ x_2 - x_3, & y_2 - y_3, & z_2 - z_3 \\ x_2 + x_1, & y_2 + y_1, & z_2 + z_1 \\ 2x_2, & 2y_2, & 2z_2 \\ x_2 + x_3, & y_2 + y_3, & z_2 + z_3 \end{vmatrix} ; \quad \pm \begin{vmatrix} x_3 - x_1, & y_3 - y_1, & z_3 - z_1 \\ x_3 - x_2, & y_3 - y_2, & z_3 - z_2 \\ x_3 + x_1, & y_3 + y_1, & z_3 + z_1 \\ x_3 + x_2, & y_3 + y_2, & z_3 + z_2 \\ 2x_3, & 2y_3, & 2z_3 \end{vmatrix}$$

and the peaks expected in the Patterson function will be found at:

$\pm (x_1 - x_2, y_1 - y_2, z_1 - z_2)$ Multiplicity 2

$\pm (x_2 - x_3, y_2 - y_3, z_2 - z_3)$ Multiplicity 2

$\pm (x_3 - x_1, y_3 - y_1, z_3 - z_1)$ Multiplicity 2

around the origin, and at:

$\pm (x_1 + x_2, y_1 + y_2, z_1 + z_2)$ Multiplicity 2

$\pm (x_2 + x_3, y_2 + y_3, z_2 + z_3)$ Multiplicity 2

$\pm (x_3 + x_1, y_3 + y_1, z_3 + z_1)$ Multiplicity 2

$\pm (2x_1, 2y_1, 2z_1)$ Multiplicity 1

$\pm (2x_2, 2y_2, 2z_2)$ Multiplicity 1

$\pm$ ($2x_3$, $2y_3$, $2z_3$) Multiplicity 1

A three-dimensional Patterson function sharpened to 'point atoms at rest' (B = 3) was calculated and in it a set of peaks were located that precisely satisfied the conditions for P-P vectors in space group $P\bar{1}$ with three phosphorus atoms to the asymmetric unit (table 1).

An F_o synthesis was calculated phased on these three phosphorus atom positions which confirmed them, and which contained $\approx$ 200 other significant peaks. From these, 72 were selected to represent atoms (by consideration of peak shape and site, and by comparison of the F_o synthesis with the Patterson function).

An F_o synthesis was calculated phased on the trial structure (figure 8) which confirmed the structure.

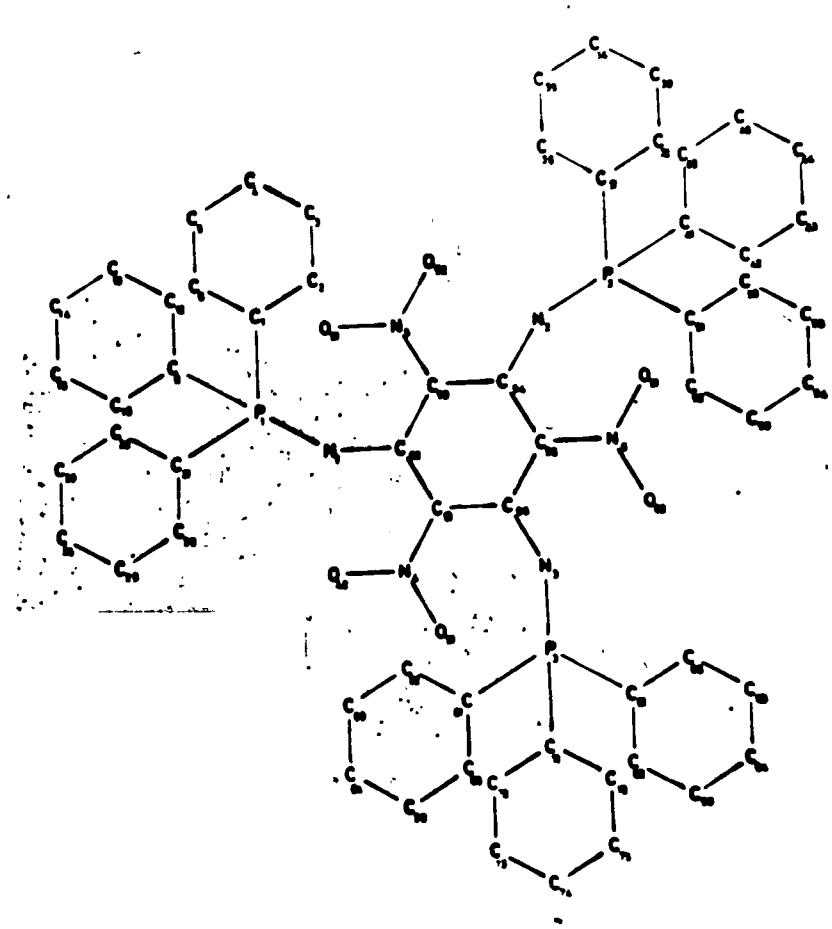


Figure 8

The trial structure with individual isotropic temperature factors was refined by least squares with a block diagonal approximation to the full matrix (p. 8). Five matrix blocks were used, one for the overall scale factor and temperature factors, one for the positional parameters of each triphenyl phosphine group and one for the positional parameters of the benzotrifuroxan fragment.

This required 301 refinement parameters, while the least squares refinement programme was limited to 180 parameters; the calculation, therefore, was restricted to the refinement of two or three blocks at one time and a procedure was followed that needed two separate calculations for the refinement of each parameter once and that rearranged the sequence of the blocks at the end of each complete least squares cycle.

After six rounds of refinement with unit weights for all observations, the reliability factor (R) was 19%. A difference Fourier synthesis was calculated which showed no remarkable features except a plane of residual electron density about the point $0,0,\frac{1}{2}$ (figure 9). This plane was thought to represent a toluene molecule, statistically disordered throughout the crystal, in two orientations (figure 10).

The toluene parameters, with a separate matrix block for the positional parameters, were included in the least squares refinement*

*The programme had, by this stage, been adapted[3] to accept as many as 400 parameters.

and two rounds of refinement were calculated with a weight (w) for each observation where (w) is given by Equation (1), $P_3 = {}^2/_3P_2$, the R factor was 14.8%, the data measurement was checked and after three more rounds of refinement, with the weighting parameters unchanged, the R factor was 13.3%.

The structure is shown in figures XI, XII, the projection onto the least squares best place of the central C_6 ring in figure XIII and the bond lengths and angles in figures XIV, XV. (For full details of co-ordinates, bond lengths and angles, and e.s.d.'s, see p. 208)

In the final structure, (figures XI, XII) the co-ordinates of the toluene molecule ~~is~~ are distorted, which is not unexpected for the molecule is not held rigidly in the crystal lattice and probably vibrates (close contacts to each atom are given in table 2). Also the molecule is in two orientations related by a centre of symmetry (figure 11) and for the purpose of least squares refinement both orientations must be included in one unit cell. However, the positions of some of the atoms in one orientation are less than 0.5Å from the positions of other atoms in the second orientation and under these conditions, the expressions which are derived by Taylor's expansion for use in the least squares process are no longer even approximately linearly independent and the refinement is not strictly valid. A technique is available in this laboratory for refinement in these circumstances (see Chapter 2), and though it is neither difficult nor arduous to employ, in terms of computer time used and computer store needed, for this structure, it is too expensive to be justified.

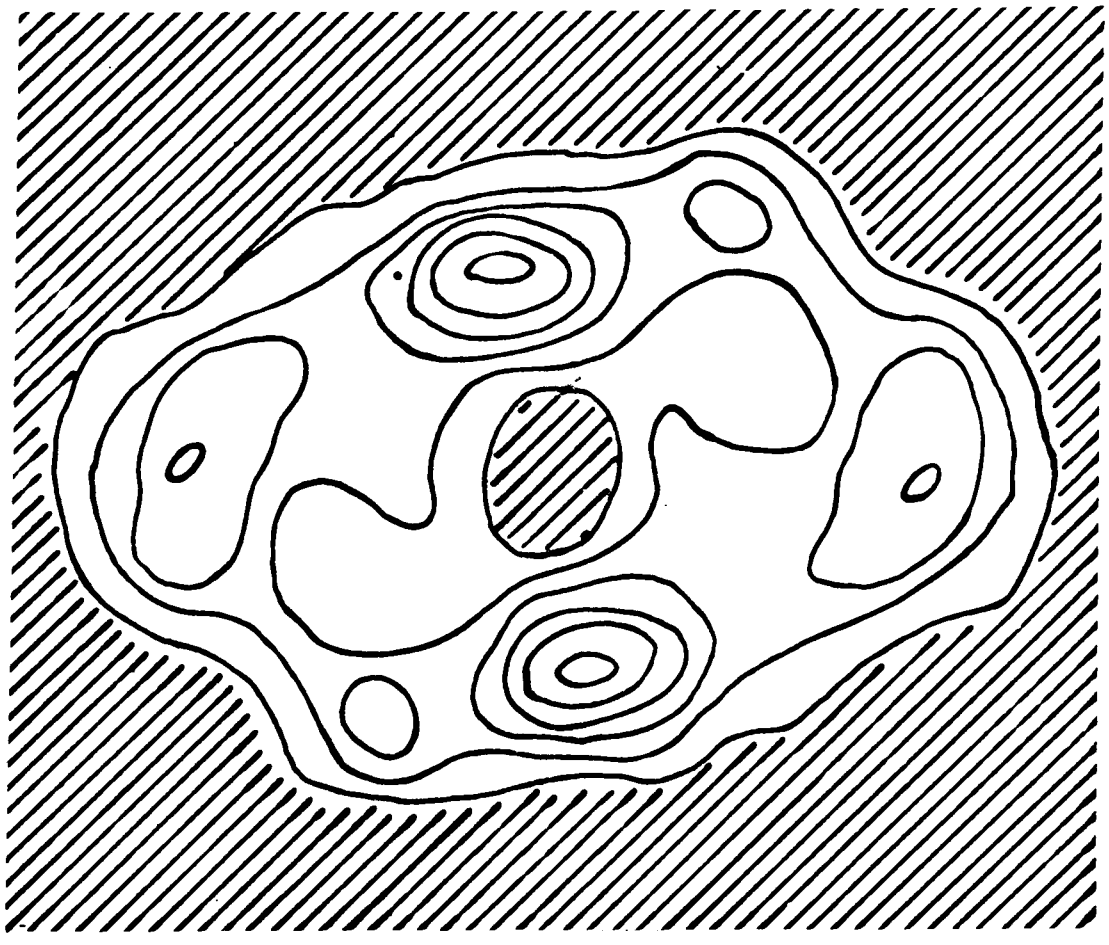


Figure 9

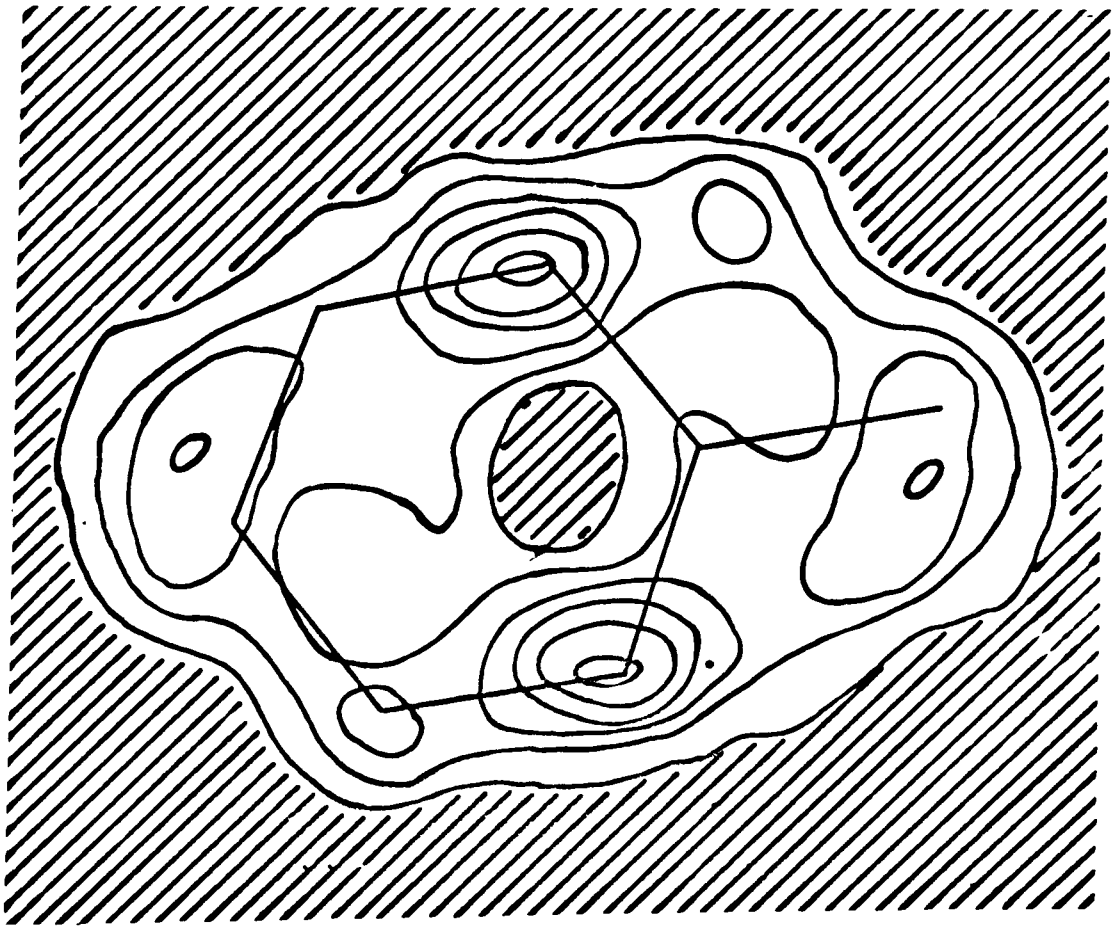


Figure 10

Atom pair	Atomic separation (Å)
$C_{102} - C_5$	3.91
$C_{103} - C_4$	3.77
$C_{103} - C_5$	3.83
$C_{104} - C_{42}$	3.94
$C_{104} - C_{43}$	3.73
$C_{104} - C_{51}$	3.54
$C_{105} - C_{16}$	3.62
$C_{105} - C_{52}$	3.57
$C_{106} - C_5$	3.84
$C_{106} - C_{16}$	3.81
$C_{107} - C_4$	4.00

Table 2. The short contact distances to the atoms of the toluene molecule.

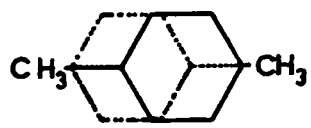


Figure 11

The geometry of the molecule is constructed upon an equilateral triangle of phosphorus atoms (of side 7Å), with the benzotrifuroxan fragment bonded between three triphenyl phosphine groups (figure XIV). The plane of the C_6 ring of the fragment is inclined slightly to the plane through the three phosphorus atoms (figure XI). The benzotrifuroxan residue forms a plane perpendicular to axis a and the molecule, together with other molecules related by the centres of symmetry, forms a layer structure stacking up a (figure XII) where phenyl groups either fit into spaces in adjacent layers, or arrange their planes to be parallel to the planes of neighbouring phenyl groups (figure XI).

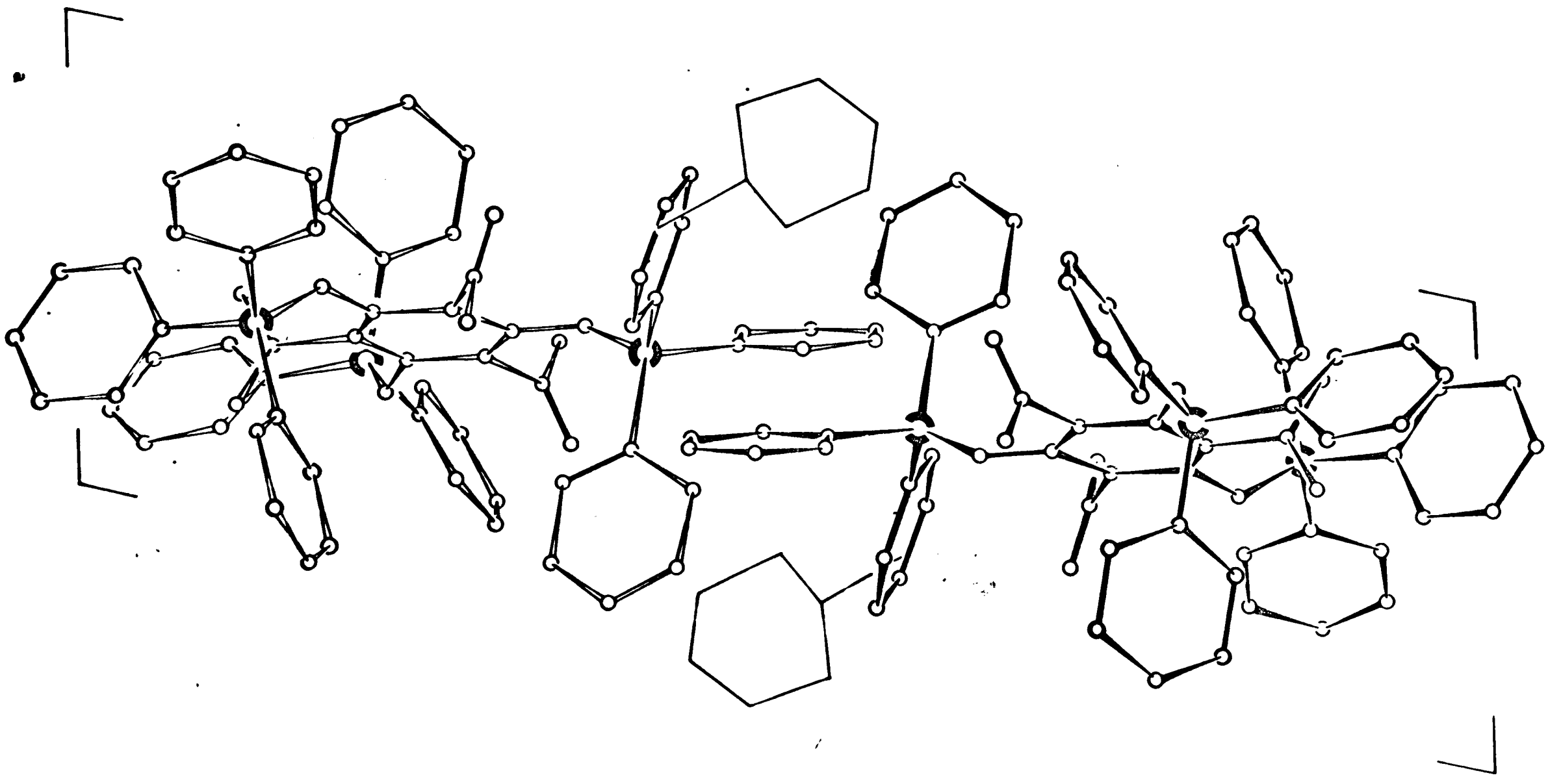


Figure XI Yellow Compound Projection (0 1 0)

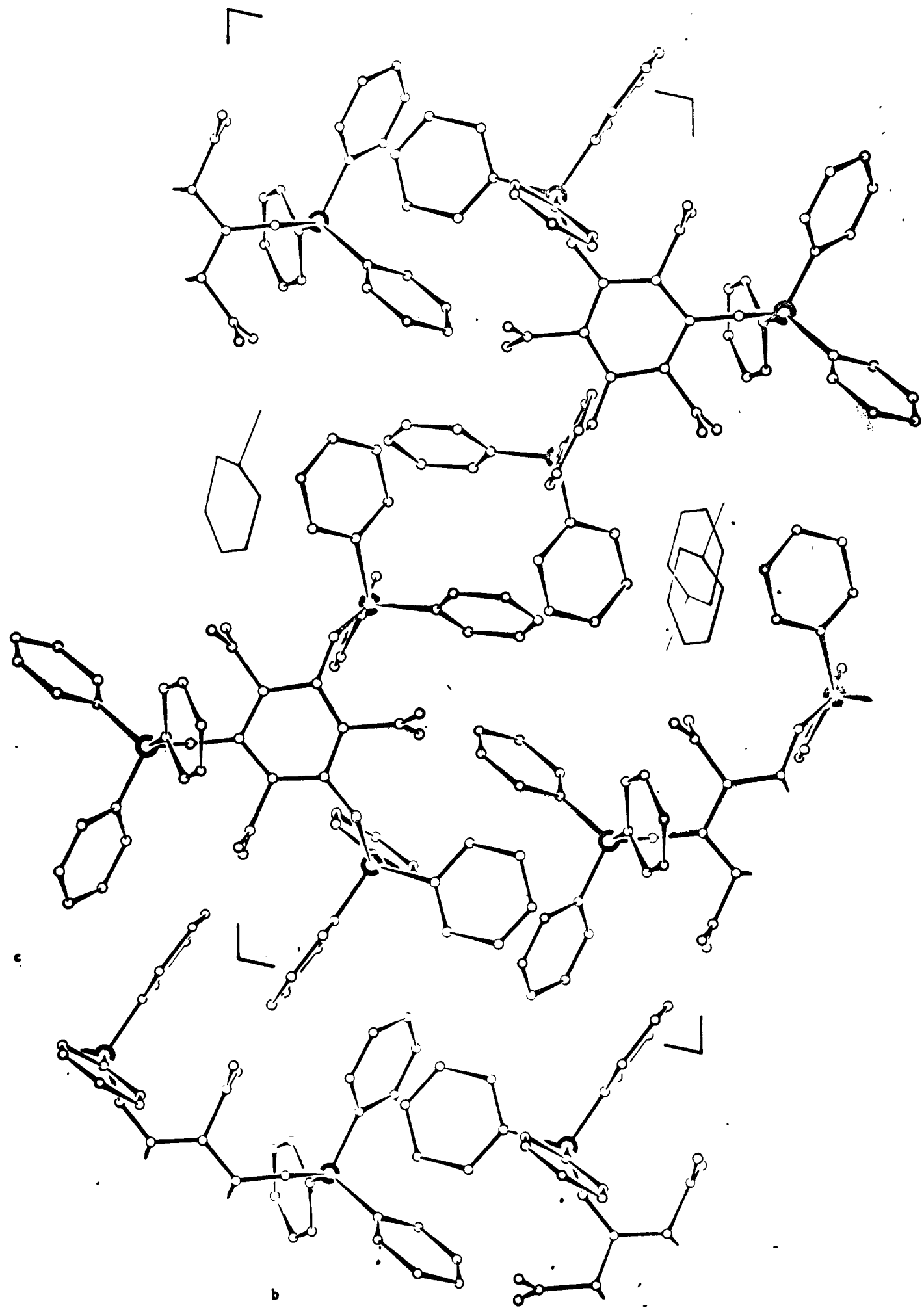


Figure XII Yellow Compound Projection (1 0 0)

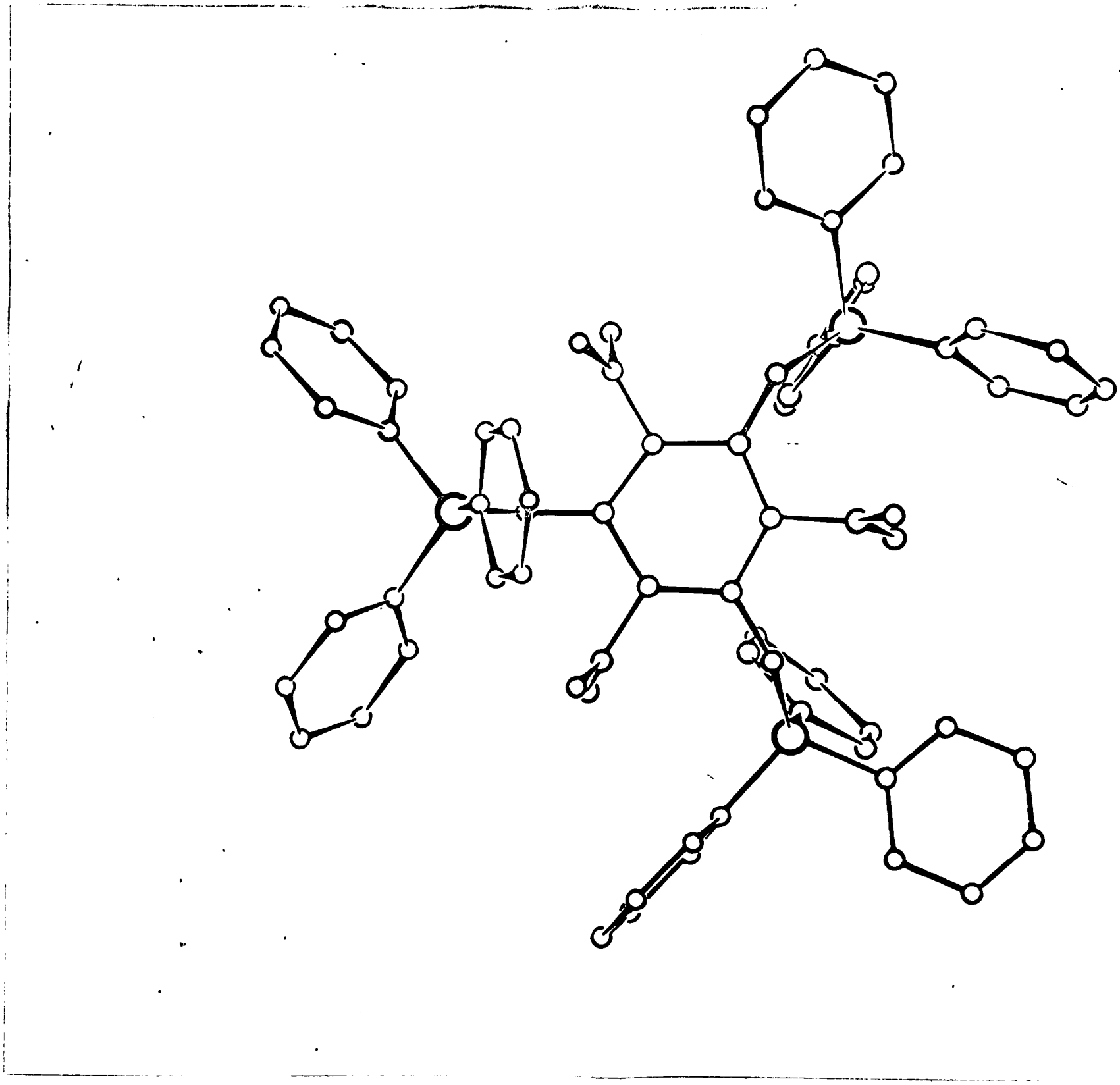


Figure XIII Yellow Compound

Projection onto the least squares best plane of the central C_6 ring.

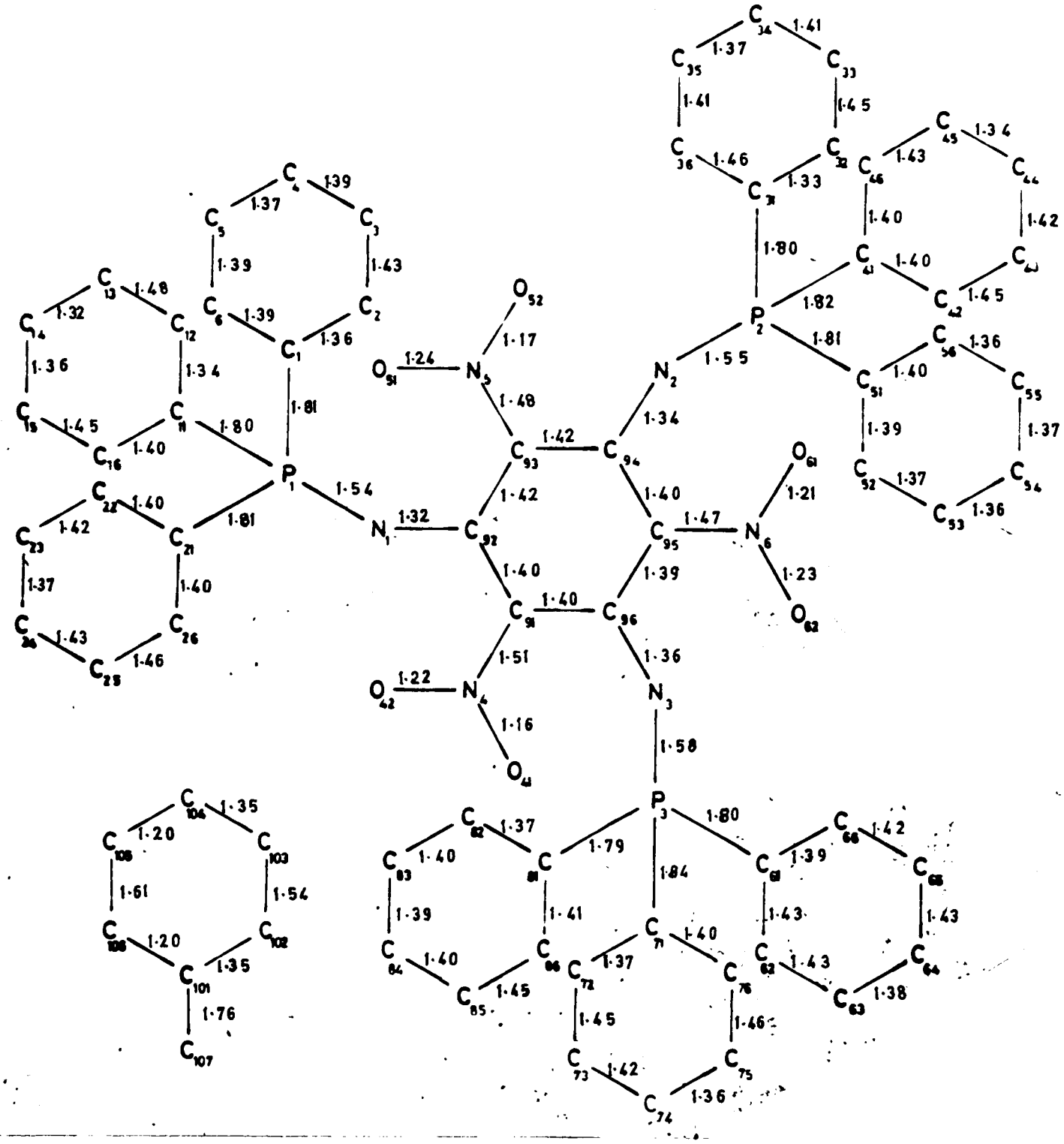


Figure XIV Yellow Compound Interatomic Distances (Å)

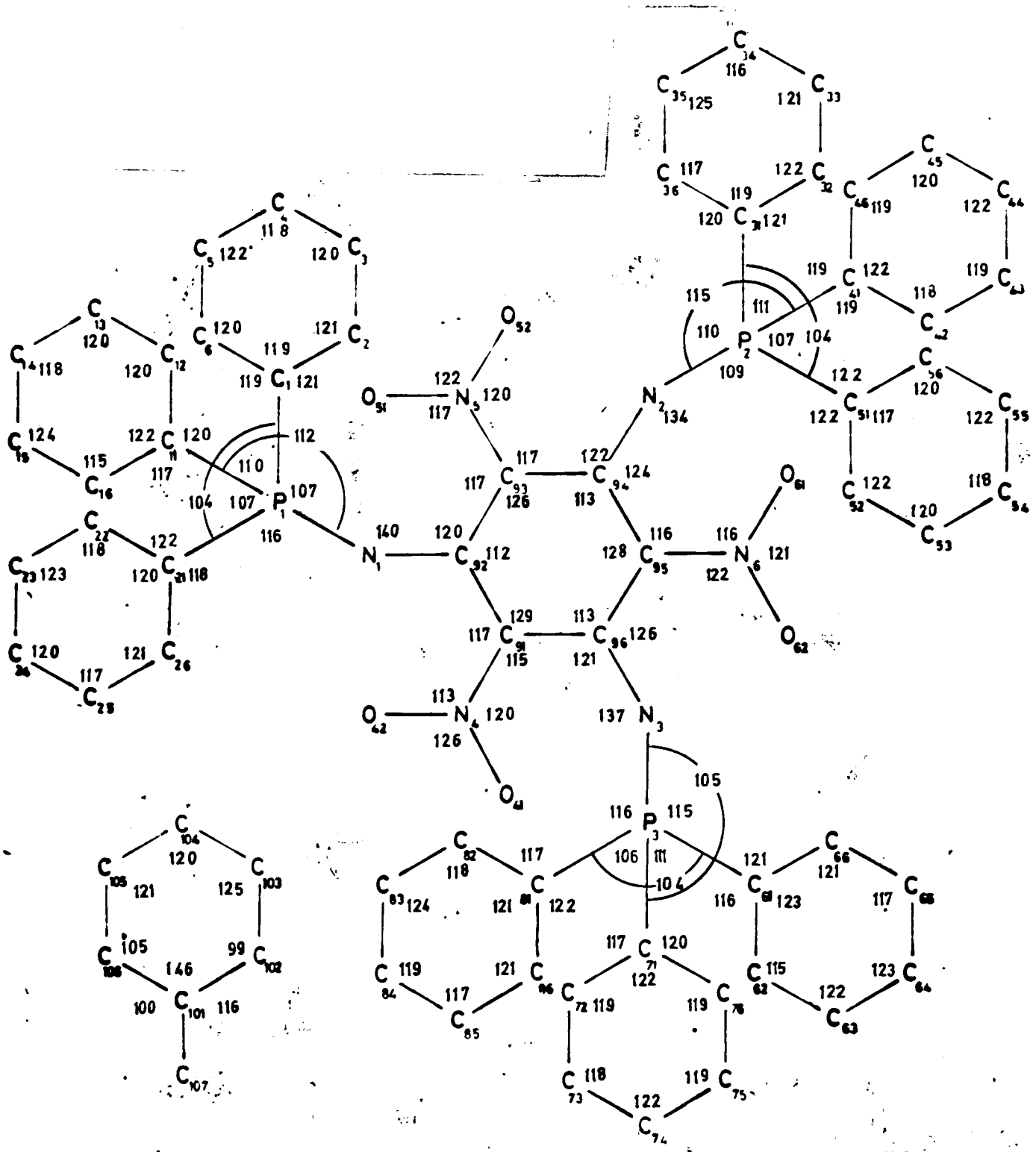


Figure XV Yellow Compound Bond angles

BLUE COMPOUND

Crystal data: Monoclinic plates; a = 9.258 ± 0.004, b = 16.44 ± 0.02, c = 14.843 ± 0.017Å; γ = 111.47° ± 0.02; Space group Pb; Cu-K_α radiation; μ = 14.29 cm.$^{-1}$; M.pt. = 262°C; D_m = 1.3657 g.cm^{-3} which gave an estimated molecular weight of 864 and two molecules to the unit cell. From the structure analysis the molecular formula is ($C_{48}H_{30}N_8O_4P_2$), M = 869; Z = 1.988. 3273 independent reflections were used in the initial calculations. 165 reflections were removed when the data measurement was checked.

The total yield of the blue compound from all the 'runs' of the reduction of benzotrifuroxan was never recorded but it can hardly have exceeded 20 mg. The sample exists as a few jagged needle platelets, so it was without much hope that one crystal, less misshapen than the others, was mounted and a survey X-ray photograph taken. Surprisingly, the diffraction pattern was sharp and continued to the Cu-K_α limit.

Three-dimensional intensity data photographs were collected with rotation about the unique axis c. The Unicam camera on which the X-ray photographs were taken is designed so that for an equi-inclination angle greater than 10°, the direct beam backstop no longer casts a shadow upon the X-ray film. For non-zero layers of the intensity data photographs, axial reflections (001) were clearly present when (l) was both odd and even. The significance of this was not appreciated at the time, and since the diffraction pattern exhibited systematic

absences consistent with an axial glide, it was assumed that the crystal was in some common space group such as $P2_1/b$.

Once the intensity data had been collected, the crystal was remounted for survey photography (with a sample of one crystal only one does not remount the crystal for survey photographs before taking intensity data photographs!). When the zero layer Weissenberg photograph taken with rotation about a monoclinic non-unique axis was examined, the only systematic absence present was that due to an axial glide, and so the space group of the crystal was either Pb or P2/b. Although Nowacki[9] records only four examples of a compound crystallising in space group Pb compared with 26 examples for P2/b, from the pattern of intensities and from the morphology of the crystal (plate 1) it was suspected that the crystal was in the acentric space group Pb.

The data was corrected for Lorentz and polarisation factors only and a three-dimensional Patterson function sharpened to 'point atoms at rest' (B = 3) was calculated. This contained no Harker section at Z = 0 and the space group was assigned to Pb.

There was no information on the chemical formula of the compound, but from the calculated molecular weight (864) and assuming that any phosphorus atoms present were in the form of triphenyl phosphine groups (262) it was thought that two phosphorus atoms were present in the asymmetric unit.

In space group Pb, with two independent atoms at:

x_1, y_1, z_1 $\qquad\qquad$ x_2, y_2, z_2

The vectors between them are:

$(x_1 - x_2, y_1 - y_2, z_1 - z_2)$	$(x_2 - x_1, y_2 - y_1, z_2 - z_1)$
$(0,\frac{1}{2},2z_1)$	$(x_2 - x_1, \frac{1}{2} + y_2 - y_1, z_2 + z_1)$
$(x_1 - x_2, \frac{1}{2} + y_1 - y_2, z_1 + z_2)$	$(0,\frac{1}{2},2z_2)$
$(0,\frac{1}{2},-2z_1)$	$(x_2 - x_1, \frac{1}{2} + y_2 - y_1, -z_2 - z_1)$
$(x_1 - x_2, \frac{1}{2} + y_1 - y_2, -z_1 - z_2)$	$(0,\frac{1}{2},-2z_2)$
$(x_1 - x_2, y_1 - y_2, -z_1 + z_2)$	$(x_2 - x_1, y_2 - y_1, -z_2 + z_1)$

and in the Patterson function peaks would appear at:

$\pm (x_1 - x_2, y_1 - y_2, z_1 - z_2)$	Multiplicity 2
$\pm (0,\frac{1}{2},2z_1)$	Multiplicity 2
$\pm (0,\frac{1}{2},2z_2)$	Multiplicity 2
$\pm (x_1 - x_2, \frac{1}{2} + y_1 - y_2, z_1 + z_2)$	Multiplicity 2

In the Patterson function a set of peaks was located which satisfied only the conditions for P-P vectors in space group Pb, with two phosphorus atoms to the asymmetric unit, (table 1).

Two minimum functions[10] were calculated with superpositions of the vectors $(x_1 - x_2, y_1 - y_2, z_1 - z_2)$ and $(x_1 - x_2, \frac{1}{2} + y_1 - y_2, z_1 + z_2)$ respectively upon the origin. (The regions of Patterson space about the peaks at $(0,\frac{1}{2},2z)$ were confused and no superposition was calculated using these vectors.)

By inspection of the Patterson function and the minimum functions it was possible to identify a tetrahedron of atoms around each phosphorus atom and to see faint outlines for several phenyl groups.

The same tetrahedron of atoms was observed in an F_o synthesis phased on the positions of the phosphorus atoms.

An F_o synthesis was calculated phased on the positions of two phosphorus atoms and the four atoms (treated as carbon) tetrahedrally arranged about them, and from a scrutiny of two F_o syntheses, the minimum and Patterson functions, the positions of four phenyl groups were established, two groups attached to each phosphorus atom. Another F_o synthesis was calculated phased on the positions of 26 atoms, the positions of these atoms adjusted and the position of another phenyl group located.

This procedure was followed through eight successive F_o syntheses until the positions of two phosphorus atoms and four phenyl groups attached to each phosphorus had been established. The eighth F_o synthesis was phased on 50 atoms (2P + 48C) and the resulting peaks which represented carbon atoms were all approximately the same height and proportional in size to the peaks representing the phosphorus atoms. In previous F_o syntheses the indications for atoms in phenyl groups were often faint and frequently the presence of a C_6 group was deduced as much by the behaviour of the background electron density as by the presence of peaks representing atoms. In fact, until almost the entire molecule had been deciphered, atoms whose positions had yet to be established were never represented by peaks with a height greater than three times the average background. Figure 12(a) shows a section through the plane of the $P\text{-}C_{(40\text{-}46)}$, for the F_o synthesis phased on $2(Pc_4)$; and figure 12(b) shows the same plane in the final structure.

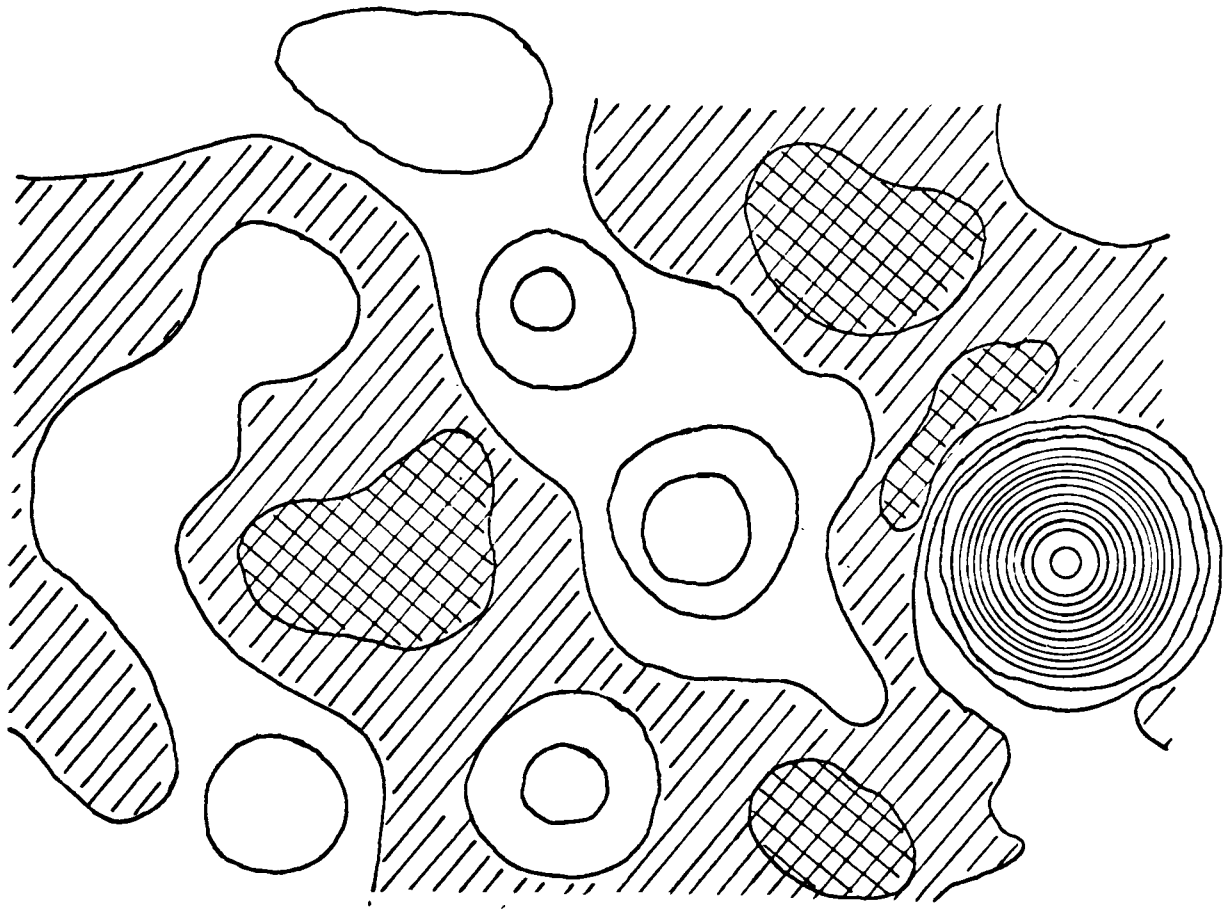


figure 12

A difference Fourier synthesis was calculated phased on the positions of 50 atoms, and around two phenyl groups, one attached to each phosphorus atom, indications were found of hetero-atoms of a benzotrifuroxan fragment. As the planes of these two groups were parallel and approximately 3Å apart, the molecular compound given in figure 13 was proposed as a trial structure.

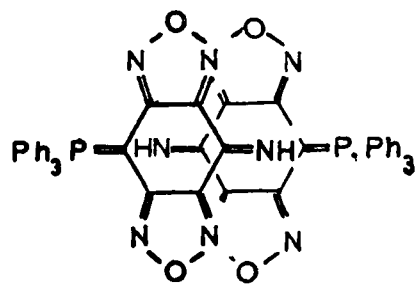


Figure 13.

The trial structure with individual isotropic temperature factors on all atoms was refined by least squares for three cycles, a difference Fourier synthesis was calculated, the atomic positions of the trial structure adjusted and the refinement procedure repeated.

No matter how the positions of the atoms of the benzotrifuroxan fragments were altered, on refinement the C_6 rings would not remain planar, the temperature factors of the hetero-atoms para to the phosphorus always increased to an unlikely value, and the carbon atoms para to the phosphorus atoms approached each other until they were between 2 and 2.5Å apart.

Finally the refinement was allowed to continue further than could be thought prudent, the C_6 rings deformed into a boat conformation, the temperature factors of the para-hetero-atoms continued to increase and the para-carbon atoms approached each other until they were 1.6Å apart.

The Patterson function, minimum functions and F_o syntheses were rechecked and the positions of the atoms of the benzotrifuroxan

fragments re-established without any conditions of planarity imposed upon them. The trial structure (figure 14) with individual isotropic temperature factors was refined by least squares with a block diagonal approximation to the full matrix (p. 8) which used four blocks, one for the overall scalefactor and temperature factors, and three for the positional parameters of the two triphenylphosphine groups and the benzotrifuroxan fragments respectively.

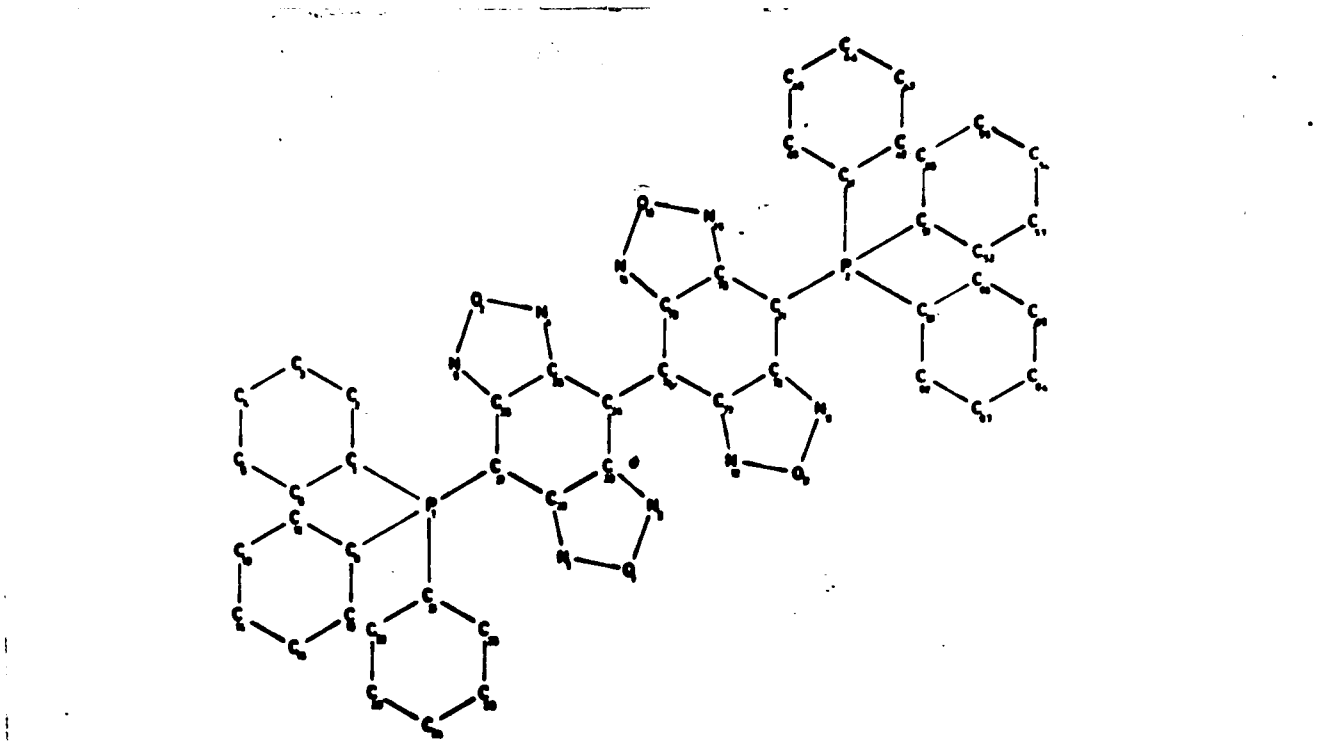


Figure 14

Three rounds of refinement were calculated with unit weights and three rounds with a weight (w) for each intensity observation where (w) is given in Equation (1) and $P_3 = {}^3/2P_2$.

After six rounds, the reliability factor (R) was 15.4%. The data measurement was checked and the refinement continued with the same weighting parameters for four more rounds. The R factor is now 10.9%.

The structure is shown in figures XVI, XVII and the bond lengths and bond angles in figures XVIII, XIX. (For full details of co-ordinates etc., see p.238).

In the blue compound, the two phosphorus atoms are 10Å apart and in projection onto the P-P axis, the molecule is 18Å long with the two triphenyl phosphine groups situated at either end. (Figure XVI). It is these 'bulky groups' separated by the rigid (p. 81) less space-filling, benzotrifuroxan fragments, which make it difficult to pack the molecules efficiently into the crystal lattice. An axial glide is the one of the space group symmetry operation that can be applied to such a molecule without causing large unfilled spaces in the crystal lattice.

It can be thought that the unusual geometry of the molecule caused it to crystallise in the uncommon space group Pb, and conversely, from considerations of the space group it was possible to deduce the general shape of the molecule at an early stage in the structure analysis (p.52)

For the purpose of crystal packing, the compound may be considered as shaped like a regular dumbell with the $C_{\infty v}$ axis inclined at an angle to the axial glide, the molecules then pack together with the end of one molecule situated close to the middle of another (figures XVII, 15,16).

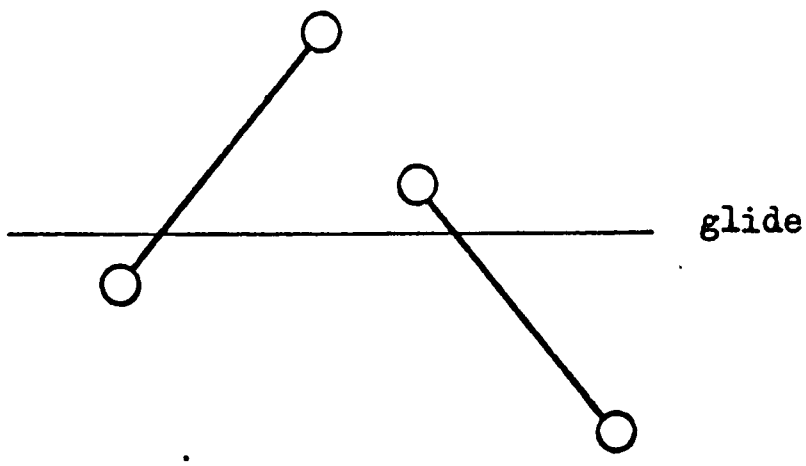


Figure 15

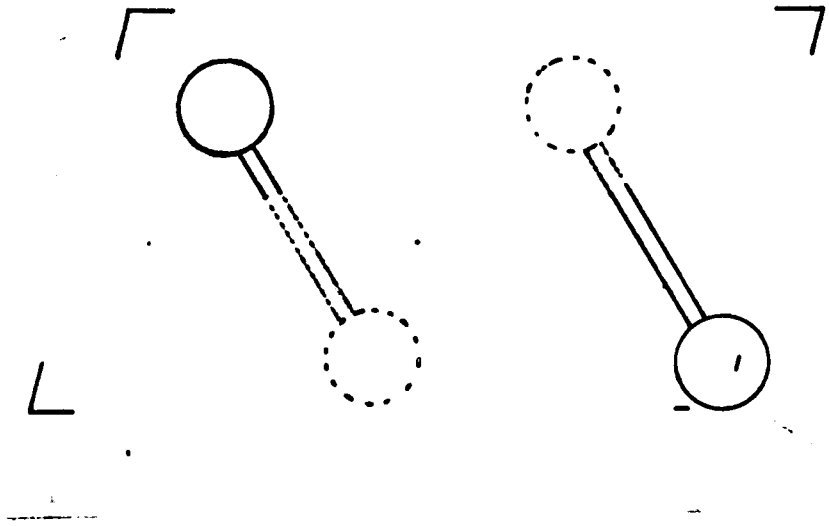


Figure 16

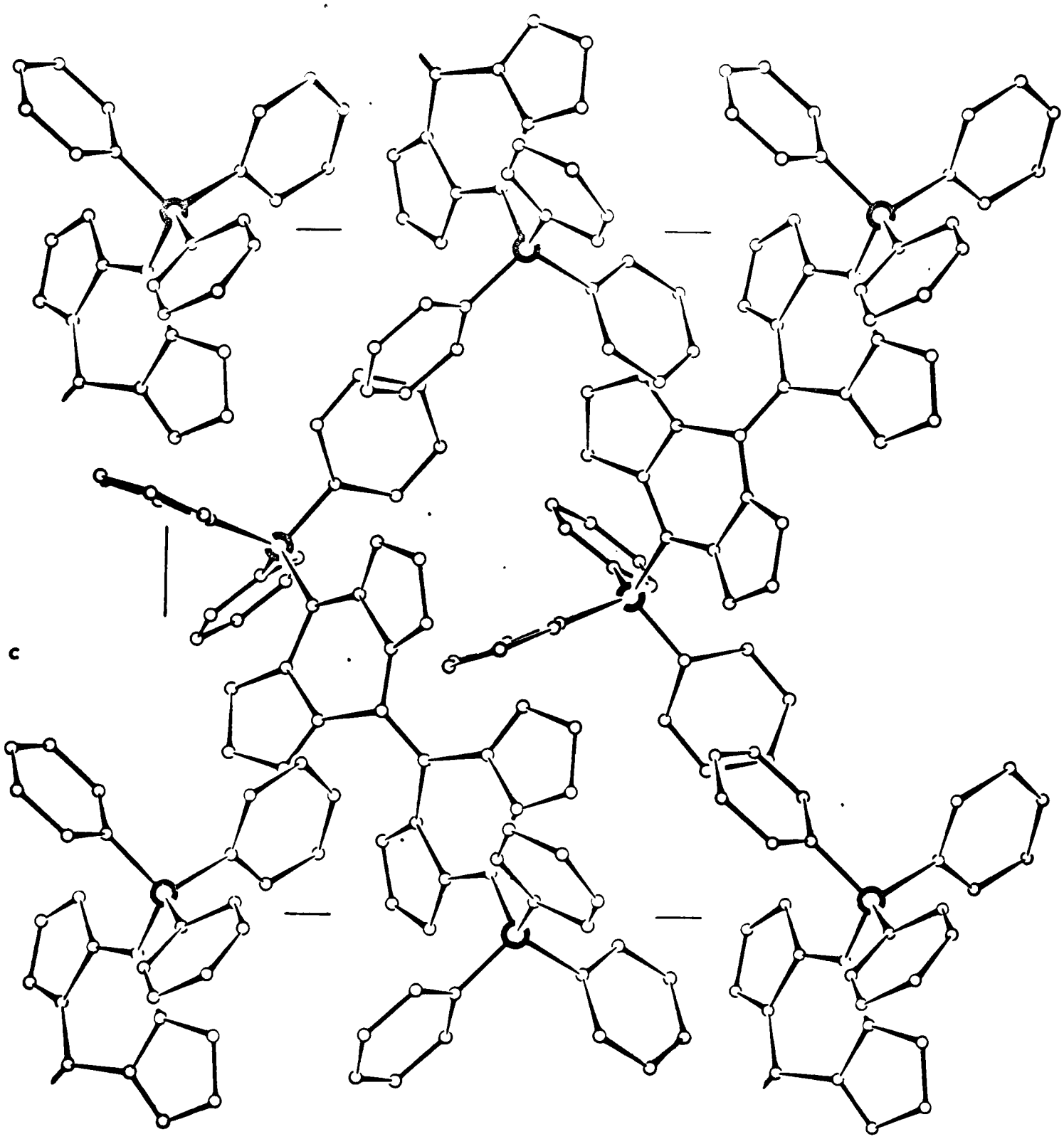


Figure XVI Blue Compound Projection (1 0 0)

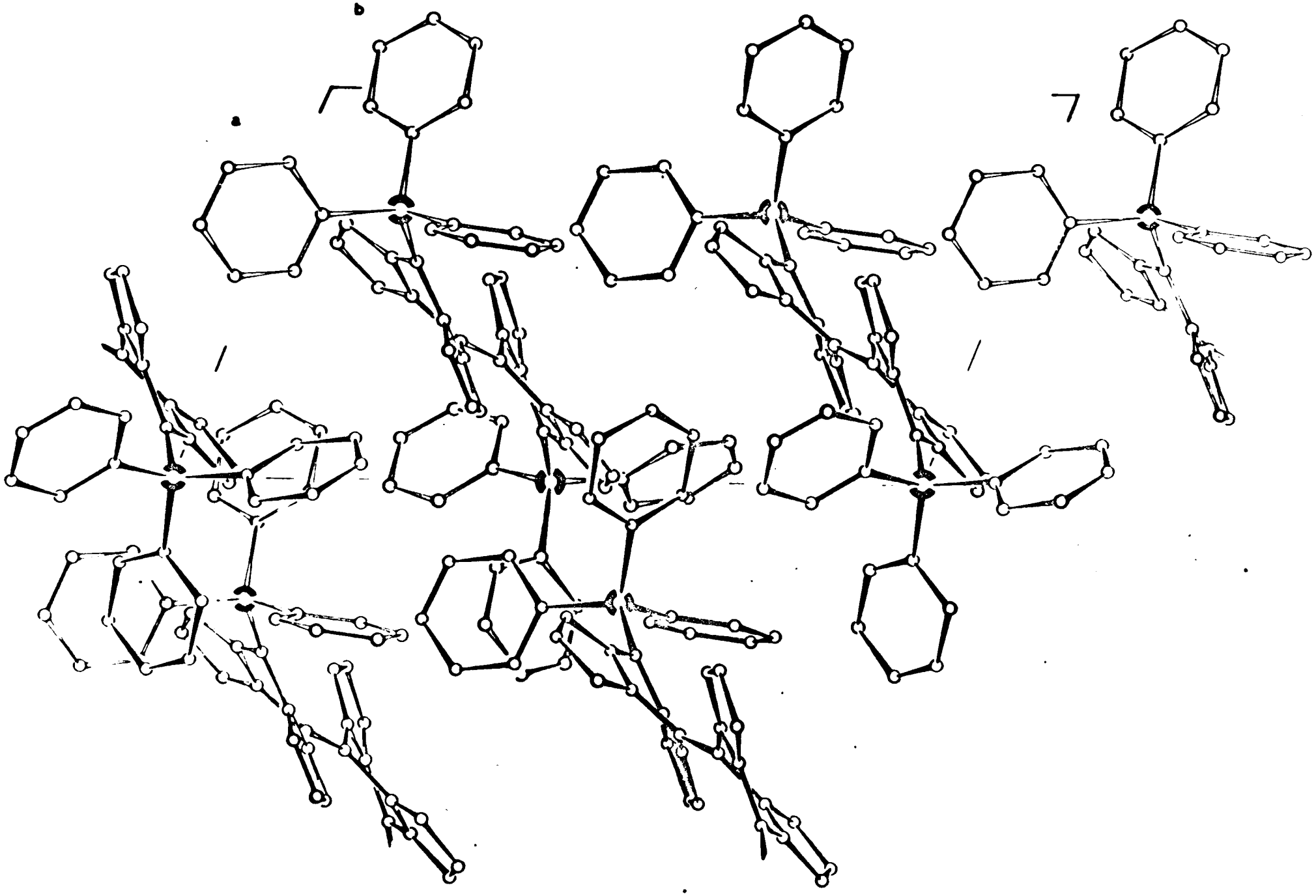


Figure XVII Blue Compound Projection (0 0 1)

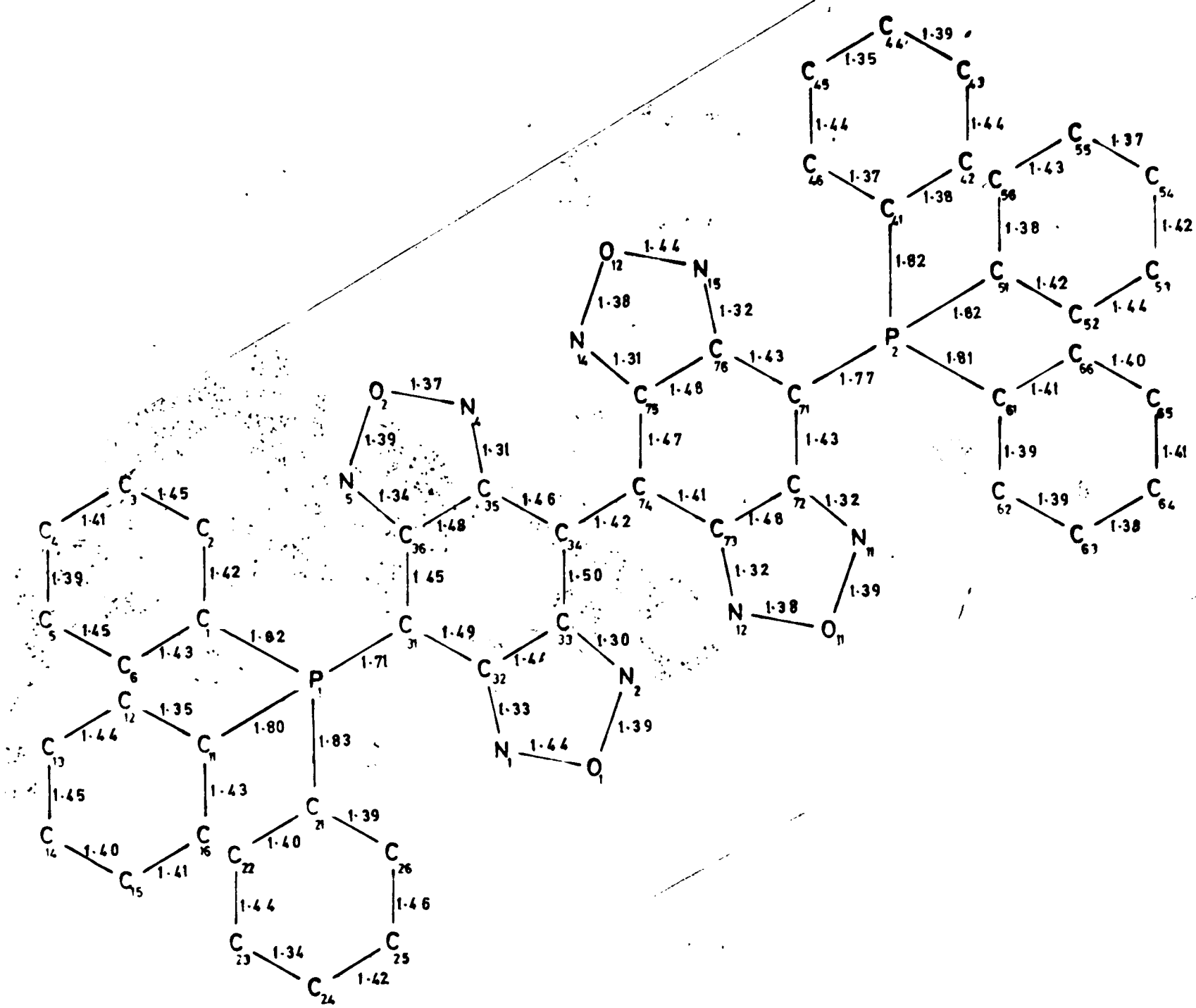


Figure XVIII Blue Compound Interatomic Distances (Å)

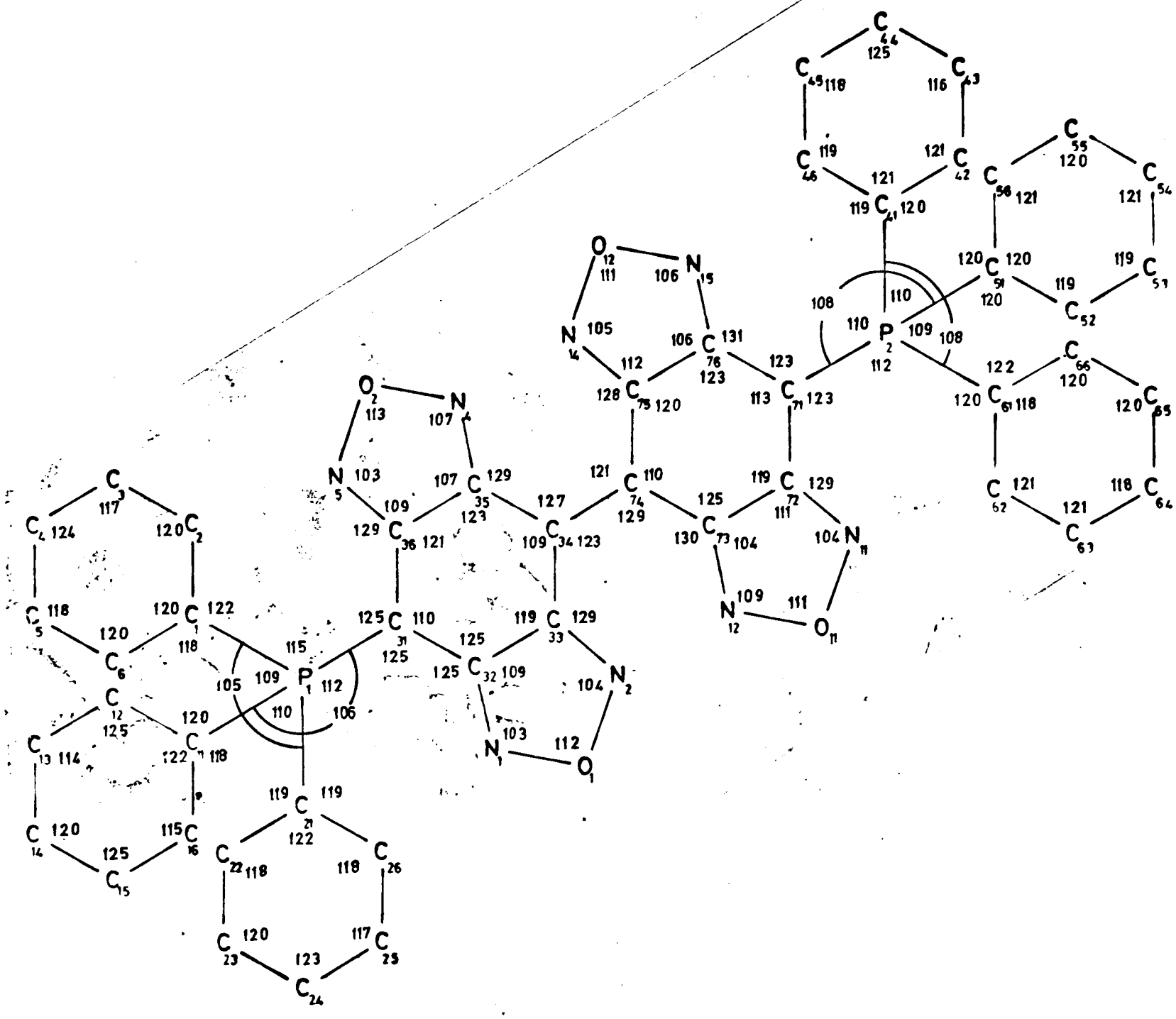


Figure XIX Blue Compound Bond Angles

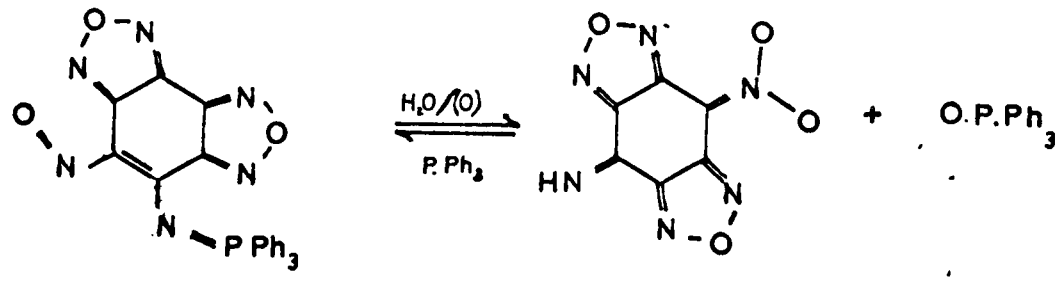
IDENTITY OF THE ATOMS

The hetero-atoms in the coloured compounds were identified both with chemical knowledge and from the residual electron density at atomic locations in a difference Fourier synthesis, phased on the full structure, but where the light atoms were treated as carbon. In most cases the behaviour of the individual isotropic temperature factors (U_{iso}) in the subsequent least squares refinements confirmed the identification.

The average temperature factors of some of the related atoms in the coloured compounds are given in table 3. In each molecule U_{iso} increases as the distance from the centre of the molecule of the atom concerned, and there are no marked anomalies.

These indications could be misleading and, wherever possible, independent chemical evidence for the identities of the atoms was obtained.

The light green and red compounds are closely related; the red can be prepared by gentle oxidation of an $MeOH/CHCl_3$ solution of the green, and the green compound is isolated from a reaction between the red compound and triphenyl phosphine is benzene solution (p.160).

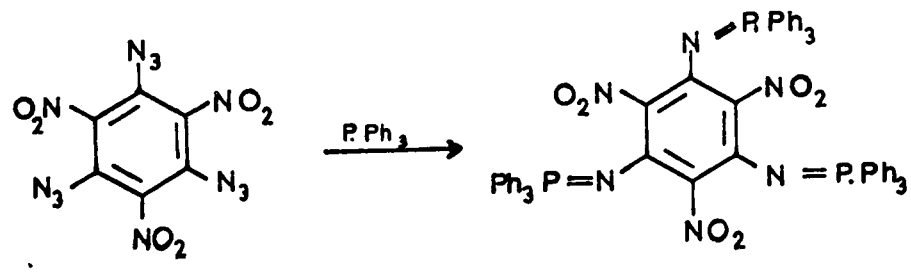


Type of atom(s)	Average U_{iso}
Red compound	
Carbon atoms (heterocycle C_6 ring)	0.03753
Furazan nitrogen atoms	0.05290
Furazan oxygen atoms	0.06238
Nitro nitrogen atoms	0.03604
Nitro oxygen atoms	0.05015
Imine nitrogen	0.03604
Ph_3PO oxygen atom	0.05597
Phenyl carbon atoms (attached to P)	0.03015
Light green compound	
Phenyl carbon atoms (attached to P)	0.05665
Phosphimino nitrogen atom	0.05352
Carbon atoms (heterocycle C_6 ring)	0.05730
Furazan nitrogen atoms	0.07668
Furazan oxygen atoms	0.08761
Nitroso nitrogen atom	0.06362
Nitroso oxygen atom	0.08020
Blue compound	
Carbon atoms (central C_6 rings)	0.04152
Furazan nitrogen atoms	0.05316
Furazan oxygen atoms	0.05565
Yellow compound	
Phenyl carbon atoms (attached to P)	0.06166
Phosphimino nitrogen atom	0.05392
Carbon atoms (central C_6 ring)	0.05042
Nitro nitrogen atoms	0.07115
Nitro nitrogen atoms	0.09285

Table 3

In the red compound, the temperature factors of the imino nitrogen atom is a little lower and the phosphine oxide oxygen atom a little higher than expected, but there can be little doubt as to the identity of these atoms. The presence of Ph_3PNH from an aqueous oxidation is most unlikely, and if the red compound heterocycle contained a 'quinone type' oxygen atom the green compound could not be prepared from it by the action of triphenyl phosphine.

The yellow compound can be prepared by the action of triphenyl phosphine on sym-triazido trinitrobenzene in benzene solution.



..... (1)

The evidence is less convincing than it appears, for the yellow derivative from reaction (1) was one of at least four other products (T.L.C.); however, the derivative can be reduced by phenyl hydrazine in the presence of pyridine to hexa amino-benzene and the yellow compound is similarly reduced*(p.161).

*This is contrary to the report[1] of Miss J. Evans, who observed that phenyl hydrazine (in the absence of pyridine) did not reduce the yellow compound

DISCUSSION

Although the main objective of this part of the research was the investigation of the chemistry of the reduction by triphenyl phosphine, each of the structures that were determined have themselves several interesting features. In general they present a number of curious conjugated systems, and in particular include the first three dimensional structure analyses of aromatic furazan compounds.

It is sometimes convenient to discuss the molecular structures of the coloured compounds in terms of interatomic bond orders rather than the corresponding bond lengths, for with bond orders the distribution of the π electrons in the heterocycles is clear while it is not immediately obvious with the bond lengths.

Semi-empirical relationships have been derived[11,13] between an observed interatomic bonding distance and the corresponding calculated bond order. For C=C and C=N bonds these are:

$$(C=C) \qquad \text{Bond length} = 1.51 - 0.17p \qquad \ldots\ldots (2)$$

$$(C=N) \qquad \text{Bond length} = 1.48 - 0.21p \qquad \ldots\ldots (3)$$

where (p) is the π bond order.

There is less information about N-O bonds and their orders but some of the known values have been tabulated (figure 17).[12]

For a series of simple aromatic compounds (pyrolle, pyridine p-nitroaniline),[11] equations (2), (3) and figure 17 have been found to give good agreement between observed bond lengths[14] and the lengths calculated with bond orders from Huckel and SCF computations* (see following page).

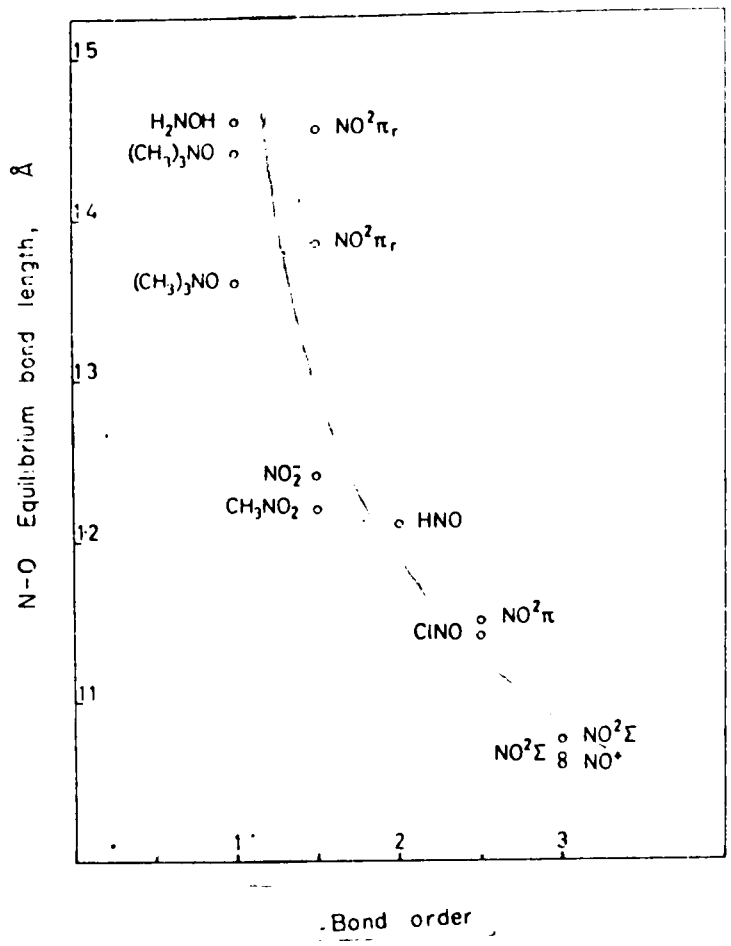


Figure 17

The same computations also gave good agreement between the observed and the calculated UV and visible absorption spectra.

*The choice of resonance parameters in heterocycles like the ooloured compounds is a complex problem, and no really successful computations were carried out with these compounds.

The red compound

The bond orders for the benzotrifuroxan fragment, calculated from the bond lengths (p. 22) are given in figure 18. The bond lengths and angles will be found on p.196.

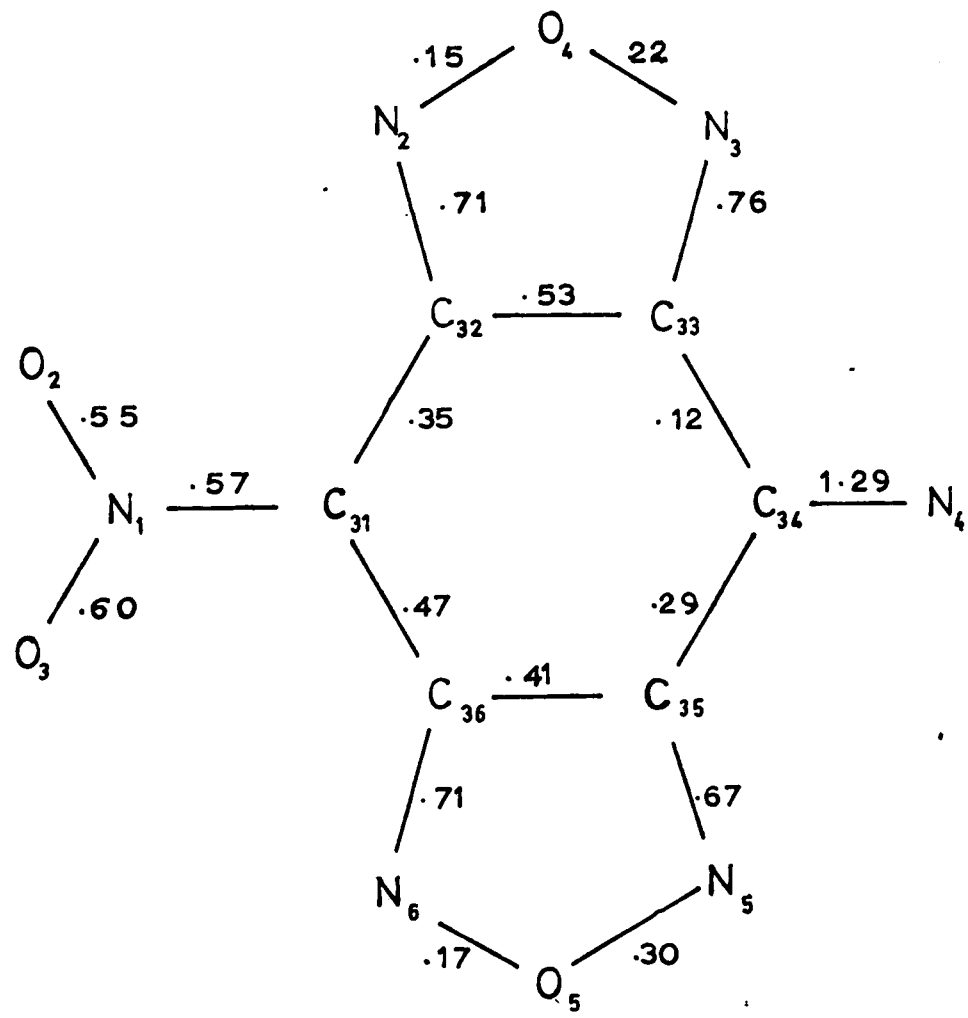
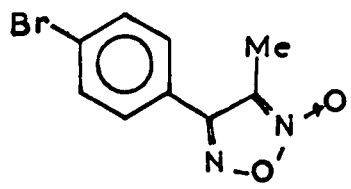


Figure 18

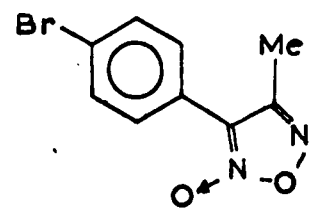
The C-C bond length in benzene[15] is 1.397Å so that the bonds C(33)-C(32), C(32)-C(31), C(31)-C(36) and C(36)-C(35) with a mean length of 1.44Å correspond more closely to the 'single' bond in quinone[16] (1.467Å) and the C-C bond in glyoxime[17] (1.449Å).

In the furazan rings, the mean C=N, N-O and intracyclic C-C bonds are 1.33, 1.39 and 1.43Å respectively, which compare with the corresponding average distances over the red compound, the light green compound and benzotrifurazan of 1.323, 1.408 and 1.437 and with 1.300, 1.380 and 1.421 for furazan[22] itself. Benzofurazan[18] is the only other reported aromatic furazan structure (1951 , solved in projection, space group Pa). The distances for C=N and C-C (1.35, 1.43Å) are in tolerable agreement with those recorded here , the N-O distance (1.20Å) is somewhat shorter.

The C=N bond lengths of the rings are in agreement with those of xanthazole[19] monohydrate (1.33Å) but better comparisons are found in recent structures of benzotrifuroxan[20] (mean 1.329Å) and the 5 N-oxide of 4 methyl,3(p-bromophenyl),1,2,5-oxadiazole[21] (I,II) where the mean C=N bond length is 1.314Å . The C=N bond length in glyoxime[17] is 1.284Å



(I)



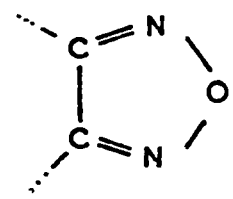
(II)

The N-O distance (1.408Å) in these systems is less well documented. The corresponding bonds in furoxan systems are non-equivalent. In benzotrifuroxan[20] the mean trigonal nitrogen N-O and the exposed nitrogen N-O bond lengths are 1.476 and 1.389Å respectively and compare with

corresponding average distances (1.432, 1.371Å) in the systems (I,II). The N-O distance in the simple furazan[22] is 1.380 and glyoxime[17] is 1.397Å.

From a consideration of the bond orders in the furazan rings (figure 18) and from a comparison with the C=N bond length in glyoxime it is clear that a large proportion of the π electron density is concentrated between the carbon and nitrogen atoms. The N-O bond is practically a single bond; the mean N-O-N bond angle in the red compound is 112° which is closer to the angle expected for an sp^3 hybridisation than an sp^2. With sp^3 hybridisation the two oxygen (p) lone pairs will be inclined at an angle to, and away from, the π system of the rest of the molecule. There is some π density in the region of the intracyclic C-C bond, but the mean bond order (0.47) is similar to the order in butadiene (0.477)[14].

The structure of a furazan ring, therefore, is best written as (III),



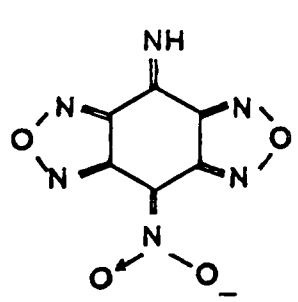
(III)

The whole of the nitro group of the red compound has a high π density, the two N-O bonds are equivalent (mean length 1.27Å) within three e.s.d.'s and are similar to those of p-nitroaniline[23] (1.29, 1.25Å). The N-OH and N-O bond lengths in nitric acid[24] are 1.41 and 1.22Å respectively. The C-N bond of this group (1.36Å) is short compared to the corresponding bond (1.49Å) in the yellow compound which must be a single bond (p.75).

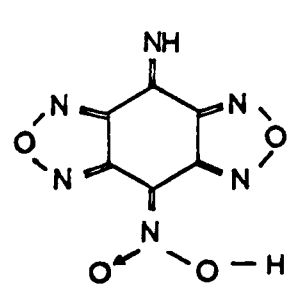
The imino nitrogen bond length of 1.21Å is exceedingly short (the carbon to nitrogen bond in CH_3CN is[25] 1.157Å) and suggests that a (p) lone pairs of the nitrogen atom is interacting strongly with the π system of the rest of the molecule.

From the bond orders over the whole heterocycle it appears that the molecular π electrons are almost divided into two portions, with the imino C=N bond forming a separated system.

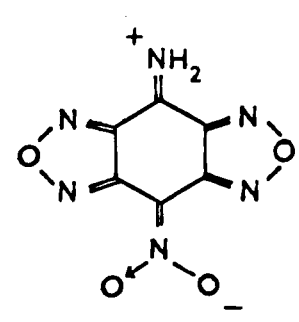
The bond lengths (and bond orders) are in agreement with a structure (IV) rather than the structure (V) or (VI).



(IV)



(V)



(VI)

The crystal structure of triphenyl phosphine oxide has not yet been reported, the structure of triphenyl phosphine[26], however, is known where the average P-C bond lengths are 1.828Å. The mean P-C bond length in the phosphine oxide of the red compound is 1.78Å and both this bond and the phenyl C-C bond have lengths within the range of acceptable values (p. 81)

The P=O bond length is significantly longer (1.64Å) than a similar bond[27] in $(EtO)_3PO$ (1.44Å)[28] and $(PhO)_3PO$ (1.43Å). Since the benzotrifurazan

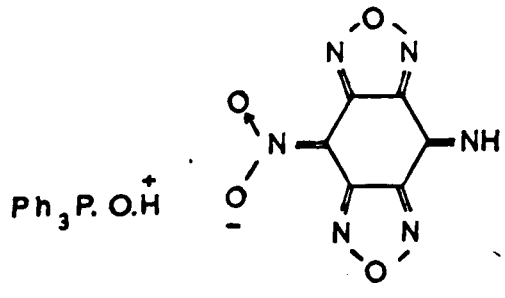
fragment is written as an anion (IV) it is thought by analogy with amine oxides that the phosphine oxide is protonated (VII).

$Ph_3P.OH^+$

(VII)

Salt like crystalline adducts: $Ph_3POH^+\ OH^-$ and $R_3POH^+\ Br^-$ have been prepared.[29,30]

The distance P(1)-O(2) is 3.01Å which is short for a non-bonded contact distance, but rather long for an O...H...O hydrogen bond.[31] As the nitro N-O bonds are equivalent, the red compound is probably the ion pair (VIII).

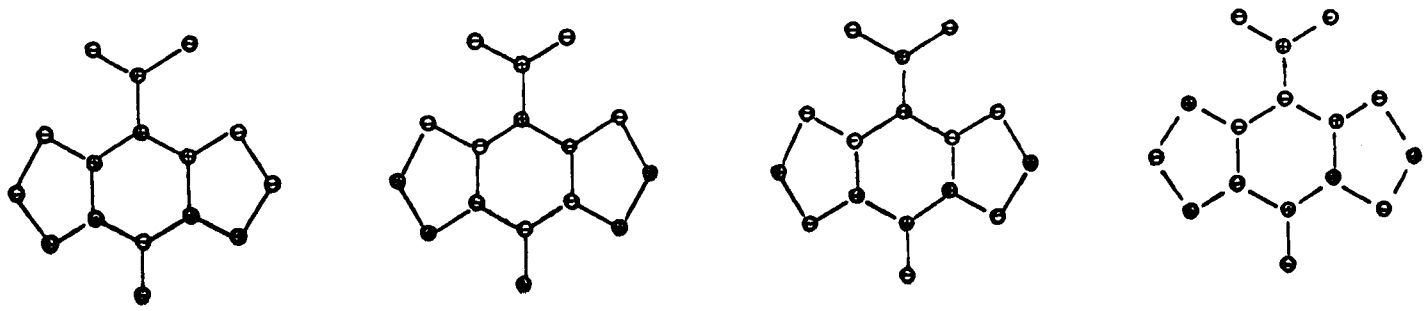


(VIII)

The shortest planar separation between two molecules of the heterocycle is 3.25Å, the projection of one onto the least squares best plane of the other is shown in figure 4. $Ph_3POH^+\ OH^-$ is colourless and it seems likely that the red colour of the compound is caused by intermolecular charge transfer between the heterocyoles. The UV and visible

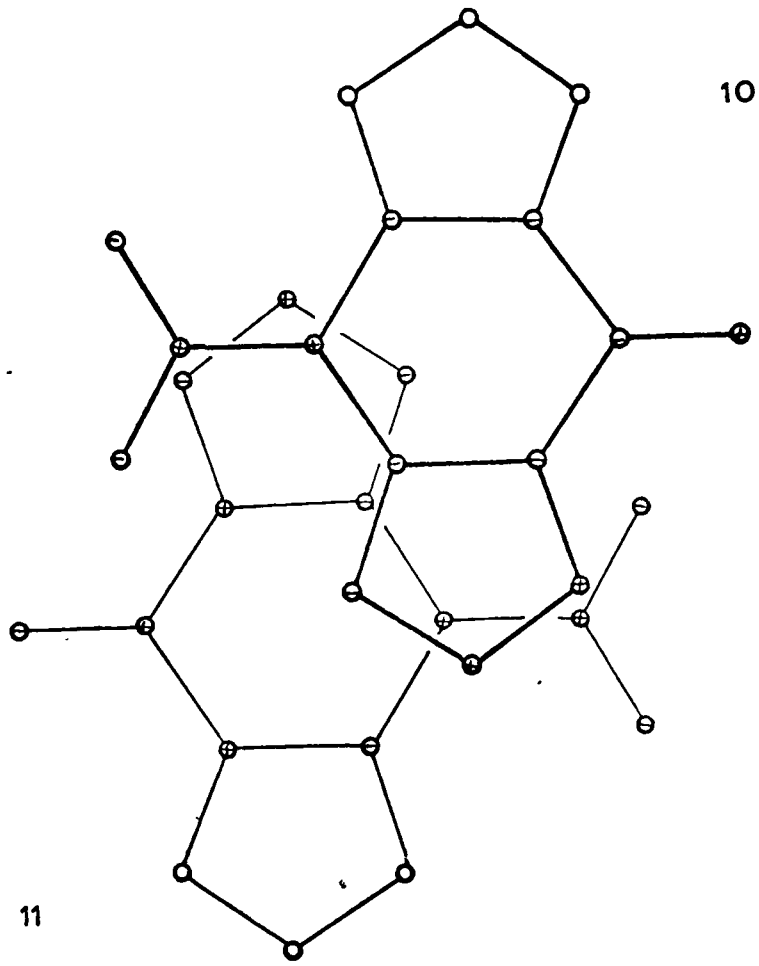
spectrum has a smooth broad based absorption band (typical of charge transfer) with a maximum at 4820Å.

The simple Huckel calculation for the heterocycle of the red compound is given in Appendix (IV). Figure 19 shows the polarities of the atomic orbitals of the two highest energy filled and lowest energy unfilled molecular orbital (there are 10 bonding orbitals). Figure 20 shows the polarities in the region of the overlap of the two molecules for the orbital 10 and 11. It can be seen that the polarities match closely and that consequently charge transfer is at least possible.



9 10 11 12

Figure 19



10

11

Figure 20

The light green compound

The bond orders are given in figure 21, details of the bond lengths and bond angles can be found on p. 31, 202

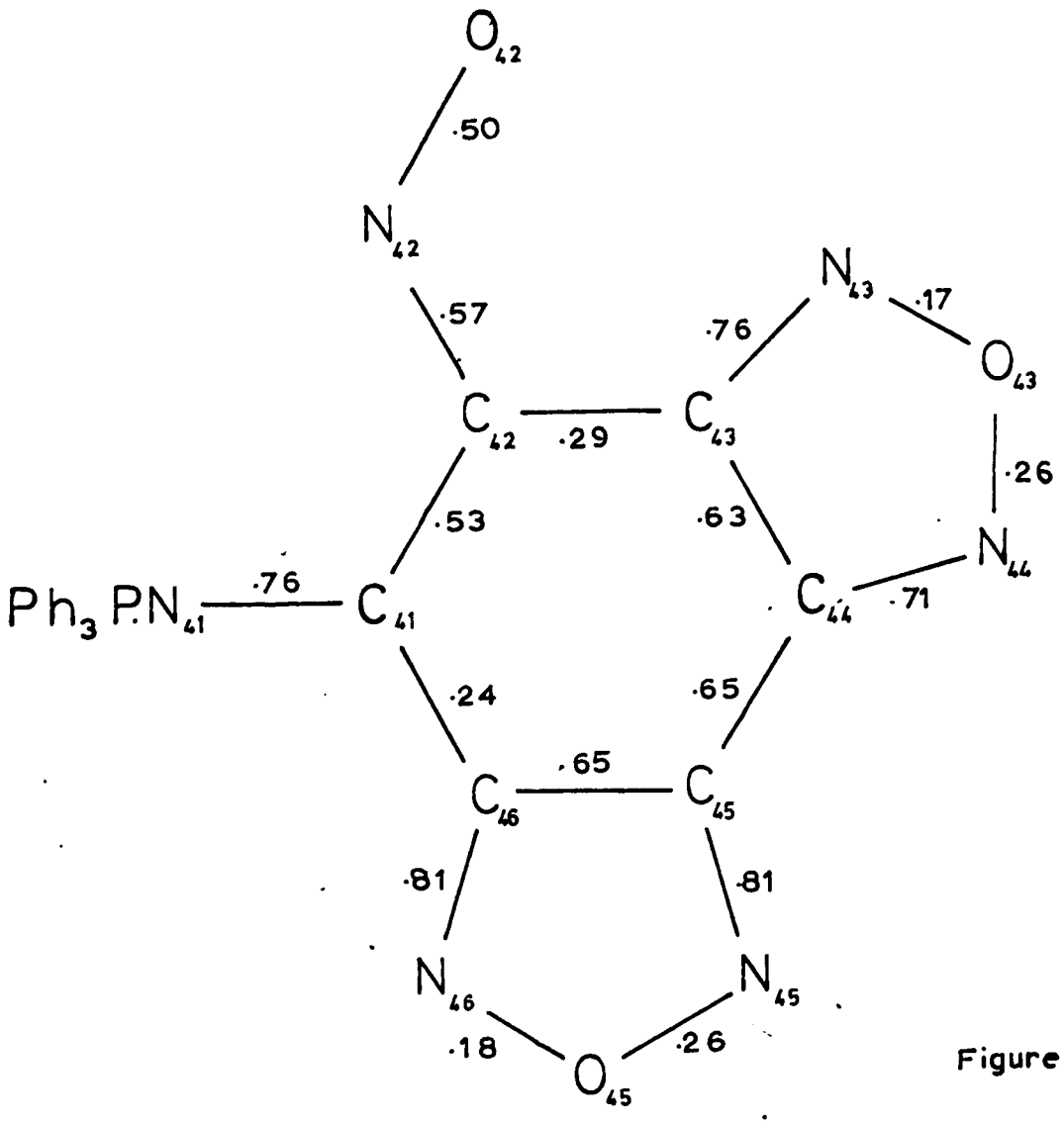
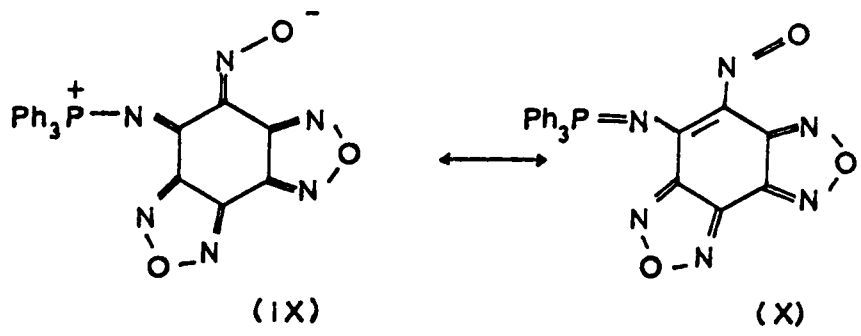


Figure 21

There is no significant difference between the bond lengths of the intracyclic N-O and C=N bonds of the red and green compounds, though the mean C=N distance is slightly shorter (1.318Å) in the green compound. The bonds C(43)-C(44), C(44)-C(45) and C(45)-C(46) with an average length of 1.41A are closer to those of benzene[15] (1.397Å) than the single bonds of quinones[16] (1.467Å). This, together with the fact that 1,2,3,4-benzodifuroxan (and can consequently the difurazan) can

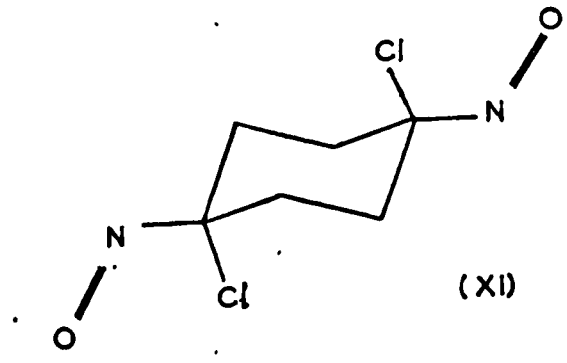
be prepared[32] while 1,2,4,5-benzodifuroxan cannot,[33] suggests that the two adjacent furazan rings together form a delocalised π system.

The longer lengths (1.46, 1.47A) of the bonds C(42)-C(43), C(41)-C(46) and the shorter length (1.42Å) of bond C(41)-C(42) indicates a tendency toward a double bond for C(41)-C(42), while the short N-O bond length and the relatively longer C-N length (1.27, 1.36Å) of the nitroso group suggests a similar tendency in the N-O bond. The molecule can be written in two forms:



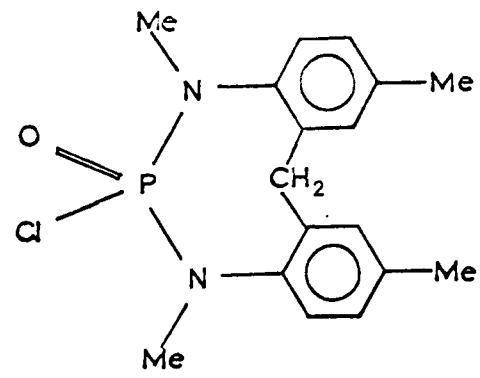
(IX) (X)

The structure of nitrosobenzene has not been reported, but the N-O and C-N bond lengths in 1,4-dichloro-1', 4' dinitrosocyclohexane[34] (XI) are 1.20 and 1.39Å respectively, which suggests that form (IX) predominates in the molecular structure.



(XI)

The P-N bond (1.63Å) is longer than the average phosphorus to nitrogen distance of 1.57Å for $(PNCl_2)_3$[35] and 1.56Å for the yellow compound. It is comparable, however: with the P-N distances (1.64, 1.65Å) in:



where the nitrogen atoms deviate[36] by less than 0.1Å from the planes of the three atoms bonded to them. This too is in agreement with form (IX).

The phenyl C-C bond lengths are within the range of acceptable values as are the mean P-C distances (1.79Å).

In the crystal, the minimum plane to plane separation of two heterocycles is 3.5 - 3.6Å so there is little opportunity for intermolecular charge transfer and the green colour is probably caused[37] by the $n-\pi^*$ (N) transition in the nitroso group.

The yellow compound

The bond orders of the benzotrifuroxan residue are given in figure 22, details of bond lengths and angles will be found on p.45, 208.

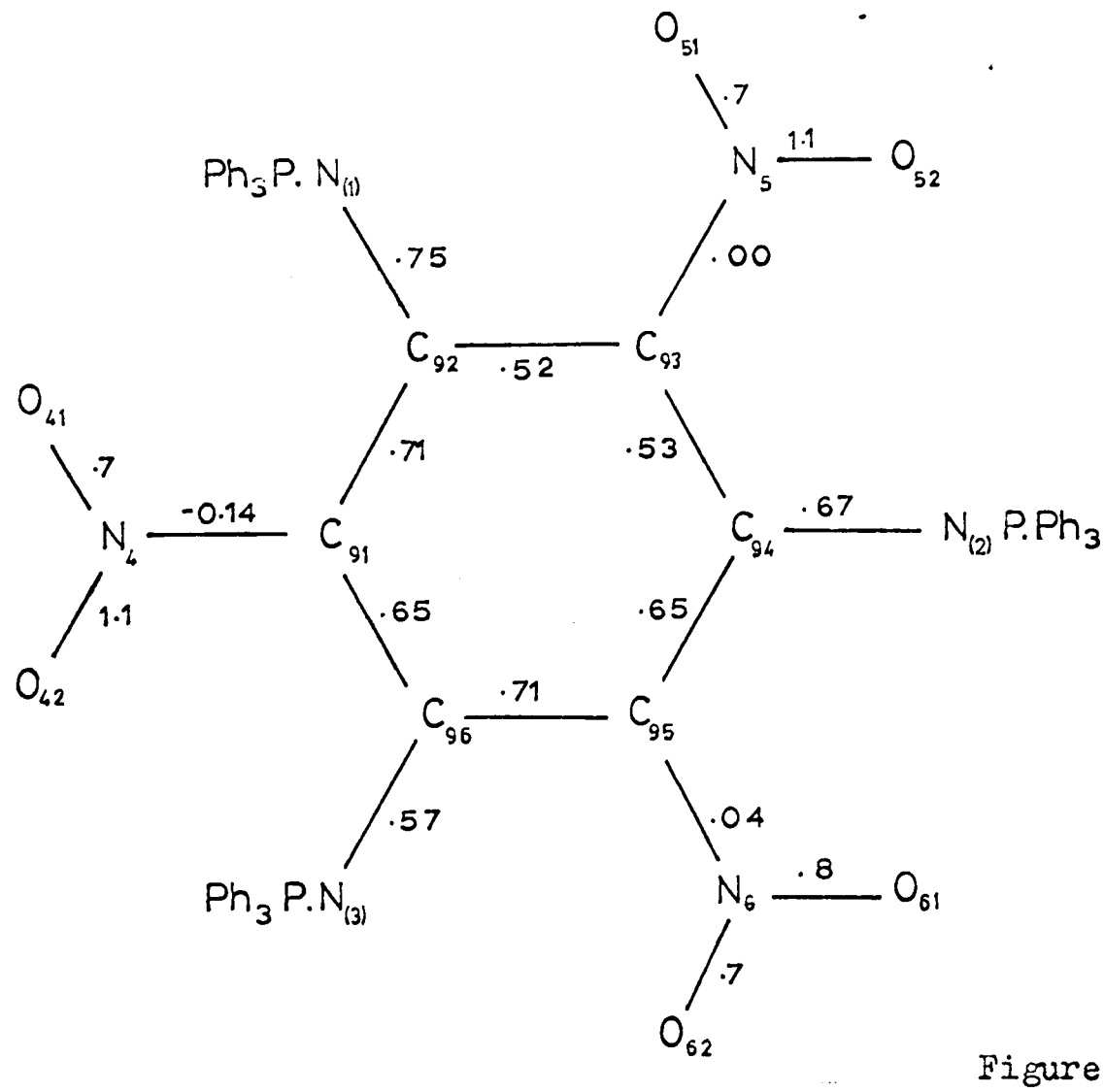
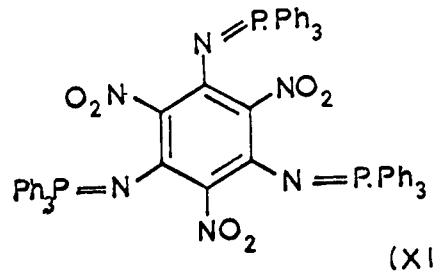


Figure 22

In the central C_6 ring the C-C bond lengths (mean 1.405Å) are benzenoid,[15] the planes of the nitro groups are approximately perpendicular to the plane of this ring and the nitro C-N bonds (mean 1.49Å) are single bonds, (it is reassuring to observe that the bond orders, calculated from the observed lengths, are around zero). The nitro N-O distances (mean 1.205Å) are within the range of expected values.[31]

The P-N bond lengths (1.54, 1.55, 1.58Å) are shorter than the average phosphorus to nitrogen distance of 1.59Å in $(PNCl_2)_3$[35] and 1.62Å at the phosphorus atom bonded to the phenyl groups[38] in gem, $P_3N_3Cl_4Ph_2$. The average C-N-P angle is 137° which is distorted from the 120° of sp^2 hybridisation by a $p_\pi - d_\pi$ interaction between the nitrogen lone pair and an available (d) orbital on the phosphorus. (The corresponding angle in the light green compound is 130°.)

The nitro π electrons can not interact with the π-system of the rest of the molecule and with the short P-N bond length, the yellow compound can only be written in one reasonable form (XII), which explains the differences between the corresponding bonds in the yellow and green compounds,



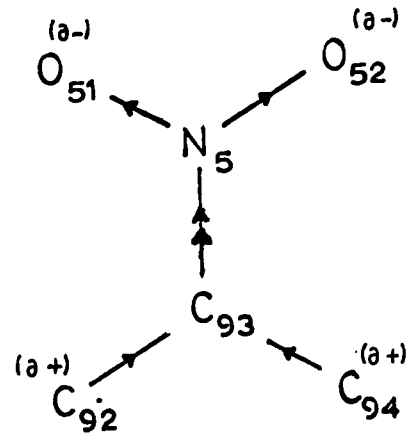
(XII)

never the less, there is considerable conjugation of the phosphimino C-N bonds for their lengths (1.32, 1.34, 1.36Å) are close to those of the furazan ring and it is possible that the molecular π system covers not only the central C_6 ring, but through[39] the (d) orbitals of the phosphorus atoms, the phenyl groups as well, with these phenyl

groups feeding electrons towards the centre. The mean P-C bond (1.809Å) is marginally longer than the equivalent bond in the red and light green compounds (1.78, 1.79Å) but the mean C-C bond (1.397Å) is precisely that expected for a benzenoid system so that it is difficult to judge the extent of the π delocalisation.

The central ring is seriously distorted; the average C-C-C angles at the nitro and phosphimino groups are 127° and 113° respectively. Similar angular distortions in nitro substituted benzenoid systems have been observed,[40] and for these it was suggested[41] that the cause was $\sigma-\sigma$ bond repulsions rather than π interactions. In the yellow compound there is no possibility of π interactions and since there are no abnormally short contacts between the nitro oxygen and neighbouring atoms (C(22)-O(42) is the shortest contact (3.05A), but almost all the other close approaches are in the range 3.2 - 3.5Å), $\sigma-\sigma$ bond repulsions are the most plausible explanation of the distortion.

The N-O bonds of the nitro group will be polarised and this will cause a marked polarisation of the C-N bond (XIII).



(XIII)

The shift of (σ) electrons toward nitrogen in the C-N bond will reduce the $\sigma-\sigma$ electron repulsions between the bonds: C(93)-N(5), and

C(93)-C(92), C(93)-N(5) and C(93)-C(94) but not between C(92)-C(93) and C(93)-C(94). The effect is to apply a 'clockwise' couple on the bond C(92)-C(93) and an 'anticlockwise' couple on C(93)-C(94) which will open out the angle C(92)-C(93)-C(94) from 120°.

The blue compound

The bond orders are given in figure 23; details of bond lengths and angles will be found on p.58, 220.

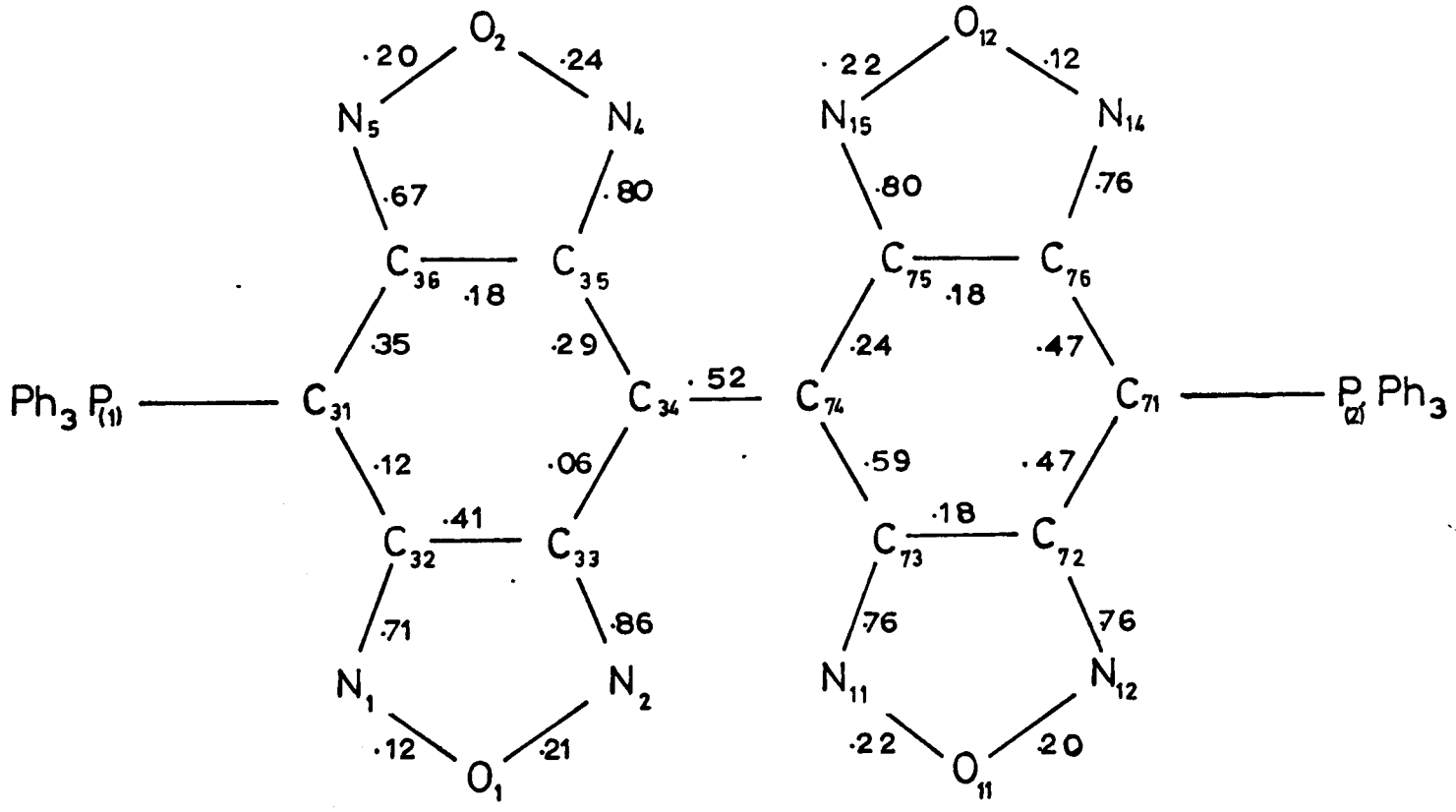


Figure 23

The central difurazan heterocycles are distorted[42] from the plane. The central C_6 rings are in boat conformations, with C(31), C(34), 0;25, 0.34A above, and O(1), O(2), 0.54, 0.65Å below the plane through C(32), C(33), C(35), C(36) and with C(71), C(74), 0.26, 0.30Å above and O(11), O(12), 0.63, 0.62Å below the plane through C(72), C(73), C(75), C(76). The two 'boats', inverted one with respect to the other are joined at C(34)-C(74). Schematically, the molecule is shown in figure 24 (see also, p.56)

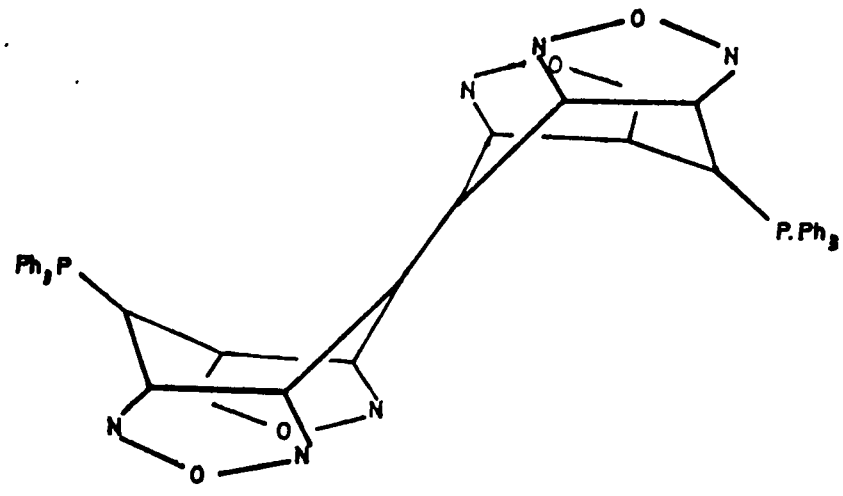
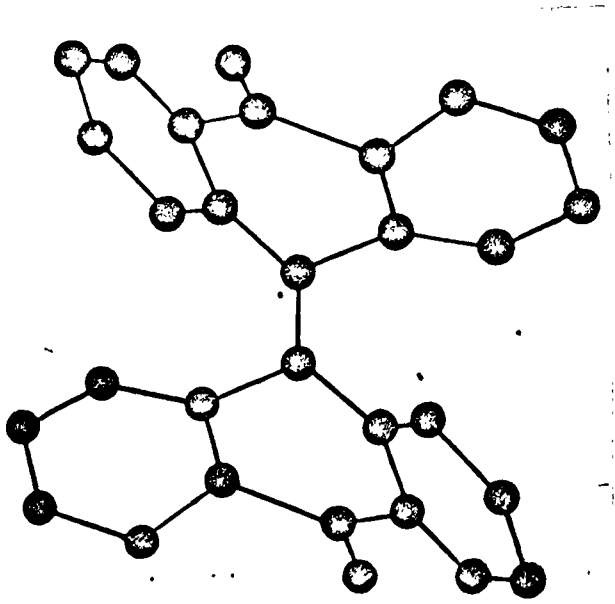


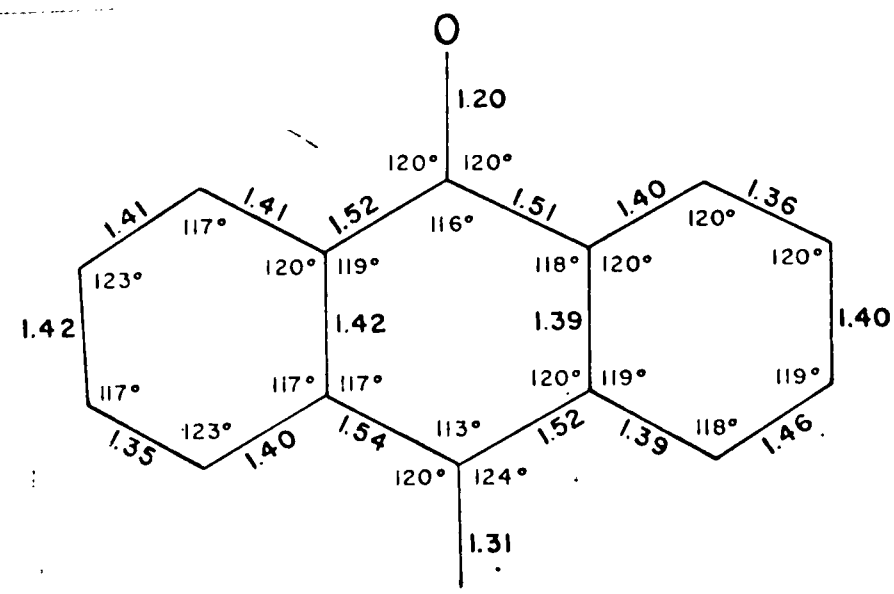
Figure 24

There is a good precedent for such deformation amongst the

structures of 'overcrowded aromatic compounds' and one such compound (dianthronylidene)[44] has the same distortion (figure 25a) as the blue compound.



(a)



(b)

Figure 25

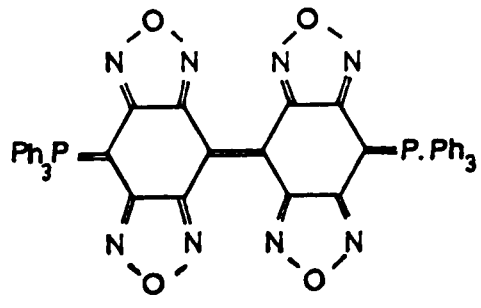
Although the R factor for the blue compound is 10.9%, the interatomic distances in the central C_6 ring initially present little coherent pattern. The mean C=N and N-O bond lengths (1.319, 1.397Å), however, are comparable with those in the furazan rings of the green compound, the red compound and benzotrifurazan (p. 66). It appears that the deformation of the C_6 rings does not interfere with the π system of the heterocyclic rings, particularly as throughout the difurazan substrates the trigonal carbon atoms deviate[42] by less than 0.06Å (mean 0.038Å) from the planes of the three atoms bonded to them.

For dianthronylidene[44] it was concluded that the molecule consisted: "of a central ethylenic group attached by single bonds to a normal benzene ring which in turn were linked by single bonds to the carbonyl group", (figure 25b). Similarly, the blue compound can be thought to consist of a central ethylenic group linked by quinone type single bonds (1.467Å) to furazan rings which in turn are attached to phosphoranes by similar single bonds (XIV).

The mean furazan intracyclic C-C bond (1.47A) is comparable with the corresponding bond (1.46A) in benzotrifurazan, the bond C(34)-C(74), (1.42Å) is one of the shortest of the system and of the remaining bonds C(71)-C(72) and C(71)-C(76) at 1.43Å have probably been determined shorter than they should be (see below).

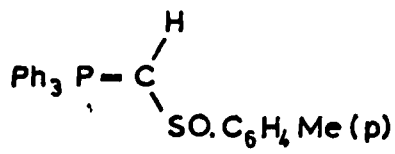
The phosphorus P=C bonds (1.71, 1.77Å) appear to be non-equivalent. The author can see no justification for this and suspects that the anomaly is caused by blocked matrix refinement of a large acentric

structure. The mean phenyl P-C bond lengths are not significantly different in the two phosphine groups (P(1)-C, P(2)-C, 1.817, 1.816Å) so that either C(31) or C(37) has refined into a slightly incorrect position.

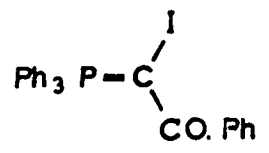


(XIV)

The evidence for the expected length of a P=C bond is conflicting. The P=C bond[6] in the dark green compound is 1.77Å but in both the Wittig intermediates XV, XVI,[46,47] is 1.71A. The suggested distance for P-C single[48] and triple[49] bonds are 1.843 and 1.542Å which by interpolation give a phosphorus to carbon double bond of 1.697Å. Pauling suggests 1.665Å.[50]



(XV)



(XVI)

The balance of the evidence is weighted in favour of the shorter P=C bond length of $\approx$1.71Å, in which case the co-ordinates of atom C(71) in the blue compound are incorrectly determined and this would be in agreement with formula (XIV).

Refinement at a late stage of the analysis with the co-ordinate of the two phosphorus atoms and the atoms of the benzotrifuroxan residue in the same matrix block failed to alter the P=C distances. A better experiment would have been the refinement of the trial structure with the parameters blocked in this manner. In terms of the computer time required, such a refinement is very expensive (30 - 40 hours) and has not yet been done.

The phenyl mean P-C and C-C bond lengths (1.816, 1.408Å) are within the range of acceptable values.

The blue compound, unlike dianthronylidene[44], is not obviously pyrochromic and with no UV and visible spectrum it is impossible to reach any conclusion as to the source of the colour.

Phase analysis

In the 'heavy atom method', the contribution from the heavy atom dominates the structure factors of the crystal, so that the true phases (α) of the structure factors will not differ greatly from the phases (α_H) due to the heavy atom alone.

Phosphorus is the heaviest atom in any of the structures discussed here and since its scattering power is six times that of

carbon and less than four times that of oxygen, the phosphorus contribution would not be expected to dominate the structure factors.

If there are (N) atoms in the unit cell of a centrosymmetric crystal and (Q) atoms in a partial structure, then the proportion (P) of correctly determined phases from the contribution of the partial structure can be related[51] to a function (σ^2), where:

$$\sigma^2 = \sum_{i=1}^{Q} f_{Qi}^2 \Big/ \sum_{i=1}^{N} f_{Ni}^2$$

and (f) is the scattering factor(at a Bragg angle of 40°).

This relation is shown in figure 26, for a partial structure with

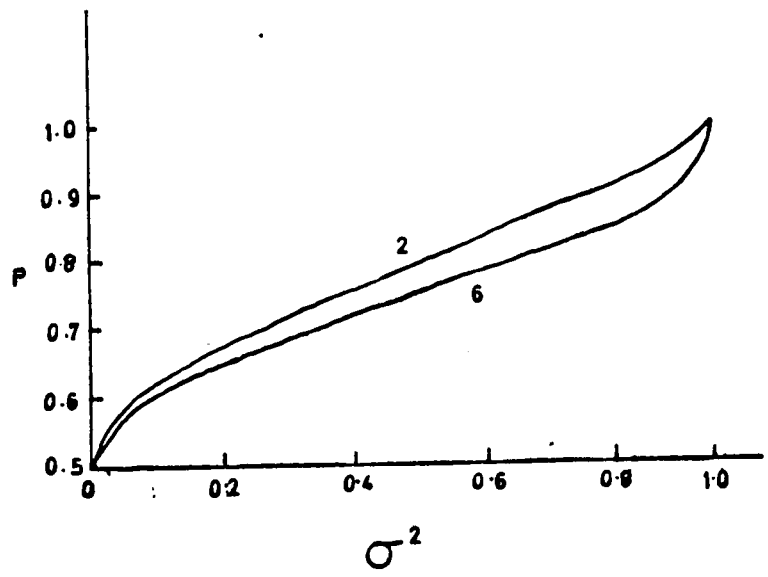


Figure 26

two and six heavy atoms in the unit cell. Table 4 gives the theoretical and the observed proportion (P) of correct phases for the red, light green and yellow compounds with contributions to the structure factors in each case from the phosphorus atoms alone.

Compound	P(theoretical)	P(obs.)
Red	0.63	0.79
Light green	0.64	0.76
Yellow	0.66	0.80

Table 4

There is a large discrepancy between the predicted and observed values of (P). The relation between (σ^2) and (P) appears only to hold when the heavy atom (or atoms) concerned is not at the centre of an approximately spherically symmetric environment of light atoms.

The phosphorus atom, surrounded by phenyl carbon atoms is at the centre of such an environment and clearly the contributions to the phases from these light atoms is similar to the contribution from the phosphorus atoms alone.

If the function (σ^2) is modified to include the scattering matter from the first two concentric spheres of light atoms around the phosphorus atoms ($P(C_3)_4$), then the value of (σ^2) is $\approx$ 0.40 and and P(theoretical) has the corresponding value of $\approx$ 0.75.

Theoretical phase predictions have also been made[52] for the acentric case, where (P_a) is the proportion of phases within a given number of

degrees of the correct value.

The relation between (P_a) and (σ^2) for phase discrepancies not greater than 30°, 60° and 90° is given in figure 27.

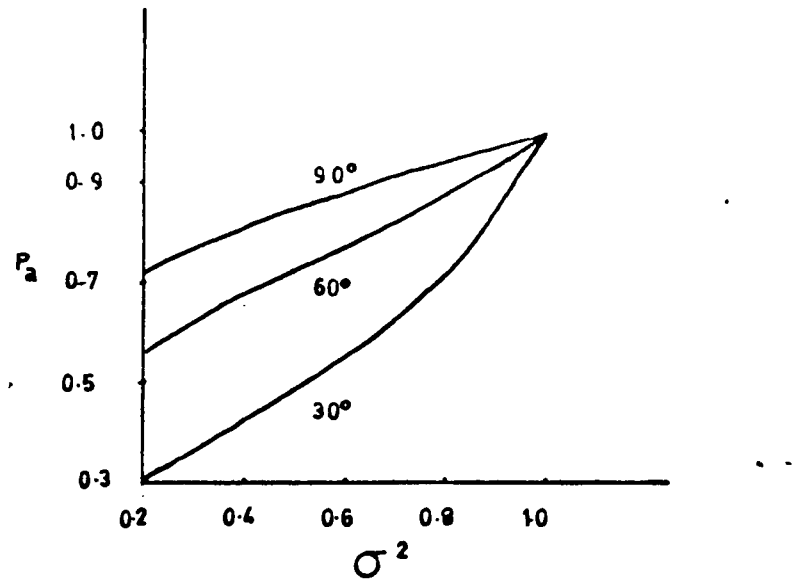


Figure 27

Table 5 shows the theoretical and observed values of (P_a) for the blue compound with contributions to the phases from the phosphorus atoms only

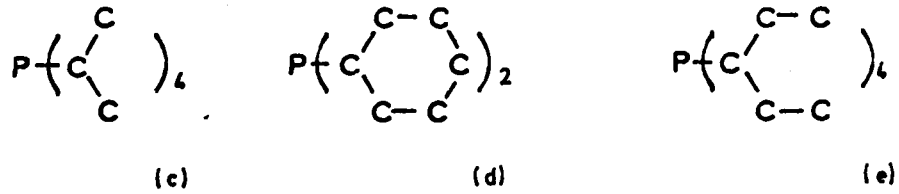
	P_a(theoretical)	P_a(obs.)
Within 30°	0.28	0.49
Within 60°	0.54	0.71
Within 90°	0.70	0.82

Table 5

The proportion of phases correct within the limits is much higher

than expected, and in the case of the blue compound, which is based upon a $P(C_6)_4$ unit, the development of P_a(obs) has been examined as the number of atoms in the partial structure is increased.

Figure 28 shows the proportion of phases that are correct within progressive intervals of 10° between 0° and 180° for the partial structures: 2P, (a); $2P(C)_4$, (b); $2P(C_3)_4$, (c); $2P(C_6)_2$, (d); $2P(C_5)_4$, (e); 2P, (f).

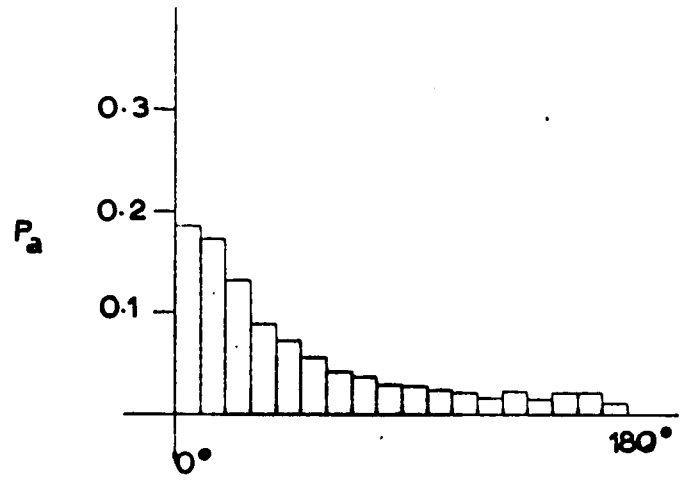


(c) (d) (e)

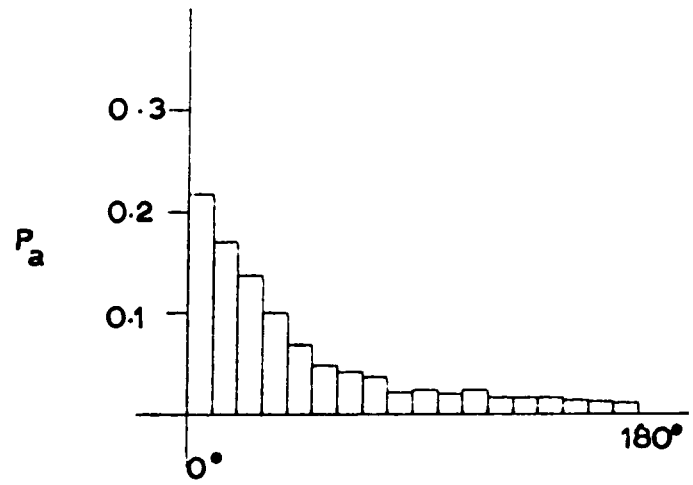
The proportion of phases determined correctly within a tolerance of 30°, 60°, and 90° is given in table 6.

	30°	60°	90°
2P	0.49	0.71	0.82
$2P(C)_4$	0.52	0.74	0.84
$2P(C_3)_4$	0.62	0.83	0.90
$2P(C_6)_2$	0.59	0.80	0.89
$2P(C_5)_4$	0.72	0.88	0.94

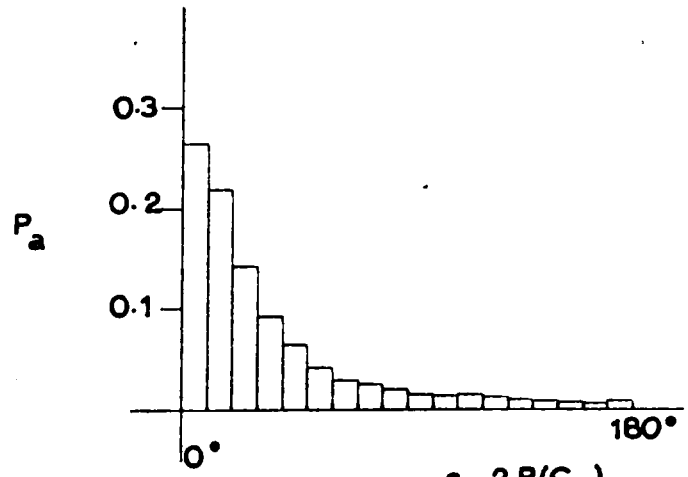
Table 6



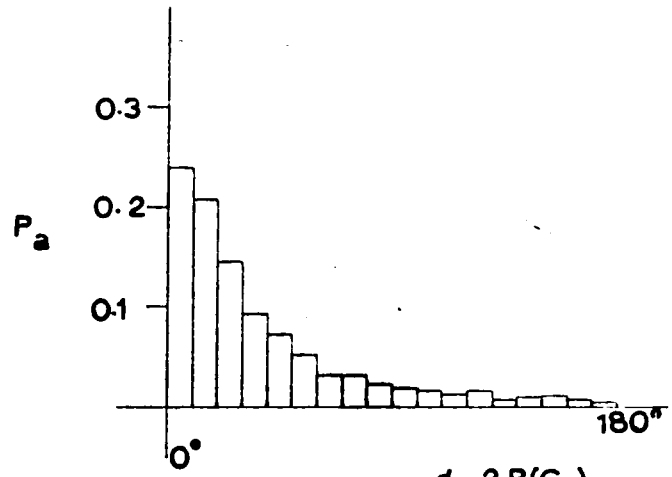
a. 2P



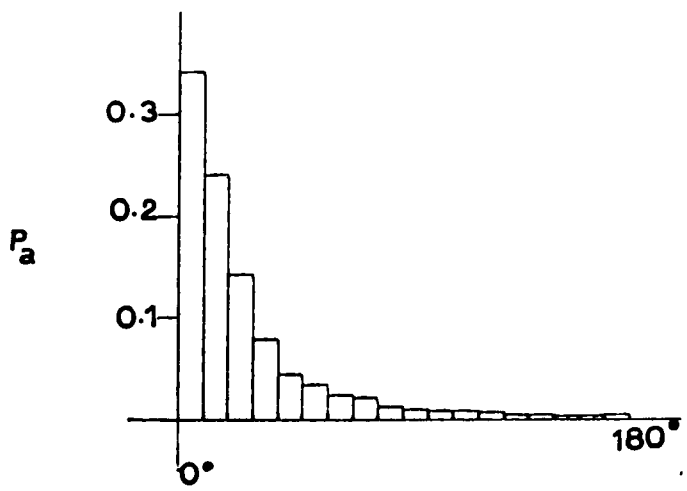
b. $2P(C)_4$



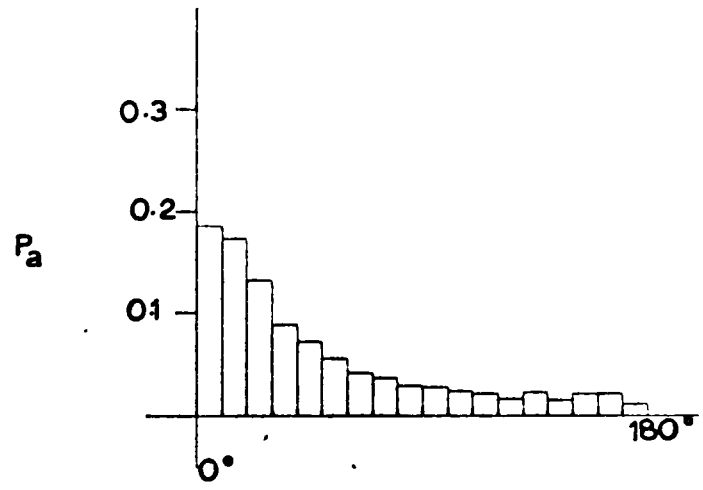
c. $2P(C_3)_4$



d. $2P(C_6)_2$



e. $2P(C_5)_4$



f. 2P

The total scattering matter in the spherical environment $2P(C_3)_4$ is the same as in the non-spherical environment $2P(C_6)_2$ and as expected the proportion of phases correctly determined within the lower limits is higher for the spherical environment than for the non-spherical.

A series of phase analyses were carried out which observed the value of (P_a) for the partial structure of phosphorus atoms alone in various ranges of the absolute value of the structure factors for the whole structure.

It was discovered that, apart from some of the very weak structure amplitudes, the phases from the trial structure in poor agreement with the correct values were equally distributed among the ranges.

Another similar series of phase analyses observed (P_a) over various ranges of $|(|F_o| - |F_c|)|$* of the phosphorus phased calculation. Again, apart from those with a very weak (F_o), the large phase discrepancies were well distributed among the ranges.

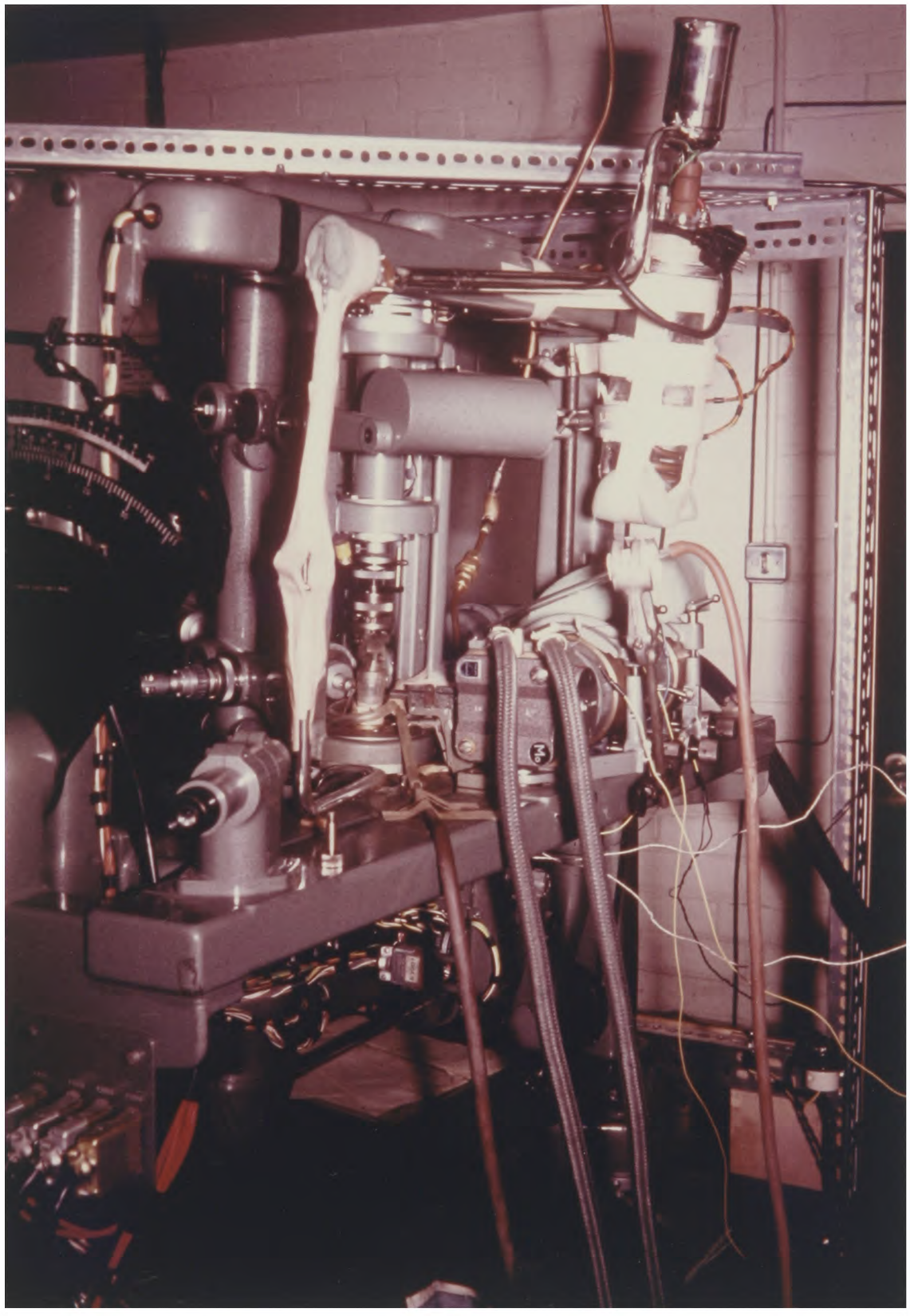
It seems, therefore, that any weighted Fourier series would have been little help for the determination of this structure. The weak observations could have been usefully removed, and this had been done as the normal routine.

* The function : $|(|Fo| - |Fc|)|/(|Fo| + |Fc|)$ was observed.

CHAPTER 2

The molecular complex of triethyl phosphate with benzotrifurazan

PLATE 2



Linear diffractometer fitted with the low temperature attachment

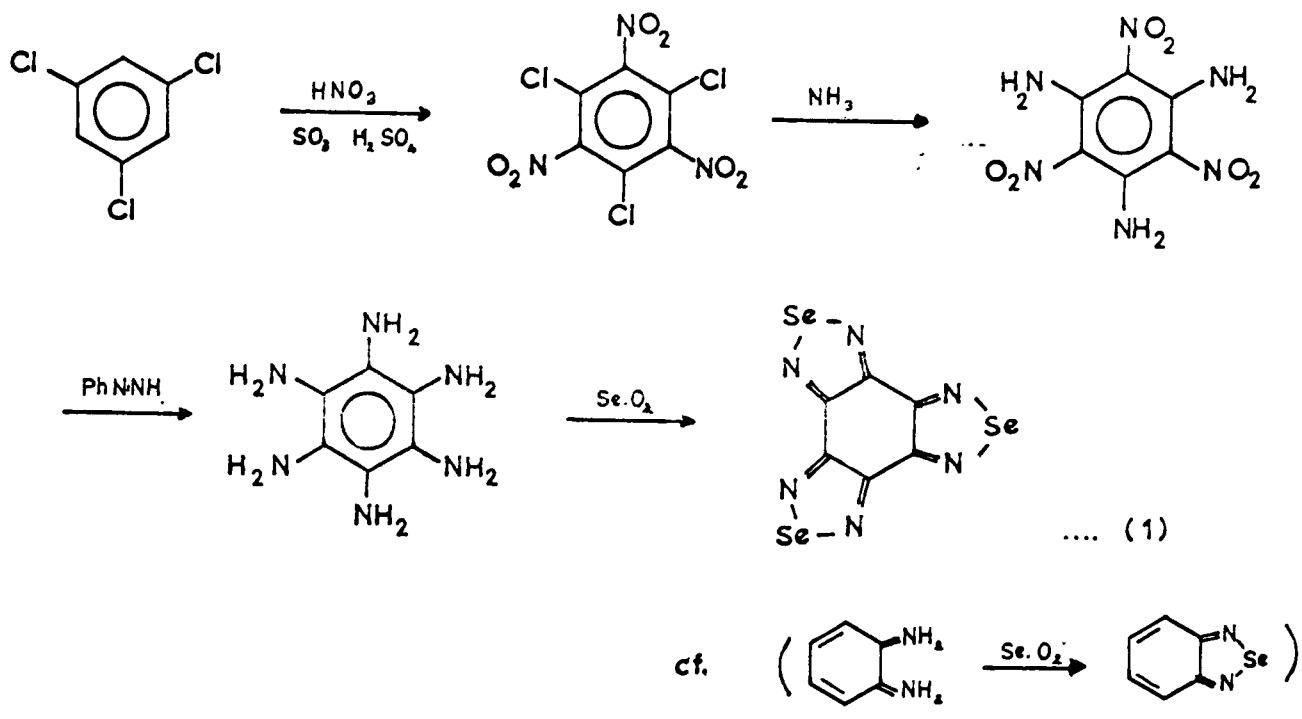
INTRODUCTION

The 1:1 complex of benzotrifurazan with triethyl phosphate is separated[53] as colourless needles from the reduction of benzotrifuroxan by triethyl phosphite in benzene solution. The crystals are easily purified by sublimination and are highly deliquescent.

Molecular weight determinations suggest[54] that the component molecules remain associated in solution, and shifts of the order -20 cm^{-1}. have been observed[53] in the P=O stretching frequency. However, the visible and U.V. spectrum of the complex is the sum of the spectra of the components so that there is no spectroscopic evidence for intermolecular charge transfer.

In order to resolve the question of the nature of this complex, three-dimensional, X-ray, Weissenberg data were collected at room temperature and a structure analysis attempted.

The X-ray diffraction patterns showed thermal diffuse scatter and a sharp temperature cut off at a Bragg angle of 40°. The diffraction patterns defied detailed interpretation. After many unsuccessful attempts to solve the structure analysis by Patterson methods, molecular transforms, direct methods in projection (Kilean projection)[55] and an attempt to make the selenium analogue of benzotrifurazan (1), the opportunity was provided to examine the complex at low temperatures.



Growth and mounting of crystals

The room temperature data had been collected photographically with an exposure time of four days and with Cu-K_α radiation.

The use of a linear diffractometer, fitted with a low temperature attachement was loaned for a short period*. With this instrument it was necessary to use MoK_α radiation, but the sample of the complex contained no crystals of a suitable size for such an X-ray source. Simple recrystallisation failed to produce any larger crystals, but it was found that if the crystals were sealed in contact with saturated solution (solvent 40/60 petroleum ether) and every few hours the temperature alternately raised and lowered between 5°C and 25°C; then the larger crystals in the sample grew at the expense of the smaller.

Two suitable crystals were grown by this method over a period of

*Our thanks to Professor Dorothy Hodgkin

three months.

Triethyl phosphate is a liquid (m.pt. -52°C) and as a solvent possesses much the same ubiquity as dimethyl sulphoxide. Although the two components of the complex appear to be strongly associated, any attempt to mount the crystal with shelac or some type of cement causes the phosphate ester to dissociate from the benzotrifurazan and dissolve the mounting.

The hygroscopic crystals had to be mounted in Lindermann glass capillaries, and for room temperature photography it was sufficient to wedge the crystals against the walls of the tube, but the coefficient of expansion was greater for the glass than for the crystal so that on cooling to -120°C the fragile crystals splintered.

Lindermann glass capillaries are not of uniform bore, being narrower in the middle than at the ends. A portion of a 1 mm. bore tube with the narrower bore was cut into two pieces, the ends of these pieces gently curled over in a flame, and they were then cracked, on one side, longitudinally (figure 1a).

One of the two pieces was introduced into the remaining (larger bore) fragment of the capillary and the crystal then inserted with the second piece to hold it in place (figure 1b). The ends of the



(a) (b) Figure 1

outer capillary were then sealed so that they held the inner capillaries firmly. The longitudenal cracks in the inner tubes allowed the glass to expand and contract without putting too much pressure upon the crystal.

Low temperature attachment

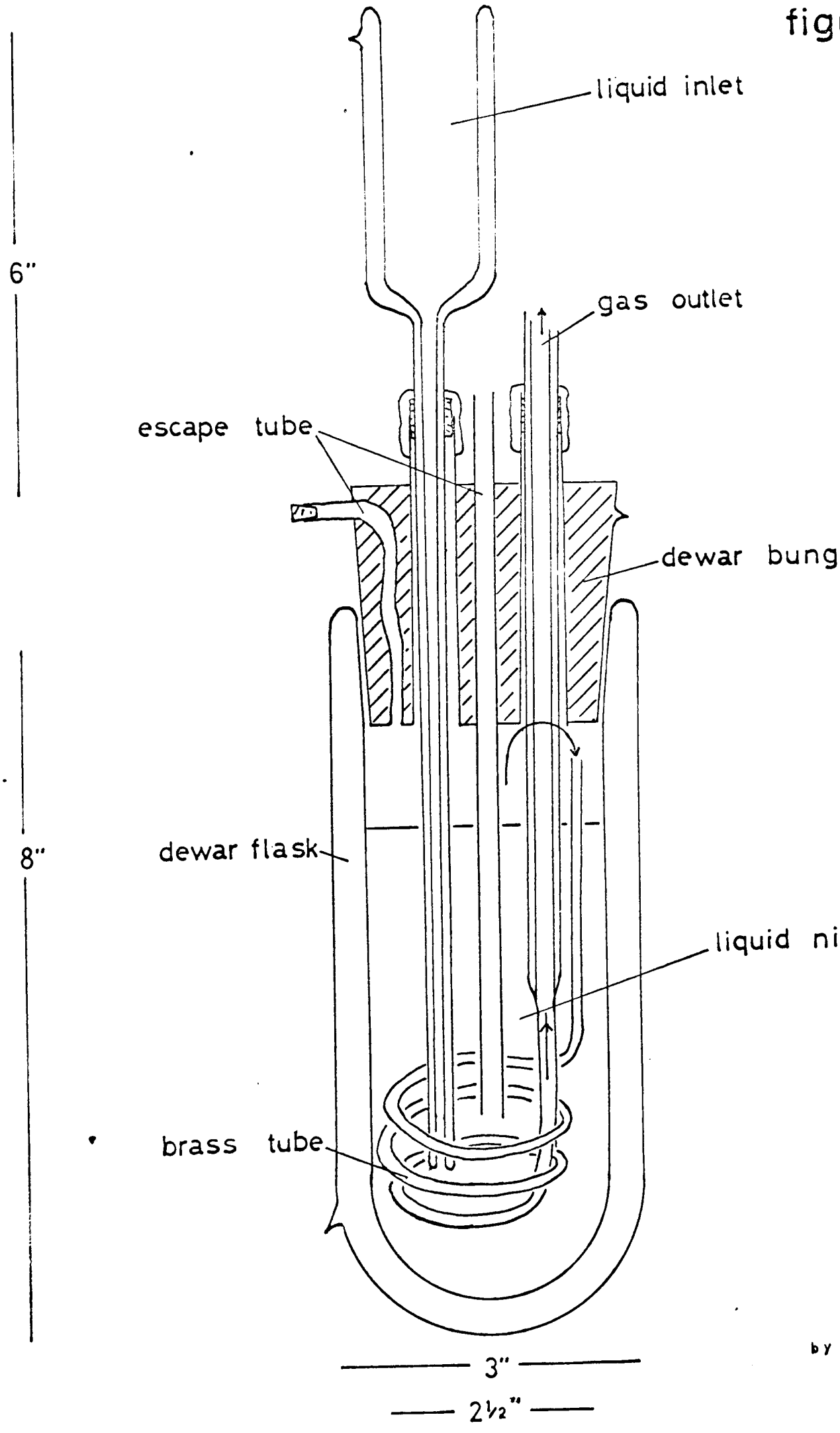
The crystal was cooled by placing it in a stream of nitrogen which had been generated from a source of liquid nitrogen (plate 2). The liquid gas, contained in a Dewar flask*, was allowed to boil under the action of conducted and radiant heat from the room; the gas was then passed in a copper coil back through the liquid (figure 2). The flask was attached to one of the uprights of the cradle of the linear diffractometer (figure 3); the escaping gas was passed along dewar tubes to the bottom of the cradle and up through a hole beneath the crystal.

The crystal was mounted in plasticine in a brass cup that was screwed onto a goniometer head, and fastened to the cup was a brass collar. Around the collar was a milar sleeve, frilled at the lower edge, which projected downwards over the end of the dewar tube coming upwards.

Around the outside of the sleeve was a brass tube coming upwards from underneath which was fixed to an air supply and resting on the

*The dewar was designed[56] by Dr. Viswamitra but had never been used successfully for a structure analysis.

figure 2



by courtesy :

Viswamitra

Low temperature attachment (schematic) on the linear diffractometer

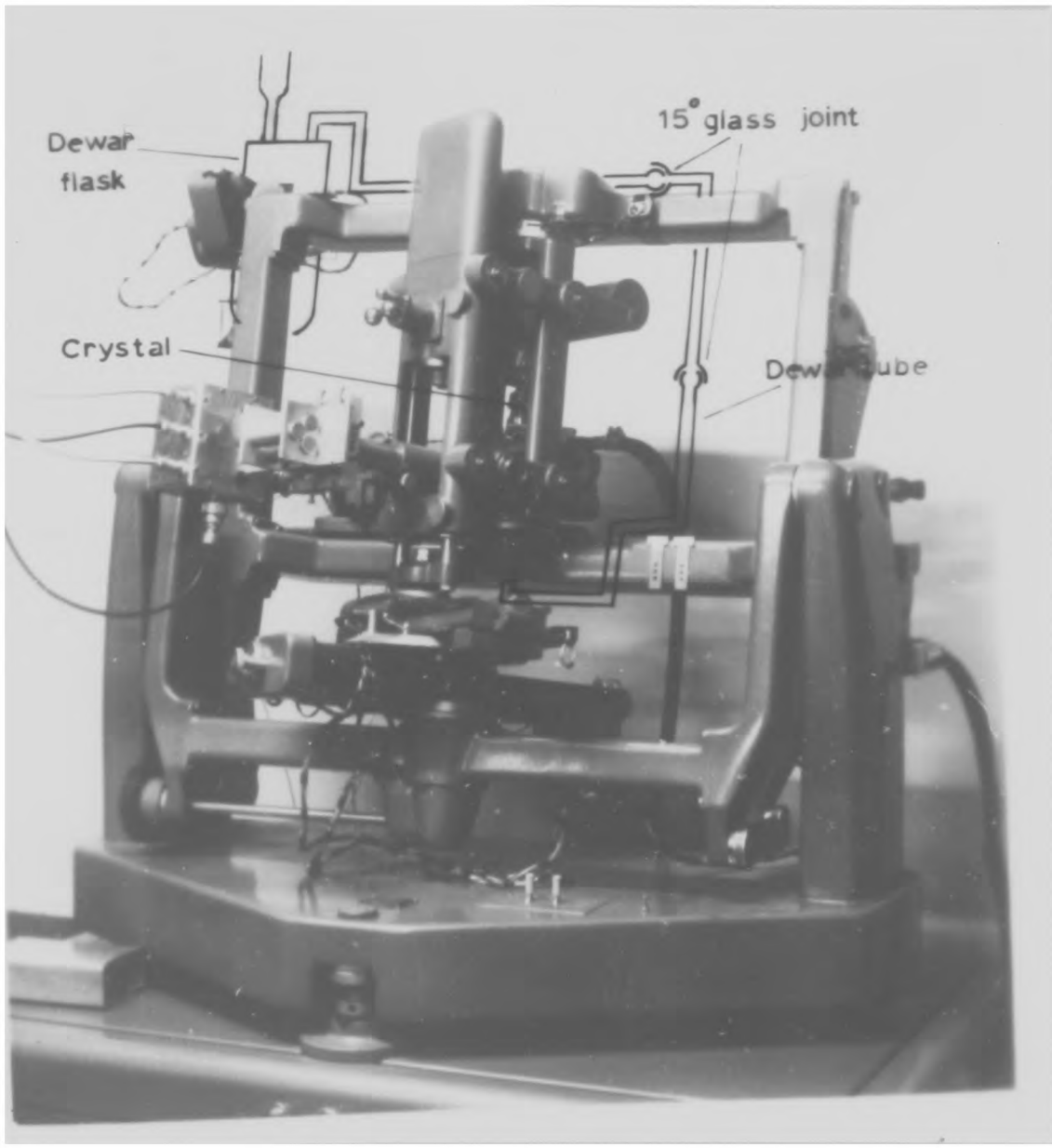


Figure 3.

Photograph by courtesy

Prof. D.C.Philips.

central plate of the cradle wasa circular polythene tube, also attached to an air supply, with holes bored in it so that jets of air were projected onto the sleeve (figure 4).

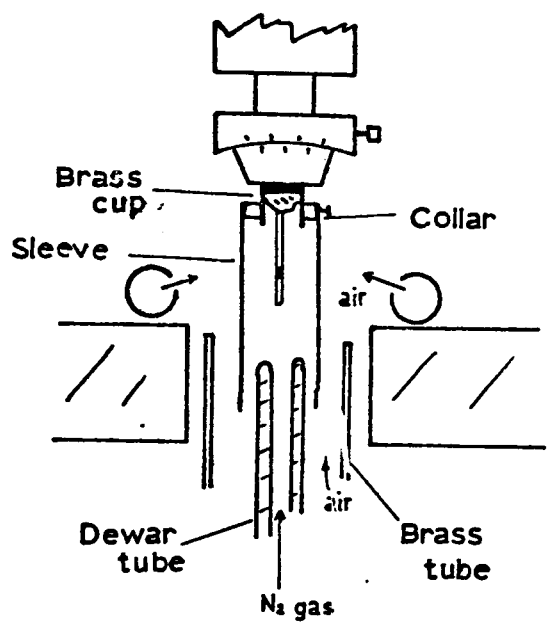


Figure 4

The outer brass tube which passed a stream of air all round the sleeve, stopped water vapour diffusing back against the slow stream of cold nitrogen from the crystal chamber, (filter pump principle) while the jets of air from the polythene tube prevented condensation forming on the sleeve.

A thermocouple junction was positioned at the mouth of the dewar tube, and down the tube was a small heating coil which warmed the stream of cold gas to any required temperature between 70°C and -150°C.

It was found that with the dewar constantly kept (by manual filling) between $^1/_3$ and $^2/_3$ full, the gas coming into the crystal chamber remained at $-120^{\circ}C \pm 3^{\circ}C$. and that the system could be maintained at $-120^{\circ}C$ for $\simeq$16 hours before condensation and icing within the crystal chamber became a serious problem.

Accurate setting of the crystal, however, was difficult, for the milar sleave tended to catch on the lower tubes and since at low temperatures it ceased to be flexible the alignment of the crystal was distorted. With the arcs of the goniometer head set to zero, the crystal had to be aligned in the plasticine by hand to within 1° of its correct setting before data measurement was possible and even then after every hour of measurement the setting had to be checked and the arcs frequently corrected.

Because the low temperature could only be maintained for a relatively short time, and because the instrument was on loan only for a limited period*, it was decided to collect three-dimensional X-ray intensity data at $22^{\circ}C$ and $-120^{\circ}C$ with Mo-K_{α} radiation without balanced filters.

The pulse height analyser[57] was critically set to reject white radiation streaks, and a test showed the measurement of equivalent reflections to be within 10% of each other, (comparable to the precision of this particular instrument).

*three weeks

STRUCTURE ANALYSIS

Crystal data: Monoclinic needles; $\underline{a}$ = 7.702, $\underline{b}$ = 8.869, $\underline{c}$ = 13.131Å; $\underline{\alpha}$ = 90°, $\underline{\beta}$ = 90°, $\underline{\gamma}$ = 107.0°; m.pt. = 67°C; D_m = 1.4040 g.cm.$^{-3}$, D_c for $2(C_{12}H_{15}N_6O_7P)$ 1.4199 g.cm.$^{-3}$; Mo-K_α radiation, μ = 1.460 cm.$^{-1}$; space group $P2_1$; 1030 independent reflections were measured on a Hilger and Watts linear diffractometer; 71 reflections were removed when the data measurement was checked.

The accurate aligning of a crystal on a linear diffractometer poses no problems when the axis of rotation of the reciprocal lattice is colinear with an axis of the lattice. Ipso facto, this condition is always satisfied if the unique axis of a monoclinic crystal is the axis of rotation, but is not necessarily satisfied when the axis is non unique. The reciprocal axial lengths for Mo-K_α radiation are: $\underline{a}^*$ = 0.0964, $\underline{b}^*$ = 0.0838, $\underline{c}^*$ = 0.0541, with the axis $\underline{a}^*$ inclined at an angle of 17.0° to the axis of rotation.

With rotation about $\underline{a}$, the origin of the reciprocal lattice on the third layer (h = 3) will have moved 0.0845 reciprocal lattice units along the axis $\underline{b}^*$ so that the lattice point $(3\ \bar{1}\ 0)$ is almost co-incidental with the rotation axis. The reflection $3\ \bar{1}\ 0$ had one of the largest observed intensities and it was possible accurately to align the axis $\underline{a}$ of the crystal collinear with the rotation axis by means of this reflection.

Three dimensional, intensity data were collected, up to an equi-inclination angle (μ) of $\approx$13°, with rotation about the unique axis $\underline{c}$

and the non unique axis a.

The data was corrected for the Lorentz and polarisation factors, but no absorption correction was necessary.

Three dimensional Patterson function, sharpened to 'point atoms at rest' (B = 3) was calculated. In the function, a pattern of peaks was discovered about the origin which represented the inter-atomic vectors of a benzotrifurazan molecule (figure 5). From this pattern the orientation of the molecule was deduced and it was clear that the plane of the molecule was in (or almost in) the zone of the unique axis. In such a situation, with space group $P2_1$, a systematic set of non Harker intermolecular vectors are generated (figure 6) which give rise to a regular pattern of peaks (figure 7) about the Harker section in the Patterson function. This pattern was located in the Patterson function so that it was possible to determine the position of the benzotrifurazan molecule in the unit cell.

The central peak of the pattern was observed to be more than twice as large as expected, and it was discovered that it represented not only the separation of the mid points of the two benzotrifurazan molecules in the cell, but also the separation of the two phosphorus atoms. Further by the application of the two-fold axis in Patterson space, the vectors generated between the phosphorus atom and the atoms of the nearest benzotrifurazan molecule were themselves intimately intermingled with the vectors between the two benzotrifurazan molecules.

From an inspection of the Patterson function and from considerations of molecular packing in the crystal it was deduced that the phosphorus

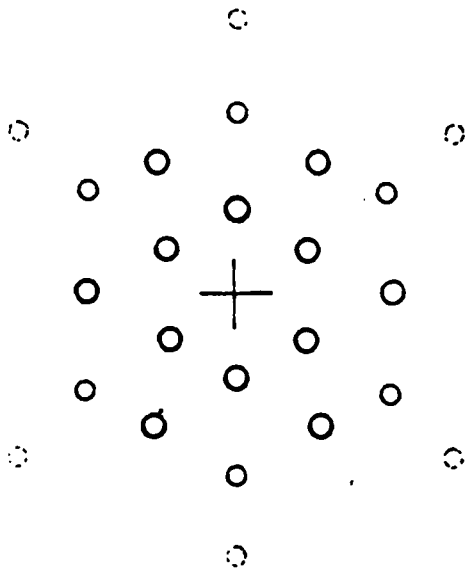


Figure 5.

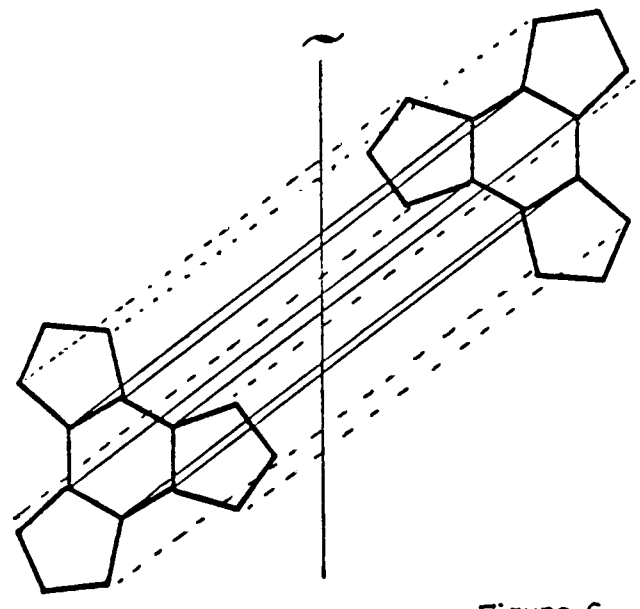


Figure 6

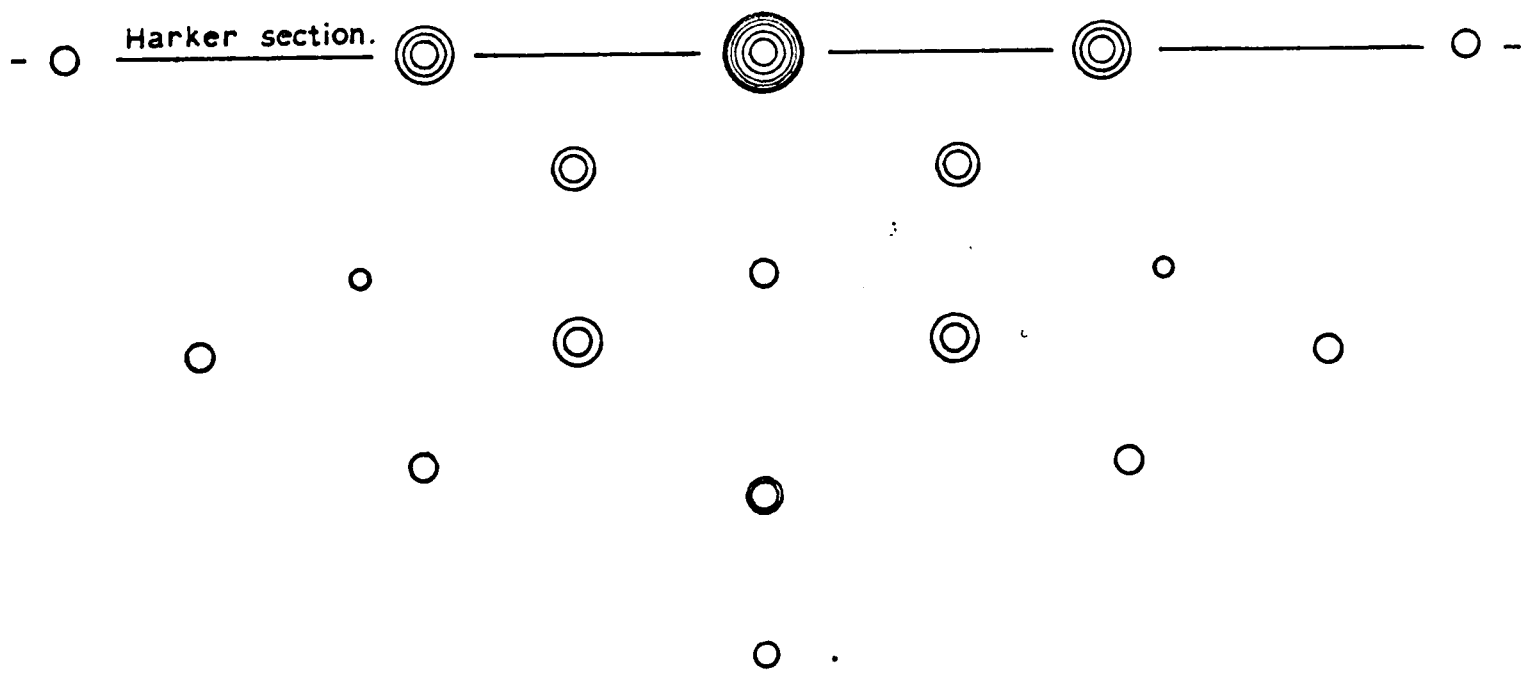


Figure 7

(The plane, perpendicular to the Harker section, through the Benzotrifurazan vectors.)

atom and the centre of the benzotrifurazan molecule had the same y and z co-ordinates and that their x/a co-ordinates differed by $\frac{1}{2}$. The structure given in Figure 8 was proposed.

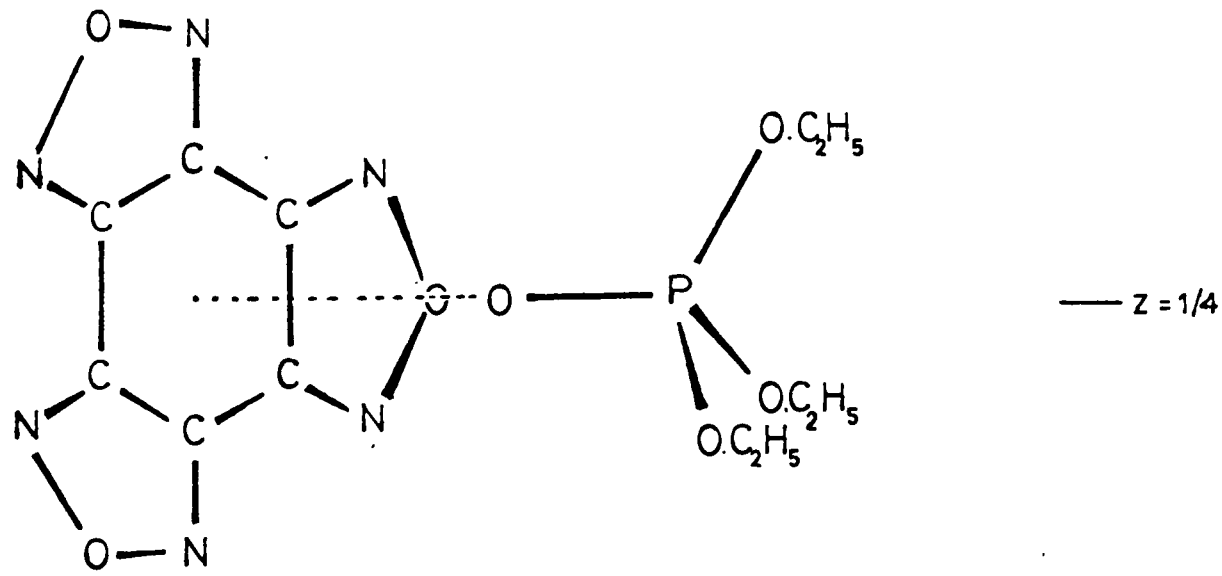


Figure 8

Although the solution of the Patterson function seemed rigourously correct, no attempt was made to refine the trial structure by least squares. Instead an F_o synthesis was calculated phased on the position of the phosphorus atom from which the positions of a (PO_4) and a (C_6N_6) unit were determined. These positions were essentially the same as those derived from the Patterson function. An F_o synthesis phased on the positions of the ~~17 atoms revealed the positions of the~~

17 atoms revealed the positions of the remaining 9 atoms, and confirmed the solution of the Patterson function.

From figure 4 it can be seen that only a few atoms break the mirror plane (at $z = \frac{1}{4}$) that would have been expected had the space group been $P2_1/m$.

In these circumstances the expressions derived by Taylor's expansion for the normal equations used in least squares refinement are no longer even approximately linearly independent, and the matrix that is calculated to determine the shifts in positional parameters is ill conditioned, with rows and columns that are very similar. Consequently when the matrix is inverted, conditions of singularity are inherent, but are seldom discovered and the resulting parameter shifts can be wildly inaccurate.

Therefore, the trial structure (figure 9) with individual isotropic temperature factors was refined by full matrix least squares with conditions of constraints imposed upon interatomic distances. Values for the interatomic distances were derived by analogy with similar bonds in the coloured compounds, in benzotrifuroxan and in published structures of phosphate esters.

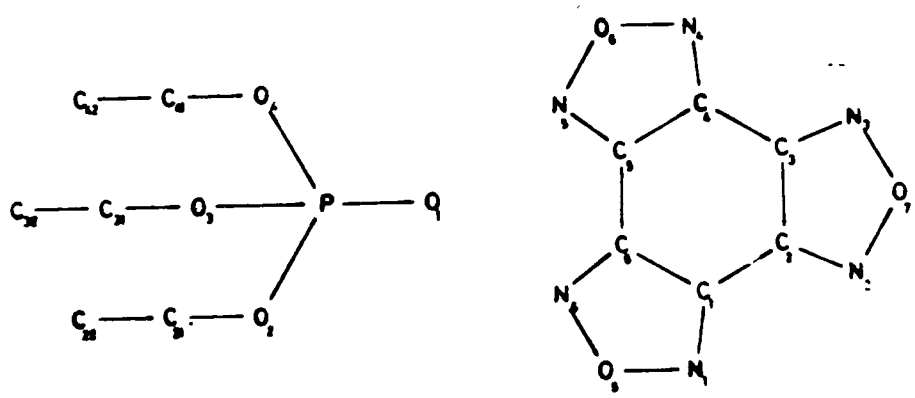


Figure 9

The condition that an interatomic distance within a molecule must be of a given length to a given standard deviation can be expressed in a form that is compatible with the normal equations for the minimisation of $w(|F_o| - |F_c|)^2$, (Appendix II).

This condition therefore may be treated as a further observational equation and the derivatives may be added into the full matrix during a refinement cycle, which removes the inherent singularities. The extent to which any constraint dominates the full matrix is a function of the tolerance applied to that constraint, and during the refinement of the trial structure of the complex, the standard deviations were adjusted to permit interatomic distances to vary between ±0.03Å (Appendix II).

After three rounds of refinement with unit weights, the reliability factor (R) was 23%. The three most intense reflections (the diffractometer is known to measure very intense reflections incorrectly) and reflections where the recorded intensity was less than two e.s.d.'s of the recording were removed. After three more cycles of refinement with a weight (w) applied to each intensity observations where:

$$w = \frac{1}{(1 + ((|F_o| - P_2)/P_2)^2)^{\frac{1}{2}}} \qquad (p.s)$$

The R factor was 14.7%.

The structure is shown in figures XX, XXI, XXII, the projection onto the least squares best plane of the benzotrifuroxan molecule in

in figure XXIII and the bond lengths and angles in figures XXIV and XXV. (Full details of atomic parameters, e.s.d.'s, bond lengths and angles, and atomic parameters with reference to orthogonal axes are found on p.196.

In the structure, the benzotrifurazan molecules and the phosphate ester form alternating stacks parallel to a, (figure XXI), there is no close contact between atoms in adjacent stacks, but within the stacks, the P=O bond is almost co-incident with the three-fold axis of the nearest benzotrifurazan molecule (figure XXIII) and the oxygen atom O(1) is only 2.51 Å from the plane of this molecule.

Room temperature structure

On cooling to low temperatures there was no significant change in cell parameters: a = 7.84, b = 9.06, c = 13.30Å; γ = 107.0° (22°C); a = 7.702, b = 8.869, c = 13.131Å; γ = 107.0°, (-120°C) and no change in space group. Predictably, the thermal diffuse scatter at room temperature disappeared, while reflections with a Bragg angle greater than 40° appeared at low temperatures. (497 independent reflections were collected on the diffractometer at 22°C. and 1030 at -120°C.).

However, the pattern of intensities changed remarkably as the temperature was lowered. Figure 10 shows a trace of the line of reciprocal space 0k2 at various temperatures between 22°c. and -120°C. It is perhaps significant that the most obvious alterations occur above -60°C. for a cooling curve (figure 11) shows that triethyl phosphate

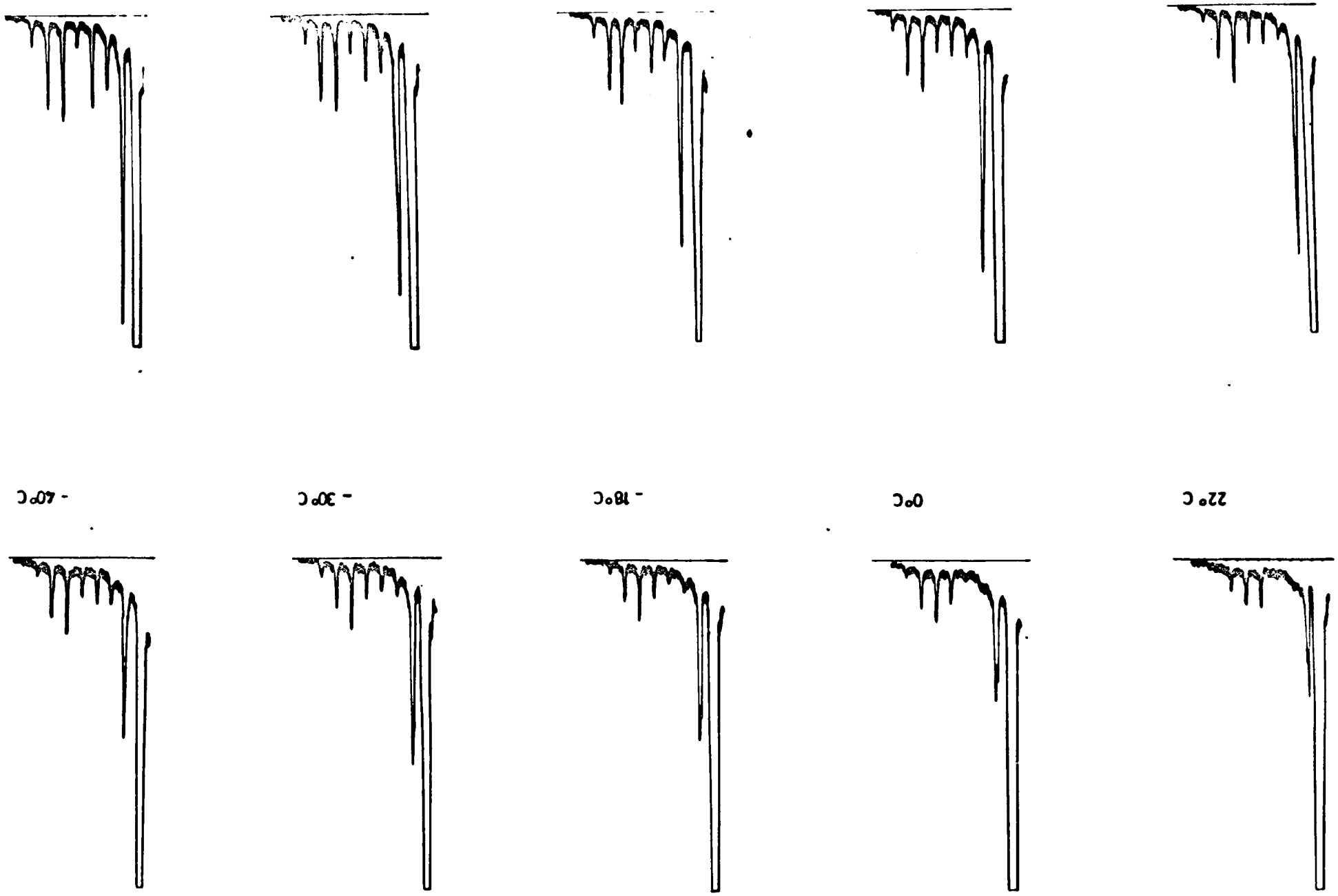


Figure 10

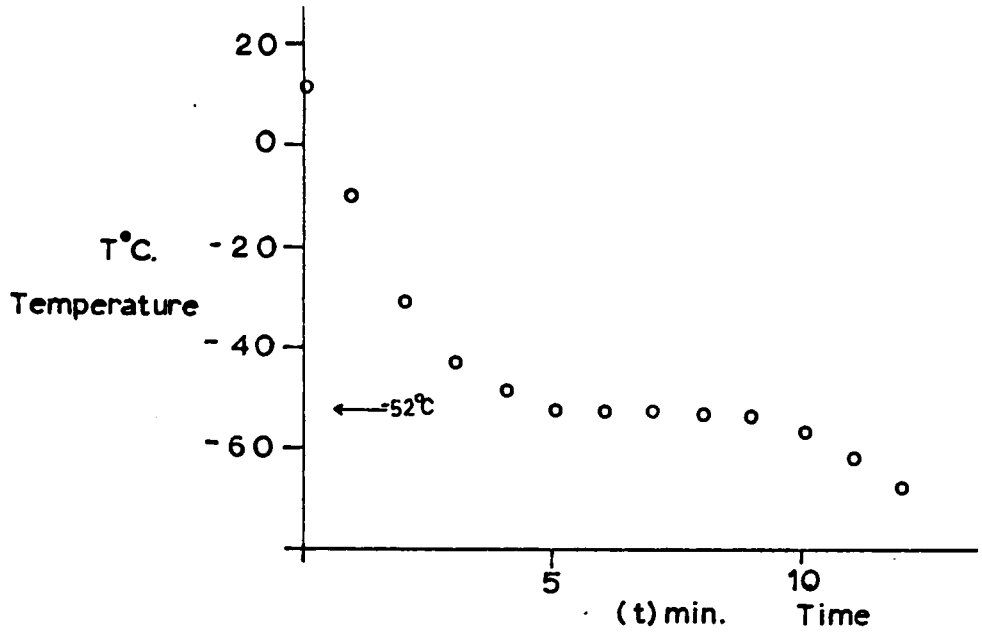


Figure 11

melts at -52°C.

When the atomic parameters of the low temperature structure were refined with the photographic data collected at room temperature the R factor was 20%. The main features of the structure were unchanged and closely resembled the trial model that had been suggested for this room temperature structure. The isotropic temperature factors were greatly increased (for tables and co-ordinates, see p. 196) particularly those temperature factors of the atoms on the periphery of the molecules.

It is suggested that in the crystal at room temperature, the molecules occupy the same relative positions as at -120°C., but that the phosphate ester is librating about an axis through the P=O bond and that this causes a similar (though less marked) libration of the benzotri-furazan molecule. The libration is slowly damped as the temperature

drops to $-60^{\circ}C.$, and below that temperature individual atomic vibrations only are successively restricted.

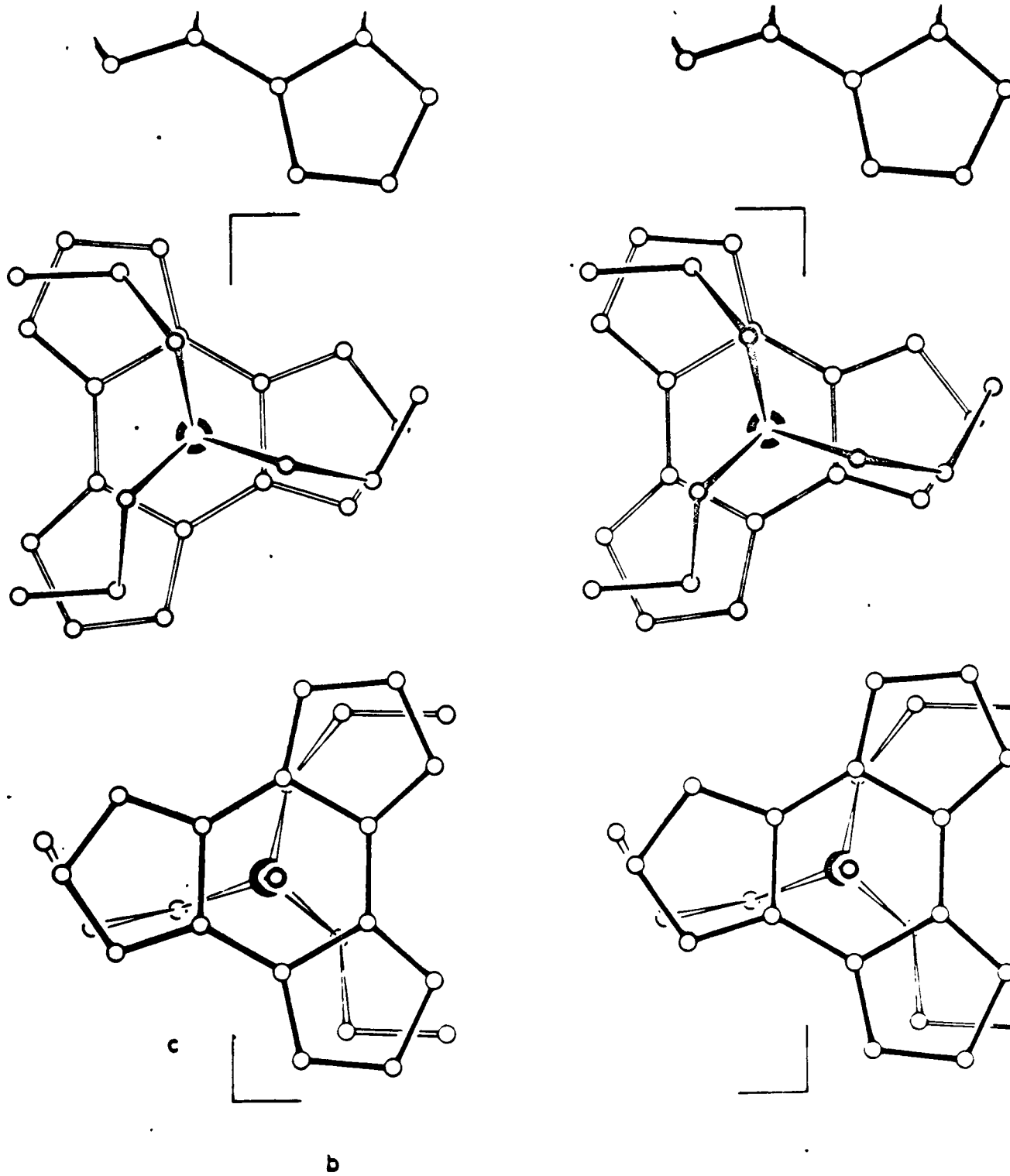


Figure XX Phosphate complex (-120°C.) Projection (1 0 0)

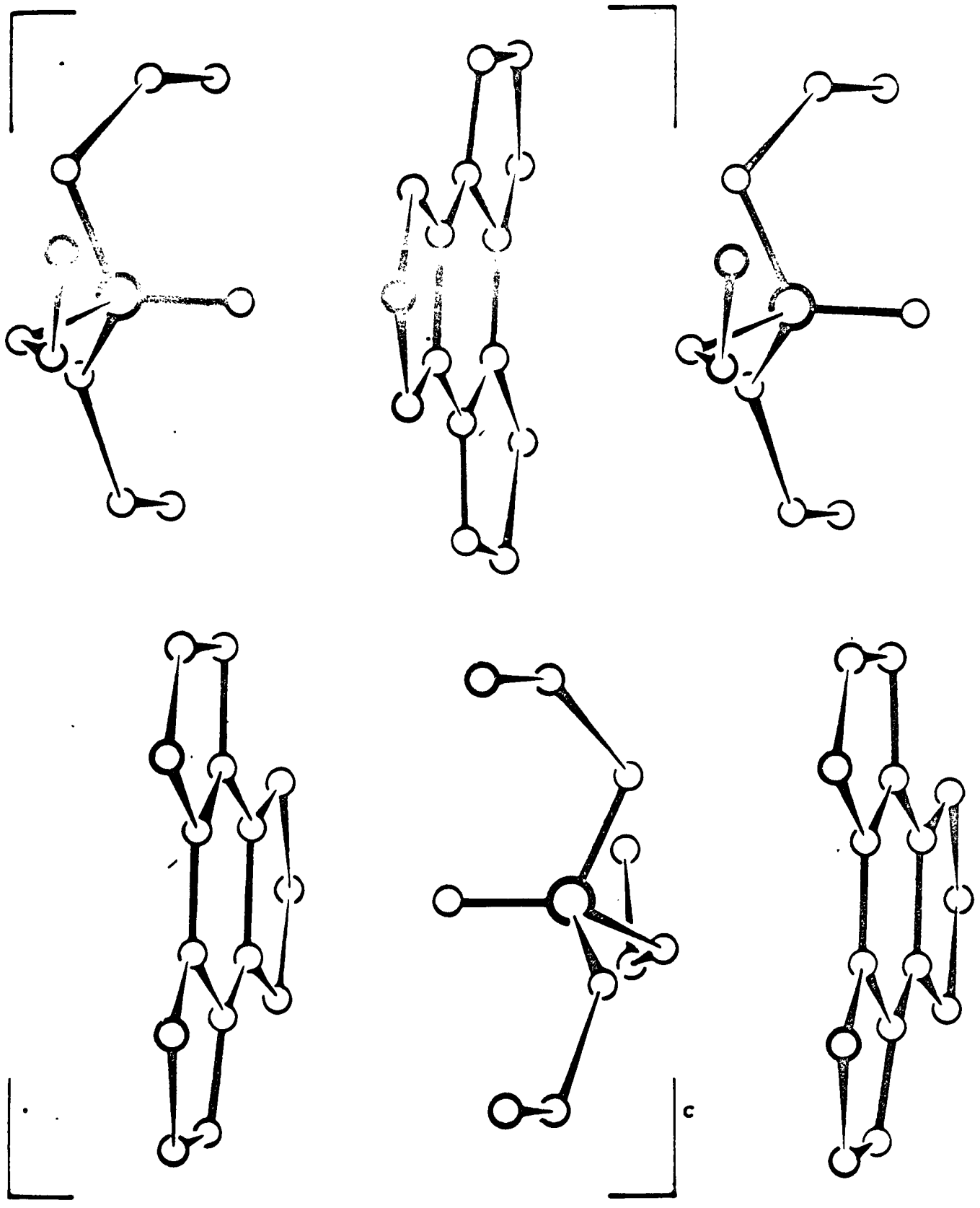


Figure XXI · Phosphate complex (-120°C.) -- Projection (0 1 0)

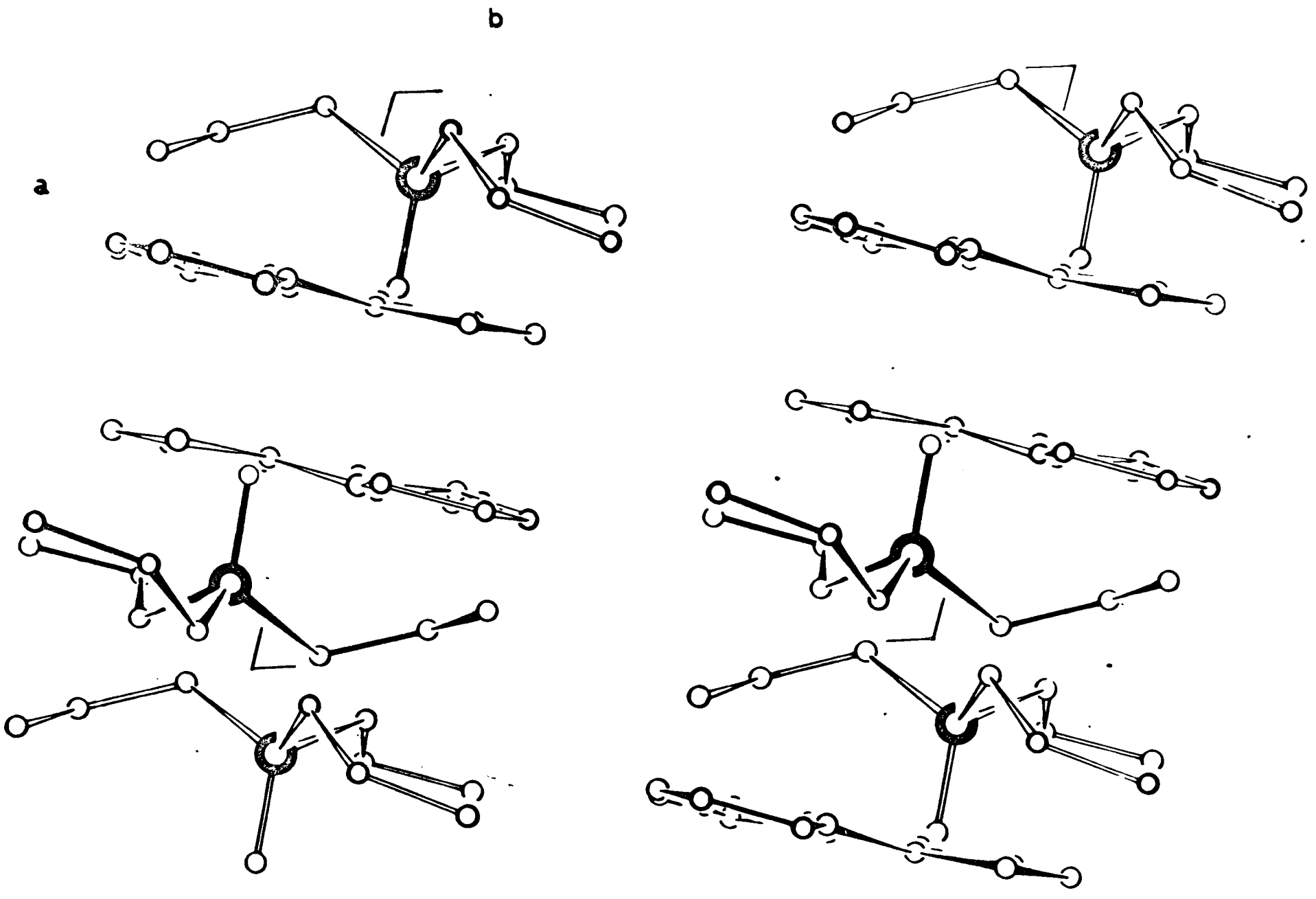
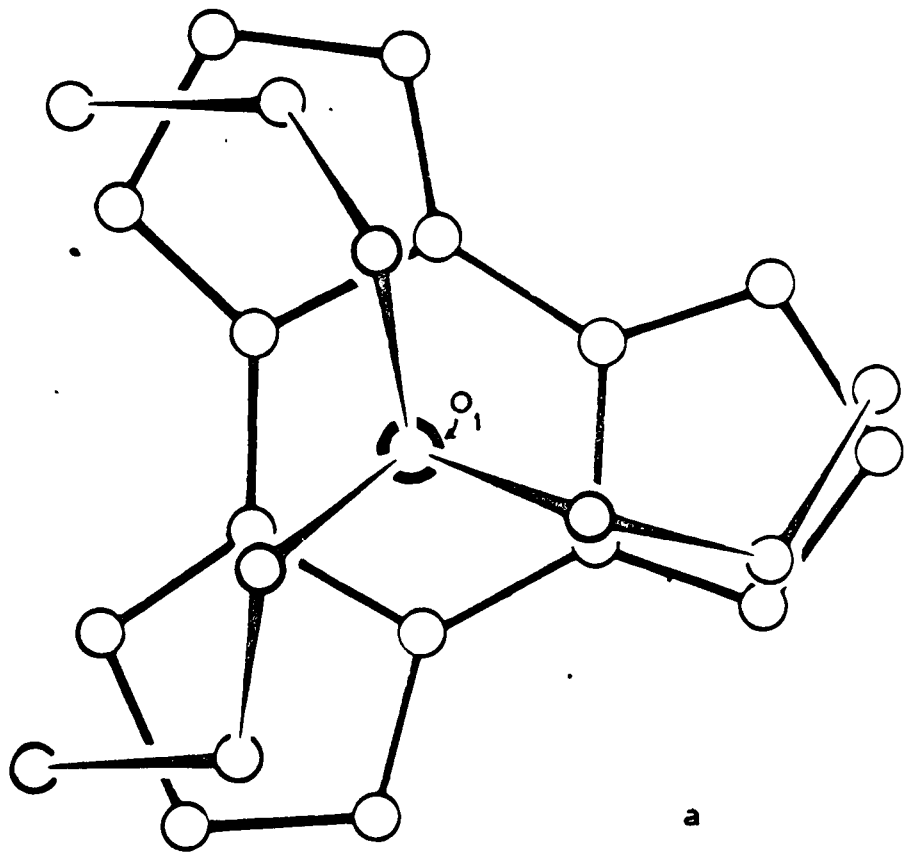


Figure XXII Phosphate complex (-120°C.) Projection (0 0 1)



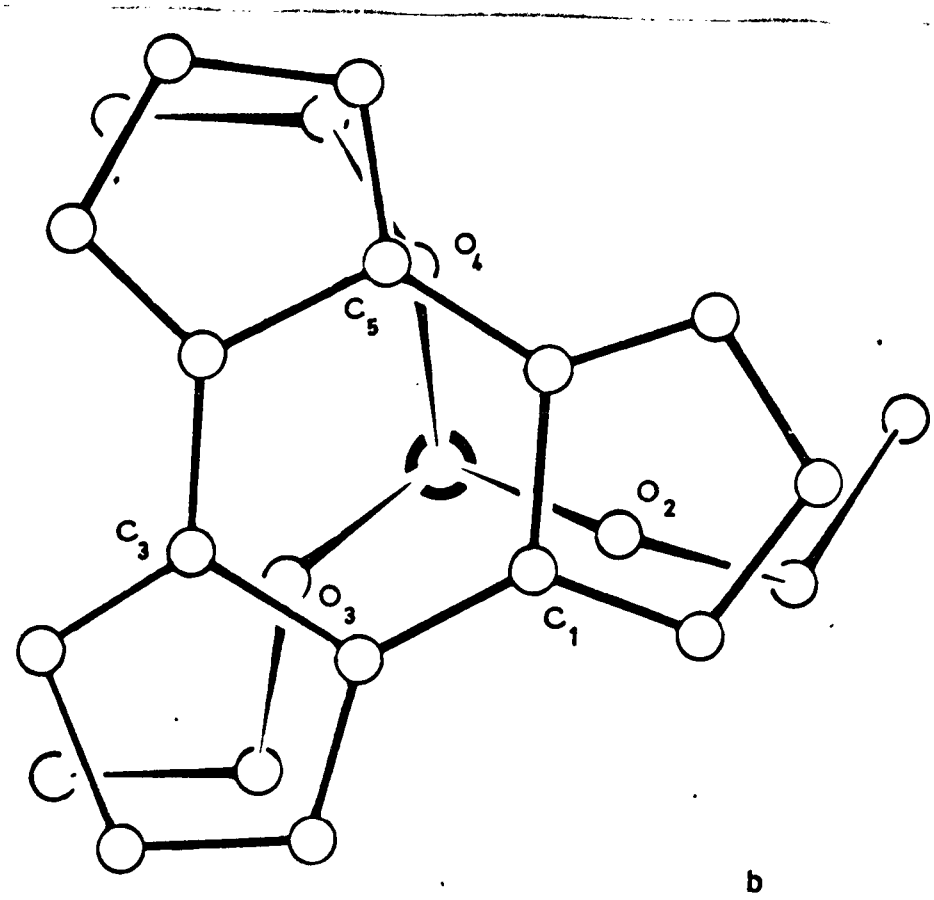
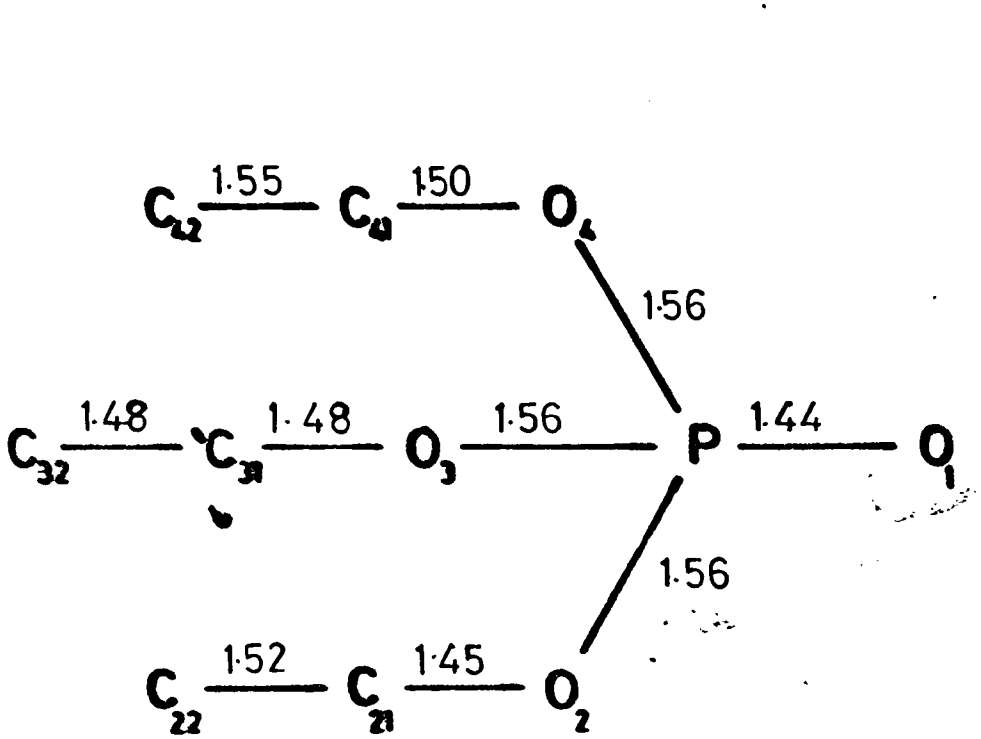


Figure XXIII Phosphate Complex (-120°C.) Projection onto the least squares best plane of the C_6 ring.



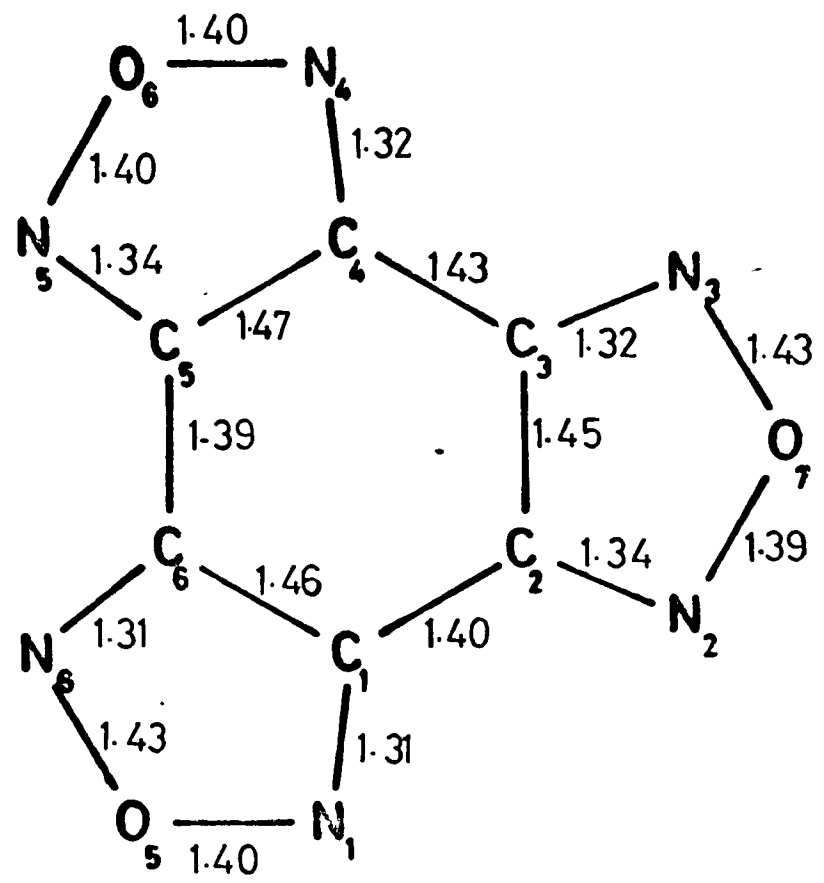
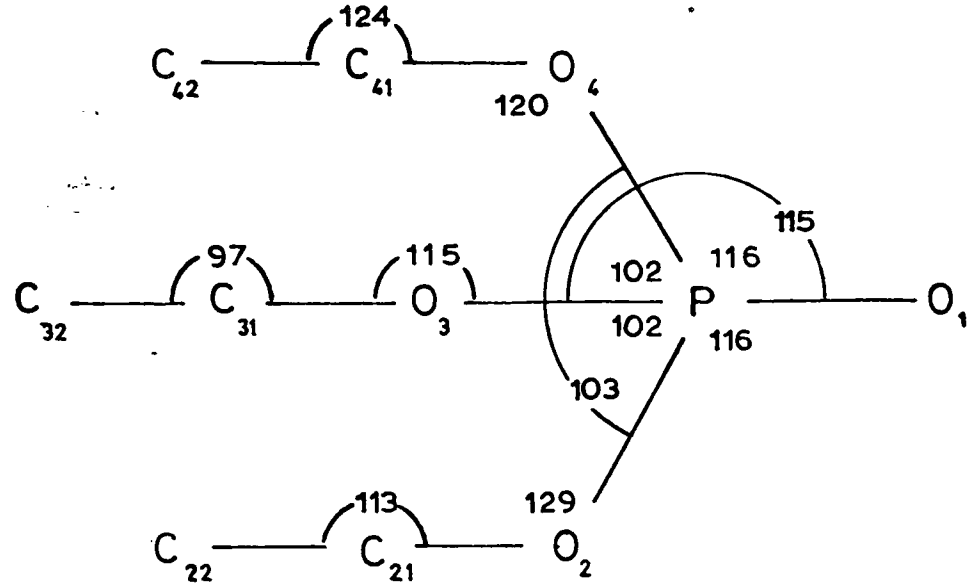


Figure XXIV Phosphate complex (-120°C.) Distances



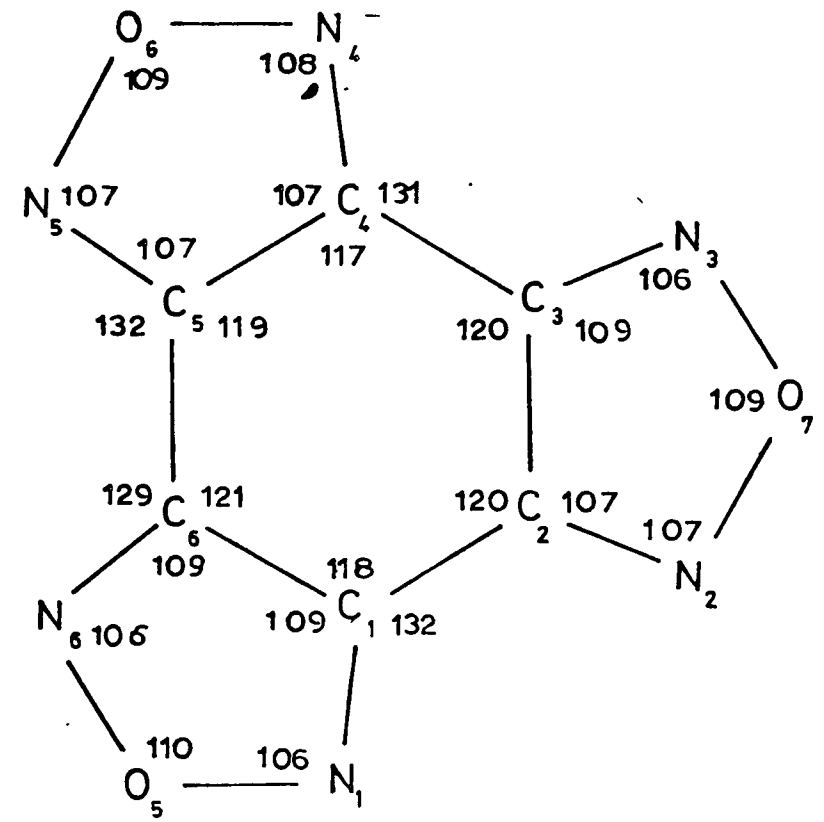


Figure XXV Phosphate complex (-120°C.) Angles

Discussion

The bond lengths, but not the bond angles of the phosphate ester were constrained during the refinement to be reasonable. Values for the P=O and bridging P-O distances were derived by analogy with the structure[28] of $(PhO)_3PO$ and values of the C-O and C-C distances were obtained from the literature. The P=O and P-O bonds were constrained to be 1.43 and 1.56Å respectively and did not alter significantly with refinement.

The C-O and C-C bonds were constrained to be 1.47[±0.03]Å (epodixe C-O)[14] and 1.54Å (aliphatic C-C).[14] The corresponding mean lengths, after refinement, are 1.48 and 1.52Å but the spread of values is large.

The bond angles at the phosphorus atom are in good agreement with those observed in $(PhO)_3PO$ but the angles at the carbon and oxygen atoms are less reasonable. A difference Fourier synthesis indicates that the positions of these light atoms are somewhat disordered. Consequently, the inter bond angles are a compromise forced by the bond length constraints.

The temperature factor of C(22) is significantly higher than the temperature factors of the other terminal carbon atoms (U_{iso}: 0.132, 0.091 0.074 respectively). Carbon atom C(22) lies between atoms C(32) and C(42) of the ester related by a cell translation in b and is free to vibrate perpendicular to the bc face. Carbon atoms C(32) and C(42) are 3.29, 3.27Å from oxygen atoms in adjacent trifurazan molecules (figure xx) and, held by polar interactions are less free to vibrate.

Values for the interatomic distances in the benzotrifurazan molecule were obtained by analogy from the structure of benzotrifuroxan.[20] Not only these bond lengths, but also the interatomic distances between non-bonded atoms were constrained during the refinement. The latter restriction imposes certain bond angles upon the molecule, but does not require the molecule to be planar. Table 1 gives the constrained and the mean refined bond lengths and angles in the heterocycle.

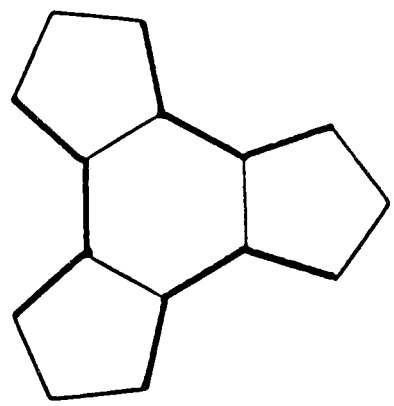
	Bond	Constrained length	Refined length
Intercyclic	C-C	1.43Å	1.46Å
Intracyclic	C-C	1.44Å	1.41Å
	C-N	1.33Å	1.33Å
	C=N	1.33Å	1.33Å
	N-O	1.40Å	1.41Å
	Angle	**Constrained**	**Refined**
	C-C-C	120°	119°
	C-N-O	107°	107°
	N-O-N	110°	109°
Intracyclic	C-C-N	108°	108°

Table 1

The C=N and N-O bond lengths* are of little interest as they hardly changed during the refinement, but there is a striking change in the C-C bond lengths.

*For a discussion of the furazan system, see p.66

An alternation in the (C-C) bond lengths is observed and it can be thought of as another example of the π character of a multicyclic conugated system oollecting[58](wherever possible) on the periphery of the ring (I).



(I)

The P=O bond is almost co-incident with the three fold axis of the nearest benzotrifurazan molecule, and the oxygen atom O(1) is 2.51Å from the plane of this molecule. The oxygen atoms O(2), O(3) and O(4) are respectively 3.08, 3.11 and 2.97Å from the carbon atoms C(1), C(3) and C(5) of a second benzotrifurazan molecule (figure xxiii b). This close approach of oxygen atom O(1) to the plane of the C_6 ring suggests a specific interaction between the ring π electrons and the phosphate ester oxygen.

Shifts of the order -20cm.$^{-1}$ have been observed in the P=O

stretching frequency and the complex is reported to be as much as 50% associated in solution. The visible and UV spectrum in either ethanol or chloroform solutions is the sum of the spectra of the components so there is no evidence for intermolecular charge transfer.

The room temperature cyrstal structure suggests that the P=O bond remains on the three fold axis of benzotrifurazan even when ester alkyl groups are librating, but dimethyl aniline will replace the ester to form a red dimethylanilene : benzotrifurazan complex in benzene solution.

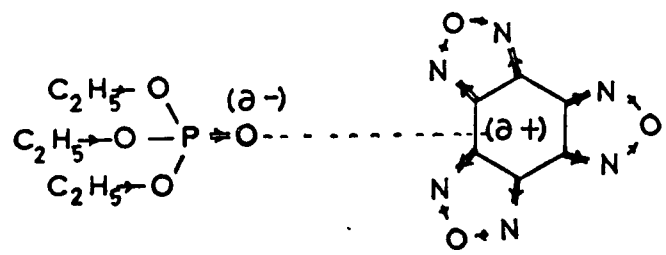
The observations on the strength of the phosphate ester complex appear confusing, but in fact they can be explained in terms of a weak polar (or charge transfer) interaction between the ester and the heterocycle.

That the complex remains associated in carbon tetrachloride is not surprising for CCl_4 is one of the least polar of common solvents. Ethanol is distinctly polar and so, to a less extent, is chloroform. If the complex is a weak 'polar' association, it will be dissociated in ethanol and, probably, in chloroform and the UV and visible spectrum will be the sum of the spectra of the components in the same solvents.

The ester complex is crystallised from light petroleum (a non-polar solvent) and the components are probably associated in solution. The crystal structure at room temperature is built upon a skeleton of benzotrifurazan molecules with interstitial phosphate ester molecules. The P=O bond:benzotrifurazan interaction orients the molecules on crystallisation and once arranged in the crystal lattice, the alkyl carbon to benzotrifurazan contact distances do not permit the axis of

the phosphoryl bond to deviate much from the zone of the three fold axis of benzotrifurazan.

The complex is probably best written as:



The complex superficially resembles the bromine benzene complex[45], and the (σ) type interaction of the P=O bond is similar to the interaction in some carbonyl compound complexes[73], but until some measurement is made of the energy of interaction between the components of the phosphate complex it is difficult to compare this complex with the others.

PHASE ANALYSIS

The relationship has already been discussed for (Pa), the proportion of phases correct within a given number of degrees from a partial structure, and (σ^2), a function related to the scattering matter in the partial structure, (p.83)

Figure 13 shows the phase discrepancies in intervals of 10° plotted against (Pa(obs.)) for the complex at -120°C. with partial structures of the phosphorus atom alone, and the PO_4 unit. Table 2 gives the theoretical and observed proportions (Pa) of the phases correct within 30°, 60° and 90° for the same two partial structures.

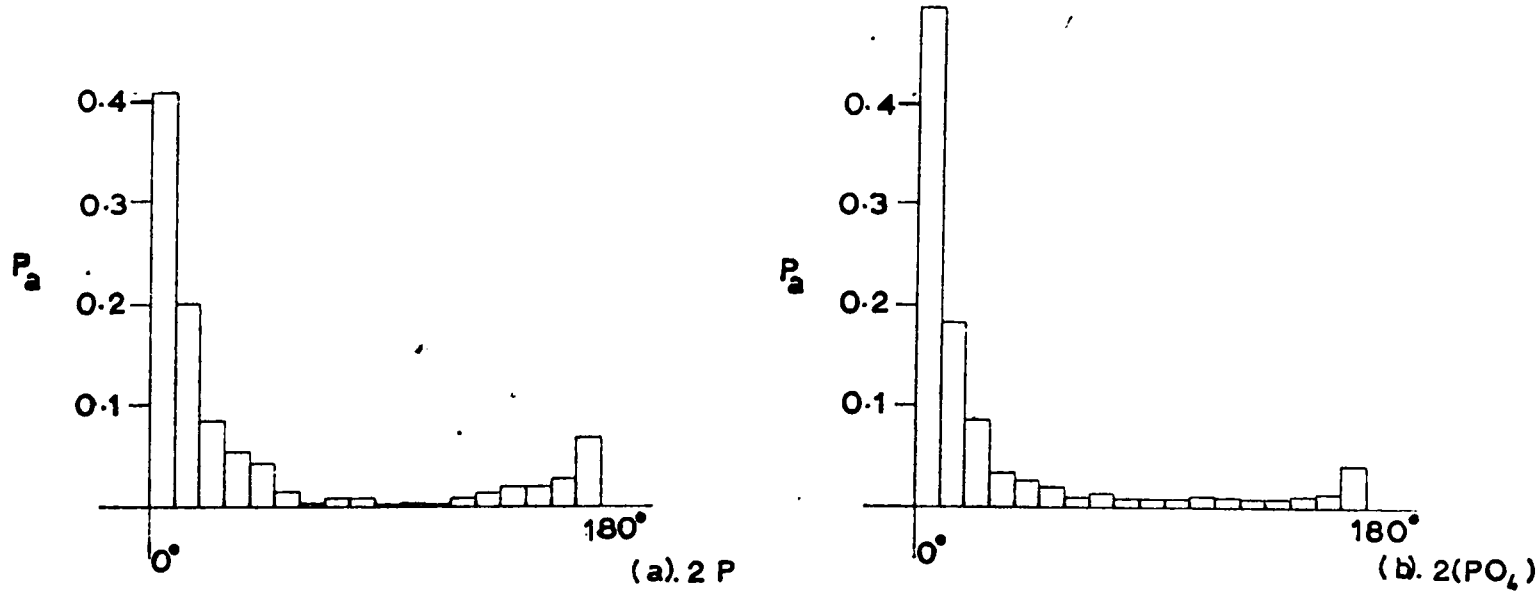


Figure 13

	Pa(theoretical)		Pa(obs.)	
	(P)	(PO_4)	(P)	(PO_4)
30°	0.30	0.35	0.69	0.76
60°	0.55	0.64	0.81	0.84
90°	0.70	0.74	0.83	0.88

Table 2

As with the coloured compounds, there is a large difference between the observed and calculated values of (Pa) and although the explanation for this difference probably includes the approximately spherical atomic environment of the phosphorus atom, the observation from figure 13 that (Pa) for any 10° range reaches a minimum around 90° and increases again toward 180° suggests that there is another factor involved. (11.8% of the phases in figure 13a have an error greater than 150°.)

Figure 14 shows an analysis of the distribution (p) of the phases of the final structure between 0° and 180° in intervals of 10°. It was found that 84.3% of these phases were within 30° of either 0° or 180°, which reflects the close approximation to the crystal molecular packing for centric space group $P2_1/m$ that can be seen in figure (XX). Had the structure been in the centric space group, (P) would have been 0.65 for the partial structure of the phosphorus atom alone.

It is hardly surprising therefore that initially it was impossible to refine the trial structure of the complex with data, collected at room temperatures, where the intensity observations were limited to reflections with a Bragg angle of less than 40°.

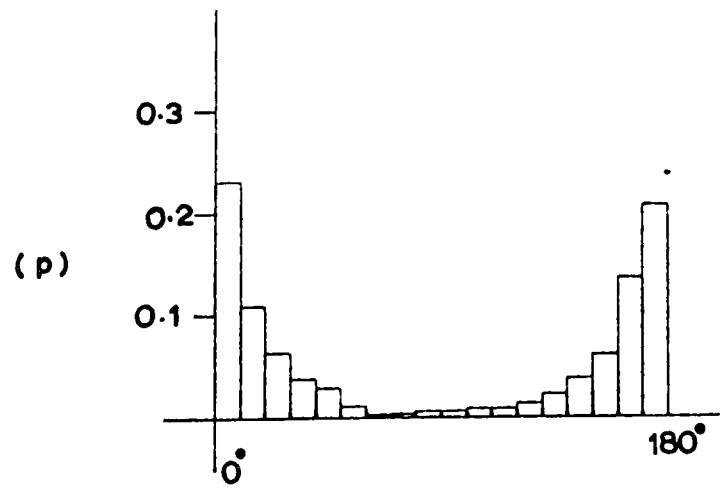


Figure 14.

A series of phase analyses were carried out which observed the value of (Pa) for the partial structure of phosphorus atoms alone in various ranges of the absolute value of the structure factor (F_o), and also over various ranges of the function (ϕ):

$$\phi = |(|F|_o - |F_c|)| / (|F_o| + |F_c|).$$

It was found that the large phase discrepancies were concentrated among the weaker structure factors and among the higher values of the function (ϕ), so that Fourier maps calculated with phases from the partial structure would have been more reliable if the Fourier coefficient had been weighted by ($1-\phi$) or by some similar function.

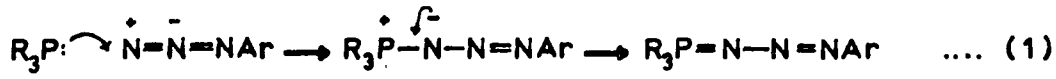
Unfortunately, because of the experience with the phase analysis of the blue compound, no such weight was applied.

CHAPTER 3

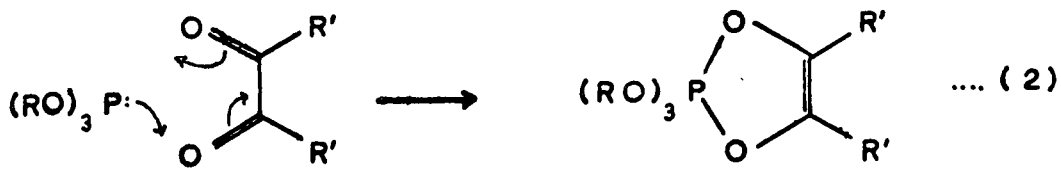
Mechanisms for the reduction of benzotrifuroxan by organo-phosphorus (P_{III}) compounds

INTRODUCTION

The reaction mechanisms in organo-phosphorus chemistry are not yet well classified, but many of them appear to be controlled by the curious biphilic[59] property of the phosphorus atom. The term 'biphilic' was introduced from co-ordination chemistry to describe the phosphorus ligand (PX_3) which can, in favourable circumstances , donate electrons to a substrate to form σ bonds and simultaneously accept them at the same centre to form π bonds. This phenomenon, particularly when its definition is enlarged to include the possibility of the formation of a second σ bond, has wide applications in organic chemistry. Reactions (1)[60], (2)[61] are typical examples.



.... (1)



.... (2)

Many characteristic reactions of P(III) compounds terminate with the formation of the phosphoryl P=O bond. When phosphorus forms a bond with oxygen $p\pi$-$d\pi$ interactions can occour between both filled

oxygen (p) orbitals and two unfilled phosphorus (d) orbitals. Such an interaction is thought to explain the remarkable strength of the phosphoryl bond, (table 1).[62]

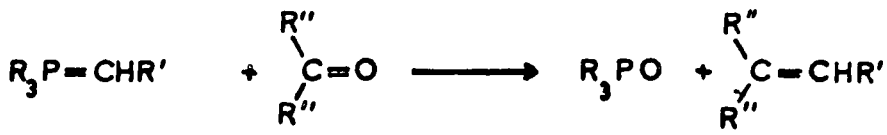
Bond	-Δ H (heat of formation)
N-O	53 K.Cals/mole
P-O	83 "
P=O	120-150 "
P-N	60 "
P=N	100 "

Table 1

The mechanisms of three general reactions (the Wittig, the Arbusov and the Perkow reactions) have been carefully studied, and to place the reduction of benzotrifuroxan in context it will be useful to discuss these in a little detail for they represent the only available mechanistic models.

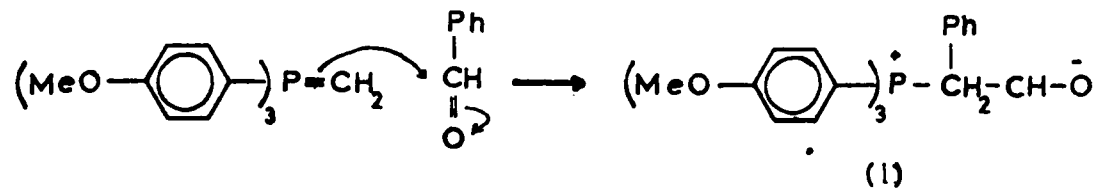
Wittig reaction[63]

Phosphoranes react with a carbonyl compound to produce an olefin.



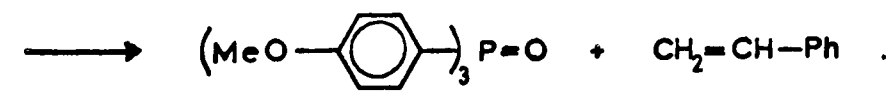
The reaction is thought to go through a four centre rearrangement

with an initial nucleophilic attach by the phosphorane upon the carbonyl carbon.



(I)

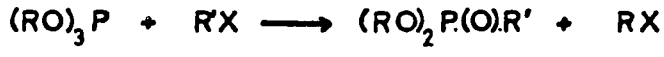




The intermediate (I)[64] and a similar four membered cyclic intermediate[65] have been isolated.

Arbusov reaction[66]

Trialkyl phosphites (or phosphines) react with alkyl halides to produce phosphonate esters.



The reaction is thought to proceed in two stages, an initial nucleophilic attack by the phosphite upon the carbon of the halide followed by dealkylation of the alkoxyphosphonium cation by the displace anion.

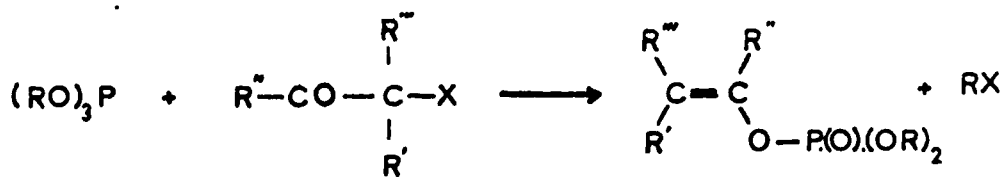




Thermographic measurements[67] distinguish two exothermic processes (presumably the two stages of the reaction) and crystalline salt like compounds[68] containing an ion similar to the supposed alkoxyphosphonium cation have been prepared.

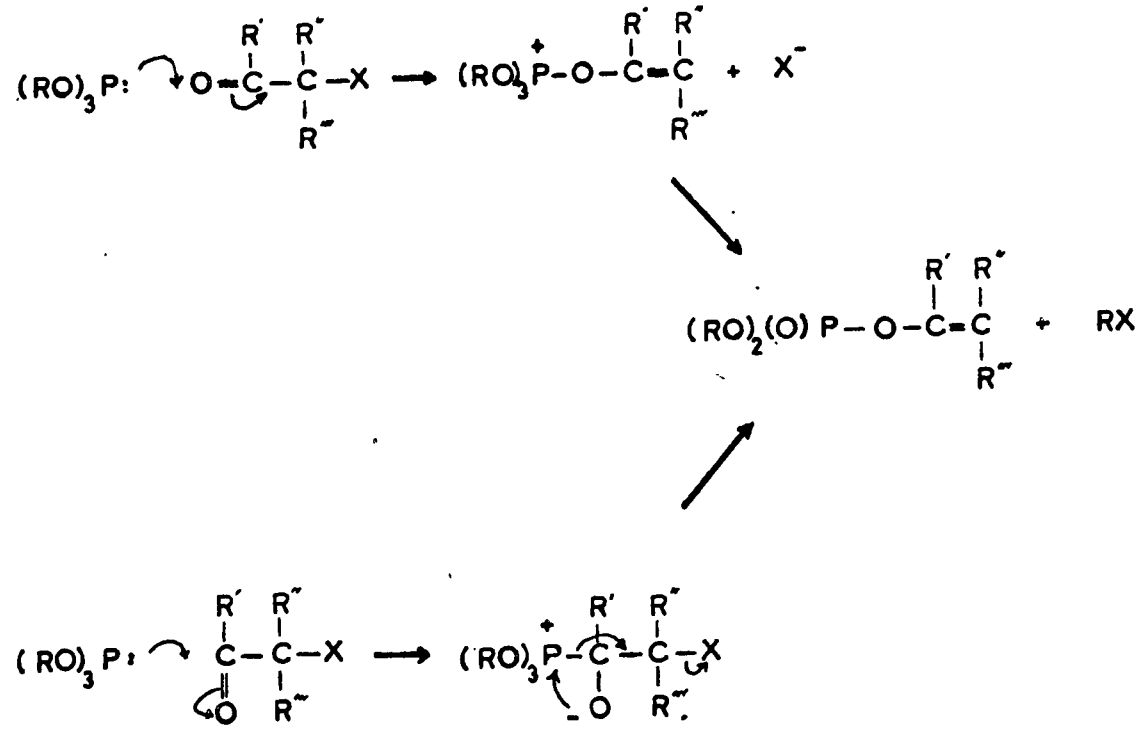
Perkow reaction[69]

Trialkyl phosphites react with α-halogenated carbonyl compounds to give enol phosphate esters with elimination of an alkyl halide.



The mechanism is the least well understood of the three, for the initial nucleophilic attack of the phosphite can occur at one of four sites; the carbon, the carbonyl carbon, the carbonyl oxygen or the halogen.

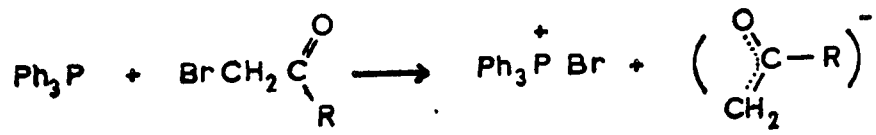
Phosphites are thought to attack either at the carbonyl carbon, or the carbonyl oxygen with a similar mechanism to the Arbusov reaction.

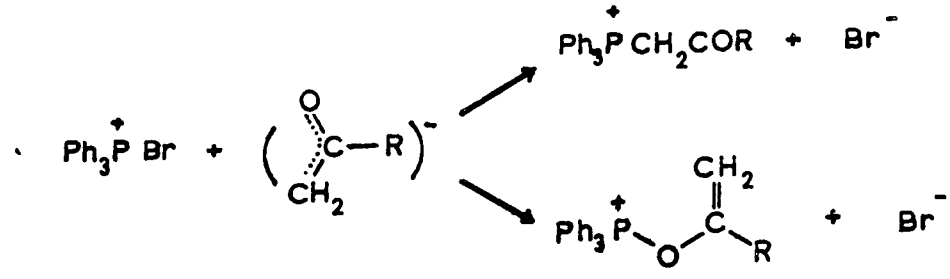


At the moment there is insufficient evidence to decide between

the two alternative sites for attack.

When the phosphite is replaced by a phosphine, the initial attack is thought[70] to occur at the halogen and the reaction, passing through an enolate intermediate, gives one of two possible produots.



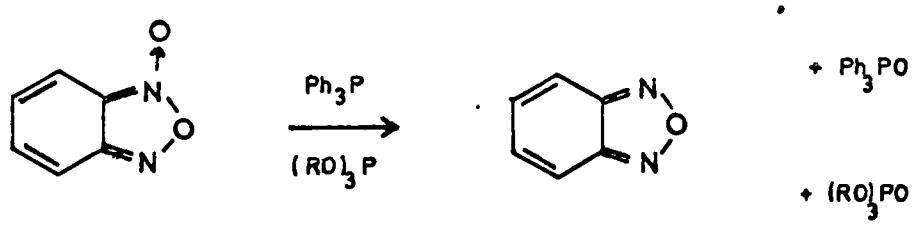


Hudson[71] has investigated the reaction with a series of α-brominated ketones and has related the product composition to the expected electron distribution in the enolate ion intermediate.

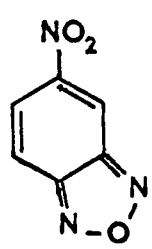
Employing the 'frontier electron concept' (Appendix IV) he found that when the ratio of the frontier electron density on the oxygen and carbon atom (fo/fc) was high, bond formation to oxygen was observed and enol phosphonium salts formed, when the ratio was low keto phosphonium salts were produced.

Reaction of P(III) compounds with simple furoxans and related compounds

Triphenyl phosphine[72] and trialkyl phosphites reduce benzo furoxan to the corresponding furazan*; they do not react with benzofurazan, benzotrifurazan or 3,4 nitro benzo - furazan(II).



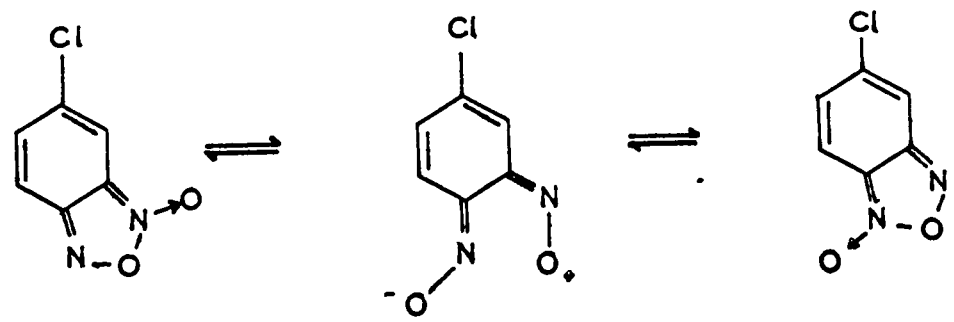
.... (3)



No reaction.

(III)

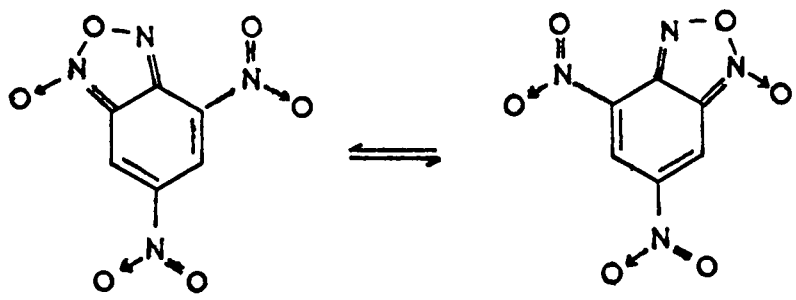
The furoxan ring itself is not a rigidly bonded system for no two isomers of 3,4 chloro benzofuroxan can be isolated at room temperature (though they can be obtained at low temperatures).



.... (4)

*Reaction with the phosphine also produces some ortho nitroaniline[1]

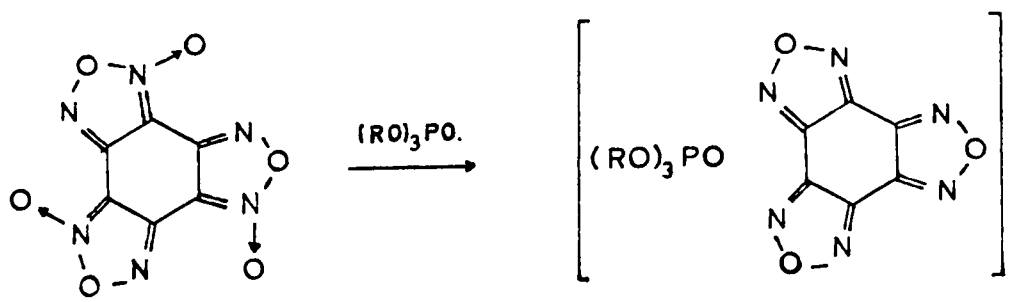
From IR spectroscopic evidence a related equilibrium (5) may occur in 4,6 dinitro benzofuroxan, and although trialkyl phosphites reduce this dinitro furoxan to 4,6 dinitro benzofurazan, the reaction with triphenyl phosphine is complex. When carried out in benzene solution it produces Ph_3PO and three or four green and brown products (T.L.C.) which with reaction (3) suggests that the nitro group adjacent to the furoxan influences the reduction. This reaction, however, has not been thoroughly studied.

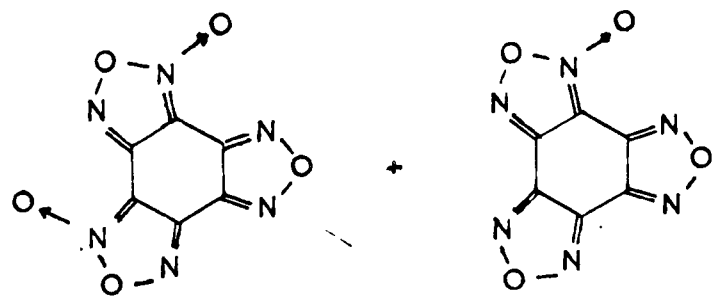


....(5)

REDUCTION OF BENZOTRIFUROXAN

The reduction of benzotrifuroxan by trialkyl phosphites gives[53] the best yields when an excess of the phosphite is slowly added to a boiling benzene solution of the furoxan*. The reported yield of the triethyl phosphate complex is 60% and minor products include benzodifuroxan monofurazan and benzomonofuroxan difurazan.





The reduction was carried out with a series of P(III) compounds in corresponding molecular concentrations (wherever possible) and the results are summarised in table 2. (For experimental details,

*The reaction sometimes is explosive with pure reagents.

see p.159)

Phosphite	Conditions	Reaction time
$(EtO)_3P$	Refluxing benzene (80°)	30 mins.
$(CH_2{:}CH_2O)_3P$	Refluxing benzene (80°)	90 mins.
$(CH_2{:}CH_2O)_3P$	Refluxing toluene (110°)	30 mins.
$(Cl.CH_2CH_2O)_3P$	Refluxing toluene (110°)	3-4 hours
$(EtO)_2.Cl.P$	Pure reagents (50°)	2 hours
Br_3P	Pure reagents (150°)	12 hours
Cl_3P	Pure reagents (150°)	No reaction[53]

Table 2

The reactivity trend is clear, but unfortunately no systematic kinetic studies have yet been done.

In contrast the reaction of triphenyl phosphine with benzotrifuroxan in benzene is complex[1]. An examination of the product showed that it contained no benzotrifurazan or benzotrifuroxan, but the presence of triphenyl phosphine oxide indicated that a reaction had occurred.

The first product to be isolated[1] was the yellow compound, (m.pt.> 330°C.) readily available because of its low solubility in almost all common solvents. The isolation of the other pure products was difficult for the product mixtures contained up to nine different compounds (T.L.C.) contaminated with large excesses of triphenyl

phosphine oxide.

By a combination of column chromatography (silica) and fractional crystallisation four other compounds were obtained[1]. The products are known by trivial names and recognised by their melting points and IR spectra.

Yellow compound	m.pt.	330°
Red compound	m.pt.	168° (dec.)
Blue compound	m.pt.	262° (dec.)
Green compound	m.pt.	268° (dec.) (Light green compound)
Dark green compound	m.pt.	148° (dec.)

When the reduction is carried out in protolytic solvents (acetone, MeOH/EtOAc) at room temperature the predominent product is the dark green compound; if the solution is heated, the yellow compound is formed as well.

Reduction by triphenyl phosphine

Benzotrifuroxan forms many molecular complexes where it is the acceptor[74]. Triphenyl phosphine behaves as a nucleophile in many reactions (Arbusov, Perkow). It is likely, therefore, that the initial stage of the reduction of benzotrifuroxan is nucleophilic attack by the phosphine upon the heterocycle.

Site of attack

There are several sites in benzotrifuroxan where nucleophilic attack could occur, and in view of Hudson's success in predicting the products of the Perkow reaction (p.130) it was decided to investigate the frontier electrons of benzotrifuroxan.

Benzotrifuroxan has 12π molecular orbitals and 18 atoms. If ψ(n) is the wave function of the (nth) molecular orbital, ∅(m) the atomic orbital on the (mth) atom and C(mm) the mixing coefficient for the atomic orbital ∅(m) of the wave function ψ(n) then by LCAO:

$$\psi(n) = C(n1)\emptyset(1) + C(n2)\emptyset(2) + \ldots\ldots\ C(n18)\emptyset(18).$$

In the frontier electron hypothesis it is argued[75] that for nucleophilic attack, electrons on the substrate must be perturbed by the approaching nucleophile and promoted into a higher-energy unfilled molecular orbital. Atomic orbitals with a high mixing coefficient (Cmn) contribute strongly to the molecular orbital ψ(n). Orbitals that contribute strongly to the highest energy filled molecular orbitals are regarded as the most profitable sites for approach of nucleophile.

A discussion of the frontier electron concept, a full Hückel calculation for benzotrifuroxan and the coefficient matrix for the equivalent SCF treatment is given in Appendix IV (p.177,192)

The energy levels for the 12 molecular orbitals are given in

table 3, and it can be seen that the three highest filled orbitals are practically degenerate. Electron density is proportional to ψ^2 so that the electron density from molecular orbital $\psi(n)$ at an atomic site (m) is proportional to $(C(mm))^2$ and the electron density provided by the three highest molecular orbitals at an atomic site in benzotrifuroxan is given by:

$$C(m10)^2 + C(m11)^2 + C(m12)^2$$

Orbital	Energy (ev)
1	-17.77
2	-17.58
3	-17.58
4	-15.75
5	-15.74
6	-15.72
7	-13.86
8	-12.21
9	-12.21
10	-10.09
11	-10.08
12	-10.07

Table 3 (Energies of benzotrifuroxan molecular orbitals (SCF))

Figure 1 shows the values of $\sum_{n=10}^{12} C(mn)^2$ (rounded to two decimal places)

at each atomic site for the highest three π molecular orbitals (SCF).

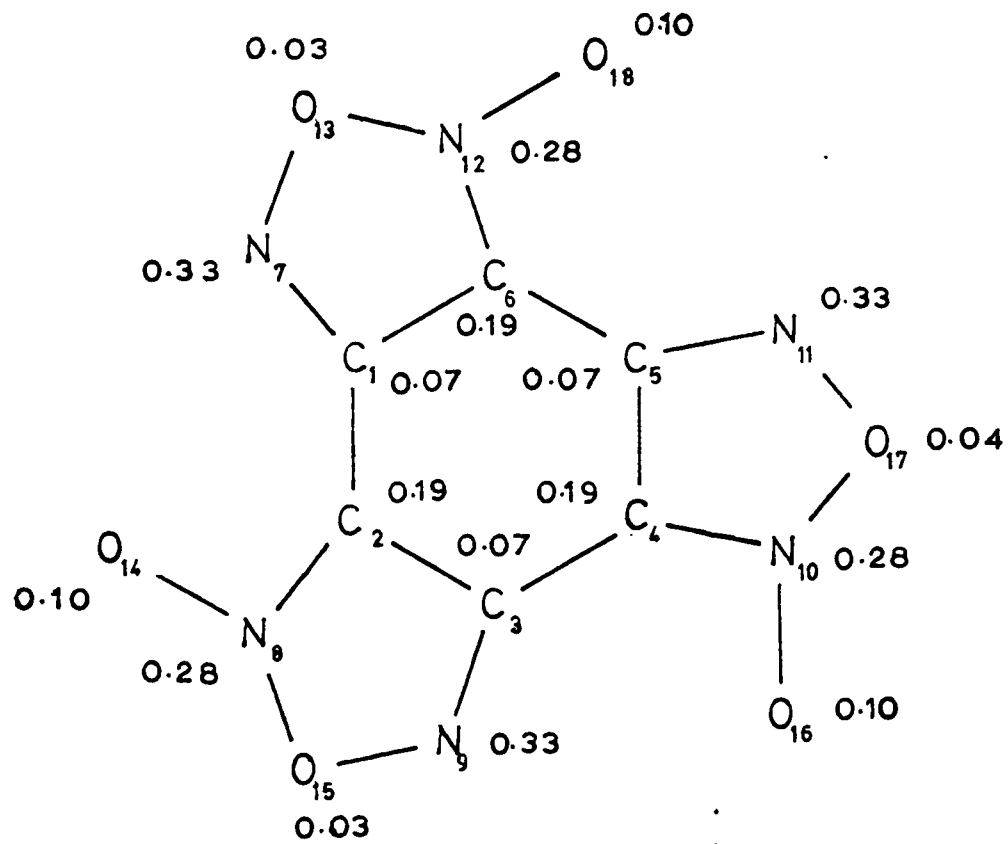


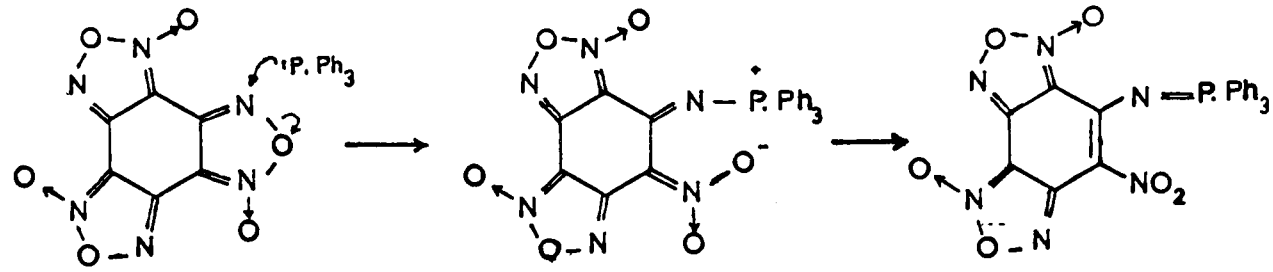
Figure 1

Nucleophilic attack, therefore, will occur most readily at N(7), N(9), N(11) (the exposed nitrogen). Attack is also indicated at N(8), N(10), N(12), but the environment of these atoms would discourage the approach of a nucleophile. Some attack can also be expected at C(2), C(4), C(6) particularly if the exposed nitrogen site is protected (by protonation, p.150)

Reaction mechanisms

The mechanism of the reduction can be explained largely in terms of nucleophilic attack by the phosphine at an exposed nitrogen atom of

a furoxan system, and for the yellow, the green (and the red) compounds such an attack is proposed as the first stage (7).



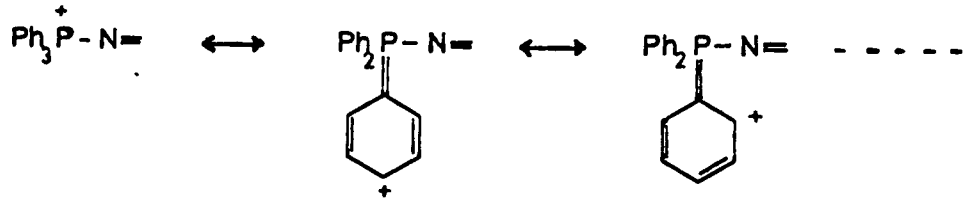
(III)

.... (7)

Although triphenyl phosphine is observed to reduce benzofuroxan (reaction 3) a swift and simple elimination of Ph_3PO from intermediate (III) is not plausible. If the elimination occurred once, presumably it could be repeated three times, and benzotrifurazan would be formed (Ph_3P does not attack furazan systems). Benzotrifurazan is not found[1] among the products of the reduction. There are two factors that may inhibit the elimination:

The positive charge in intermediate(III) though formally written upon the phosphorus atom can be delocalised over the phenyl groups (8), and this would discourage intra-molecular nucleophilic attack by the adjacent nitro group. Also the phosphorus atom must attack the exposed nitrogen atom from above (or below) the plane of benzotrifuroxan, and as it approaches from one side of the plane, the interoyclic oxygen

atom will be expelled from the other side, thus removing it from the immediate vicinity of the phosphorus (figure 2).



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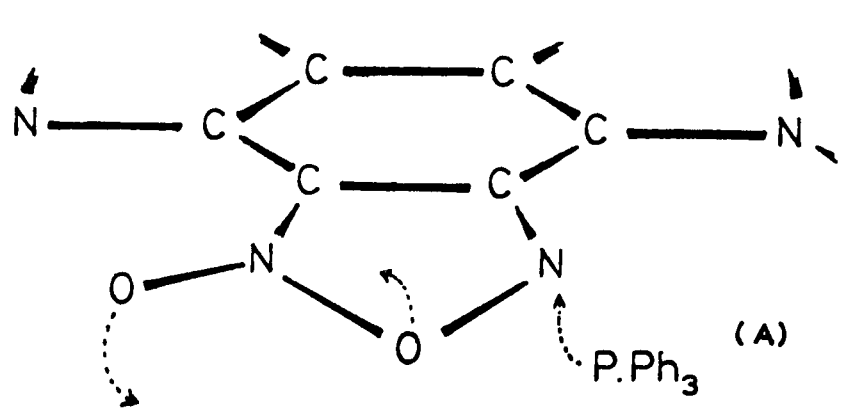
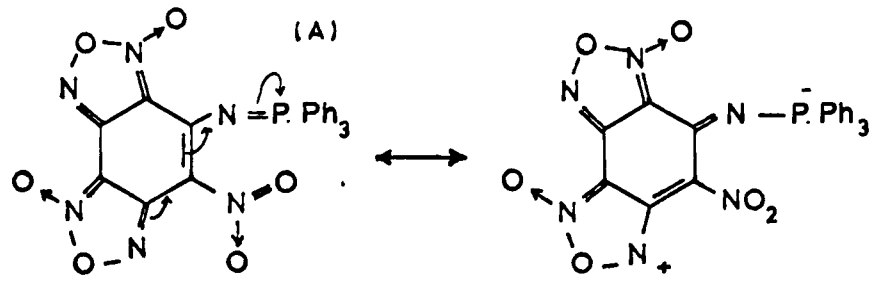


(A)

Figure 2

If a combination of these two factors inhibits the simple elimination, the next stage of the reaction would be an attack by a second phosphine molecule (B). The exposed nitrogen atoms in intermediate (III) are no longer equivalent, however, for one will be polarised (9) by the phosphine group (A). Attack at this nitrogen would yield a dinitro intermediate (IV) with the remaining exposed



....(9)

nitrogen activated (V) by both bonded phosphine groups. No dinitro derivatives have yet been isolated from the reaction and it is proposed that attack by a third phosphine molecule follows quickly after the second to produce the yellow compound (10).

Attack at the less favoured exposed nitrogen site in intermediate (III) could also give the dinitro intermedieate (IV) but in this case the extracyclic oxygen of the attacked furoxan system will be forced into the vicinity of the phosphine group (A), and by a concerted mechanism (figure 3) a six membered cyclic intermediate (VI) could be formed (reaction 11).

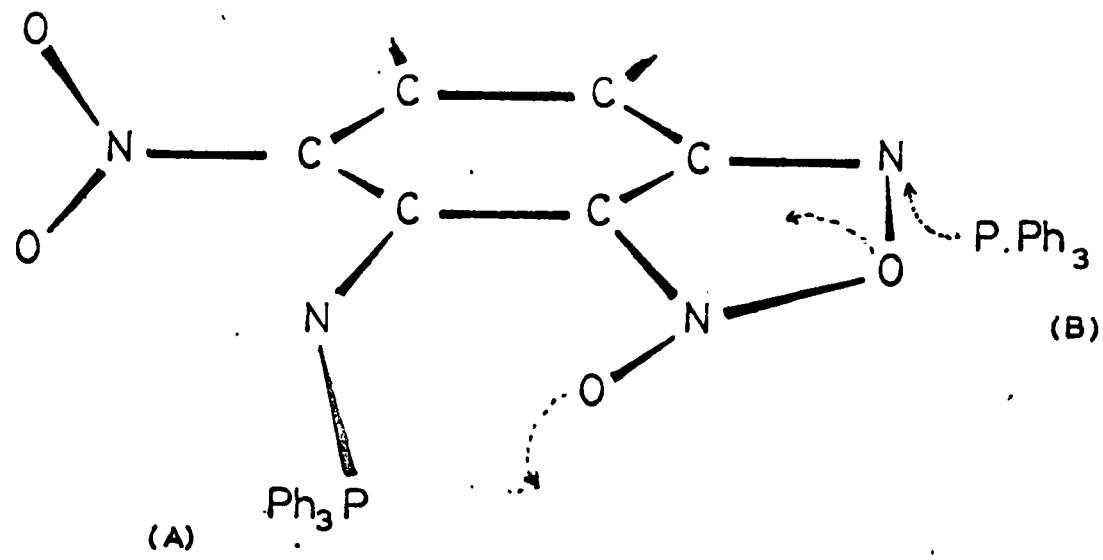
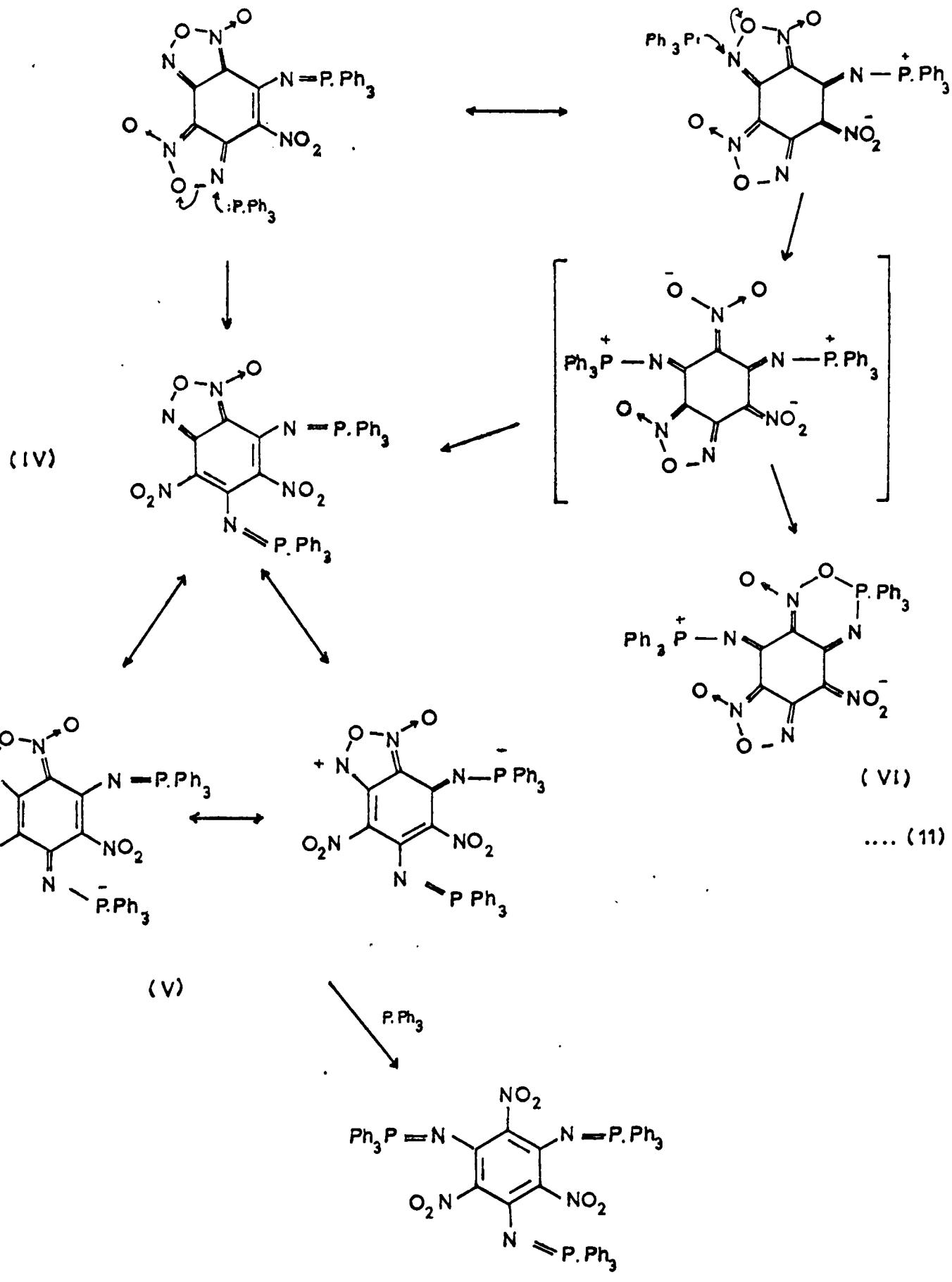


Figure 3


(IV)
(V)
(VI)
.... (11)
P.Ph3
Yellow Compound
.... (10)

The ring intermediate (VI) cannot be planar for C=N bonds are 1.33Å, bridging P-O bonds ≈ 1.60Å and P-N bonds ≈ 1.64Å. If the trigonal nitrogen atom remains in the plane of the three atoms bonded to it, then the extracyclic oxygen will be above (and the phosphorus below) a plane through N=C-C=N. Elimination of Ph_3PO could occur as a concerted action with the extracyclic oxygen sweeping over the top of the N=C-C=N plane as the bond between the nitrogen and the phosphorus atoms is broken and Ph_3PO departs beneath, (figure 4, reaction 12).

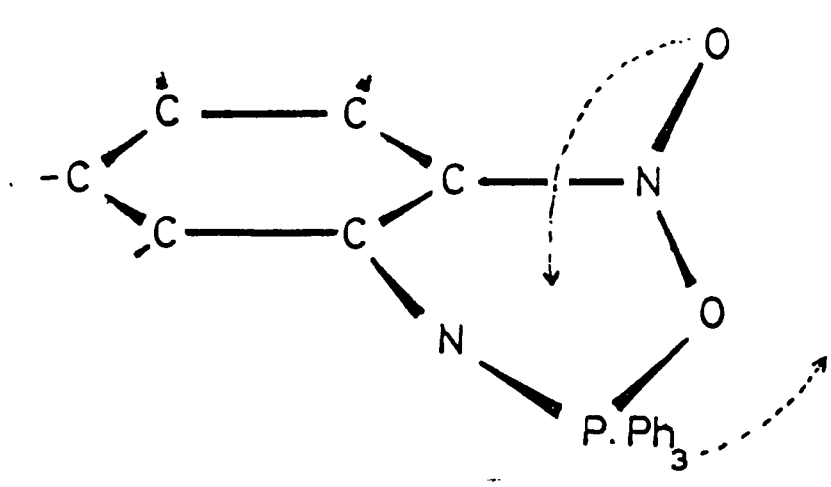
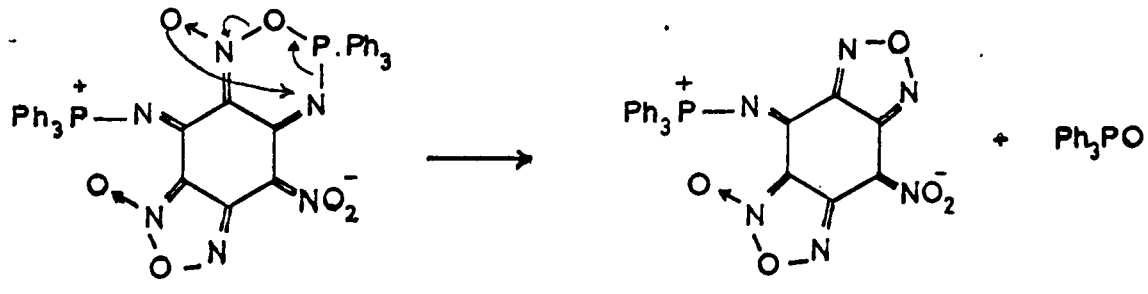


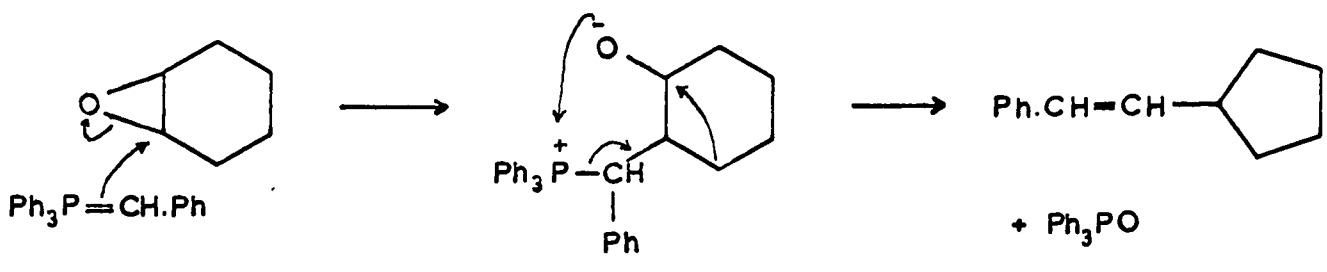
Figure 4



(VI) (VII)

.... (12)

A five membered ring rearrangement has been reported[76] in a reaction similar to the Wittig reaction (figure 5, reaction 13).



....(13)

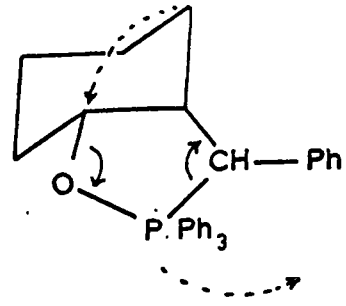
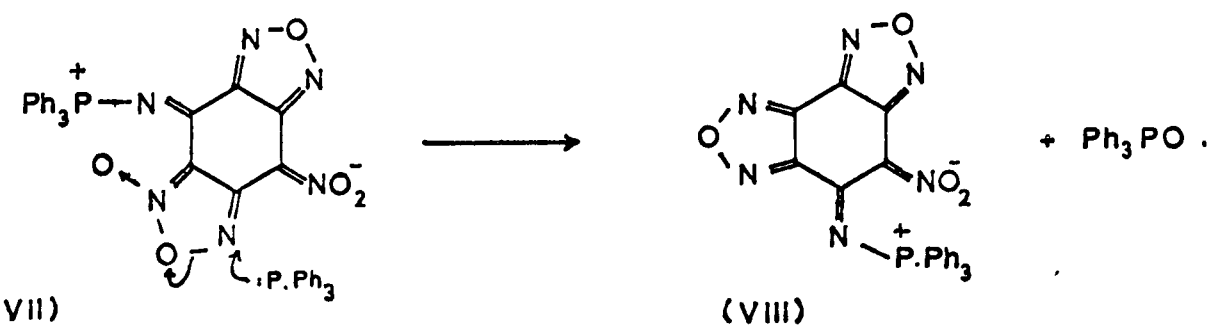


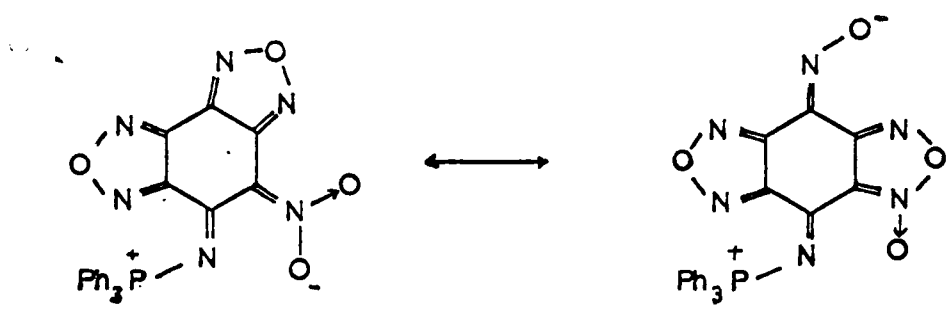
Figure 5.

A similar sequence to reactions 11, 12 could now follow at the remaining exposed nitrogen atom in intermediate (VII).



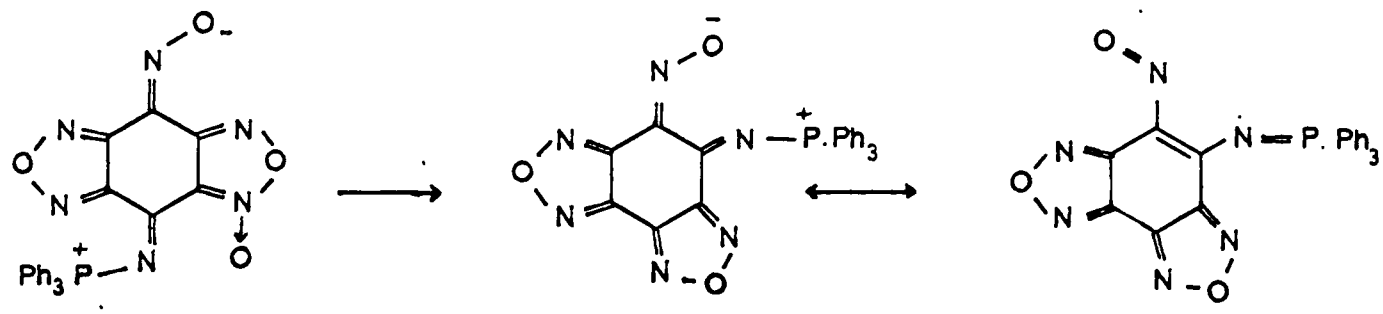
(VII) (VIII)

An interaction between a nitro group and an adjacent furazan ring has been reported,[77] so that intermediate (VIII) can be written in two forms. Reduction of the furoxan system (reactions 11, 12)



(VIII) (IX)

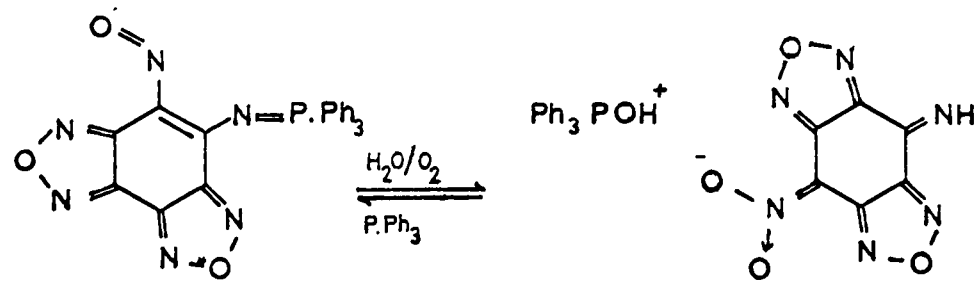
with intermediate (IV) would produce the green compound (Light Green Compound).



Green Compound

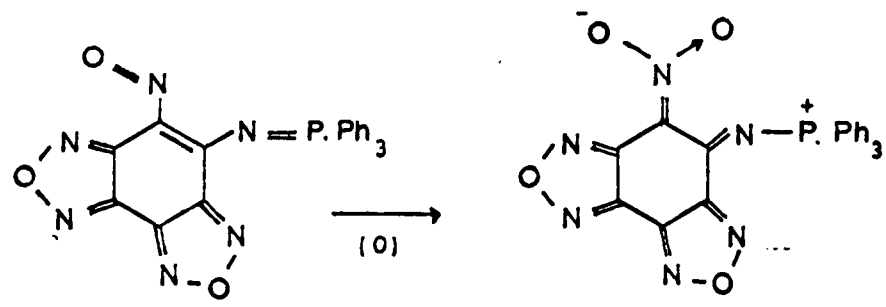
The red and the green compounds are very closely related, and it is likely that the red compound which is isolated is not formed during the course of the reaction. If a benzene solution of the red compound is treated with triphenyl phosphine it produces (among other

products) the green compound (T.L.C.). Conversely, if a 1:10 $MeOH/CHCl_3$ solution of the green compound is left open in the atmosphere it slowly turns to the red (T.L.C.). A drop of water hastens the process which is rapid with a drop of H_2O_2. (Plate 1d shows the red and the green compound crystallising together from a slow evaporation of 1:10 $MeOH/CHCl_3$ solution of the green compound.)

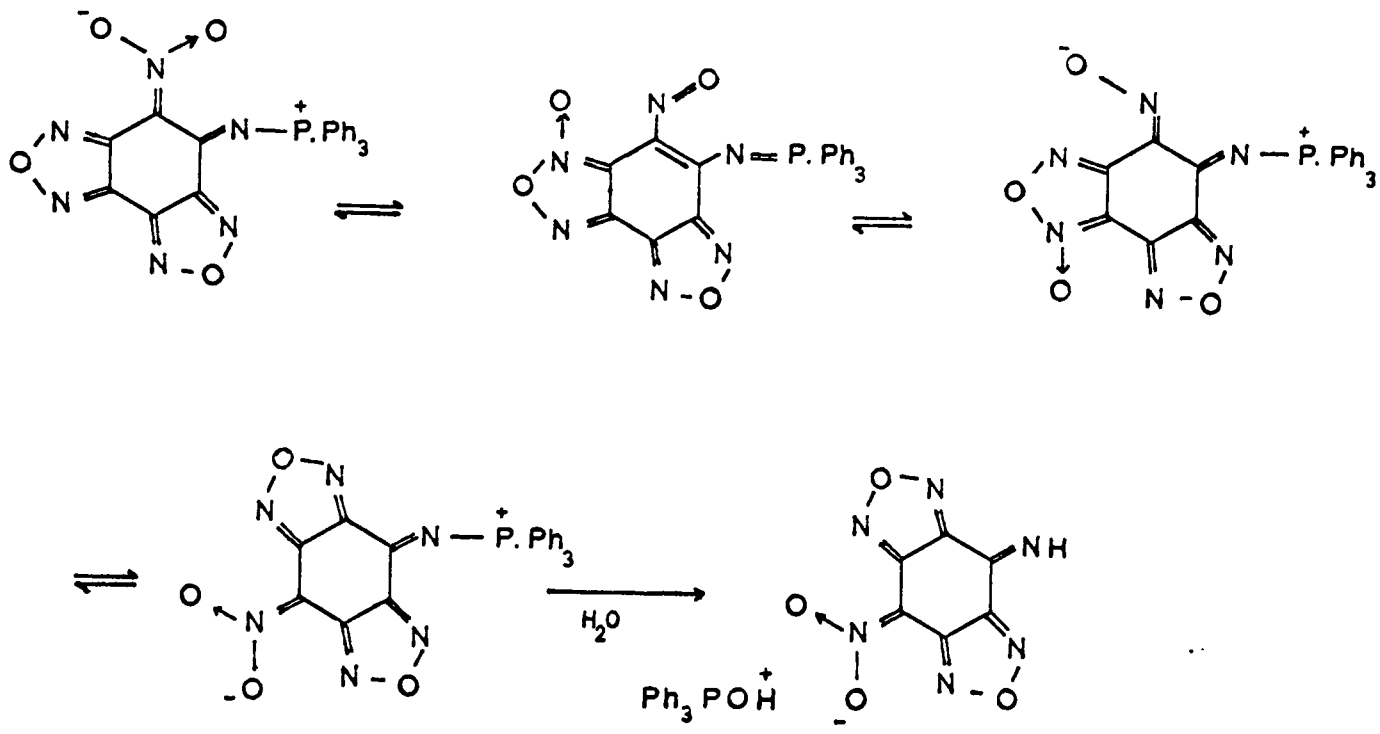


Since the benzotrifuroxan reduction is carried out with an excess of the phosphine, any red compound that may be formed is converted to the green.

A mechanism for the production of the red compound from the green would be oxidation of the nitroso group followed by rearrangement

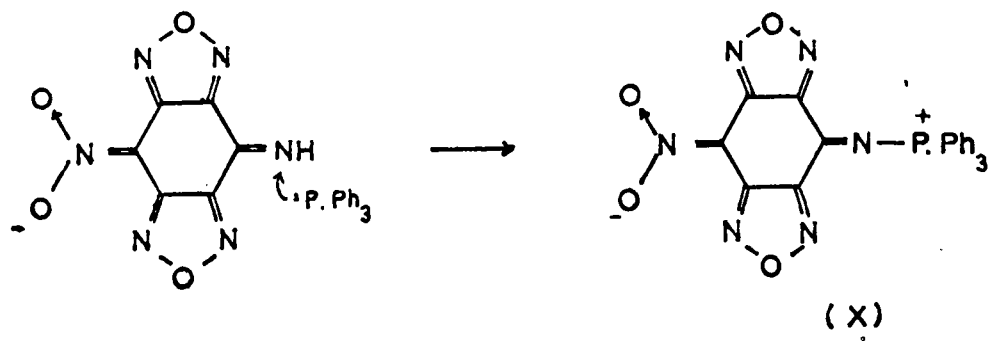


and hydrolysis. It is curious to note that the rearrangement (cf. reaction 4) would pass through a nitroso furoxan system (p.145)



Red Compound.

Conversion of the red compound to the green would follow attack at the imino group by the phosphine.

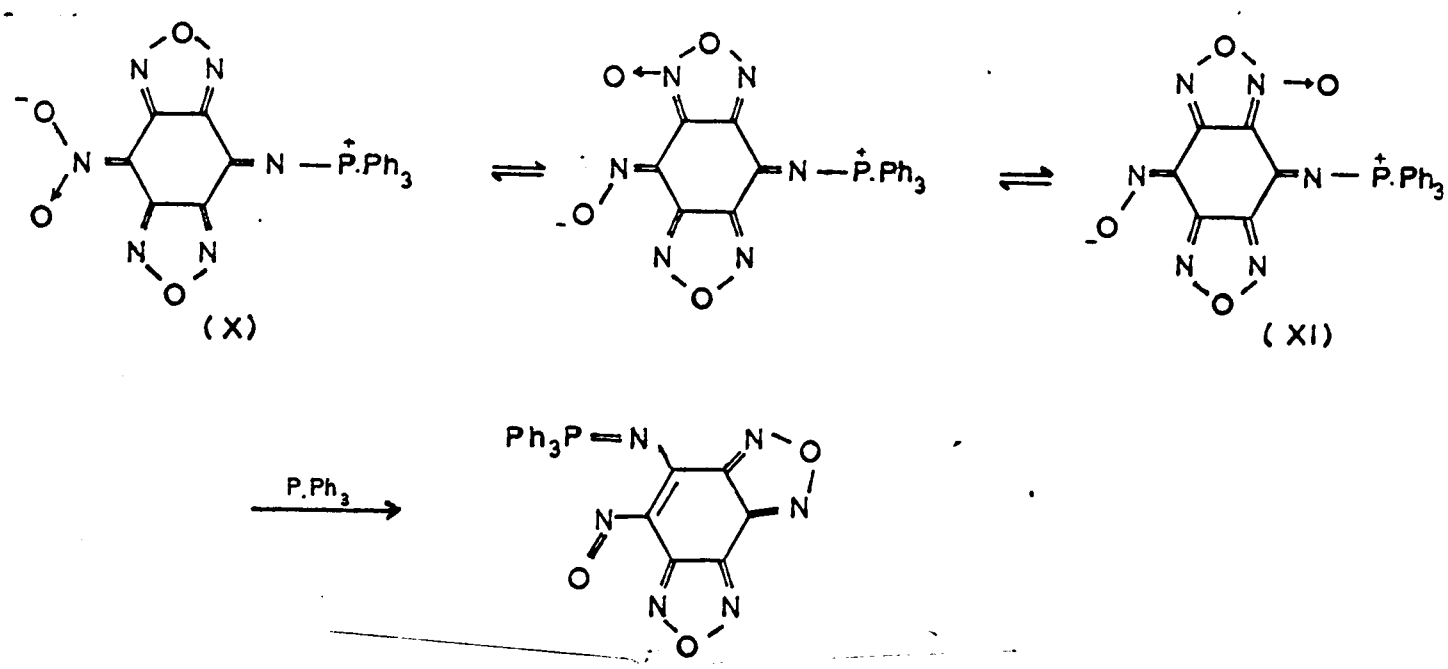


(X)

There is a report[78] of a reaction of type:

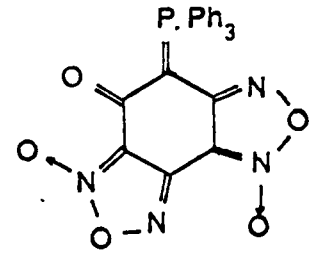


Rearrangement of intermediate (X) followed by phosphine attack gives the green compound. Intermediate (XI) is proposed during the

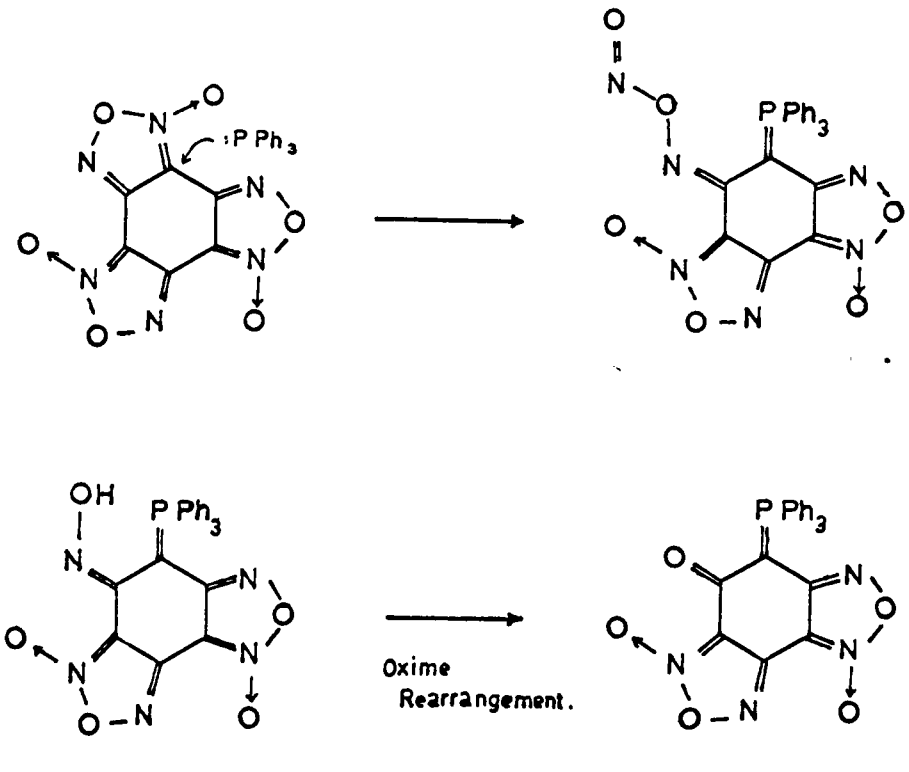


sequence that produces the green compound, and it is possible that if at this stage the reaction mixture, during reduction of the trifuroxan, does not contain an excess of the phosphine, then the intermediate (X) would be isolated and on crystallisation (from MeOH) hydrolyse to give the red compound.

Dark Green compound



This structure was determined[1] by Miss J. M. Evans who suggested the following mechanism:

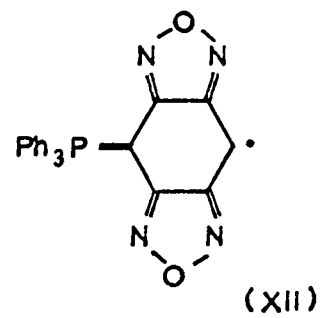


It is perhaps significant that the dark green compound is the major product from the reduction in protolytic solvents. The protons could be though to provide a protecting layer about the hetero-atoms blocking nucleophilic attack at these sites which leaves the carbon sites as the most likely to be attacked (p.138) This is the only compound to be isolated that contained furoxan rings.

Blue compound

Any mechanism for the blue compound must explain the distorted difuroxan dimer, for the corresponding C_6 ring of the red compound is planar. It is sterically possible that a difuroxan dimer could be formed with the planes of the C_6 rings inclined to each other (as with hindered biphenyls) and although this would introduce some problems with the π electron system, phosphorus seems a sufficiently versatile electron donor/acceptor to overcome them.

Dimerisation through a free radical (XII) as the last stage in a mechanism is a possible explanation. Russell Saunders coupling



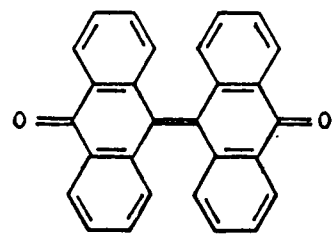
(XII)

predicts that such a radical might be distorted from the expected

planar difurazan molecule.

The blue compound is a most extraordinary molecule and it has but one close parallel in the literature (p. 80).

Dianthronylidene (XIII) is prepared[79] from anthacene by the action of fuming nitric acid in sunlight. The reaction has not been investigated but the dimerisation sounds like a free radical mechanism.



(XIII)

Reaction mechanisms can be written to produce the radical (XII) but they are unqualified speculation, and the author is unwilling to discuss them further.

Reduction by trialkyl phosphites

The reactivity sequence (p.134) of the phosphites in the reduction of benzotrifuroxan follows the same order as their nucleophilic strengths:

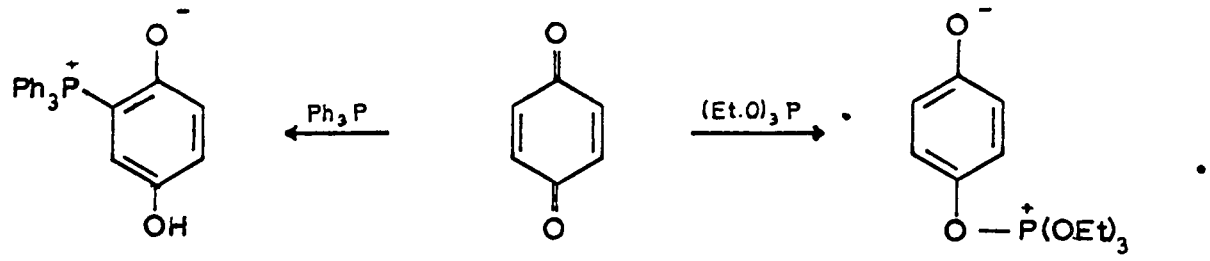
$$(EtO)_3P > (CH_2{:}CH_2O)_3P > (Cl.CH_2CH_2O)_3P > (EtO)_2.Cl.P$$

This suggests that the mechanism involves nucleophilic attack by the

phosphite. The weak reduction by Br_3P is consistent with such a conclusion while the absence of any reaction with Cl_3P indicates that a radical mechanism is unlikely.

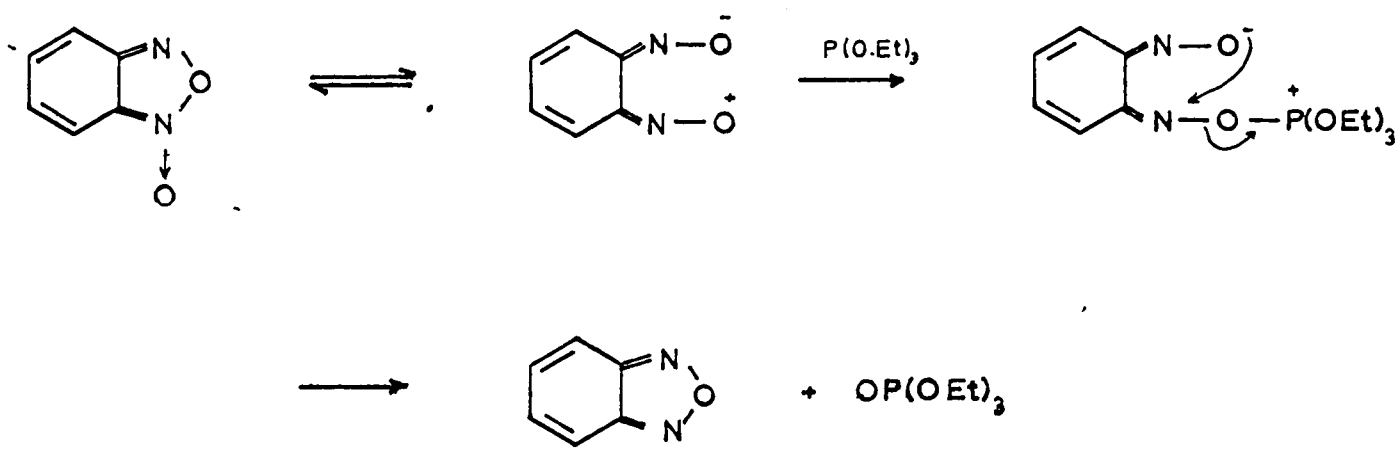
The trialkyl phosphite group, unlike the triphenyl phosphine group (p. 140), cannot delocalise any charge placed upon the phosphorus atom, and the heat of formation of the P=O bond is 151 K.cals/mole for triethyl phosphate[80], and 128 K.cals/mole for triphenyl phosphine oxide.[81] These two factors alone are probably responsible for the different behaviour of the two reductants.

There is some evidence that alkyl phosphites prefer to attack an oxygen atom rather than a nitrogen or carbon atom if a choice is available (reaction 14).[82] A mechanism for the reduction of benzofuroxan



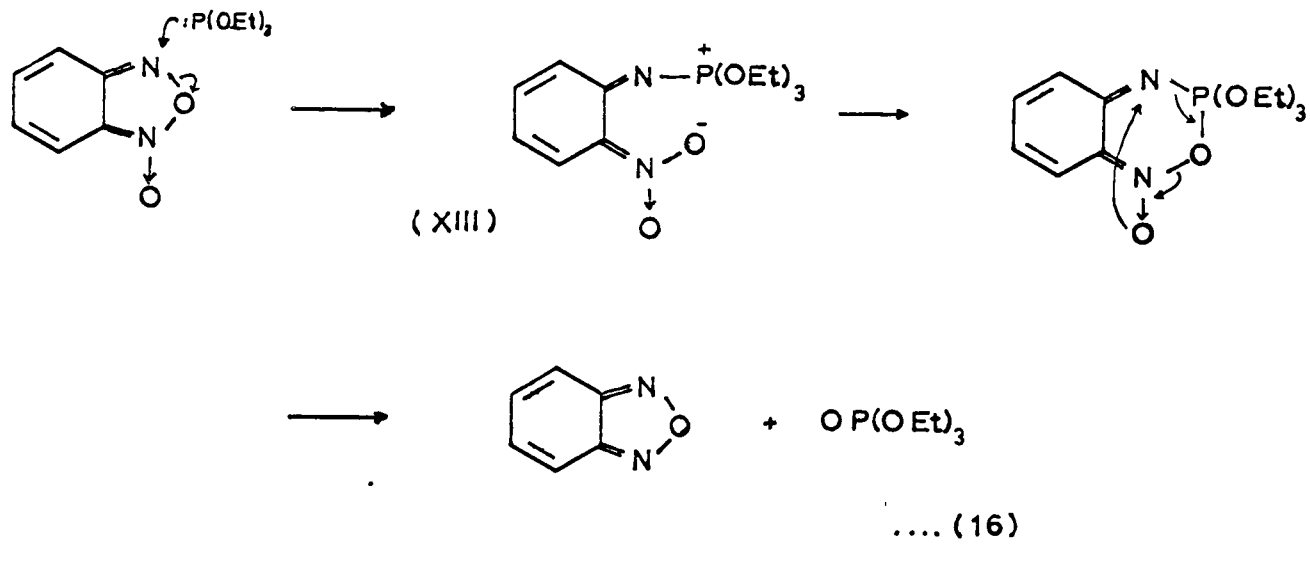
..... (14)

by attack at the extracyclic oxygen has been proposed (reaction 15)[73]



.... (15)

An alternative mechanism to reaction (15) proposes nucleophilic attack by the phosphite at the exposed nitrogen atom of the furoxan, (reaction 16).



.... (16)

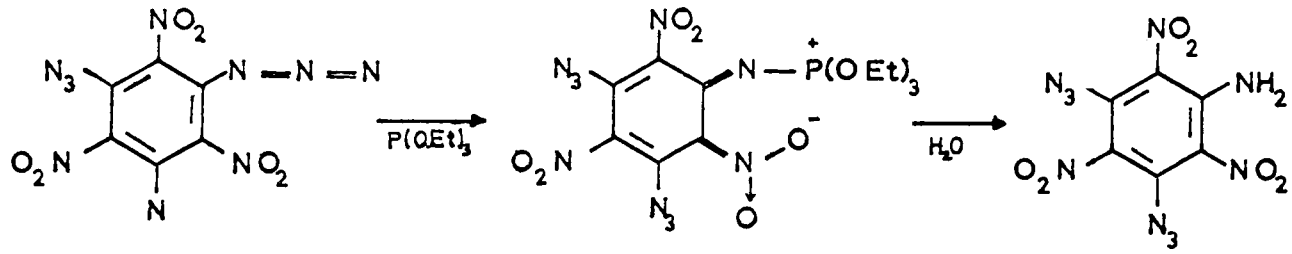
With either mechanism, the reduction of benzotrifuroxan is seen as a stepwise process, removing one oxygen atom at a time, controlled by the strength of the phosphate ester P=O bond. (The difuroxan monofurazan and the difurazan monofuroxan are both products of the reaction.)

There is little evidence to distinguish the two mechanisms, but one observation may be significant.

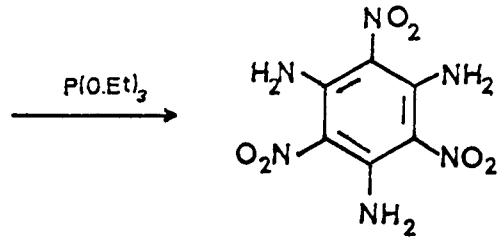
When a benzene solution sym-triazido trinitrobenzene is treated with triethyl phosphite the products are a mixture of benztrifurazan and sym-triamo trinitrobenzene. When benzotrifuroxan, in an identical sample of the solvent, is treated with triethyl phosphite no sym-triamino trinitrobenzene is isolated.

This suggests that attack at oxygen is the more likely of the

two reduction mechanisms, for the intermediate (XIII) that would be formed by the attack at the exposed nitrogen atom of a furoxan is similar to the intermediate (XIV) formed in the reaction between a phosphite and an azide.



(XIV)



..... (17)

The presence of benzotrifurazan among the products of reaction (17) can be explained by the formation of benzotrifuroxan by the pyrolysis of the azide from heat generated during the reaction (such a pyrolysis is the normal method of preparing benzotrifuroxan).[53]

APPENDIX I

EXPERIMENTAL SECTION

Melting points were measured on a Kofler block.

Microanalyses are by Bernhardt of Germany.

Infra-red spectra (IR) were measured on a Unicam S.P.200 infra-red spectrometer.

Thin layer chromatography (TLC) was carried out on unbaked silica 'H' plates, developed with iodine.

Chemical analysis of the coloured compounds

Chemical analysis by combustion was carried out on the red, light green and yellow compounds; each of the samples left incombustible residues.

The chemical analysis figures C(obs) and the chemical composition C(calc), calculated from the X-ray structure analysis, are given below.

	Red compound		Light green compound		Yellow compound	
	C(obs)	C(calc)	C(obs)	C(calc)	C(obs)	C(calc)
C.	57.4	57.6	61.2	61.8	70.1	70.0
H.	3.6	3.4	3.3	3.2	4.7	4.6
N.	16.4	16.8	16.9	18.0	6.7	7.7
P.	4.3	6.2	4.3	6.6	7.8	8.6
$O._{sub.}$	19.3	16.0	14.3	10.4	10.7	8.8

Attempt to prepare benzotriselazan

a. Sym-trichloro trinitrobenzene[83]

10g. of 1,3,5 trichlorobenzene was dissolved in a mixture of 100ml. fuming sulphuric acid (20% SO_3) and 50ml. fuming nitric acid. The solution was refluxed for 5 hours, then cooled and poured into a large volume of water. Sym-trichloro trinitrobenzene separated as a colourless solid, was filtered, washed and recrystallised from alcohol.

M.pt. 193°; yield 79%.

b. Sym-triamino trinitrobenzene[83]

2.5g. of sym-trichlorotrinitrobenzene were dissolved in 100ml. of alcohol. The solution was boiled under reflux and NH_3 gas passed through it for ½ hour. The highly insoluble sym-triamino trinitrobenzene separated as a yellow powder. The suspension was filtered and the solid washed. M.pt.<330°d; yield 87%.

c. Hexaminobenzene[84]

1.2g. of sym-triamino trinitrobenzene were dissolved in 6ml. of a reasonably pure sample of phenylhydrazine (purified by crystallisation) and the solution heated to 120° until no more gas was evolved. 5ml. of phenylhydrazine was added and the temperature raised to 140°* for two hours. The solution was cooled, diluted with benzene and small brown needles of hexaminobenzene collected by filtration. These were recrystallised from phenylhydrazine. The crystals slowly turned black on exposure to light. M.pt. 250°d; yield 35%.

d. Benzotriselazan



*Higher temperatures cause the reaction to explode; this is contrary to the reported preparation

Hexaminobenzene is sparingly soluble in water. 1g. of it was contained in a porous thimble at the lower end of a refluxing column. 3g. of SeO_2 dissolved in 40ml. of water was refluxed so that the returning liquid passed through the thimble. After four hours the solution was cooled, made acidic (HCl) and a microcrystalline brown solid filtered off. The IR spectrum of this solid was very similar to the spectrum of benzoselazan and quite different from that of hexaminobenzene. It included the proposed C=N stretching (1620 $cm.^{-1}$) of benzoselazan.

The solid, however, was insoluble in all common solvents and it was suspected that if a selenium nitrogen bond had been formed the compound that was isolated was a Ph:N.Se.N:Ph polymer.

e. Benzoselazan[85.18]

1g. of SeO_2 was added to an aqueous solution of 1g. of ortho phenylenediamine at room temperature. An immediate reaction took place and a solid was formed. After $\frac{1}{2}$ hour, the mixture was heated to 80° for 10 minutes, made weakly acidic (HCl) and shaken with ether. The solid benzoselazan is deposited from the ether solution on evaporation and is recrystallised from aqueous alcohol as faintly cream long needles. M.pt. 72.3°; yield 83%.

NOTE This compound is slightly volatile and has been shown[86] to be highly toxic. It should not be prepared unless extensive precautions are taken for the vapour will pass through human epidermis. (cont.)

Reduction of benzotrifuroxan

The reduction of benzotrifuroxan by trialkyl phosphites and triphenyl phosphine were carried out in an identical manner to that reported[1,53] by Miss J. M. Evans (D. Phil. Thesis, 'Reduction of Furoxans', Oxford University, 1966).

a. Reduction of benzotrifuroxan by phosphorus tribromide

0.5g. of benzotrifuroxan was heated under reflux at 150° with 4ml. of phosphorus tribromide in an atmosphere of nitrogen at a pressure of 30mm. During the reaction, yellow square prismatic crystals were formed on the sides of the reflux column. These were identified by their IR spectrum as phosphorus oxybromide (Br_3PO). (P=O stretching frequency 1270cm.$^{-1}$ and the complex P-Br stretching absorption maxima slightly modified from that of PBr_3.) After 12 hours, the mixture was cooled and washed with boiling petroleum ether (40/60). On cooling the petroleum ether, small white filament like crystals separated. These were sensitive to the atmosphere, liberating bromine but an IR spectrum indicated that they contained benzotrifurazan and phosphorus oxybromide.

NOTE (cont.) Because of a minor accident with benzoselazan, work on the preparation of the triselazan was discontinued after the supposed polymer had been prepared.

Reaction of 3,4 nitrobenzofurazan, benzotrifurazan and benzofurazan with triphenyl phosphine

In turn, 3,4 nitrobenzofurazan, benzofurazan and benzotrifurazan were refluxed for 24 hours with triphenyl phosphine in toluene and benzene solution. At the end the starting materials were recovered, and thin layer chromatography showed that no other compound had been formed.

Inter-conversion of the red and light green compounds

0.05g. of the light green compound was dissolved in 2ml. of a 1:10 mixture of carefully purified MeOH and $CHCl_3$. A drop of H_2O_2 (from 20 vol. solution diluted 100 times) was added to the solution which turned red. The solvent was allowed to evaporate and small crystals were collected. They were identified as the red compound by their melting point (167°), by comparison of IR spectra and by thin layer chromatography.

0.02g. of the red compound was dissolved in 2ml. of benzene and 0.2g. of triphenyl phosphine in 1ml. of benzene was added. The solution slowly turned green and on T.L.C. gave four distinguishable spots. One of these was identified as the light green compound and a solution of it was obtained by preparative thin layer chromatography. The IR spectra of the solution and a solution of the light green compound were similar.

A melting point of 263° (dec.) was recorded but there was insufficient of the sample for this to be reliable.

Reduction of the yellow compound

0.3g. of the yellow compound was heated to 140° with 3ml. of purified phenylhydrazine and 0.5ml. pyridine. After 1 hour, the solution was cooled, diluted with benzene, and filtered. A small quantity (0.01g.) of hexaminobenzene was collected and identified by comparison of the IR spectrum with the spectrum of a sample of hexaminobenzene prepared by the reduction of sym-triamino trinitrobenzene.

APPENDIX II

SKELETAL DIAGRAMS

Skeletal diagrams

The program for drawing the skeletal diagrams of crystal structures first calculates (and prints out) the co-ordinates (x',y',z') of the atoms and the required equivalent positions of the atoms with respect to orthogonal axes.

One of the crystal axes (o) is chosen to be coincident with the orthogonal axis (z') for which the matrix[87] is:

$$\begin{bmatrix} a\mathrm{Sin}(\beta).\mathrm{Sin}(\gamma)^* & 0 & 0 \\ -a\mathrm{Sin}(\beta).\mathrm{Cos}(\gamma)^* & b\mathrm{Sin}(\alpha) & 0 \\ a\mathrm{Cos}(\gamma) & b\mathrm{Cos}(\alpha) & c \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

where:

$$\mathrm{Sin}(\gamma)^* = (1-\mathrm{Cos}^2(\gamma))^{\frac{1}{2}}$$

$$\mathrm{Cos}(\gamma)^* = (\mathrm{Cos}(\alpha)\mathrm{Cos}(\beta) - \mathrm{Cos}(\gamma))/\mathrm{Sin}(\alpha)\mathrm{Sin}(\beta)$$

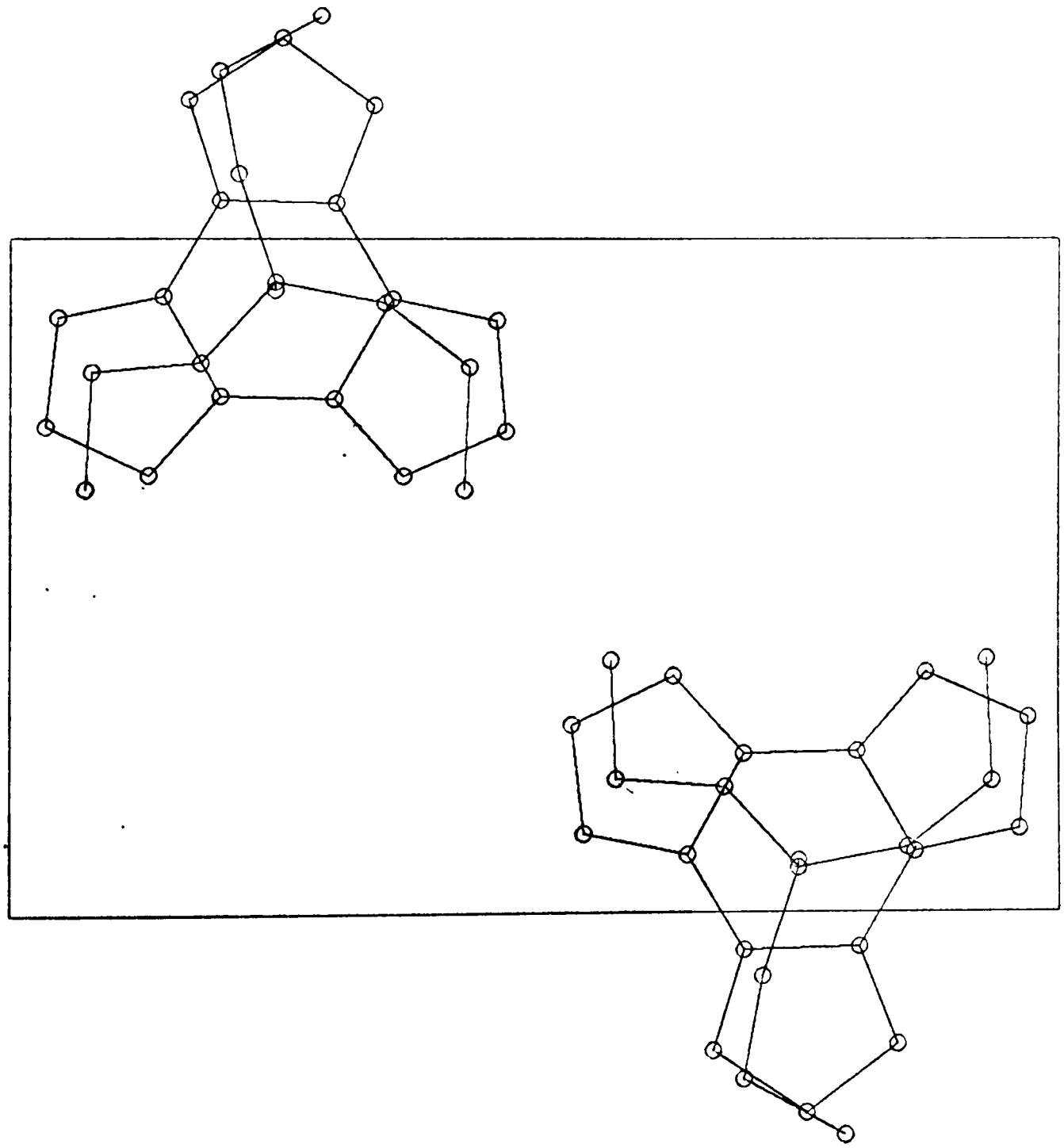
The structure diagram is drawn on an x,y graph plotter, linked on line with the KDF9 computer, in projection down (z'). The projection of the unit cell is calculated and the cell edges drawn in, then in turn each atom is represented by a small circle drawn with a centre at (x',y') and the centres are joined by a straight line for the atoms that are found to be less than 2Å apart in the crystal lattice.

The program, written in KDF9 Autocode and machine code*, and a typical plot are given below.

*The subroutines for instructing the x,y graph plotter were written by O. J. R. Hodder (Oxford University).

TEP.BTZ. 7 702 8.869 13.137

A PERPENDICULAR TO THE PAPER. B DOWN THE PAGE C ACROSS THE PAGE



```
CHAPTER  1
TITLE
VAR.SCALE.STRUCT.PLOT



1)Z'=0.1
JS91
A'=78.7
X=0
Y=2
JS76
X=.6
FETCH636;SET30;+
I=40
Y=0
JS77
Y=.4
STORE636;JS77
I=41
Y=7
JS77
Y=7.4
I=J+30
JS77
Y=14
I=42
JS77
I=K+30
Y=14.1
JS77
Y=
X=0
JS72
```

```
A'=157.2
B=12.4
HANDKEYS(0)
JUMP  2,ONE63
A'=78.7
B=24.8
2)D=E-F

D=D/B
JUMP  6,IGTD
A'=A'/D
B=B/12.4
D=DB
NL/CAPTION
SCALE=
PRINT(2/D)1,9
CAPTION
CM/A

6)Y=-F+0.15
X=-G+0.15
JS72
X=0
Y=0
JS80
%6(80)X,2
JS81
%6(86)X,2
JS81
%6(83)X,2
JS81
X=0
Y=0
JS81
```

```
D'=100
L=0(1)S
I=1(1)N
%6(D'+3K)X,3
JS70
JUMP  7,LNE0
JUMP  7,Q=63
JS80
JS75

7)J=SM+N-LN-I
JUMP  23,J=0
K=1(1)J
%6(D'+3K)A,3
D=%SQRT(AA+BB+CC+XX+YY+ZZ-2AX-2BY-2CZ+0.0000001)
JUMP  8,DGT2
JS80
%6(D'+3K)X,2
JS81
%6(D')X,2

8)REPEAT
D'=D'+3
REPEAT
REPEAT

23)Y=F-0.15
X=F+3.0

JS80
JS99
UP
```

```
40)CAPTION
A
41)CAPTION
B
42)CAPTION
C
31)CAPTION
DOWN THE PAGE.
32)CAPTION
ACROSS THE PAGE.
33)CAPTION
PERPENDICULAR TO THE PAPER.


PSA
70)FETCH607:DUP:J154LEZ:JS72:FETCH594:DUP:CAB:%F:STORE594
FETCH619:FETCH620:FETCH631:SET47:FLOAT:FETCH632:SET47:FLOAT
DUPD:OR:J119=Z:JS210:J120
119)ERASE:ERASE:ZERO
120)DUP:JS213:STORE619:DUP:JS212:STORE620:JS80
X=1/A'
FETCH622:DUP:+F:FETCH619:DUP:=Q11:/F:JS108:=C12
121)Q11:+F:DUP:JS213:STORE619:DUP:JS212:STORE620
JS81:DC12:J121C12NZ:ERASE:CAB:STORE594:DUPD
NEGF:STORE620:NEGF:STORE619:JS72:STORE620:STORE619:EXIT1

71)JS80:JS81:SET5:FETCH1=127
119)SET8:=C15
109)SHC6:DUPD:JS92:DC15:J109C15NZ:ERASE:ERASE:EXIT1

72)FETCH631:FETCH619:FETCH594:%F:JS109:-:STORE631
FETCH632:FETCH620:FETCH594:%F:JS109:-:STORE632:EXIT1
```

```
108)FIX;SET47;-;=C15;SHAC15;EXIT1

85)=I14;I15;ABS;M15;ABS;VR;MAX;DUP;=C14;SET3;J86V;SHL2
86)I14;AND;=M14;NEG;/;=Q15;SET3;SHC-2
87)Q15;+;Q14;J88NV;SHL-16
88)JS90;DC14;ZERO;NOT;STR;ERASE;NOT;OR;J87C14NZ;ERASE;EXIT1

80)SETB20;J82
81)SETB40
82)FETCH594;DUP;FETCH619;%F;JS108;REV;FETCH620;%F;JS108;CAB
101)FETCH633;J89=;DUP;JS90
89)STORE633;DUP;FETCH632;-;=M15;STORE632;DUP;FETCH631;-;=I15
STORE631;COTOQ15;M15;DUP;J83=Z;DUP;ABS;NEG;NOT;=C15
ZERO;SIGN;SHA-1;NOT;NEG;SHL2
83)I15;DUP;J84=Z;DUP;ABS;NEG;NOT;=+C15;ZERO;SIGN;SHA-1
NOT;NEG
84)OR;J85C15NZ;DUP;J154=Z

90)FETCH624;=Q1
98)SETB77;AND;DC1;FETCH626;SHL6;OR;DUP;STORE626;J95C1NZ
FETCH625;=Q2;=M1M20;SET8;=C1;J96C2NZ;I1;DUP;=I2;DUP
SET31;+;=M2;FETCH623;=C2;W02;I1;=M1;=I1
97)SET32;=RC2
96)Q2;STORE625;ZERO
95)ERASE;Q1;STORE624;EXIT1

91)SETB20;SET9;OUT;DUP;STORE623;=RC2;ZERO;=TR
MANUALQ2;RTN2;J94TR;TYPE
GRAPH PLOTTER PLEASE
94)SET8;=C1;SET544;=I1;SET512;=M1;SET520;DUP;JS98
STORE633;ZERO;STORE632;ZERO;STORE631;J97

92)REV;DUP;J153LE7;NEG;NOT;REV;DUP;JS90;J92
```

```
99)SETB20;JS90;SET263;ZERO;JS92;FETCH623;SET6;OUT;EXIT1

116)JS80;FETCH631;=I13;ZERO;STORE631;FETCH632;=M13
ZERO;STORE632;SET3=127;=M12;EXIT1

PSA


75)JS116;FETCH=127;FETCH636;DUP;=TR
ABS;J110NTR;SET14;JS114
110)FRB;SET8;=C13;DUP;EVEN
111)SHAD6;J112V;DC13;J111C13NZS;SET1;=+C13
112)SHAD-6;ERASE
113)ZERO;SHLD6;SET2;+;JS114;DC13;J113C13NZ;DUP
117)ERASE;ERASE;FETCH631;I13;+;STORE631
FETCH632;M13;+;STORE632;EXIT1

114)=M15;M12M15H
106)SET6;=C12;FETCH632;SET16;DUP;=+M13;-;STORE632;SETB20
115)=I12;ZERO;SHLD4;DUP;J153=Z
107)ZERO;REV;SHLD-2;SHL3;REV
SHC4;I12;JS101;DC12;SETB40;J115C12NZ;ERASE;ERASE;EXIT1

76)JS264;JS116;I7;=RM7;CUTC98
126)MOM7QM;SET8;=C7
125)ZERO;SHLD6;SETB75;J117=;JS123;DC7;J125C7NZ;ERASE;J126
123)DUP;J114=Z
SET17;-;DUP;SET16;SIGN;J122LTZ;SET20;J114LE
JS114;ZERO;SETB17;J107
122)SET3;+;DUP;J105LTZ;J103C8NZ;DUP;SET11;SIGN;J114LEZ
DUP;SET14;SIGN;J102LEZ;SET2;-;SET13;J114NE;ERASE;SETB524
SHC-9;JS106;SET7;FETCH2=127;J113
105)NC8;DC8
104)ERASE;EXIT1
103)SET2;+;SET12;J114=;SET13;J114=
102)ERASE;ZERO;J114
```

```
77)FETCH636;DUP;J154LEZ;DUP;SET127;SIGN;J154GTZ;JS282;DUP
J154=Z;JS116;ZERO;SHLD35;SET3;+;SET6;/I;DUP;SET7;-
NEG;=RC6;SHL3;=C7;=M6;SHL-35;=+M6;MOM6Q;SHLC7
124)ZERO;SHLD8;SETB177;AND;SETB177;J117=;ZERO;REV;SHLD-6;=C8
SHC6;JS123;DC6;J124C6NZ;ERASE;MOM6Q;SET6;=C6;J124

EVEN
127)=B1212121212121212
=B1205051206111106
=B0201010204101004
=B0000000065600000

=B2577652033400000
=B2573676025727720
=B7151540067734527
=B4677662625760000
=B5127677272672633

=B3657000026550000
=B4660000073400000

=B7565663347752571
=B3551736055456753
=B3531523535315235
=B5277652727315577
=B2566733747373400
=B2731762727370000
=B6532376065373400
=B2577652065275620
=B5375257765275637
=B6773452725667000
=B2737340027470000
=B2732756027726560
=B2654516027574401
```

```
PSA
CLOSE


CHAPTER  0
27)A'=0
B'=20
C'=30
H=£/180
A:9
B:96
C:10
D:100
D'=100
E=0
F=0
G=0
Z=0
READ(I)
READ(J)
READ(K)
READ(AI)
READ(AJ)
READ(AK)
READ(A(I+3))
READ(A(J+3))
READ(A(K+3))

L=4(1)6
A(L+3)=%SIN(HAL)
AL=%COS(HAL)
REPEAT
```

```
B1=1
B3=1
B5=1
READ(T)
JUMP  30,T=0
Q=1(1)T
READ(B(2I-1+60))
READ(B(2I+60))
READ(B(2J-1+60))
READ(B(2J+60))
READ(B(2K-1+60))
READ(B(2K+60))
REPEAT

30)L=0(1)10
CL=0
REPEAT

A0=%DIVIDE(A4A5-A6,A7A8)
A10=%SQRT(1-A0A0)
C1=A1A8A10
C4=-A1A8A0
C5=A2A7
C7=A1A5
C8=A2A4
C9=A3

%7(A')C1,0
NL/CAPTION
ORTHOG•MATRIX
NE LINE
L=0(3)6

M=1(1)3
```

```
PRINT(C(L+M))2,4
REPEAT
NEWLINE
REPEAT

READ(Q)
L=1(1)Q
READ(C1)
READ(C2)
READ(C(I+2))
READ(C(J+2))
READ(C(K+2))
READ(C6)
READ(C7)
NEWLINE
PRINT(C1)2,0
PRINT(C2)2,0
NEWLINE

2)P=0(1)T
D1=C3R(1+6P)+3(2+6P)
D2=C4R(3+6P)+R(4+6P)
D3=C5R(5+6P)+R(6+6P)
%7(B')D1,3
C'=%26(A',B',3,1,3)
%6(C')D1,3

PRINT(D1)12,3
PRINT(D2)4,3
PRINT(D3)4,3
%7(D'+3PQ)D1,3
JUMP  3,E61D2
E=D2
3)JUMP  4,D2GTF
F=D2
4)JUMP  5,D1GTG
G=D1
5)JUMP  6,HGTD1
H=D1
6)NEWLINE
REPEAT
D'=D'+3
JUMP  1,ZGT1

REPEAT

JUMP  1,ZGT1
Z=2
S=T
T=2
N=N
Q=1
D'=80
M=0(1)36
BM=0
REPEAT
B1=1
B9=1
B13=1
B15=1
C3=1
C4=1
C5=1
NEWLINE
NEWLINE
JUMP  2
1)DOWN  1/1
JUMP  27
PSA
END
CLOSE

:
```

APPENDIX III

CONSTRAINED REFINEMENT

The program for constrained least squares refinement was written by G. Ford (Oxford University) and the calculations were carried out on an English Electric KDF9 computer at this university.

Constrained refinement[88.]

In the method of constrained refinement, subsidiary conditions, related to the separation of specified atoms, are treated as further observational equations, and the squares of the residuals, suitably weighted, resulting from the conditions are added to the sum of the weighted squares of the residuals derived from the usual observational equations.

The actual procedure for adding in the subsidiary residuals is complex and for full detaisl, G. Ford, D. Phil. Thesis, Oxford University, 1968, should be consulted.

By imposing certain interatomic separations it is possible to define exactly a given geometry for a molecule and by allowing a small lattitude for the interatomic separations it is possible to calculate the best 'fit' for a molecule of an approximate geometry to the observed structure factors. The geometry is defined in three stages: (1) the distances between bonded atoms are assigned, (2) the distances between non-bonded atoms of atom triplets are assigned to determine the bond angles, (3) the distances of the atoms of the molecule to a 'null' atom ~6Å from the molecule are assigned to impose such conditions as planarity upon groups of atoms which are not imposed by the second stage.

In a molecule which has (N) atoms at positions: x_1, y_1, z_1; x_2, y_2, z_2 ..... $\underline{X}_{(N-1)}$; $\underline{X}_{(N)}$, with reference to crystallographic axes: a_x, a_y, a_z, ($\underline{A}$), certain distances ($\underline{r}_{ik}$) are to be prescribed for select pairs of atoms (i), (k), and the parameters ($\underline{X}_i$), ($\underline{X}_k$) are to be adjusted so that

the actual distance ($\underline{r}_{ik}$) with a weight (w_{ik}) gives the best fit with the observational data.

The sum of the weighted residuals (R_1) related to this requirment is:

$$R_1 = \sum_{i,k.} w_{ik}((G(\underline{X}_i - \underline{X}_k)^2)^{\frac{1}{2}} - \underline{r}_{ik})^2 \qquad \ldots\ldots (1)$$

Where (G) is the transformation matrix, derived from ($\underline{A}$), for converting the co-ordinates ($\underline{X}$) with reference to the crystallographic axis ($\underline{A}$) to the co-ordinates ($\underline{X}'$) with reference to orthogonal axes.

$$\underline{X}_i = \underline{X}_i^o + \Delta_i \qquad \ldots\ldots (2)$$

where ($\underline{X}_i^o$) is the initial parameter and (Δ_i) is the shift.

From (2), differentiating (R_1) with respect to the parameters ($\underline{X}_i$) and neglecting all powers of the shifts

$$\tfrac{1}{2}(\partial R_1/\partial \underline{X}_i) = \sum_{i,k.} w_{ik}((\underline{r}_{ik}/\underline{r}_{ik}^o)(G_{ik}^2(\Delta_i - \Delta_k)) + (1 - \underline{r}_{ik})r_{ik}^o G_{ik}(\Delta_i - \Delta_k) + G_{ik}(\underline{r}_{ik}^o - \underline{r}_{ik}) \qquad \ldots\ldots (3)$$

where $(G_{ik}) = G(\underline{X}_i^o - \underline{X}_k^o)/\underline{r}_{ik}^o$.

The weighted sum of the residuals (R_2) that is usually minimised in structure factor least squares refinement is:

$$R_2 = \Sigma w_F(|F_o| - |F_c|)^2$$

$$\tfrac{1}{2}(\partial R_2/\partial \underline{X}_i) = \sum_{i,k.} w_F((\partial F_o/\partial \underline{X}_k)(\partial F_o/\partial \underline{X}_i)\Delta_k -$$

$$-(F_o - F_o)\partial^2 F_c/\partial \underline{X}_i \partial \underline{X}_k \cdot \quad _i - (F_o - F_o)\partial F_c/\partial \underline{X}_i)$$

..... (4)

In the least squares refinement with specified distance requirements, the linear equations to be solved for the shifts are obtained by setting the sums of (3) and (4) to zero:

$$\partial R_1/\partial \underline{X}_i + \partial R_2/\partial \underline{X}_i = 0$$

In this particular version of the constrained refinement program, the terms from equations (3), (4) are added together into a full matrix and the shifts are then calculated.

The weights for the prescribed interatomic distances ($(\underline{r}_{ik})$Å) are the e.s.d.'s of these lengths and reasonable values for the refinement of the phosphate complex were obtained from the empirical formula:

$$w_{ik} = 0.025 + (\underline{r}_{ik} - 1.4)0.001 .$$

APPENDIX IV

MOLECULAR ORBITAL SECTION

Calculations that are not specifically worked through in the text, were calculated on the KDF9 computer with a program that was written by N. Saunders (Oxford University).

HÜCKEL APPROXIMATION[89]

The Hückel approximation is an inexact, but simple, method of investigating the π electrons of conjugated molecules and though it is crude, it determines certain properties of these molecules to a useful degree of accuracy.

A π molecular orbital $\psi(n)$ can be expressed as a linear combination of pπ atomic orbitals $\phi(m)$ where (m) refers to the mth. atom. It is assumed that the atomic orbitals (ϕ) are independent and normalised.

The molecular orbitals therefore can be written:

$$\psi(n) = N \sum_m a_{(nm)} \phi_{(m)}$$

where a(nm) is the coefficient of the atomic orbital and the normalising factor (N) is given by:

$$1/N^2 = \int \left(\sum_m a_{(nm)} \phi_{(m)}\right)^2 d\tau$$

$$= \sum_m a^2_{(nm)} \int \phi_{(m)} \phi_{(m)} d\tau + \sum_{\substack{m,p \\ m \neq p}} a_{(nm)} a_{(np)} \int \phi_{(m)} \phi_{(p)} \, d\tau$$

$\phi(m)$, $\phi(p)$ are normalised and independent so that the second integral is zero and the first is equal to $a^2(nm)$.

$$1/N^2 = \sum_m a^2_{(nm)}$$

The energy E(n) of the molecular orbital is given by

$$E(n) = \int (\psi(n) \, H. \, \psi(n)) d\tau$$

Hence:

$$E(n) = N^2\left(\sum_m a^2_{(nm)} \int \left(\phi_{(m)}^{H} \cdot \phi_{(m)} d\tau\right) + \sum_{\substack{m,p \\ m \neq p}} \left(a_{(nm)} a_{(np)} \int \left(\phi_{(m)}^{H} \cdot \phi_{(p)} d\tau\right)\right)\right)$$

The integrals in the first sum (coulomb integral) represent the energy of the individual $\phi(m)$'s and are usually represented by (α). The integrals in the second sum (resonance integrals) are assumed to be zero unless the orbitals $\phi(m)$, $\phi(p)$ are those of adjacent atoms in the molecule, and are represented by (β).

Numerical values for (α) and (β) for atoms of the second row of the periodic table are quoted in the literature.[91]

Secular equation

If a set of wave functions $\psi(n)$ are denoted by $\psi(1)$, $\psi(2)$ ... $\psi(i)$, the energies of the eigenstates of the molecule can be obtained by solving the determinental equation:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1i} - ES_{1i} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2i} - ES_{2i} \\ \cdot & & & \\ H_{i1} - ES_{i1} & H_{i2} - ES_{i2} & \cdots & H_{ii} - ES_{ii} \end{vmatrix} = 0$$

where:

$$H_{gh} = \int \psi_{(g)}^{H} \cdot \psi_{(h)} d\tau \quad \text{and} \quad S_{gh} = \int \psi_{(g)} \psi_{(h)} d\tau .$$

H is the Hamiltonian operator.

If the molecule possess some symmetry, the axes of symmetry may be used to define the axes of the wave function, so that each function is normalised and orthogonal to the others. The terms $S_{(gh)}$ then become zero thus simplifying the secular equation which is further simplified by the Hückel approximation where many of the term $H_{(gh)}$ are also set to zero.

Butadiene

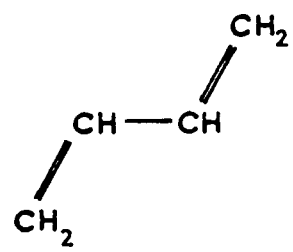
It is illustrative to consider the wave function for trans-butadiene. This molecule belongs to the symmetry group C_{2h}. The character of the π system can be determined by considering the behaviour of the atomic orbitals during the symmetry operations of the group. An orbital whose position is unchanged contributes a value of one to the character and one that is inverted through its centre contributes a value of minus one.

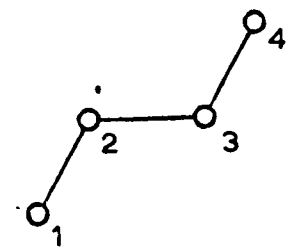
The π character of butadiene is given below, and from the character table of C_{2h} the characters of the irreducible representations for the wave functions can be obtained by inspection.

C_{2h}	E	C_2	i	σ_h
Ag	1	1	1	1
Bg	1	-1	1	-1
Au	1	1	-1	-1
Bu	1	-1	-1	1
$\Gamma\pi$	4	0	0	-4

$\Gamma_\pi = 2Bg + 2Au$

The wave function can be written by LCAO:





$$\psi(Au) = 1/\sqrt{2}\ (\phi_1 + \phi_4);\quad 1/\sqrt{2}\ (\phi_2 + \phi_3)$$

$$\psi(Bg) = 1/\sqrt{2}\ (\phi_1 - \phi_4);\quad 1/\sqrt{2}\ (\phi_2 - \phi_3)$$

The secular determinant for E(Bg) has the terms:

$$E(Bg) = \int(\psi_{Bg}\ H\psi_{Bg})\ d\tau$$

$$= \int(1/\sqrt{2}\ (\phi_1 - \phi_4)\ H.\ 1/\sqrt{2}\ (\phi_1 - \phi_4))d\tau +$$

$$\int(1/\sqrt{2}\ (\phi_1 - \phi_4)\ H.\ 1/\sqrt{2}\ (\phi_2 - \phi_3))d\tau +$$

$$\int(1/\sqrt{2}\ (\phi_2 - \phi_3)\ H.\ 1/\sqrt{2}\ (\phi_1 - \phi_4))d\tau +$$

$$\int(1/\sqrt{2}\ (\phi_2 - \phi_3)\ H.\ 1/\sqrt{2}\ (\phi_2 - \phi_3))d\tau$$

$$= H_{11} + H_{12} + H_{21} + H_{22}$$

$H_{11} = \alpha$; $H_{12} = H_{21} = \beta$; $H_{22} = \alpha - \beta$; $(\alpha = 0.)$

$$\begin{bmatrix} -E & \beta \\ \beta & -\beta-E \end{bmatrix} = 0$$

$$E^2 + E\beta - \beta^2 = 0$$

$$E = (-1 \pm \sqrt{5})\beta / 2$$

$$E = 0.62\beta \; ; \; -1.62\beta$$

Similarly fo E(Au)

$$E^2 - E\beta - \beta^2 = 0$$

$$E = 1.62\beta \; ; \; -0.62\beta$$

To determine the bond orders in butadiene it is necessary to find the correct combinations of the terms in $\psi(Au)$ and $\psi(Bg)$.

$$(Au) = 1/(1 + x^2)^{\frac{1}{2}} \; (\phi_1 + \phi_4 + x\phi_2 + x\phi_3)$$

$$E = \beta(1 \pm\sqrt{5})/2$$

$$E = 1/(1 + x^2)(\int\psi'(Au)\ H.\ \psi'(Au)d\tau + x^2 \int\psi''(Au)\ H.\ \psi''(Au)d\tau + 2x \int\psi'(Au)\ H.\ \psi''(Au)d\tau$$

$$\beta(1 +\sqrt{5})/2 = 1/(1 + x^2)(\alpha + x^2(\alpha + \beta) + 2x\beta)$$

$$x = 0.618$$

$$\psi(Au) = 0.37\ \phi_1 + 0.61\ \phi_2 + 0.61\ \phi_3 + 0.37\ \phi_4$$

$$\psi(Bg) = 0.62\ \phi_1 + 0.37\ \phi_2 - 0.37\ \phi_3 - 0.61\ \phi_4$$

The bond orders for the bond C(2)-C(3) is

$$\text{Au} \quad 2(0.61)^2 = 0.72$$

$$\text{Bg} \quad -2(0.37)^2 = \underline{-0.27}$$

$$\underline{\underline{0.45}}$$

The bond order for the bond C(1)-C(2) is

$$4(0.37)(0.61) = \underline{\underline{0.90}}$$

Benzotrifuroxan

In the case of benzotrifuroxan, the Hückel approximation is complicated by the presence of hetero-atoms and the consequent polarisation of the π electrons. To some extent this effect can be compensated by the careful choice of resonance and coulomb integral parameters.

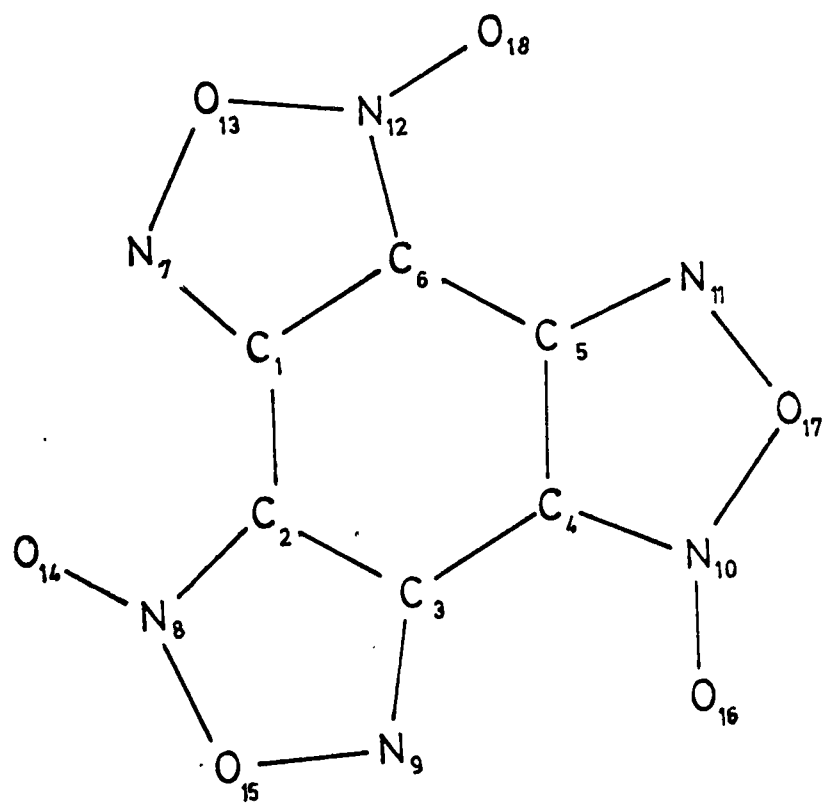
From the literature, the following values are acceptable:[91]

$$\alpha_C = 0; \quad \alpha_N = 0.5\beta_o; \quad \alpha_O = 2\beta_o$$

$$\beta_{CC} = 0.75\beta_o; \beta_{NO} = \beta_o; \quad \beta_{CN} = 0.9\beta_o$$

where (β_o) is the resonance integral for ethylene.

The atoms in benzotrifuroxan are numbered as follows:



Benzotrifuroxan is in group C_{3h} and the electron character is:

$$\Gamma_\pi = 6A'' + 6E''$$

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5
A'	1	1	1	1	1	1
E'	1	ϵ	ϵ^*	1	ϵ	ϵ^*
	1	ϵ^*	ϵ	1	ϵ^*	ϵ
A''	1	1	1	−1	−1	−1
E''	1	ϵ	ϵ^*	−1	$-\epsilon$	$-\epsilon^*$
	1	ϵ^*	ϵ	−1	$-\epsilon^*$	$-\epsilon$

$\epsilon = \text{Cos } 2/3 - i\text{Sin } 2/3$

The wave equations are:

$$\psi A'' = \frac{1}{\sqrt{3}}((\phi_1 + \phi_3 + \phi_5); (\phi_2 + \phi_4 + \phi_6); (\phi_7 + \phi_9 + \phi_{11}); (\phi_8 + \phi_{10} + \phi_{12}); (\phi_{13} + \phi_{14} + \phi_{17}); (\phi_{14} + \phi_{16} + \phi_{18}))$$

$$\psi^{(1)} E'' = \frac{1}{\sqrt{N}}((\phi_1 + e\phi_3 + e^*\phi_5); (\phi_2 + e\phi_4 + e^*\phi_6); (\phi_7 + e\phi_9 + e^*\phi_{11}); (\phi_8 + e\phi_{10} + e^*\phi_{16}); (\phi_{13} + e\phi_{15} + e^*\phi_{17}); (\phi_{14} + e\phi_{16} + e^*\phi_{18});$$

$$\psi^{(2)} E'' = \frac{1}{\sqrt{N}}((\phi_1 + e^*\phi_3 + e\phi_5); (\phi_2 + e^*\phi_4 + e\phi_6); (\phi_7 + e^*\phi_9 + e\phi_{11}); (\phi_8 + e^*\phi_{10} + e\phi_{12}); (\phi_{13} + e^*\phi_{15} + e\phi_{17}); (\phi_{14} + e^*\phi_{16} + e\phi_{18}))$$

Since $\psi^{(1)} E''$ and $\psi^{(2)} E''$ are degenerate, a linear combination of them is also an acceptable wave function:

$$\psi^{(1)} E'' + \psi^{(2)} E'' = \frac{1}{\sqrt{6}}((2\phi_1 - \phi_3 - \phi_5); (2\phi_2 - \phi_4 - \phi_6); (2\phi_7 - \phi_9 - \phi_{11}); (2\phi_8 - \phi_{10} - \phi_{12}); (2\phi_{13} - \phi_{15} - \phi_{17}); (2\phi_{14} - \phi_{16} - \phi_{18}))$$

$$\frac{\psi^{(1)}{}_{E''} - \psi^{(2)}{}_{E''}}{i} = \frac{1}{\sqrt{2}}\left(\left(\phi_3 - \phi_5\right); \left(\phi_4 - \phi_6\right); \left(\phi_9 - \phi_{11}\right); \left(\phi_{10} - \phi_{12}\right); \left(\phi_{15} - \phi_{17}\right); \left(\phi_{16} - \phi_{18}\right)\right).$$

The secular determinants are:

$$A'' \quad \begin{vmatrix} -E & 1.5\beta & .9\beta & 0 & 0 & 0 \\ 1.5\beta & -E & 0 & .9\beta & 0 & 0 \\ .9\beta & 0 & .5\beta-E & 0 & \beta & 0 \\ 0 & .9\beta & 0 & .5\beta-E & \beta & \beta \\ 0 & 0 & \beta & \beta & 2\beta-E & 0 \\ 0 & 0 & 0 & \beta & 0 & 2\beta-E \end{vmatrix} = 0$$

$$E'' \quad \begin{vmatrix} -E & .33\beta & .9\beta & 0 & 0 & 0 \\ .33\beta & -E & 0 & .9\beta & 0 & 0 \\ .9\beta & 0 & .5\beta-E & 0 & \beta & 0 \\ 0 & .9\beta & 0 & .5\beta-E & \beta & \beta \\ 0 & 0 & \beta & \beta & 2\beta-E & 0 \\ 0 & 0 & 0 & \beta & 0 & 2\beta-E \end{vmatrix} = 0$$

These can be solved for E(E") and E(A") by determining the latent roots of the determinental matrix. They are:

E(E")	E(A")	(in units of (β_o))
-3.04, -3.04	-3.10	
-2.19, -2.19	-2.17	
-1.19, -1.19	-1.62	
-0.60, -0.60	-0.68	
0.71, 0.71	0.71	
1.30, 1,30	1.86	

Benzotrifuroxan coefficient matrix (Hückel)

Molecular orbitals (sequentially in increasing energy)

Atoms	1	2	3	4	5	6
1	0.12172	-0.02719	0.10089	-0.08954	0.02551	-0.05464
2	0.13209	0.12434	0.02036	-0.06780	-0.00488	0.00965
3	0.12172	0.10097	-0.02690	0.06686	0.06479	-0.05464
4	0.13209	-0.04410	-0.11811	0.02968	0.06115	0.00965
5	0.12172	-0.07378	-0.07400	0.02268	-0.09030	-0.05464
6	0.13209	-0.08024	0.09725	0.03812	-0.05628	0.00965
7	0.19952	-0.12869	0.24272	-0.19236	0.11280	-0.14779
8	0.25259	0.35893	0.00887	-0.14547	-0.08707	0.11433
9	0.19952	0.27454	-0.00991	0.19387	0.11019	-0.14779
10	0.25259	-0.17178	-0.31528	-0.00267	0.16952	0.11433
11	0.19952	-0.14555	-0.23281	-0.00150	-0.22299	-0.14779
12	0.25259	-0.18715	0.30640	0.14814	-0.08244	0.11433
13	0.40984	-0.30280	0.52644	-0.24297	0.16677	-0.19754
14	0.17173	0.25808	0.00638	-0.59944	-0.35880	0.50628
15	0.40984	0.60731	-0.00099	0.26591	0.12703	-0.19754
16	0.17173	-0.12351	-0.22669	-0.01101	0.69853	0.50628
17	0.40984	-0.30452	-0.52545	-0.02294	-0.29380	-0.19754
18	0.17173	-0.13456	0.22031	0.61045	-0.33973	0.50628

	7	8	9	10	11	12
1	0.36788	-0.45797	-0.11586	0.11809	-0.28299	-0.07313
2	0.35507	-0.25728	-0.32945	-0.17514	0.39783	-0.04942
3	0.36788	0.32932	-0.33868	0.11809	0.20483	-0.20851
4	0.35507	0.41395	-0.05809	-0.17514	-0.15612	0.36924
5	0.36788	0.12864	0.45454	0.11809	0.07816	-0.23164
6	0.35507	-0.15667	0.38753	-0.17514	-0.24172	-0.31062
7	0.07022	-0.25875	-0.20114	0.38055	-0.31942	0.25375
8	0.02582	-0.23195	-0.05550	-0.32829	0.33129	0.20164
9	0.07022	0.30356	-0.12351	0.38055	-0.06440	-0.40601
10	0.02582	0.16404	-0.17312	-0.32829	-0.34027	0.18608
11	0.07022	-0.04482	0.32465	0.38055	0.38382	0.14723
12	0.02582	0.06791	0.22862	-0.32829	0.00898	-0.35772
13	-0.25247	0.23456	-0.03379	-0.03946	0.22207	0.09224
14	-0.05091	0.21382	0.05116	0.18591	-0.17774	-0.10619
15	-0.25247	-0.08802	0.22003	-0.03946	-0.19092	0.14620
16	-0.05091	-0.15122	0.15959	0.18591	0.18256	-0.09984
17	-0.25247	-0.14654	-0.18625	-0.03946	-0.03116	-0.23844
18	-0.05091	-0.06260	-0.21075	0.18591	-0.00482	0.20802

Benzotrifuroxan coefficient matrix (Hückel)

Molecular orbitals (sequentially in increasing energy)

Atoms	13	14	15	16	17	18
1	0.15487	-0.18930	-0.29385	-0.41248	-0.21488	0.37719
2	0.11772	-0.14060	-0.22507	0.45066	-0.19285	-0.38103
3	0.15487	0.34913	-0.01701	0.02015	0.46466	0.37719
4	0.11772	0.26522	-0.00922	-0.39234	-0.29385	-0.38103
5	0.15487	-0.15983	0.31086	0.39233	-0.24978	0.37719
6	0.11772	-0.12462	0.23430	-0.05831	0.48671	-0.38103
7	-0.31877	0.37124	0.22551	0.26856	0.06535	-0.14254
8	-0.35129	-0.02162	0.43766	-0.32369	0.07028	0.15689
9	-0.31877	-0.38091	0.20875	-0.07769	-0.26525	-0.14254
10	-0.35129	-0.36822	-0.23755	0.22271	0.24518	0.15689
11	-0.31877	0.00968	-0.43426	-0.19087	0.19991	-0.14254
12	-0.35129	0.38984	-0.20011	0.10098	-0.31546	0.15689
13	0.24705	-0.28040	-0.00936	-0.11200	0.07581	-0.00372
14	0.09714	0.00597	-0.12094	0.07358	-0.01598	-0.03052
15	0.24705	0.14830	-0.23816	0.12165	0.05910	-0.00372
16	0.09714	0.10175	0.06564	-0.05062	-0.05573	-0.03052
17	0.24705	0.13210	0.24751	-0.00965	-0.13490	-0.00372
18	0.09714	-0.10772	0.05530	-0.02295	0.07171	-0.03052

Benzotrifuroxan S.C.F. (self consistent field) orbital energies derived with the Hückel basis.

Orbital	Energy (e.v.)	Orb.	E. (e.v.)
1	-17.774335	10	-10.093099
2	-17.581030	11	-10.080603
3	-17.578509	12	-10.066739
4	-15.745108	13	-2.197861
5	-15.741362	14	-1.872545
6	-15.724814	15	-1.857503
7	-13.859443	16	0.755113
8	-12.211470	17	0.758761
9	-12.207714	18	2.854952

7 iterations

Benzotrifuroxan coefficient matrix (SCF)

Molecular orbitals

Atom	1	2	3	4	5	6
1	0.12125	-0.07870	-0.02440	-0.08266	0.06682	0.06437
2	0.14822	0.03802	-0.13974	-0.03046	0.02987	0.01418
3	0.11997	0.06148	-0.05767	-0.00627	-0.07991	0.09512
4	0.14856	0.10310	0.10046	-0.00813	-0.03437	0.02768
5	0.12098	0.02034	0.08054	0.06539	0.05998	0.06980
6	0.15007	-0.13710	0.03696	0.03734	0.01717	0.01866
7	0.13364	-0.15916	0.01002	-0.21775	0.12947	0.13350
8	0.26519	0.12996	-0.36036	-0.00213	0.08390	-0.09316
9	0.13109	0.07191	-0.14489	0.01672	-0.19986	0.20469
10	0.26692	0.24905	0.28892	-0.08385	-0.06783	-0.06465
11	0.13266	0.09071	0.13334	0.19172	0.16583	0.13586
12	0.27076	-0.37263	0.06764	0.09048	-0.06041	-0.06212
13	0.34211	-0.48906	0.07205	-0.49169	0.26258	0.28500
14	0.30202	0.15873	-0.44426	-0.01885	0.46564	-0.52514
15	0.33441	0.18469	-0.46409	0.06027	-0.44293	0.43802
16	0.30477	0.30822	0.35614	-0.46124	-0.38265	-0.36432
17	0.33692	0.31178	0.38712	0.40957	0.38103	0.28073
18	0.30935	-0.45993	0.08479	0.50731	-0.33177	-0.35402

Atom	7	8	9	10	11	12
1	0.35296	-0.26570	-0.40331	-0.23561	-0.07195	-0.07684
2	0.33110	-0.39653	-0.05409	0.40683	0.04924	0.13512
3	0.35162	-0.21615	0.43264	0.05335	0.18225	-0.17709
4	0.33001	0.14874	0.37294	-0.15989	-0.28039	0.28606
5	0.35210	0.48293	-0.02809	0.14125	-0.19576	-0.08919
6	0.33105	0.24623	-0.31491	-0.18300	0.37069	0.12656
7	0.12479	-0.25686	-0.25310	-0.33969	-0.38337	-0.25777
8	0.04797	-0.15761	-0.11238	0.43596	-0.05352	0.29238
9	0.12268	-0.08837	0.34744	-0.16109	0.31141	-0.45577
10	0.04736	-0.02043	0.19373	-0.26989	-0.19229	0.41037
11	0.12424	0.34832	-0.09666	0.37006	-0.20536	-0.38513
12	0.04749	0.17615	-0.07895	-0.05758	0.47782	0.21765
13	-0.26986	0.06106	0.25019	0.18513	-0.04495	0.01810
14	-0.09860	0.15974	0.11450	-0.26585	0.03455	-0.17553
15	-0.26903	0.18605	-0.17834	-0.12902	-0.12028	0.07575
16	-0.09725	0.02111	-0.19639	0.16630	0.11735	-0.24724
17	-0.27012	-0.24856	-0.07261	-0.04685	0.18550	-0.01179
18	-0.09733	-0.17886	0.07958	0.03438	-0.29101	-0.12953

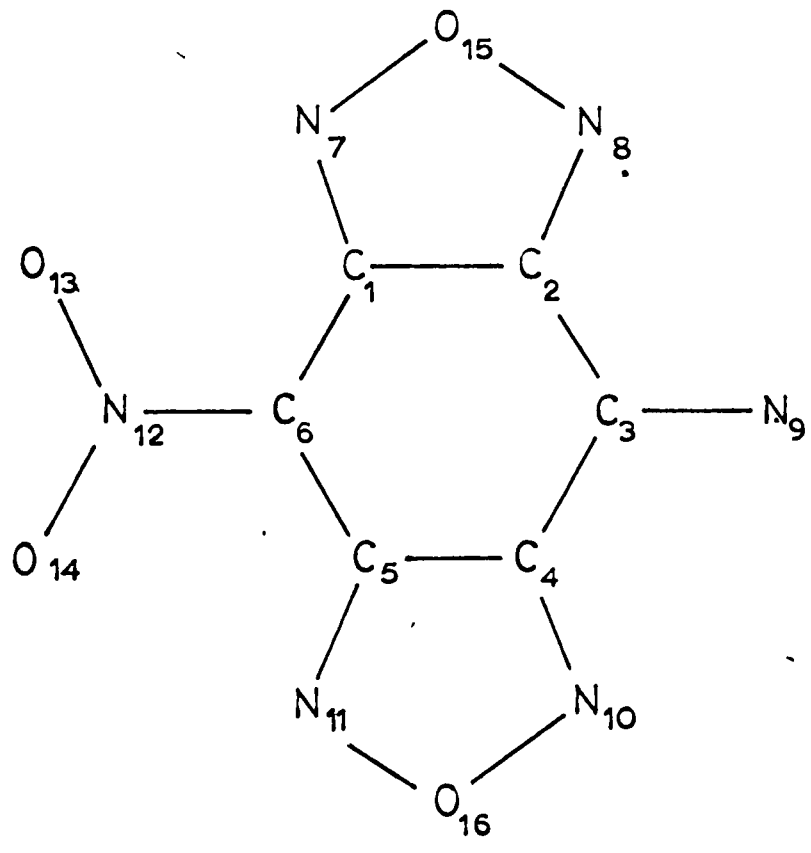
Benzotrifuroxan coefficient matrix (SCF)

Molecular orbitals

Atom	13	14	15	16	17	18
1	0.17738	-0.18302	-0.30356	0.40207	-0.27804	-0.37735
2	0.15177	0.02568	-0.30070	0.01864	0.49273	0.37657
3	0.18092	0.35287	-0.01005	-0.44233	-0.20734	-0.37693
4	0.15698	0.24598	0.17199	0.41831	-0.26175	0.37529
5	0.18187	-0.16879	0.30842	0.04145	0.48812	-0.37659
6	0.15834	-0.27295	0.12567	-0.43525	-0.23102	0.37522
7	-0.32212	0.30196	0.31593	-0.21577	0.18578	0.15644
8	-0.35336	-0.15283	0.42894	0.02018	-0.30281	-0.15716
9	-0.32479	-0.42251	0.10815	0.26833	0.09172	0.15551
10	-0.36020	-0.29303	-0.34217	-0.27251	0.13287	-0.15626
11	-0.32754	0.12015	-0.41514	-0.05443	-0.28050	0.15630
12	-0.35958	0.44548	-0.07778	0.25020	0.16847	-0.15577
13	0.17945	-0.18210	-0.05818	-0.00664	-0.07251	-0.00052
14	0.11678	0.04822	-0.13687	-0.00508	0.07905	0.03575
15	0.17002	0.14085	-0.13095	-0.05950	0.04293	-0.00015
16	0.11906	0.09387	0.10878	0.07118	-0.03483	0.03560
17	0.17218	0.04172	0.18473	0.06670	0.03085	-0.00057
18	0.11876	-0.14198	0.02526	-0.06540	-0.04385	0.03544

The red compound

The atoms of the red compound are numbered as follows:



Parameters for the Hückel Fock matrix (integers refer to the atoms)

1	2	-1.00000	1	6	-1.00000	1	7	-1.00000
3	9	-1.00000	4	5	-1.00000	4	10	-1.00000
7	7	-0.50000	7	15	-0.70000	8	8	-0.50000
10	16	-0.70000	11	11	-0.50000	11	16	-0.70000
13	13	-1.50000	14	14	-1.50000	15	15	-1.50000
2	3	-1.00000	2	8	-1.00000	3	4	-1.00000
5	6	-1.00000	5	11	-1.00000	6	12	-1.00000
8	15	-0.70000	9	9	-0.50000	10	10	-0.50000
12	12	-0.50000	12	13	-1.00000	12	14	-1.00000
16	16	-1.50000						

Energies of the molecular orbitals (units of β)

1	-2.793431	9	-0.834371
2	-2.514764	10	-0.342985
3	-2.365193	11	0.308942
4	-1.859540	12	0.594839
5	-1.565308	13	0.657298
6	-1.500000	14	1.500000
7	-1.229646	15	1.581482
8	-1.000000	16	2.362677

Red compound coefficient matrix (Hückel)

	Molecular orbital					
Atom.	1	2	3	4	5	6
1	0.25593	0.16670	-0.21711	0.07558	0.36114	-0.00000
2	0.20226	0.25627	-0.21711	0.25668	-0.08674	-0.00000
3	0.17159	0.25393	0.00000	0.45673	-0.27687	-0.00000
4	0.20226	0.25627	0.21711	0.25668	-0.08674	0.00000
5	0.25593	0.16670	0.21711	0.07558	0.36114	0.00000
6	0.35178	-0.01644	0.00000	0.07207	0.45167	-0.00000
7	0.16087	0.17937	-0.29640	-0.18821	0.20037	-0.00000
8	0.13747	0.22383	-0.29640	-0.05500	-0.22006	-0.00000
9	0.07482	0.12604	0.00000	0.33594	-0.25989	-0.00000
10	0.13747	0.22383	0.29640	-0.05500	-0.22006	0.00000
11	0.16087	0.17937	0.29640	-0.18821	0.20037	0.00000
12	0.47083	-0.37473	-0.00000	-0.01715	-0.01528	0.00000
13	0.36402	-0.36928	0.00000	-0.04769	-0.23398	-0.70711
14	0.36402	-0.36928	-0.00000	-0.04769	-0.23398	0.70711
15	0.16146	0.27814	-0.47961	-0.47351	-0.21098	-0.00000
16	0.16146	0.27814	0.47961	-0.47351	-0.21098	0.00000

Red compound coefficient matrix(Hückel)

Molecular orbital

Atom	7	8	9	10	11
1	-0.37691	-0.22361	0.01050	-0.07322	-0.01680
2	-0.37691	0.22361	0.22467	-0.14350	0.18069
3	-0.00000	0.00000	-0.20839	-0.04276	0.38973
4	0.37691	-0.22361	0.22467	-0.14350	0.18069
5	0.37691	0.22361	0.01050	-0.07322	-0.01680
6	0.00000	0.00000	0.03926	0.49923	0.00913
7	-0.08656	-0.44721	-0.25518	-0.38084	-0.18463
8	-0.08656	0.44721	0.38535	0.06676	-0.42876
9	-0.00000	0.00000	-0.62322	0.27233	-0.48178
10	0.08656	-0.44721	0.38535	0.06676	-0.42876
11	0.08656	0.44721	-0.25518	-0.38084	-0.18463
12	0.00000	-0.00000	0.01176	0.31766	0.03078
13	-0.00000	-0.00000	-0.01767	-0.27455	-0.01701
14	-0.00000	-0.00000	-0.01767	-0.27455	-0.01701
15	0.44822	-0.00000	-0.13689	0.19002	0.23736
16	-0.44822	-0.00000	-0.13689	0.19002	0.23736

	12	13	14	15	16
1	0.24659	0.26536	0.44721	-0.21509	0.38490
2	0.24659	-0.02082	-0.44721	-0.27121	-0.37723
3	0.00000	-0.20140	0.00000	0.49263	0.37473
4	-0.24659	-0.02082	0.44721	-0.27121	-0.37723
5	-0.24659	0.26536	-0.44721	-0.21509	0.38490
6	-0.00000	0.14396	0.00000	0.48696	-0.39758
7	-0.39327	-0.29756	-0.22361	0.12440	-0.13458
8	-0.39327	-0.05027	0.22361	0.15136	0.13164
9	-0.00000	0.17402	-0.00000	-0.23668	-0.13090
10	0.39327	-0.05027	-0.22361	0.15136	0.13164
11	0.39327	-0.29756	0.22361	0.12440	-0.13458
12	0.00000	-0.62535	-0.00000	-0.33995	0.16955
13	-0.00000	0.28987	-0.00000	0.11032	-0.04389
14	-0.00000	0.28987	0.00000	0.11032	-0.04389
15	0.26282	0.11287	0.00000	-0.06264	0.00053
16	-0.26282	0.11287	0.00000	-0.06264	0.00053

Frontier electron concept[75].

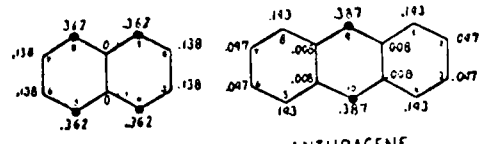
There is a quantitative correlation between reactivity and the electron configuration of the highest occupied π-orbital in the ground state of multicyclic aromatic hydrocarbons.

The wave function (ψ) for these compounds is calculated by the LCAO method where:

$$\psi = \sum_{i}^{2n} a_i \phi_i$$

and the density of each electron occupying the nth. electronic level at the ith. carbon atom is represented by $(a_i)^2$.

The electron density for the highest occupied orbital in naphthalene and anthracene is shown below and is compared with the experimental observations for oxidation and nucleophilic attack on these compounds.



Compounds	Position of the highest density of the frontier electrons	Structure of the reaction products: Oxidation	Halogenation	Nitration
Naphthalene	1,4,5,8	1,4-quinone (5,8-quinone)	1-F[1] 1-Cl 1-Br 1,4-di-Cl 1,5-di-Cl	1-NO_2 1,5-di-NO_2 1,8-di-NO_2
Anthracene	9,10	9,10-quinone	9-Cl 9,10-di-Cl 9-Br 9,10-di-Br	9-NO_2 9,10-di-NO_2

Similar results have been observed with many other aromatic hydrocarbons.

It is argued that the intermediate of these chemical reactions involve specifically the transition to the triplet state of the electrons of the highest occupied orbital of the hydrocarbon, (Frontier electrons). Such transitions are observed in photo-oxidation reactions of similar compounds.

The correlation between reactivity and the frontier electron configuration is too good to be mere coincidence and it is tempting to assume that the two factors are directly related.

The configurations, however, are calculated for the ground states of the molecules, while the approaching nucleophilic would perturb this ground state, so that there can be no rigourous basis for such an assumption.

A number of workers have objected to the concept, but, though as yet it has no sound theoretical justification, the conclusions derived from it are confirmed by experiment.

Therefore, the deductions from the frontier electron configuration of benzotrifuroxan for nucleophilic attach cannot be regarded as rigourous, but they do have a reasonable experimental justification.

APPENDIX V

Tables of atomic and structural parameters

(i) Atomic co-ordinates.

(ii) E.s.d.'s of the atomic co-ordinates.

(iii) Interatomic distances and angles with the corresponding e.s.d.'s.

(iv) Co-ordinates of the atoms (in Å) with respect to orthogonal axes.

The co-ordinates (x', y', z') with reference to orthogonal axes can be calculated form the atomic co-ordinates (x, y, z) The orthogonal axes are orientated with respect to a least squares best plane through given atoms of a structure, and these atoms have a centroid at (x", y", z").

To obtain the co-ordinates (x', y', z') subtract the centroid from the crystal co-ordinates (x, y, z) and then pre-multiply this vector ($\underline{X} - \underline{X}''$) by the transformation matrix (T).

$$(T).(\underline{X} - \underline{X}'') = (\underline{X}')$$

The transformation matrix is obtained by premultiplying the orthogonalisation matrix (p.163) by the direction cosine matrix of the plane with respect to the orthogonal axes.

The axis (c') along which the co-ordinate (z') is measured is generated perpendicular to the selected least squares best plane. The values of (z') in tables (iv) therefore indicate the perpendicular distance of the atoms from this plane.

Any such distance that is required but is not listed can be calculated from the transformation matrix which is given, and any interatomic distance or angle that is not listed can be determined with simple three dimensional trigonometry.

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Light Green compound	202
Yellow compound	208
Blue compound	220
Phosphate complex(-120°C)	233
Phosphate complex(22°C)	238

Red Compound Atomic Co-ordinates

Atom		x/a	y/b	z/c	U(iso)
P	1	0.28516	0.01161	0.18044	0.02540
C	1	0.45129	-0.01056	0.26218	0.03044
C	2	0.52282	-0.10708	0.24453	0.03690
C	3	0.65471	-0.11753	0.30641	0.05003
C	4	0.72054	-0.02712	0.38449	0.05256
C	5	0.64596	0.06689	0.40150	0.04904
C	6	0.51464	0.07655	0.34299	0.04134
C	11	0.22607	-0.12121	0.09777	0.03096
C	12	0.19172	-0.24078	0.16192	0.03850
C	13	0.15005	-0.34662	0.09759	0.04217
C	14	0.21606	-0.10478	-0.02963	0.03802
C	15	0.17047	-0.21180	-0.09134	0.04878
C	16	0.14040	-0.32984	-0.02813	0.04898
C	21	0.31271	0.15441	0.07817	0.02904
C	22	0.44736	0.21769	0.05963	0.03372
C	23	0.46504	0.32701	-0.02346	0.04420
C	24	0.34900	0.37133	-0.08619	0.05210
C	25	0.21646	0.30997	-0.06892	0.05642
C	26	0.19393	0.20021	0.01594	0.05331
O	1	0.16074	0.02477	0.26231	0.05597
C	31	0.12124	0.34205	0.49294	0.03131
C	32	0.21964	0.37436	0.40187	0.03486
C	33	0.31999	0.48720	0.39724	0.04093
C	34	0.33639	0.58208	0.48383	0.04803
C	35	0.23320	0.54451	0.57146	0.03860
C	36	0.12970	0.43162	0.57729	0.03143
N	1	0.02554	0.23391	0.49906	0.03604
N	2	0.23714	0.31258	0.31184	0.05455
N	3	0.39907	0.49657	0.30769	0.06343
N	4	0.42672	0.67522	0.47976	0.05370
N	5	0.21657	0.60858	0.66073	0.05060
N	6	0.04967	0.43128	0.66563	0.04302
O	2	0.02166	0.15829	0.42061	0.04985
O	3	-0.05786	0.21158	0.57960	0.05044
O	4	0.34811	0.38971	0.25264	0.07181
O	5	0.10612	0.54307	0.71648	0.05295

Red Compound E.s.d.'s of atomic co-ords.

Atom		x/a	y/b	z/c	U(iso)
P	1	0.00019	0.00015	0.00014	0.00042
C	1	0.00073	0.00058	0.00056	0.00139
C	2	0.00080	0.00064	0.00062	0.00156
C	3	0.00094	0.00076	0.00074	0.00196
C	4	0.00097	0.00078	0.00076	0.00204
C	5	0.00092	0.00074	0.00072	0.00193
C	6	0.00085	0.00067	0.00066	0.00169
C	11	0.00075	0.00059	0.00057	0.00141
C	12	0.00082	0.00065	0.00063	0.00160
C	13	0.00086	0.00068	0.00067	0.00171
C	14	0.00082	0.00065	0.00064	0.00161
C	15	0.00093	0.00074	0.00072	0.00191
C	16	0.00094	0.00075	0.00073	0.00194
C	21	0.00072	0.00057	0.00055	0.00137
C	22	0.00077	0.00060	0.00059	0.00149
C	23	0.00087	0.00070	0.00068	0.00178
C	24	0.00098	0.00078	0.00076	0.00205
C	25	0.00101	0.00081	0.00080	0.00217
C	26	0.00098	0.00079	0.00076	0.00208
O	1	0.00065	0.00053	0.00052	0.00149
C	31	0.00075	0.00059	0.00057	0.00142
C	32	0.00078	0.00062	0.00060	0.00152
C	33	0.00085	0.00067	0.00065	0.00167
C	34	0.00092	0.00074	0.00071	0.00188
C	35	0.00082	0.00065	0.00063	0.00161
C	36	0.00074	0.00059	0.00057	0.00142
N	1	0.00065	0.00052	0.00050	0.00131
N	2	0.00080	0.00066	0.00063	0.00177
N	3	0.00087	0.00072	0.00069	0.00201
N	4	0.00079	0.00064	0.00062	0.00175
N	5	0.00077	0.00062	0.00060	0.00166
N	6	0.00071	0.00057	0.00055	0.00148
O	2	0.00061	0.00050	0.00049	0.00136
O	3	0.00062	0.00050	0.00049	0.00137
O	4	0.00077	0.00064	0.00062	0.00185
O	5	0.00064	0.00052	0.00050	0.00142

Red Compound Distances

Atom(A)		Atom(B)	Distance(A - B)	e.s.d. (Å)
P 1	-	C 1	1.7673	0.0067
P 1	-	C 11	1.7933	0.0069
P 1	-	C 21	1.7930	0.0066
P 1	-	O 1	1.6389	0.0062
C 1	-	C 2	1.3934	0.0097
C 1	-	C 6	1.4091	0.0100
C 2	-	C 3	1.3757	0.0112
C 3	-	C 4	1.4192	0.0122
C 4	-	C 5	1.3872	0.0121
C 5	-	C 6	1.3560	0.0113
C 11	-	C 12	1.3996	0.0099
C 11	-	C 16	1.4081	0.0108
C 12	-	C 13	1.4139	0.0106
C 13	-	C 14	1.3896	0.0107
C 14	-	C 15	1.3761	0.0111
C 15	-	C 16	1.4111	0.0119
C 21	-	C 22	1.3866	0.0094
C 21	-	C 26	1.3841	0.0109
C 22	-	C 23	1.4003	0.0104
C 23	-	C 24	1.3578	0.0118
C 24	-	C 25	1.3595	0.0127
C 25	-	C 26	1.4190	0.0127
C 31	-	C 32	1.4525	0.0097
C 31	-	C 36	1.4346	0.0094
C 31	-	N 1	1.3618	0.0089
C 32	-	C 33	1.4233	0.0103
C 32	-	N 2	1.3316	0.0101
C 33	-	C 34	1.4879	0.0112
C 33	-	N 3	1.3227	0.0110
C 34	-	C 35	1.4596	0.0111
C 34	-	N 4	1.2152	0.0109
C 35	-	C 36	1.4404	0.0099
C 35	-	N 5	1.3377	0.0101
C 36	-	N 6	1.3337	0.0092
N 1	-	O 2	1.2781	0.0081
N 1	-	O 3	1.2595	0.0081
N 2	-	O 4	1.4180	0.0102
N 3	-	O 4	1.3757	0.0107
N 5	-	O 5	1.3497	0.0091
N 6	-	O 5	1.4065	0.0086

Red Compound Angles

Atom(A)	Atom(B)	Atom(C)	Angle at (B)	e.s.d.
C 1	P 1	C 11	107.21	0.313
C 1	P 1	C 21	107.45	0.307
C 1	P 1	O 1	115.58	0.312
C 11	P 1	C 21	110.39	0.308
C 11	P 1	O 1	108.64	0.311
C 21	P 1	O 1	107.53	0.306
P 1	C 1	C 2	121.97	0.517
P 1	C 1	C 6	118.10	0.517
C 2	C 1	C 6	119.86	0.630
C 1	C 2	C 3	119.98	0.681
C 2	C 3	C 4	120.08	0.763
C 3	C 4	C 5	118.57	0.784
C 4	C 5	C 6	121.82	0.777
C 1	C 6	C 5	119.61	0.701
P 1	C 11	C 12	118.96	0.519
P 1	C 11	C 16	120.14	0.546
C 12	C 11	C 16	120.90	0.658
C 11	C 12	C 13	119.27	0.662
C 12	C 13	C 14	119.55	0.691
C 13	C 14	C 15	121.14	0.711
C 14	C 15	C 16	120.65	0.753
C 11	C 16	C 15	118.44	0.733
P 1	C 21	C 22	122.16	0.503
P 1	C 21	C 26	117.72	0.548
C 22	C 21	C 26	120.12	0.652
C 21	C 22	C 23	120.63	0.642
C 22	C 23	C 24	119.54	0.731
C 23	C 24	C 25	120.36	0.821
C 24	C 25	C 26	121.84	0.837
C 21	C 26	C 25	117.48	0.767
C 32	C 31	C 36	116.01	0.590
C 32	C 31	N 1	122.81	0.603
C 36	C 31	N 1	121.18	0.598
C 31	C 32	C 33	122.19	0.632
C 31	C 32	N 2	130.40	0.664
C 33	C 32	N 2	107.41	0.642
C 32	C 33	C 34	124.34	0.677
C 32	C 33	N 3	111.74	0.688
C 34	C 33	N 3	123.91	0.721
C 33	C 34	C 35	110.49	0.669

Red Compound **Angles**

Atom(A)	Atom(B)	Atom(C)	Angle at (B)	e.s.d.
C 33	C 34	N 4	122.53	0.766
C 35	C 34	N 4	126.96	0.779
C 34	C 35	C 36	126.23	0.665
C 34	C 35	N 5	126.48	0.695
C 36	C 35	N 5	107.29	0.630
C 31	C 36	C 35	120.72	0.606
C 31	C 36	N 6	129.68	0.628
C 35	C 36	N 6	109.57	0.601
C 31	N 1	O 2	118.44	0.575
C 31	N 1	O 3	119.87	0.583
O 2	N 1	O 3	121.68	0.583
C 32	N 2	O 4	105.10	0.638
C 33	N 3	O 4	104.03	0.693
C 35	N 5	O 5	106.96	0.621
C 36	N 6	O 5	104.13	0.561
N 2	O 4	N 3	111.71	0.655
N 5	O 5	N 6	112.00	0.561

Red Compound Orthogonal co-ords. (L.S. plane though heterocycle)

Centroid: 0.19581 0.42641 0.48867

Atom		x′	y′	z′ (Å)
P	1	-5.03325	-3.51975	-1.29481
C	1	-5.21593	-2.85454	-2.92199
C	2	-6.13119	-3.37622	-3.83397
C	3	-6.27978	-2.79087	-5.07008
C	4	-5.54158	-1.62387	-5.39783
C	5	-4.62507	-1.13821	-4.47678
C	6	-4.44921	-1.72350	-3.26634
C	11	-6.00767	-5.02380	-1.22415
C	12	-5.62060	-6.11922	-2.00461
C	13	-6.41121	-7.29129	-1.99150
C	14	-7.15019	-5.08825	-0.40365
C	15	-7.89780	-6.26486	-0.38537
C	16	-7.53785	-7.34902	-1.18012
C	21	-5.67526	-2.30460	-0.14169
C	22	-6.36493	-1.17829	-0.56422
C	23	-6.88487	-0.26948	0.36565
C	24	-6.70851	-0.49517	1.69292
C	25	-6.03594	-1.59713	2.11912
C	26	-5.47362	-2.52944	1.20902
O	1	-3.49785	-3.86841	-0.84081
C	31	0.14394	-1.05200	-0.01076
C	32	-1.17536	-0.44472	0.00633
C	33	-1.36053	0.96652	0.01108
C	34	-0.25140	1.95851	-0.01545
C	35	1.04058	1.28037	-0.01298
C	36	1.25463	-0.14406	-0.00384
N	1	0.33543	-2.40022	-0.02712
N	2	-2.38325	-1.00513	0.01615
N	3	-2.64238	1.29252	0.01718
N	4	-0.44820	3.15701	-0.05886
N	5	2.24452	1.86331	-0.01167
N	6	2.56249	-0.39883	0.05306
O	2	-0.69151	-3.16103	-0.01642
O	3	1.50502	-2.86761	-0.03079
O	4	-3.29434	0.08129	0.03649
O	5	3.16087	0.87406	0.04761
C′	31	2.75466	0.56294	3.25572
C′	32	4.07395	-0.04434	3.23864
C′	33	4.25912	-1.45557	3.23388
C′	34	3.15049	-2.44756	3.24041
C′	35	1.85602	-1.76942	3.25795
C′	36	1.64400	-0.34491	3.24886
N′	1	2.56317	1.91116	3.27209

Transformation	-5.4679	3.6264	9.8853
	4.5274	8.5315	0.5651
matrix	-6.4248	5.5954	-5.2093

Light Green Compound **Atomic Co-ordinates**

Atom		x/a	y/b	z/c	U(iso)
P	1	0.15970	0.38005	0.11677	0.04904
C	11	0.25692	0.50013	0.07946	0.05484
C	12	0.33221	0.58129	0.11955	0.07025
C	13	0.42037	0.67251	0.08936	0.08461
C	14	0.42361	0.68285	0.02420	0.08169
C	15	0.34506	0.60452	-0.01434	0.07852
C	16	0.26225	0.50990	0.01366	0.06645
C	21	0.02289	0.43287	0.17059	0.06032
C	22	-0.06327	0.51797	0.14680	0.07910
C	23	-0.18256	0.55625	0.18425	0.09967
C	24	-0.20692	0.51154	0.24404	0.10506
C	25	-0.11950	0.43106	0.26913	0.09378
C	26	0.00252	0.38836	0.23264	0.07061
C	31	0.30817	0.30776	0.15452	0.05480
C	32	0.36847	0.21761	0.12182	0.06980
C	33	0.49706	0.16740	0.14406	0.08842
C	34	0.56758	0.20798	0.19991	0.09310
C	35	0.50799	0.29295	0.23367	0.08770
C	36	0.37693	0.34717	0.21304	0.06608
C	41	-0.00742	0.21552	0.05637	0.05435
C	42	-0.05828	0.14554	0.10758	0.05435
C	43	-0.15718	0.04304	0.09601	0.05903
C	44	-0.21514	0.01717	0.03423	0.06209
C	45	-0.16649	0.08463	-0.01717	0.06090
C	46	-0.06637	0.18033	-0.00639	0.05311
N	41	0.07996	0.31092	0.05696	0.05352
N	42	-0.00131	0.17646	0.16565	0.06362
N	43	-0.21589	-0.03178	0.13669	0.08435
N	44	-0.30912	-0.07636	0.03630	0.07835
N	45	-0.19729	0.07704	-0.07775	0.07893
N	46	-0.03138	0.23052	-0.06043	0.06507
O	42	-0.04817	0.11410	0.21122	0.08020
O	43	-0.31217	-0.10574	0.09862	0.09502
O	45	-0.11320	0.16466	-0.10579	0.08508

Light Green Compound **E.s.d.'s of atomic co-ords.**

Atom		x/a	y/b	z/c	U(iso)
P	1	0.00019	0.00013	0.00007	0.00048
C	11	0.00074	0.00051	0.00028	0.00152
C	12	0.00099	0.00069	0.00038	0.00225
C	13	0.00085	0.00060	0.00033	0.00185
C	14	0.00095	0.00067	0.00037	0.00216
C	15	0.00093	0.00065	0.00036	0.00210
C	16	0.00083	0.00058	0.00032	0.00182
C	21	0.00078	0.00055	0.00030	0.00166
C	22	0.00097	0.00068	0.00036	0.00212
C	23	0.00112	0.00079	0.00044	0.00269
C	24	0.00118	0.00084	0.00047	0.00285
C	25	0.00111	0.00078	0.00041	0.00253
C	26	0.00087	0.00060	0.00033	0.00192
C	31	0.00074	0.00052	0.00028	0.00153
C	32	0.00086	0.00060	0.00032	0.00186
C	33	0.00103	0.00072	0.00039	0.00236
C	34	0.00107	0.00075	0.00041	0.00249
C	35	0.00103	0.00072	0.00038	0.00235
C	36	0.00084	0.00058	0.00031	0.00179
C	41	0.00073	0.00050	0.00027	0.00149
C	42	0.00073	0.00050	0.00028	0.00150
C	43	0.00077	0.00054	0.00029	0.00162
C	44	0.00080	0.00055	0.00030	0.00168
C	45	0.00078	0.00055	0.00030	0.00167
C	46	0.00072	0.00050	0.00027	0.00147
N	41	0.00059	0.00041	0.00022	0.00126
N	42	0.00081	0.00056	0.00030	0.00185
N	43	0.00064	0.00045	0.00025	0.00144
N	44	0.00073	0.00052	0.00029	0.00171
N	45	0.00075	0.00053	0.00029	0.00174
N	46	0.00067	0.00046	0.00025	0.00146
O	42	0.00061	0.00043	0.00023	0.00145
O	43	0.00069	0.00048	0.00027	0.00171
O	45	0.00064	0.00045	0.00024	0.00152

Light Green Compound **Distances**

Atom(A)		Atom(B)	Distance(A - B)	e.s.d. (Å)
P 1	-	C 11	1.7932	0.0063
P 1	-	C 21	1.7898	0.0067
P 1	-	C 31	1.7935	0.0064
P 1	-	N 41	1.6296	0.0051
C 11	-	C 12	1.4089	0.0103
C 11	-	C 16	1.3919	0.0093
C 12	-	C 13	1.4317	0.0110
C 13	-	C 14	1.3787	0.0108
C 14	-	C 15	1.3786	0.0112
C 15	-	C 16	1.4222	0.0105
C 21	-	C 22	1.4125	0.0104
C 21	-	C 26	1.4192	0.0098
C 22	-	C 23	1.4025	0.0124
C 23	-	C 24	1.3799	0.0138
C 24	-	C 25	1.3862	0.0136
C 25	-	C 26	1.4312	0.0117
C 31	-	C 32	1.4267	0.0094
C 31	-	C 36	1.4303	0.0093
C 32	-	C 33	1.3868	0.0112
C 33	-	C 34	1.3926	0.0124
C 34	-	C 35	1.3858	0.0124
C 35	-	C 36	1.4188	0.0110
C 41	-	C 42	1.4171	0.0085
C 41	-	C 46	1.4655	0.0085
C 41	-	N 41	1.3208	0.0077
C 42	-	C 43	1.4610	0.0088
C 42	-	N 42	1.3577	0.0090
C 43	-	C 44	1.4184	0.0092
C 43	-	N 43	1.3150	0.0084
C 44	-	C 45	1.3982	0.0093
C 44	-	N 44	1.3319	0.0091
C 45	-	C 46	1.3989	0.0089
C 45	-	N 45	1.3050	0.0091
C 46	-	N 46	1.3131	0.0081
N 42	-	O 42	1.2652	0.0084
N 43	-	O 43	1.4131	0.0079
N 44	-	O 43	1.3602	0.0085
N 45	-	O 45	1.3640	0.0083
N 46	-	O 45	1.3940	0.0077

Light Green Compound Angles

Atom(A)	-	Atom(B)	-	Atom(C)	Angle at (B)	e.s.d.
C 11	-	P 1	-	C 21	105.04	0.298
C 11	-	P 1	-	C 31	106.99	0.290
C 11	-	P 1	-	N 41	102.82	0.273
C 21	-	P 1	-	C 31	114.16	0.300
C 21	-	P 1	-	N 41	114.56	0.285
C 31	-	P 1	-	N 41	112.03	0.276
P 1	-	C 11	-	C 12	117.06	0.511
P 1	-	C 11	-	C 16	121.00	0.488
C 12	-	C 11	-	C 16	121.89	0.623
C 11	-	C 12	-	C 13	116.78	0.685
C 12	-	C 13	-	C 14	121.17	0.693
C 13	-	C 14	-	C 15	121.28	0.729
C 14	-	C 15	-	C 16	119.29	0.703
C 11	-	C 16	-	C 15	119.48	0.635
P 1	-	C 21	-	C 22	115.96	0.522
P 1	-	C 21	-	C 26	120.67	0.508
C 22	-	C 21	-	C 26	123.35	0.640
C 21	-	C 22	-	C 23	119.04	0.735
C 22	-	C 23	-	C 24	118.23	0.856
C 23	-	C 24	-	C 25	123.51	0.916
C 24	-	C 25	-	C 26	120.48	0.824
C 21	-	C 26	-	C 25	115.26	0.668
P 1	-	C 31	-	C 32	118.73	0.482
P 1	-	C 31	-	C 36	120.55	0.479
C 32	-	C 31	-	C 36	120.37	0.586
C 31	-	C 32	-	C 33	121.92	0.667
C 32	-	C 33	-	C 34	117.87	0.769
C 33	-	C 34	-	C 35	121.28	0.815
C 34	-	C 35	-	C 36	123.08	0.768
C 31	-	C 36	-	C 35	115.41	0.633
C 42	-	C 41	-	C 46	115.66	0.527
C 42	-	C 41	-	N 41	129.59	0.559
C 46	-	C 41	-	N 41	114.67	0.523
C 41	-	C 42	-	C 43	120.42	0.546
C 41	-	C 42	-	N 42	115.91	0.565
C 43	-	C 42	-	N 42	123.53	0.577
C 42	-	C 43	-	C 44	120.43	0.570
C 42	-	C 43	-	N 43	129.44	0.586
C 44	-	C 43	-	N 43	109.91	0.567
C 43	-	C 44	-	C 45	120.07	0.597

Light Green Compound Angles

Atom(A)	Atom(B)	Atom(C)	Angle at (B)	e.s.d.
C 43	C 44	N 44	109.37	0.585
C 45	C 44	N 44	130.51	0.631
C 44	C 45	C 46	119.23	0.590
C 44	C 45	N 45	131.94	0.640
C 46	C 45	N 45	108.82	0.585
C 41	C 46	C 45	123.93	0.553
C 41	C 46	N 46	126.08	0.554
C 45	C 46	N 46	109.97	0.549
F 1	N 41	C 41	129.55	0.438
C 42	N 42	O 42	115.57	0.603
C 43	N 43	O 43	103.52	0.511
C 44	N 44	O 43	104.51	0.562
C 45	N 45	O 45	106.21	0.567
C 46	N 46	O 45	104.28	0.503
N 43	O 43	N 44	112.66	0.526
N 45	O 45	N 46	110.68	0.505

Light Green Compound Orthogonal co-ordinates

(plane through benzotrifuroxan fragment)

Centroid: -0.12162 0.10333 0.04875

Atom		x'	y'	z' (Å)
P	1	0.22079	4.19596	-0.14576
C	11	-1.01474	5.50485	-0.20610
C	13	-1.51385	7.86553	-0.27804
C	12	-0.53188	6.83060	-0.36050
C	14	-2.86628	7.58150	-0.17616
C	15	-3.32383	6.28567	-0.06783
C	16	-2.35570	5.20738	-0.04620
C	21	1.14696	4.37235	-1.65131
C	22	0.37325	4.59612	-2.84097
C	23	1.04704	4.62591	-4.07742
C	24	2.42868	4.46175	-4.10932
C	25	3.16913	4.31377	-2.96691
C	26	2.57384	4.24742	-1.65058
C	31	1.19103	4.45874	1.34225
C	32	0.84794	3.71309	2.53025
C	33	1.42340	3.97423	3.73372
C	34	2.35714	5.02486	3.80102
C	35	2.72944	5.71699	2.68001
C	36	2.17835	5.47983	1.49796
C	41	-0.31480	1.58361	-0.00092
C	42	0.99497	1.01893	-0.01149
C	43	1.18457	-0.42248	0.04684
C	44	0.07207	-1.30289	-0.00424
C	45	-1.22677	-0.76696	-0.01447
C	46	-1.41660	0.61550	-0.00410
N	41	-0.68782	2.84451	-0.06754
N	43	2.30027	-1.12360	0.03931
N	42	2.01516	1.92437	0.01608
N	44	0.49231	-2.55601	-0.04265
N	45	-2.40923	-1.34264	-0.03404
N	46	-2.69773	0.90936	0.03986
O	42	3.17590	1.41944	0.00435
O	43	1.83991	-2.45346	-0.01630
O	45	-3.32252	-0.34767	0.05131

Transformation matrix	-0.3947	-3.7208	19.9927
	4.5909	9.0110	6.0543
	7.2259	-7.2010	-2.7543

Yellow Compound — Atomic Co-ordinates

Atom		x/a	y/b	z/c	U(iso)
C	1	0.57829	0.26654	0.46349	0.06023
C	2	0.59961	0.33674	0.51507	0.07769
C	3	0.64806	0.31387	0.56681	0.08995
C	4	0.66743	0.21716	0.56932	0.08129
C	5	0.64624	0.14776	0.52153	0.08500
C	6	0.60554	0.17184	0.47123	0.07203
C	11	0.30505	0.27711	0.38936	0.05840
C	12	0.20728	0.23045	0.33978	0.09517
C	13	0.03126	0.21789	0.32938	0.10873
C	14	-0.03109	0.24765	0.36978	0.09457
C	15	0.07475	0.29959	0.41937	0.13497
C	16	0.24557	0.31073	0.43312	0.11296
C	21	0.64385	0.43866	0.41077	0.06430
C	22	0.57380	0.51000	0.39383	0.07984
C	23	0.68181	0.62078	0.39981	0.09662
C	24	0.84950	0.66053	0.42038	0.08599
C	25	0.92458	0.59016	0.43818	0.10709
C	26	0.81536	0.47620	0.43137	0.08786
N	1	0.55344	0.21762	0.36014	0.05122
P	1	0.52037	0.29467	0.40261	0.05064
C	31	0.29173	-0.29784	0.23960	0.06177
C	32	0.17080	-0.29683	0.26398	0.07111
C	33	0.08993	-0.38248	0.29105	0.09063
C	34	0.13787	-0.47079	0.29224	0.08546
C	35	0.26656	-0.46778	0.26814	0.08629
C	36	0.35040	-0.38497	0.24221	0.07922
C	41	0.61028	-0.15082	0.21801	0.06460
C	42	0.69401	-0.15489	0.26859	0.09085
C	43	0.87364	-0.11480	0.27935	0.12063
C	44	0.95607	-0.07516	0.23868	0.09664
C	45	0.87281	-0.07614	0.18981	0.08887
C	46	0.69512	-0.11222	0.17845	0.07715
C	51	0.30410	-0.26036	0.13340	0.06128
C	52	0.18217	-0.24018	0.10084	0.07385
C	53	0.11669	-0.29237	0.04732	0.08970
C	54	0.17258	-0.36564	0.02417	0.09541
C	55	0.29663	-0.38395	0.05566	0.07693
C	56	0.36177	-0.33419	0.10874	0.06975
N	2	0.32568	-0.09966	0.21629	0.05584
P	2	0.38576	-0.19322	0.20429	0.05228
C	61	0.22710	0.29423	0.13971	0.06470
C	62	0.18712	0.38234	0.12571	0.08075
C	63	0.03207	0.38177	0.13557	0.08815

Yellow Compound Atomic Co-ordinates

Atom		x/a	y/b	z/c	U(iso)
C	64	-0.06791	0.30291	0.15839	0.09200
C	65	-0.02568	0.21664	0.17315	0.09543
C	66	0.12609	0.21520	0.16319	0.07887
C	71	0.56285	0.42884	0.12313	0.05878
C	72	0.64632	0.50526	0.17171	0.07461
C	73	0.75473	0.61503	0.16942	0.08770
C	74	0.77056	0.63949	0.11746	0.08918
C	75	0.68370	0.56462	0.07072	0.09582
C	76	0.57615	0.45420	0.07346	0.08466
C	81	0.36540	0.20914	0.06152	0.06087
C	82	0.48715	0.18468	0.04311	0.06773
C	83	0.44332	0.11483	-0.00786	0.08291
C	84	0.28478	0.07185	-0.04151	0.08761
C	85	0.15898	0.09825	-0.02449	0.09656
C	86	0.20349	0.17161	0.02816	0.07415
N	3	0.52337	0.26013	0.17421	0.05471
P	3	0.42089	0.29266	0.12789	0.05204
C	91	0.53098	0.23417	0.26536	0.05073
C	92	0.50958	0.17734	0.30722	0.05104
C	93	0.44500	0.06272	0.28746	0.04821
C	94	0.40267	0.00868	0.23206	0.05171
C	95	0.43062	0.07984	0.19648	0.05029
C	96	0.48982	0.19248	0.20942	0.05018
N	4	0.61040	0.35686	0.28193	0.07407
O	41	0.75381	0.40181	0.29741	0.09860
O	42	0.51046	0.39946	0.27541	0.09078
N	5	0.41058	-0.00575	0.32800	0.06958
O	51	0.50819	-0.04902	0.34081	0.10345
O	52	0.29422	-0.01818	0.34672	0.08995
N	6	0.37547	0.02864	0.13841	0.06980
O	61	0.47441	0.00399	0.11775	0.08943
O	62	0.23737	0.01235	0.11159	0.08490
C	101	0.06041	0.01478	0.52174	0.11869
C	102	-0.09638	-0.03425	0.52717	0.11056
C	103	-0.18967	-0.06077	0.46700	0.15264
C	104	-0.11953	-0.02532	0.42627	0.17483
C	105	0.02739	0.02778	0.43443	0.14946
C	106	0.14762	0.05989	0.49399	0.12005
C	107	0.20194	0.06336	0.58514	0.19939

Yellow Compound **E.s.d.'s of atomic co-ords.**

Atom		x/a	y/b	z/c	U(iso)
P	1	0.00031	0.00021	0.00010	0.00070
C	1	0.00129	0.00082	0.00039	0.00266
C	2	0.00155	0.00097	0.00048	0.00337
C	3	0.00165	0.00105	0.00051	0.00365
C	4	0.00157	0.00101	0.00050	0.00343
C	5	0.00167	0.00105	0.00053	0.00375
C	6	0.00147	0.00093	0.00046	0.00314
C	11	0.00131	0.00082	0.00041	0.00268
C	12	0.00180	0.00109	0.00055	0.00401
C	13	0.00194	0.00118	0.00060	0.00445
C	14	0.00181	0.00112	0.00058	0.00409
C	15	0.00232	0.00140	0.00072	0.00564
C	16	0.00190	0.00115	0.00058	0.00432
C	21	0.00137	0.00084	0.00041	0.00279
C	22	0.00153	0.00098	0.00047	0.00335
C	23	0.00186	0.00114	0.00055	0.00411
C	24	0.00172	0.00105	0.00051	0.00368
C	25	0.00190	0.00121	0.00058	0.00438
C	26	0.00167	0.00104	0.00050	0.00364
N	1	0.00096	0.00060	0.00029	0.00198
P	2	0.00034	0.00021	0.00010	0.00071
C	31	0.00132	0.00080	0.00040	0.00272
C	32	0.00144	0.00090	0.00043	0.00298
C	33	0.00169	0.00107	0.00050	0.00381
C	34	0.00163	0.00101	0.00049	0.00352
C	35	0.00168	0.00103	0.00050	0.00366
C	36	0.00158	0.00100	0.00048	0.00347
C	41	0.00136	0.00084	0.00042	0.00279
C	42	0.00166	0.00101	0.00050	0.00358
C	43	0.00213	0.00128	0.00064	0.00490
C	44	0.00181	0.00111	0.00057	0.00410
C	45	0.00175	0.00106	0.00054	0.00385
C	46	0.00159	0.00098	0.00047	0.00337
C	51	0.00133	0.00083	0.00040	0.00272
C	52	0.00149	0.00093	0.00046	0.00318
C	53	0.00170	0.00107	0.00053	0.00381
C	54	0.00177	0.00105	0.00054	0.00391
C	55	0.00159	0.00099	0.00049	0.00342
C	56	0.00145	0.00091	0.00045	0.00311
N	2	0.00102	0.00064	0.00031	0.00214
P	3	0.00034	0.00021	0.00010	0.00070
C	61	0.00132	0.00083	0.00040	0.00267
C	62	0.00154	0.00096	0.00046	0.00328
C	63	0.00170	0.00106	0.00051	0.00374

Yellow Compound E.s.d.'s of atomic co-ords.

Atom		x/a	y/b	z/c	U(iso)
C	64	0.00170	0.00108	0.00052	0.00379
C	65	0.00175	0.00109	0.00053	0.00391
C	66	0.00158	0.00099	0.00048	0.00340
C	71	0.00127	0.00080	0.00039	0.00258
C	72	0.00148	0.00093	0.00045	0.00311
C	73	0.00172	0.00107	0.00053	0.00384
C	74	0.00171	0.00108	0.00055	0.00385
C	75	0.00185	0.00118	0.00058	0.00424
C	76	0.00167	0.00105	0.00051	0.00371
C	81	0.00135	0.00083	0.00040	0.00276
C	82	0.00145	0.00090	0.00044	0.00301
C	83	0.00160	0.00099	0.00049	0.00338
C	84	0.00175	0.00106	0.00052	0.00381
C	85	0.00178	0.00110	0.00055	0.00399
C	86	0.00156	0.00097	0.00048	0.00340
N	3	0.00099	0.00062	0.00030	0.00208
C	91	0.00120	0.00075	0.00036	0.00238
C	92	0.00119	0.00075	0.00036	0.00239
C	93	0.00113	0.00071	0.00034	0.00221
C	94	0.00120	0.00075	0.00036	0.00239
C	95	0.00118	0.00074	0.00036	0.00234
C	96	0.00120	0.00075	0.00036	0.00239
N	4	0.00133	0.00076	0.00036	0.00256
O	41	0.00125	0.00073	0.00035	0.00266
O	42	0.00110	0.00067	0.00033	0.00247
N	5	0.00120	0.00071	0.00034	0.00239
O	51	0.00123	0.00075	0.00037	0.00285
O	52	0.00113	0.00067	0.00034	0.00248
N	6	0.00124	0.00072	0.00036	0.00247
O	61	0.00111	0.00068	0.00033	0.00249
O	62	0.00111	0.00066	0.00033	0.00241
C	101	0.00789	0.00442	0.00227	0.01639
C	102	0.00596	0.00354	0.00177	0.01051
C	103	0.00764	0.00428	0.00285	0.01696
C	104	0.00630	0.00506	0.00292	0.01811
C	105	0.00736	0.00390	0.00211	0.01517
C	106	0.00466	0.00294	0.00156	0.00865
C	107	0.00647	0.00461	0.00260	0.01721

Yellow Compound Distances

Atom(A)		Atom(B)	Distance(A - B)	e.s.d. (Å)
P 1	-	C 1	1.8117	0.0112
P 1	-	C 11	1.8042	0.0114
P 1	-	C 21	1.8109	0.0116
P 1	-	N 1	1.5354	0.0085
C 1	-	C 2	1.3548	0.0169
C 1	-	C 6	1.3941	0.0165
C 2	-	C 3	1.4334	0.0191
C 3	-	C 4	1.3865	0.0194
C 4	-	C 5	1.3732	0.0195
C 5	-	C 6	1.3926	0.0189
C 11	-	C 12	1.3353	0.0186
C 11	-	C 16	1.3982	0.0192
C 12	-	C 13	1.4819	0.0220
C 13	-	C 14	1.3268	0.0223
C 14	-	C 15	1.3682	0.0246
C 15	-	C 16	1.4452	0.0249
C 21	-	C 22	1.4028	0.0172
C 21	-	C 26	1.3977	0.0179
C 22	-	C 23	1.4211	0.0200
C 23	-	C 24	1.3652	0.0208
C 24	-	C 25	1.4276	0.0214
C 25	-	C 26	1.4551	0.0212
N 1	-	C 92	1.3224	0.0128
P 2	-	C 31	1.7974	0.0113
P 2	-	C 41	1.8168	0.0117
P 2	-	C 51	1.8094	0.0114
P 2	-	N 2	1.5527	0.0090
C 31	-	C 32	1.3255	0.0162
C 31	-	C 36	1.4551	0.0172
C 32	-	C 33	1.4490	0.0185
C 33	-	C 34	1.4071	0.0195
C 34	-	C 35	1.3701	0.0194
C 35	-	C 36	1.4116	0.0192
C 41	-	C 42	1.4025	0.0178
C 41	-	C 46	1.3988	0.0174
C 42	-	C 43	1.4467	0.0222
C 43	-	C 44	1.4165	0.0232
C 44	-	C 45	1.3409	0.0210
C 45	-	C 46	1.4341	0.0196
C 51	-	C 52	1.3879	0.0167

Yellow Compound **Distances**

Atom(A)		Atom(B)	Distance(A - B)	e.s.d. (Å)
C 51	-	C 56	1.3977	0.0165
C 52	-	C 53	1.3728	0.0190
C 53	-	C 54	1.3653	0.0204
C 54	-	C 55	1.3747	0.0197
C 55	-	C 56	1.3559	0.0161
N 2	-	C 94	1.3369	0.0131
P 3	-	C 61	1.7977	0.0114
P 3	-	C 71	1.8427	0.0110
P 3	-	C 81	1.7856	0.0115
P 3	-	N 3	1.5847	0.0087
C 61	-	C 62	1.4333	0.0169
C 61	-	C 66	1.3954	0.0172
C 62	-	C 63	1.4335	0.0191
C 63	-	C 64	1.3794	0.0201
C 64	-	C 65	1.4263	0.0204
C 65	-	C 66	1.4146	0.0197
C 71	-	C 72	1.3957	0.0164
C 71	-	C 76	1.3701	0.0176
C 72	-	C 73	1.4569	0.0190
C 73	-	C 74	1.4265	0.0205
C 74	-	C 75	1.3584	0.0214
C 75	-	C 76	1.4649	0.0210
C 81	-	C 82	1.3689	0.0164
C 81	-	C 86	1.4152	0.0172
C 82	-	C 83	1.4026	0.0180
C 83	-	C 84	1.3901	0.0196
C 84	-	C 85	1.4005	0.0207
C 85	-	C 86	1.4570	0.0198
N 3	-	C 96	1.3577	0.0130
C 91	-	C 92	1.3968	0.0141
C 91	-	C 96	1.3975	0.0141
C 91	-	N 4	1.5091	0.0144
C 92	-	C 93	1.4220	0.0137
C 93	-	C 94	1.4216	0.0137
C 93	-	N 5	1.4754	0.0135
C 94	-	C 95	1.3956	0.0140
C 95	-	C 96	1.3856	0.0140
C 95	-	N 6	1.4682	0.0140
N 4	-	O 41	1.1620	0.0144
N 4	-	O 42	1.2231	0.0138
N 5	-	O 51	1.2368	0.0140
N 5	-	O 52	1.1715	0.0134
N 6	-	O 61	1.2126	0.0135
N 6	-	O 62	1.2293	0.0135

Yellow Compound Angles

Atom(A)	Atom(B)	Atom(C)	Angle at (B)	e.s.d.
C 1	P 1	C 11	109.77	0.510
C 1	P 1	C 21	103.90	0.513
C 1	P 1	N 1	107.75	0.479
C 11	P 1	C 21	106.57	0.520
C 11	P 1	N 1	112.14	0.486
C 21	P 1	N 1	116.04	0.493
P 1	C 1	C 2	121.46	0.895
P 1	C 1	C 6	119.17	0.856
C 2	C 1	C 6	119.35	1.083
C 1	C 2	C 3	120.63	1.178
C 2	C 3	C 4	119.76	1.241
C 3	C 4	C 5	118.42	1.265
C 4	C 5	C 6	121.87	1.277
C 1	C 6	C 5	119.86	1.150
P 1	C 11	C 12	120.31	0.966
P 1	C 11	C 16	117.37	0.947
C 12	C 11	C 16	122.29	1.218
C 11	C 12	C 13	119.65	1.312
C 12	C 13	C 14	120.11	1.443
C 13	C 14	C 15	118.32	1.546
C 14	C 15	C 16	124.28	1.653
C 11	C 16	C 15	114.70	1.389
P 1	C 21	C 22	121.91	0.896
P 1	C 21	C 26	117.71	0.910
C 22	C 21	C 26	120.24	1.117
C 21	C 22	C 23	117.88	1.184
C 22	C 23	C 24	123.43	1.362
C 23	C 24	C 25	120.07	1.356
C 24	C 25	C 26	116.86	1.340
C 21	C 26	C 25	121.44	1.248
P 1	N 1	C 92	139.70	0.751
C 31	P 2	C 41	111.36	0.521
C 31	P 2	C 51	103.78	0.513
C 31	P 2	N 2	109.57	0.495
C 41	P 2	C 51	107.40	0.521
C 41	P 2	N 2	114.96	0.504
C 51	P 2	N 2	109.13	0.497
P 2	C 31	C 32	121.38	0.888
P 2	C 31	C 36	119.60	0.856
C 32	C 31	C 36	119.01	1.069

Yellow Compound **Angles**

Atom(A)	Atom(B)	Atom(C)	Angle at (B)	e.s.d.
C 31	C 32	C 33	122.04	1.132
C 32	C 33	C 34	120.59	1.220
C 33	C 34	C 35	115.96	1.249
C 34	C 35	C 36	125.15	1.279
C 31	C 36	C 35	117.13	1.148
P 2	C 41	C 42	118.97	0.910
P 2	C 41	C 46	119.09	0.897
C 42	C 41	C 46	121.91	1.124
C 41	C 42	C 43	117.56	1.259
C 42	C 43	C 44	119.17	1.460
C 43	C 44	C 45	122.15	1.453
C 44	C 45	C 46	120.00	1.334
C 41	C 46	C 45	119.10	1.179
P 2	C 51	C 52	121.50	0.879
P 2	C 51	C 56	121.03	0.868
C 52	C 51	C 56	116.88	1.058
C 51	C 52	C 53	122.02	1.180
C 52	C 53	C 54	120.25	1.315
C 53	C 54	C 55	118.18	1.327
C 54	C 55	C 56	122.52	1.263
C 51	C 56	C 55	120.11	1.140
P 2	N 2	C 94	134.17	0.766
C 61	P 3	C 71	110.91	0.505
C 61	P 3	C 81	104.10	0.521
C 61	P 3	N 3	114.96	0.489
C 71	P 3	C 81	105.81	0.508
C 71	P 3	N 3	104.74	0.471
C 81	P 3	N 3	116.04	0.493
P 3	C 61	C 62	116.46	0.852
P 3	C 61	C 66	120.72	0.891
C 62	C 61	C 66	122.78	1.083
C 61	C 62	C 63	115.36	1.123
C 62	C 63	C 64	121.56	1.275
C 63	C 64	C 65	122.72	1.320
C 64	C 65	C 66	116.54	1.272
C 61	C 66	C 65	121.01	1.198
P 3	C 71	C 72	117.16	0.837
P 3	C 71	C 76	120.40	0.900
C 72	C 71	C 76	122.32	1.096
C 71	C 72	C 73	118.69	1.117

Yellow Compound Angles

Atom(A)	Atom(B)	Atom(C)	Angle at (B)	e.s.d.
C 72	C 73	C 74	118.35	1.244
C 73	C 74	C 75	121.78	1.370
C 74	C 75	C 76	119.42	1.377
C 71	C 76	C 75	119.38	1.239
P 3	C 91	C 92	117.47	0.873
P 3	C 81	C 86	121.87	0.888
C 82	C 81	C 86	120.63	1.081
C 81	C 82	C 83	118.06	1.117
C 82	C 83	C 84	123.81	1.236
C 83	C 84	C 85	119.38	1.308
C 84	C 85	C 86	117.29	1.285
C 81	C 86	C 85	120.62	1.169
P 3	N 3	C 96	137.24	0.743
C 92	C 91	C 96	128.55	0.937
C 92	C 91	N 4	116.65	0.880
C 96	C 91	N 4	114.80	0.875
N 1	C 92	C 91	128.02	0.926
N 1	C 92	C 93	119.71	0.885
C 91	C 92	C 93	112.03	0.873
C 92	C 93	C 94	125.76	0.883
C 92	C 93	N 5	116.70	0.839
C 94	C 93	N 5	117.45	0.842
N 2	C 94	C 93	122.00	0.898
N 2	C 94	C 95	124.19	0.920
C 93	C 94	C 95	113.36	0.877
C 94	C 95	C 96	127.53	0.934
C 94	C 95	N 6	115.87	0.877
C 96	C 95	N 6	116.31	0.882
N 3	C 96	C 91	120.75	0.901
N 3	C 96	C 95	126.28	0.918
C 91	C 96	C 95	112.64	0.896
C 91	N 4	O 41	120.32	1.005
C 91	N 4	O 42	113.30	0.933
O 41	N 4	O 42	126.33	1.105
C 93	N 5	O 51	117.44	0.921
C 93	N 5	O 52	120.39	0.938
O 51	N 5	O 52	122.17	1.035
C 95	N 6	O 61	116.45	0.934
C 95	N 6	O 62	122.34	0.942
O 61	N 6	O 62	121.20	1.015

Yellow Compound (clathrate toluene) Distances and angles

Atom(A)		Atom(B)	Distance(A - B)	e.s.d. (Å)
C 101	-	C 102	1.3424	0.0792
C 101	-	C 106	1.1911	0.0744
C 101	-	C 107	1.7565	0.0880
C 102	-	C 103	1.5495	0.0820
C 103	-	C 104	1.3497	0.0978
C 104	-	C 105	1.2011	0.0921
C 105	-	C 106	1.6132	0.0700

Atom(A)		Atom(B)		Atom(C)	Angle at (B)	e.s.d.
C 102	-	C 101	-	C 106	146.17	6.129
C 102	-	C 101	-	C 107	111.16	4.859
C 106	-	C 101	-	C 107	100.25	4.820
C 101	-	C 102	-	C 103	99.32	4.673
C 102	-	C 103	-	C 104	125.14	5.861
C 103	-	C 104	-	C 105	120.72	6.880
C 104	-	C 105	-	C 106	121.66	5.596
C 101	-	C 106	-	C 105	105.14	4.520

Yellow Compound Orthogonal co-ords. (L.S. plane C_{91}- C_{96})

Centroid: 0.46811 0.12587 0.24967

Atom		x′	y′	z′ (Å)
P	1	-3.71862	1.60266	-0.61140
C	1	-5.35891	1.06497	-0.19638
C	2	-6.47617	1.72989	-0.44283
C	3	-7.76361	1.24966	-0.03244
C	4	-7.87290	0.08955	0.57791
C	5	-6.72400	-0.75113	0.82122
C	6	-5.46785	-0.21261	0.47381
C	11	-3.53004	1.48497	-2.47684
C	12	-2.37026	1.08988	-3.01171
C	13	-2.22589	1.01480	-4.47406
C	14	-3.26470	1.27122	-5.25915
C	15	-4.41651	1.73099	-4.68129
C	16	-4.64938	1.77305	-3.25576
C	21	-3.76037	3.36649	-0.27142
C	22	-3.33453	4.34826	-1.17842
C	23	-3.35101	5.73256	-0.74808
C	24	-3.74043	6.09991	0.50180
C	25	-4.18421	5.11611	1.44674
C	26	-4.14949	3.72467	1.02232
N	1	-2.67441	0.76201	0.06795
P	2	0.89969	-3.80785	0.84937
C	31	-0.11153	-5.28907	0.41562
C	32	-0.80070	-5.32622	-0.71598
C	33	-1.58470	-6.42238	-1.10107
C	34	-1.63781	-7.61936	-0.27374
C	35	-0.94843	-7.53434	0.90727
C	36	-0.19299	-6.41890	1.32896
C	41	0.71996	-3.43917	2.60566
C	42	-0.50430	-3.68682	3.24357
C	43	-0.63892	-3.26491	4.62084
C	44	0.46098	-2.64604	5.26398
C	45	1.63942	-2.46840	4.61938
C	46	1.79270	-2.83795	3.27224
C	51	2.59405	-4.45420	0.60604
C	52	3.35016	-4.09335	-0.48666
C	53	4.62606	-4.51400	-0.69730
C	54	5.20012	-5.37927	0.18919
C	55	4.47341	-5.75334	1.29457
C	56	3.20692	-5.32190	1.51444
N	2	0.61610	-2.76605	-0.14091
P	3	3.13847	2.54406	-0.89124
C	61	2.72648	2.57707	-2.64234
C	62	3.10115	3.72311	-3.36731
C	63	2.75547	3.75499	-4.75900

Yellow Compound **Orthogonal co-ordinates.**

Atom		x'	y'	z' (Å)
C	64	2.07066	2.70473	-5.33408
C	65	1.67336	1.54880	-4.59901
C	66	2.01630	1.52268	-3.22732
C	71	3.42905	4.24775	-0.25513
C	72	2.30342	5.02753	0.01476
C	73	2.49491	6.39718	0.47303
C	74	3.82846	6.88058	0.62483
C	75	4.90655	6.11510	0.31305
C	76	4.70386	4.73542	-0.13571
C	81	4.72548	1.72736	-0.84169
C	82	5.25067	1.44655	0.39084
C	83	0.46525	0.74729	0.44674
C	84	7.18794	0.36118	-0.67617
C	85	6.69841	0.67245	-1.95011
C	86	5.44205	1.41028	-2.02017
N	3	2.01614	1.94496	0.05055
C	91	-0.29089	1.30209	0.01962
C	92	-1.39295	0.44434	-0.00738
C	93	-1.00449	-0.92352	-0.00382
C	94	0.33213	-1.40759	0.00814
C	95	1.28870	-0.39144	0.00757
C	96	1.06749	0.97612	-0.01564
N	4	-0.58486	2.77908	0.11718
O	41	-0.85811	3.25647	1.14071
O	42	-0.45748	3.36909	-0.91657
N	5	-2.08844	-1.92074	-0.09965
O	51	-2.37613	-2.54010	0.94157
O	52	-2.64025	-2.11020	-1.10549
N	6	2.68628	-0.82684	-0.10547
O	61	3.25377	-1.09606	0.93173
O	62	3.26575	-0.96355	-1.13691
C	101	-7.17558	-2.22611	-3.74150
C	102	-7.43990	-2.82302	-4.91442
C	103	-5.99843	-2.92779	-5.47312
C	104	-4.90722	-2.35845	-4.91916
C	105	-4.98898	-1.75367	-3.83464
C	106	-6.39487	-1.58337	-3.11214
C	107	-8.65499	-1.86601	-2.86574

0.6253	0.6014	-25.1912
-0.2761	12.6768	-3.4189
2.8076	-4.6038	-2.3983

Transformation matrix

Blue Compound Atomic Co-ordinates

Atom		x/a	y/b	z/c	U(iso)
P	1	1.00000	0.50000	-0.02605	0.04072
C	1	0.99051	0.59455	-0.08535	0.04012
C	2	1.05854	0.61964	-0.17187	0.07002
C	3	1.03861	0.69204	-0.21968	0.06998
C	4	0.96096	0.73946	-0.17407	0.07487
C	5	0.89520	0.71835	-0.08931	0.07550
C	6	0.91080	0.64452	-0.04295	0.06171
C	11	1.19126	0.52650	0.02127	0.05075
C	12	1.21838	0.47309	0.08278	0.07160
C	13	1.36507	0.48851	0.12566	0.07556
C	14	1.49133	0.56352	0.09027	0.09397
C	15	1.46220	0.61491	0.02271	0.08538
C	16	1.31398	0.60125	-0.01380	0.05859
C	21	0.96668	0.41557	-0.11251	0.05554
C	22	0.84751	0.40369	-0.17552	0.06793
C	23	0.81533	0.33329	-0.23981	0.08267
C	24	0.89155	0.27824	-0.23539	0.08911
C	25	1.01325	0.28840	-0.17320	0.09689
C	26	1.04993	0.36022	-0.10846	0.07376
C	31	0.87282	0.46419	0.06160	0.04656
C	32	0.90192	0.49977	0.15529	0.03713
C	33	0.81797	0.45699	0.23421	0.03939
C	34	0.69099	0.36829	0.22508	0.04033
C	35	0.62598	0.35770	0.13455	0.04163
C	36	0.71590	0.40065	0.05364	0.04610
N	1	1.01220	0.57508	0.17946	0.04864
N	2	0.86378	0.50632	0.30521	0.04521
N	4	0.48593	0.31085	0.10730	0.05986
N	5	0.62331	0.37935	-0.01905	0.05570
O	1	0.98212	0.58066	0.27389	0.05008
O	2	0.48029	0.32581	0.01685	0.06349

Blue Compound Atomic Co-ordinates

Atom		x/a	y/b	z/c	U(iso)
P	2	0.30905	0.15668	0.53445	0.03410
C	41	0.11278	0.13190	0.49246	0.03774
C	42	0.04623	0.06182	0.43562	0.05166
C	43	-0.10736	0.04248	0.40047	0.07486
C	44	-0.18203	0.09816	0.42781	0.08083
C	45	-0.12002	0.16684	0.48354	0.06792
C	46	0.03365	0.18428	0.51854	0.05692
C	51	0.34682	0.23416	0.62680	0.04043
C	52	0.36539	0.32228	0.60902	0.05622
C	53	0.39661	0.38333	0.68283	0.06906
C	54	0.40731	0.35309	0.77153	0.08153
C	55	0.38713	0.26725	0.78735	0.07309
C	56	0.35887	0.20760	0.71387	0.06413
C	61	0.32365	0.05599	0.57461	0.04404
C	62	0.46801	0.04877	0.58051	0.05186
C	63	0.48406	-0.02681	0.61233	0.06229
C	64	0.35631	-0.09865	0.63736	0.06637
C	65	0.20803	-0.09272	0.63168	0.06498
C	66	0.19225	-0.01569	0.60176	0.04806
C	71	0.44397	0.20620	0.44805	0.03943
C	72	0.59177	0.27293	0.46523	0.04205
C	73	0.68830	0.31912	0.38832	0.04490
C	74	0.64466	0.30691	0.29698	0.04390
C	75	0.53043	0.21810	0.28303	0.03636
C	76	0.43245	0.17083	0.35888	0.04042
N	11	0.66811	0.29567	0.54225	0.05184
N	12	0.82072	0.36874	0.42524	0.06038
N	14	0.50920	0.16920	0.21131	0.05580
N	15	0.34753	0.09276	0.32733	0.04785
O	11	0.81185	0.35648	0.51757	0.05455
O	12	0.39673	0.09063	0.23583	0.05447

Blue Compound E.s.d.'s of atomic co-ords.

Atom		x/a	y/b	z/c	U(iso)
P	1	0.00000	0.00000	0.00023	0.00073
C	1	0.00121	0.00068	0.00083	0.00260
C	2	0.00178	0.00100	0.00114	0.00391
C	3	0.00177	0.00101	0.00114	0.00400
C	4	0.00187	0.00104	0.00123	0.00419
C	5	0.00184	0.00106	0.00120	0.00428
C	6	0.00158	0.00089	0.00105	0.00354
C	11	0.00145	0.00082	0.00097	0.00320
C	12	0.00178	0.00099	0.00116	0.00405
C	13	0.00195	0.00108	0.00121	0.00436
C	14	0.00231	0.00130	0.00152	0.00588
C	15	0.00212	0.00116	0.00137	0.00493
C	16	0.00163	0.00091	0.00104	0.00351
C	21	0.00148	0.00083	0.00098	0.00339
C	22	0.00178	0.00098	0.00110	0.00383
C	23	0.00199	0.00112	0.00126	0.00475
C	24	0.00207	0.00115	0.00130	0.00489
C	25	0.00230	0.00129	0.00146	0.00561
C	26	0.00185	0.00103	0.00114	0.00409
C	31	0.00147	0.00081	0.00093	0.00297
C	32	0.00117	0.00067	0.00080	0.00239
C	33	0.00124	0.00068	0.00083	0.00250
C	34	0.00125	0.00071	0.00082	0.00254
C	35	0.00130	0.00073	0.00086	0.00263
C	36	0.00140	0.00077	0.00089	0.00284
N	1	0.00113	0.00065	0.00074	0.00243
N	2	0.00108	0.00062	0.00070	0.00231
N	4	0.00132	0.00074	0.00082	0.00293
N	5	0.00124	0.00070	0.00081	0.00271
O	1	0.00093	0.00053	0.00062	0.00208
O	2	0.00108	0.00061	0.00069	0.00242

Blue Compound E.s.d.'s of atomic co-ords.

Atom		x/a	y/b	z/c	U(iso)
P	2	0.00033	0.00019	0.00020	0.00065
C	41	0.00116	0.00066	0.00079	0.00251
C	42	0.00145	0.00081	0.00095	0.00310
C	43	0.00183	0.00103	0.00118	0.00420
C	44	0.00193	0.00113	0.00127	0.00470
C	45	0.00177	0.00098	0.00118	0.00401
C	46	0.00152	0.00086	0.00098	0.00326
C	51	0.00123	0.00069	0.00082	0.00256
C	52	0.00152	0.00088	0.00099	0.00335
C	53	0.00178	0.00101	0.00115	0.00406
C	54	0.00196	0.00110	0.00127	0.00462
C	55	0.00183	0.00103	0.00114	0.00431
C	56	0.00169	0.00095	0.00108	0.00372
C	61	0.00130	0.00073	0.00087	0.00285
C	62	0.00142	0.00080	0.00095	0.00302
C	63	0.00162	0.00091	0.00108	0.00374
C	64	0.00179	0.00098	0.00111	0.00383
C	65	0.00171	0.00094	0.00108	0.00369
C	66	0.00136	0.00078	0.00093	0.00303
C	71	0.00126	0.00071	0.00084	0.00258
C	72	0.00136	0.00075	0.00085	0.00268
C	73	0.00135	0.00075	0.00088	0.00277
C	74	0.00131	0.00076	0.00087	0.00274
C	75	0.00116	0.00067	0.00080	0.00238
C	76	0.00129	0.00073	0.00087	0.00262
N	11	0.00122	0.00069	0.00078	0.00262
N	12	0.00134	0.00074	0.00085	0.00292
N	14	0.00126	0.00072	0.00078	0.00272
N	15	0.00109	0.00063	0.00076	0.00245
O	11	0.00100	0.00056	0.00064	0.00214
O	12	0.00098	0.00055	0.00062	0.00214

Blue Compound Distances

Atom(A)		Atom(B)	Distance(A - B)	e.s.d. (Å)
P 1	-	C 1	1.8160	0.0116
P 1	-	C 11	1.8038	0.0138
P 1	-	C 21	1.8316	0.0140
P 1	-	C 31	1.7082	0.0136
C 1	-	C 2	1.4233	0.0202
C 1	-	C 6	1.4343	0.0189
C 2	-	C 3	1.4540	0.0235
C 3	-	C 4	1.4119	0.0242
C 4	-	C 5	1.3854	0.0247
C 5	-	C 6	1.4479	0.0230
C 11	-	C 12	1.3523	0.0216
C 11	-	C 16	1.4316	0.0205
C 12	-	C 13	1.4408	0.0245
C 13	-	C 14	1.4492	0.0282
C 14	-	C 15	1.3997	0.0293
C 15	-	C 16	1.4148	0.0248
C 21	-	C 22	1.4044	0.0215
C 21	-	C 26	1.3927	0.0220
C 22	-	C 23	1.4443	0.0247
C 23	-	C 24	1.3373	0.0266
C 24	-	C 25	1.4183	0.0287
C 25	-	C 26	1.4625	0.0273
P 2	-	C 41	1.8205	0.0115
P 2	-	C 51	1.8158	0.0120
P 2	-	C 61	1.8101	0.0127
P 2	-	C 71	1.7672	0.0123
C 41	-	C 42	1.3780	0.0176
C 41	-	C 46	1.3746	0.0181
C 42	-	C 43	1.4368	0.0219
C 43	-	C 44	1.3940	0.0252
C 44	-	C 45	1.3468	0.0249
C 45	-	C 46	1.4414	0.0219
C 51	-	C 52	1.4195	0.0185
C 51	-	C 56	1.3816	0.0196
C 52	-	C 53	1.4417	0.0221
C 53	-	C 54	1.4235	0.0248
C 54	-	C 55	1.3740	0.0250
C 55	-	C 56	1.4253	0.0231
C 61	-	C 62	1.3871	0.0182
C 61	-	C 66=	1.4076	0.0180

Blue Compound Distances

Atom(A)		Atom(B)	Distance(A - B)	e.s.d. (Å)
C 62	-	C 63	1.3869	0.0204
C 63	-	C 64	1.3816	0.0224
C 64	-	C 65	1.4134	0.0227
C 65	-	C 66	1.3992	0.0205
C 31	-	C 32	1.4944	0.0176
C 31	-	C 36	1.4507	0.0188
C 32	-	C 33	1.4390	0.0162
C 32	-	N 1	1.3335	0.0155
C 33	-	C 34	1.5071	0.0166
C 33	-	N 2	1.3024	0.0155
C 34	-	C 35	1.4565	0.0170
C 34	-	C 74	1.4227	0.0172
C 35	-	C 36	1.4844	0.0178
C 35	-	N 4	1.3065	0.0173
C 36	-	N 5	1.3423	0.0174
N 1	-	O 1	1.4385	0.0139
N 2	-	O 1	1.3891	0.0135
N 4	-	O 2	1.3693	0.0158
N 5	-	O 2	1.3995	0.0154
C 71	-	C 72	1.4289	0.0173
C 71	-	C 76	1.4338	0.0171
C 72	-	C 73	1.4770	0.0178
C 72	-	N 11	1.3239	0.0169
C 73	-	C 74	1.4079	0.0178
C 73	-	N 12	1.3178	0.0177
C 74	-	C 75	1.4704	0.0168
C 75	-	C 76	1.4758	0.0166
C 75	-	N 14	1.3047	0.0162
C 76	-	N 15	1.3212	0.0162
N 11	-	O 11	1.3894	0.0147
N 12	-	O 11	1.3833	0.0155
N 14	-	O 12	1.3785	0.0148
N 15	-	O 12	1.4370	0.0140

Blue Compound **Angles**

Atom(A)			Atom(B)			Atom(C)		Angle at (B)	e.s.d.
C	1	-	P	1	-	C	11	109•44	0.573
C	1	-	P	1	-	C	21	105•15	0.572
C	1	-	P	1	-	C	31	114•89	0.587
C	11	-	P	1	-	C	21	109•51	0.621
C	11	-	P	1	-	C	31	106•17	0.634
C	21	-	P	1	-	C	31	111•65	0.634
P	1	-	C	1	-	C	2	122•03	0.999
P	1	-	C	1	-	C	6	118•25	0.930
C	2	-	C	1	-	C	6	119•71	1.203
C	1	-	C	2	-	C	3	120•15	1.401
C	2	-	C	3	-	C	4	117•42	1.493
C	3	-	C	4	-	C	5	124•27	1.610
C	4	-	C	5	-	C	6	118•15	1.530
C	1	-	C	6	-	C	5	120•11	1.323
P	1	-	C	11	-	C	12	120•35	1.135
P	1	-	C	11	-	C	16	117•79	1.044
C	12	-	C	11	-	C	16	121•67	1.359
C	11	-	C	12	-	C	13	124•94	1.523
C	12	-	C	13	-	C	14	113•78	1.612
C	13	-	C	14	-	C	15	120•06	1.559
C	14	-	C	15	-	C	16	124•67	1.785
C	11	-	C	16	-	C	15	114•58	1.412
P	1	-	C	21	-	C	22	118•54	1.094
P	1	-	C	21	-	C	26	119•00	1.120
C	22	-	C	21	-	C	26	122•18	1.391
C	21	-	C	22	-	C	23	118•20	1.460
C	22	-	C	23	-	C	24	120•30	1.697
C	23	-	C	24	-	C	25	123•05	1.826
C	24	-	C	25	-	C	26	117•56	1.777
C	21	-	C	26	-	C	25	118•57	1.552
C	41	-	P	2	-	C	51	109•61	0.531
C	41	-	P	2	-	C	61	108•10	0.546
C	41	-	P	2	-	C	71	109•51	0.545
C	51	-	P	2	-	C	61	109•45	0.558
C	51	-	P	2	-	C	71	107•61	0.556
C	61	-	P	2	-	C	71	112•54	0.573
P	2	-	C	41	-	C	42	120•06	0.909
P	2	-	C	41	-	C	46	118•72	0.924
C	42	-	C	41	-	C	46	121•22	1.150
C	41	-	C	42	-	C	43	120•72	1.248

Blue Compound **Angles**

Atom(A)		Atom(B)		Atom(C)	Angle at (B)	e.s.d.
C 42	-	C 43	-	C 44	115.94	1.501
C 43	-	C 44	-	C 45	124.57	1.692
C 44	-	C 45	-	C 46	118.36	1.525
C 41	-	C 46	-	C 45	119.17	1.227
P 2	-	C 51	-	C 52	119.71	0.935
P 2	-	C 51	-	C 56	120.11	0.991
C 52	-	C 51	-	C 56	120.18	1.203
C 51	-	C 52	-	C 53	119.18	1.236
C 52	-	C 53	-	C 54	119.79	1.483
C 53	-	C 54	-	C 55	121.06	1.633
C 54	-	C 55	-	C 56	119.83	1.558
C 51	-	C 56	-	C 55	120.04	1.397
P 2	-	C 61	-	C 62	119.72	0.962
P 2	-	C 61	-	C 66	121.92	0.980
C 62	-	C 61	-	C 66	118.35	1.140
C 61	-	C 62	-	C 63	121.37	1.265
C 62	-	C 63	-	C 64	121.22	1.412
C 63	-	C 64	-	C 65	118.30	1.464
C 64	-	C 65	-	C 66	120.48	1.404
C 61	-	C 66	-	C 65	120.24	1.235
P 1	-	C 31	-	C 32	124.83	0.968
P 1	-	C 31	-	C 36	124.64	1.017
C 32	-	C 31	-	C 36	110.51	1.095
C 31	-	C 32	-	C 33	125.35	1.047
C 31	-	C 32	-	N 1	125.50	1.069
C 33	-	C 32	-	N 1	109.13	1.091
C 32	-	C 33	-	C 34	119.35	1.006
C 32	-	C 33	-	N 2	111.10	1.035
C 34	-	C 33	-	N 2	129.49	1.073
C 33	-	C 34	-	C 35	109.90	0.994
C 33	-	C 34	-	C 74	122.99	1.054
C 35	-	C 34	-	C 74	127.10	1.093
C 34	-	C 35	-	C 36	123.66	1.084
C 34	-	C 35	-	N 4	129.32	1.163
C 36	-	C 35	-	N 4	107.02	1.094
C 31	-	C 36	-	C 35	121.07	1.134
C 31	-	C 36	-	N 5	128.97	1.207
C 35	-	C 36	-	N 5	109.44	1.100
C 32	-	N 1	-	O 1	102.77	0.915
C 33	-	N 2	-	O 1	104.43	0.932

Blue Compound **Angles**

Atom(A)		Atom(B)		Atom(C)	Angle at (B)	e.s.d.
C 35	-	N 4	-	O 2	107.01	1.003
C 36	-	N 5	-	O 2	102.99	1.029
N 1	-	O 1	-	N 2	113.26	0.844
N 4	-	O 2	-	N 5	113.37	0.986
P 2	-	C 71	-	C 72	122.74	0.917
P 2	-	C 71	-	C 76	123.23	0.911
C 72	-	C 71	-	C 76	112.59	1.060
C 71	-	C 72	-	C 73	119.07	1.092
C 71	-	C 72	-	N 11	129.28	1.167
C 73	-	C 72	-	N 11	111.24	1.087
C 72	-	C 73	-	C 74	125.66	1.137
C 72	-	C 73	-	N 12	104.33	1.096
C 74	-	C 73	-	N 12	129.95	1.216
C 34	-	C 74	-	C 73	123.68	1.151
C 34	-	C 74	-	C 75	121.26	1.079
C 73	-	C 74	-	C 75	109.93	1.059
C 74	-	C 75	-	C 76	119.69	1.017
C 74	-	C 75	-	N 14	128.16	1.095
C 76	-	C 75	-	N 14	111.91	1.040
C 71	-	C 76	-	C 75	123.40	1.069
C 71	-	C 76	-	N 15	130.56	1.141
C 75	-	C 76	-	N 15	105.87	1.025
C 72	-	N 11	-	O 11	104.31	1.010
C 73	-	N 12	-	O 11	109.25	1.090
C 75	-	N 14	-	O 12	104.69	1.006
C 76	-	N 15	-	O 12	106.11	0.955
N 11	-	O 11	-	N 12	110.87	0.942
N 14	-	O 12	-	N 15	111.36	0.885

Blue Compound Orthogonal co-ordinates (L.S. plane C(32), C(33), C(35), C(36).)

Centroid : 0.76544 0.42878 0.14442

Atom		x'	y'	z' (Å)
P	1	-0.12394	-3.19340	0.61304
C	1	-0.09983	-4.31456	-0.78507
C	2	-0.45617	-5.68798	-0.67295
C	3	-0.51494	-6.52649	-1.86639
C	4	-0.10730	-5.95158	-3.04278
C	5	0.26652	-4.62694	-3.27537
C	6	0.28599	-3.78200	-2.08673
C	11	1.32396	-3.56326	1.67401
C	12	1.66643	-2.63074	2.64799
C	13	2.81082	-2.77034	3.51446
C	14	3.51552	-4.02649	3.35437
C	15	3.09166	-4.95040	2.39216
C	16	2.01675	-4.74320	1.49596
C	21	-1.64079	-3.63284	1.57110
C	22	-2.82635	-3.84734	0.85274
C	23	-4.03856	-4.10777	1.59676
C	24	-4.03107	-4.06546	2.93541
C	25	-2.85196	-3.86117	3.69432
C	26	-1.69619	-3.61984	2.96338
P	2	-0.09041	7.55603	0.65983
C	41	-1.49604	7.96699	-0.43002
C	42	-2.78437	7.86937	0.06174
C	43	-3.90716	8.10098	-0.79256
C	44	-3.60427	8.47357	-2.11690
C	45	-2.35727	8.53259	-2.62218
C	46	-1.24809	8.26855	-1.74040
C	51	1.45532	8.06123	-0.13516
C	52	1.94976	7.36299	-1.25521
C	53	3.18386	7.78329	-1.87067
C	54	3.86690	8.91205	-1.33622
C	55	3.36208	9.60233	-0.24033
C	56	2.15313	9.16767	0.35512
C	61	-0.31349	8.40959	2.20649
C	62	0.31819	8.03156	3.35112
C	63	0.18654	8.71738	4.55964
C	64	-0.60175	9.24649	4.65668
C	65	-1.25659	10.30804	3.49226
C	66	-1.09850	9.63589	2.27537

Blue Compound Orthogonal co-ordinates.

Atom		x'	y'	z' (Å)
C	31	-0.08336	-1.53091	0.25320
C	32	1.16094	-0.74630	-0.01028
C	33	1.20000	0.66911	0.01024
C	34	0.03953	1.45904	0.31127
C	35	-1.16501	0.73934	-0.00992
C	36	-1.25593	-0.71215	0.00997
N	1	2.36264	-1.26360	-0.26825
N	2	2.45324	1.06100	-0.32375
N	4	-2.33648	1.21943	-0.37312
N	5	-2.48213	-1.03962	-0.38445
O	1	3.16007	-0.09687	-0.53668
O	2	-3.11504	0.12280	-0.65461
C	71	0.00471	5.86950	0.91226
C	72	1.24595	5.11452	1.04478
C	73	1.24271	3.63769	1.07007
C	74	0.11214	2.91664	0.89709
C	75	-1.09940	3.53402	1.32095
C	76	-1.11956	5.00960	1.30209
N	11	2.45229	5.59556	1.30369
N	12	2.49068	3.31301	1.34150
N	14	-2.19040	3.03882	1.63746
N	15	-2.29952	5.26106	1.78141
O	11	3.24213	4.46609	1.47972
O	12	-2.96392	4.13868	2.14096

Transformation matrix.

4.3306	6.6033	9.4306
-3.7550	-5.0476	11.4578
7.2762	-14.1803	0.3130

Blue Compound Planes through atom triplets (central C_6 rings)

Atom		x'	y'	z' (Å)
C	31	1.50434	0.09016	0.00000
C	35	-0.84054	1.10604	0.00000
C	36	0.06368	-0.06969	-0.05936
N	5	-0.66380	-1.19620	-0.00000
C	34	1.51211	0.16223	-0.00000
C	35	0.07638	-0.06296	-0.00549
C	36	-0.94266	1.01639	-0.00000
N	4	-0.56945	-1.19862	-0.00000
C	32	0.76059	-1.13021	0.00000
C	33	-0.01371	0.08251	-0.02064
C	34	-1.51583	-0.00142	0.00000
N	2	0.75774	1.13162	0.00000
C	71	1.51107	0.11520	-0.00000
C	75	-0.87307	1.05315	-0.00000
C	76	0.08903	-0.06558	-0.02997
N	15	-0.63749	-1.16836	-0.00000
C	71	-1.47383	-0.05531	-0.00000
C	72	-0.05272	0.03428	0.05195
C	73	0.78983	-1.12775	-0.00000
N	11	0.68400	1.18306	-0.00000
C	72	0.93260	-1.00059	-0.00000
C	73	-0.10884	0.04658	0.02023
C	74	-1.49864	-0.17764	-0.00000
N	12	0.56604	1.17824	-0.00000
C	74	1.48930	0.13805	-0.00000
C	75	0.03585	-0.03112	-0.03930
C	76	-0.87932	1.07605	-0.00000
N	14	-0.60949	-1.21410	-0.00000

Blue Compound Planes though atom triplets (central C_6 rings) cont.

Atom		x'	y'	z' (Å)
C	33	-1.57483	1.20732	0.07410
C	34	-0.70185	-0.01937	0.00705
C	35	-1.53076	-1.21345	-0.08552
C	73	1.55400	1.16881	-0.08896
C	74	0.71956	0.03982	0.01743
C	75	1.53386	-1.18312	0.07591
P	2	-1.70068	-0.01568	-0.00000
C	76	0.86714	-1.18282	-0.00000
C	71	0.06329	-0.00032	-0.10630
C	72	0.83355	1.19850	-0.00000
P	1	1.69746	0.06483	0.00000
C	31	-0.00854	-0.01143	-0.04246
C	32	-0.91713	1.17424	0.00000
C	36	-0.78033	-1.23907	0.00000

Orthogonal co-ordinates (L.S. plane C(72), C(73), C(75), C(76).)

Centroid: 0.56074 0.24525 0.37387

C	71	0.06971	1.42823	-0.25582
C	72	1.23838	0.76670	-0.00047
C	73	1.13054	-0.76638	0.00048
C	74	-0.02908	-1.50458	-0.30378
C	75	-1.22649	-0.76689	-0.00048
C	76	-1.14243	0.76656	0.00047
N	11	2.44063	1.09980	0.39045
N	12	2.31684	-1.16061	0.39813
N	14	-2.39812	-1.12790	0.38960
N	15	-2.33977	1.19661	0.39685
O	11	3.12711	-0.08369	0.63246
O	12	-3.12176	0.02139	0.62564

Transformation matrix.

3.2470	7.7161	10.1125
-4.1029	-5.3955	10.7634
7.6377	-13.4720	1.4828

Phosphate Complex (-120°C) Atomic Co-ordinates

Atom		x/a	y/b	z/c	U(iso)
P	1	0.15156	0.06451	0.25150	0.02988
O	1	0.34246	0.07593	0.25120	0.03513
O	2	0.01964	-0.09588	0.21687	0.06237
O	3	0.09792	0.18473	0.18072	0.05995
O	4	0.07101	0.09536	0.35590	0.04082
C	21	0.05416	-0.24583	0.19811	0.06012
C	22	0.08392	-0.32852	0.29488	0.13177
C	31	0.17384	0.19715	0.07691	0.07863
C	32	0.23399	0.37181	0.07127	0.09092
C	41	0.19210	0.19236	0.43592	0.06503
C	42	0.27604	0.37394	0.43168	0.07379
C	1	0.63605	-0.05661	0.19895	0.03953
C	2	0.66593	0.08514	0.14509	0.03749
C	3	0.72232	0.23421	0.19900	0.03557
C	4	0.70226	0.23747	0.30721	0.03539
C	5	0.68243	0.08924	0.36297	0.03372
C	6	0.62764	-0.05194	0.30999	0.03709
N	1	0.59432	-0.20444	0.16946	0.05535
N	2	0.69188	0.11671	0.04537	0.05341
N	3	0.74676	0.34994	0.13197	0.05155
N	4	0.75614	0.35364	0.37330	0.05200
N	5	0.68289	0.12288	0.46220	0.04977
N	6	0.59044	-0.19590	0.34529	0.05282
O	5	0.56764	-0.29564	0.25817	0.06683
O	6	0.73796	0.28690	0.47069	0.06319
O	7	0.72521	0.27794	0.03394	0.06362

Phosphate Complex (-120°C) E.s.d.'s of atomic co-ords.

Atom		x/a	y/b	z/c	U(iso)
P	1	0.00055	0.00049	0.00003	0.00122
O	1	0.00129	0.00126	0.00195	0.00273
O	2	0.00221	0.00163	0.00139	0.00506
O	3	0.00230	0.00191	0.00136	0.00471
O	4	0.00190	0.00172	0.00109	0.00375
C	21	0.00350	0.00259	0.00126	0.00670
C	22	0.00651	0.00566	0.00307	0.01569
C	31	0.00509	0.00390	0.00232	0.01053
C	32	0.00471	0.00390	0.00319	0.01015
C	41	0.00415	0.00334	0.00240	0.00874
C	42	0.00473	0.00379	0.00352	0.01022
C	1	0.00370	0.00167	0.00168	0.00265
C	2	0.00364	0.00177	0.00151	0.00264
C	3	0.00317	0.00186	0.00145	0.00285
C	4	0.00333	0.00186	0.00141	0.00278
C	5	0.00349	0.00174	0.00152	0.00270
C	6	0.00368	0.00164	0.00168	0.00269
N	1	0.00366	0.00236	0.00180	0.00330
N	2	0.00373	0.00234	0.00164	0.00329
N	3	0.00385	0.00198	0.00172	0.00360
N	4	0.00372	0.00195	0.00174	0.00356
N	5	0.00355	0.00228	0.00159	0.00339
N	6	0.00355	0.00235	0.00176	0.00338
O	5	0.00208	0.00150	0.00202	0.00327
O	6	0.00326	0.00216	0.00152	0.00326
O	7	0.00307	0.00221	0.00156	0.00320

Phosphate Complex (-120°C) Distances

Atom(A)		Atom(B)		Distance(A - B)	e.s.d. (Å)
P 1	-	O 1		1.4439	0.0155
P 1	-	O 2		1.5548	0.0168
P 1	-	O 3		1.5586	0.0178
P 1	-	O 4		1.5521	0.0150
O 2	-	C 21		1.4515	0.0277
O 3	-	C 31		1.4750	0.0390
O 4	-	C 41		1.4986	0.0344
C 21	-	C 22		1.5182	0.0519
C 31	-	C 32		1.4833	0.0512
C 41	-	C 42		1.5511	0.0497
C 1	-	C 2		1.4019	0.0304
C 1	-	C 6		1.4613	0.0307
C 1	-	N 1		1.3138	0.0326
C 2	-	C 3		1.4500	0.0291
C 2	-	N 2		1.3423	0.0318
C 3	-	C 4		1.4311	0.0284
C 3	-	N 3		1.3232	0.0307
C 4	-	C 5		1.4732	0.0290
C 4	-	N 4		1.3183	0.0306
C 5	-	C 6		1.3864	0.0300
C 5	-	N 5		1.3369	0.0308
C 6	-	N 6		1.3088	0.0322
N 1	-	O 5		1.3991	0.0306
N 2	-	O 7		1.3851	0.0318
N 3	-	O 7		1.4254	0.0315
N 4	-	O 6		1.3995	0.0314
N 5	-	O 6		1.3963	0.0313
N 6	-	O 5		1.4256	0.0302

Phosphate Complex (-120°C) Angles

Atom(A)		-	Atom(B)		-	Atom(C)		Angle at (B)	e.s.d.
O	1	-	P	1	-	O	2	116.30	0.889
O	1	-	P	1	-	O	3	114.72	0.913
O	1	-	P	1	-	O	4	116.01	0.842
O	2	-	P	1	-	O	3	102.62	0.905
O	2	-	P	1	-	O	4	103.32	0.832
O	3	-	P	1	-	O	4	101.87	0.859
P	1	-	O	2	-	C	21	129.95	1.446
P	1	-	O	3	-	C	31	115.11	1.759
P	1	-	O	4	-	C	41	120.27	1.528
O	2	-	C	21	-	C	22	113.23	2.367
O	3	-	C	31	-	C	32	96.90	2.576
O	4	-	C	41	-	C	42	124.85	2.578
C	2	-	C	1	-	C	6	118.39	1.928
C	2	-	C	1	-	N	1	132.41	2.170
C	6	-	C	1	-	N	1	109.62	1.999
C	1	-	C	2	-	C	3	119.88	1.895
C	1	-	C	2	-	N	2	130.92	2.100
C	3	-	C	2	-	N	2	107.45	1.902
C	2	-	C	3	-	C	4	119.87	1.803
C	2	-	C	3	-	N	3	108.59	1.877
C	4	-	C	3	-	N	3	129.59	1.986
C	3	-	C	4	-	C	5	117.37	1.775
C	3	-	C	4	-	N	4	131.20	2.000
C	5	-	C	4	-	N	4	107.27	1.857
C	4	-	C	5	-	C	6	118.76	1.864
C	4	-	C	5	-	N	5	107.07	1.855
C	6	-	C	5	-	N	5	132.13	2.076
C	1	-	C	6	-	C	5	121.49	1.945
C	1	-	C	6	-	N	6	108.97	1.989
C	5	-	C	6	-	N	6	128.70	2.140
C	1	-	N	1	-	O	5	106.44	2.046
C	2	-	N	2	-	O	7	107.00	2.037
C	3	-	N	3	-	O	7	106.40	1.975
C	4	-	N	4	-	O	6	107.56	1.995
C	5	-	N	5	-	O	6	106.86	1.982
C	6	-	N	6	-	O	5	105.84	1.999
N	1	-	O	5	-	N	6	109.84	1.852
N	4	-	O	6	-	N	5	109.29	1.951
N	2	-	O	7	-	N	3	109.07	1.956

Phosphate Complex (-120°C) Orthogonal co-ordinates

(plane C_1- C_6)

Centroid: 0.67277 0.08959 · 0.25387

Atom		x'	y'	z' (Å)
P	1	0.02932	-0.01087	-3.95521
O	1	0.02643	-0.03018	-2.51133
O	2	0.90790	1.07605	-4.62864
O	3	0.54310	-1.31961	-4.62297
O	4	-1.36083	0.17692	-4.64041
C	21	1.56352	2.21469	-4.04420
C	22	0.63565	3.32692	-3.63949
C	31	1.79854	-1.35462	-4.04590
C	32	1.36500	-3.20511	-3.97479
C	41	-2.61545	-0.19960	-3.91549
C	42	-3.08319	-1.65038	-3.65513
C	1	1.10084	0.91865	0.02553
C	2	1.35447	-0.45451	-0.04313
C	3	0.26041	-1.39324	0.07344
C	4	-1.08731	-0.94203	-0.03777
C	5	-1.34410	0.49550	0.07493
C	6	-0.28432	1.37562	-0.04605
N	1	1.89194	1.98248	0.02256
N	2	2.49637	-1.14587	0.06940
N	3	0.75217	-2.61730	0.01535
N	4	-2.23569	-1.56189	0.07921
N	5	-2.66689	0.66999	0.00699
N	6	-0.30357	2.68025	-0.02586
O	5	1.06054	3.06525	0.01083
O	6	-3.24460	-0.59398	0.03156
O	7	2.16984	-2.46444	0.00281

Transformation	1.4087	-3.3547	-12.3111
	0.3388	-8.0648	4.4826
matrix	7.6909	-2.1270	-0.0005

Phosphate Complex (22°C) Atomic Co-ordinates

Atom		x/a	y/b	z/c	U(iso)
P	1	0.16325	0.08048	0.25150	0.06214
O	1	0.34745	0.08021	0.25162	0.09465
O	2	0.02344	-0.07994	0.22010	0.08410
O	3	0.10667	0.20571	0.18716	0.10075
O	4	0.07787	0.11843	0.35201	0.08674
C	21	0.05398	-0.23358	0.19935	0.10591
C	22	0.09180	-0.33527	0.26668	0.17850
C	31	0.17407	0.20084	0.08271	0.17002
C	32	0.24657	0.37863	0.06653	0.15477
C	41	0.19524	0.17858	0.44128	0.16564
C	42	0.28632	0.35673	0.43840	0.20363
C	1	0.60882	-0.06547	0.20458	0.07890
C	2	0.68547	0.07603	0.14907	0.07987
C	3	0.73617	0.22693	0.20445	0.07946
C	4	0.68488	0.22346	0.30927	0.07836
C	5	0.66152	0.07721	0.36792	0.07793
C	6	0.65041	-0.06363	0.31453	0.07842
N	1	0.57547	-0.21370	0.17259	0.11270
N	2	0.67710	0.10643	0.05114	0.11150
N	3	0.73226	0.33900	0.13589	0.11023
N	4	0.77196	0.34155	0.37174	0.11156
N	5	0.69846	0.11696	0.46530	0.11282
N	6	0.60121	-0.21243	0.34598	0.11290
O	5	0.55852	-0.31265	0.25880	0.13070
O	6	0.74267	0.28465	0.47307	0.13133
O	7	0.72461	0.27233	0.03685	0.13110

Phosphate Complex (22°C) E.s.d.'s of atomic co-ords.

Atom		x/a	y/b	z/c	U(iso)
P	1	0.00133	0.00130	0.00000	0.00366
O	1	0.00256	0.00353	0.00434	0.00960
O	2	0.00329	0.00255	0.00298	0.00998
O	3	0.00437	0.00369	0.00320	0.01076
O	4	0.00412	0.00377	0.00190	0.01018
C	21	0.00673	0.00450	0.00504	0.01765
C	22	0.01132	0.01028	0.00576	0.03045
C	31	0.01433	0.00971	0.00536	0.03713
C	32	0.01141	0.00924	0.00728	0.02806
C	41	0.01041	0.00940	0.00517	0.02730
C	42	0.01390	0.00999	0.01014	0.03689
C	1	0.00552	0.00282	0.00298	0.00650
C	2	0.00595	0.00297	0.00293	0.00652
C	3	0.00522	0.00318	0.00268	0.00646
C	4	0.00579	0.00325	0.00270	0.00647
C	5	0.00671	0.00302	0.00280	0.00644
C	6	0.00585	0.00287	0.00293	0.00648
N	1	0.00714	0.00437	0.00342	0.00700
N	2	0.00791	0.00465	0.00303	0.00698
N	3	0.00770	0.00350	0.00350	0.00701
N	4	0.00726	0.00324	0.00384	0.00700
N	5	0.00803	0.00461	0.00303	0.00695
N	6	0.00730	0.00416	0.00341	0.00696
O	5	0.00430	0.00274	0.00427	0.00759
O	6	0.00777	0.00477	0.00317	0.00755
O	7	0.00678	0.00478	0.00304	0.00758

Phosphate Complex (22°) Distances

Atom(A)		-	Atom(B)		Distance(A - B)	e.s.d. (A)
P	1	-	O	1	1.4448	0.0396
P	1	-	O	2	1.5990	0.0304
P	1	-	O	3	1.5845	0.0375
P	1	-	O	4	1.5773	0.0315
O	2	-	C	21	1.5053	0.0611
O	3	-	C	31	1.4915	0.0977
O	4	-	C	41	1.5033	0.0843
C	21	-	C	22	1.5638	0.1014
C	31	-	C	32	1.5582	0.1277
C	41	-	C	42	1.5631	0.1363
C	1	-	C	2	1.4499	0.0521
C	1	-	C	6	1.4973	0.0517
C	1	-	N	1	1.3593	0.0593
C	2	-	C	3	1.5006	0.0514
C	2	-	N	2	1.3368	0.0610
C	3	-	C	4	1.4487	0.0510
C	3	-	N	3	1.3717	0.0580
C	4	-	C	5	1.5015	0.0538
C	4	-	N	4	1.3693	0.0588
C	5	-	C	6	1.4405	0.0538
C	5	-	N	5	1.3528	0.0622
C	6	-	N	6	1.3554	0.0596
N	1	-	O	5	1.4375	0.0607
N	2	-	O	7	1.4514	0.0663
N	3	-	O	7	1.4430	0.0649
N	4	-	O	6	1.4372	0.0669
N	5	-	O	6	1.4599	0.0687
N	6	-	O	5	1.4502	0.0605

Phosphate Complex (22°C) Angles

Atom(A)		-	Atom(B)		-	Atom(C)		Angle at (B)	e.s.d.
O	1	-	P	1	-	O	2	114•75	1.927
O	1	-	P	1	-	O	3	119•41	2.092
O	1	-	P	1	-	O	4	119•18	1.961
O	2	-	P	1	-	O	3	104•41	1.750
O	2	-	P	1	-	O	4	101•40	1.588
O	3	-	P	1	-	O	4	94•37	1.776
P	1	-	O	2	-	C	21	129•52	2.848
P	1	-	O	3	-	C	31	107•83	4.132
P	1	-	O	4	-	C	41	119•64	3.591
O	2	-	C	21	-	C	22	121•16	4.833
O	3	-	C	31	-	C	32	97•09	6.244
O	4	-	C	41	-	C	42	113•66	6.496
C	2	-	C	1	-	C	6	117•05	3.156
C	2	-	C	1	-	N	1	128•68	3.636
C	6	-	C	1	-	N	1	107•16	3.377
C	1	-	C	2	-	C	3	119•14	3.188
C	1	-	C	2	-	N	2	130•25	3.764
C	3	-	C	2	-	N	2	107•84	3.479
C	2	-	C	3	-	C	4	117•02	3.099
C	2	-	C	3	-	N	3	106•91	3.297
C	4	-	C	3	-	N	3	126•15	3.514
C	3	-	C	4	-	C	5	118•74	3.201
C	3	-	C	4	-	N	4	119•66	3.514
C	5	-	C	4	-	N	4	106•18	3.388
C	4	-	C	5	-	C	6	119•04	3.321
C	4	-	C	5	-	N	5	107•53	3.553
C	6	-	C	5	-	N	5	131•34	3.860
C	1	-	C	6	-	C	5	116•61	3.217
C	1	-	C	6	-	N	6	107•01	3.399
C	5	-	C	6	-	N	6	130•91	3.732
C	1	-	N	1	-	O	5	108•81	3.809
C	2	-	N	2	-	O	7	109•13	4.034
C	3	-	N	3	-	O	7	107•71	3.832
C	4	-	N	4	-	O	6	107•32	3.905
C	5	-	N	5	-	O	6	108•18	4.076
C	6	-	N	6	-	O	5	108•81	3.797
N	1	-	O	5	-	N	6	106•55	3.592
N	4	-	O	6	-	N	5	105•74	4.049
N	2	-	O	7	-	N	3	106•30	3.916

Phosphate Complex (22°C) Orthogonal co-ordinates (plane though $C_1 - C_6$)

Centroid: 0.67121 0.07908 0.25830

Atom		x'	y'	z' (Å)
P	1	0.10163	-0.23235	-3.97910
O	1	0.08628	-0.12546	-2.53830
O	2	-0.69609	0.92229	-4.74454
O	3	1.48917	-0.32127	-4.73790
O	4	-0.49079	-1.52559	-4.66059
C	21	-1.55191	2.02796	-4.18560
C	22	-2.97609	1.73681	-3.60900
C	31	2.33849	0.81315	-4.27171
C	32	3.66128	0.00706	-4.10277
C	41	-0.65321	-2.71300	-3.81283
C	42	0.35628	-3.64664	-3.49044
C	1	-0.50618	1.33715	-0.20993
C	2	0.90497	1.14230	0.04353
C	3	1.44243	-0.25477	0.14936
C	4	0.53336	-1.33587	-0.17239
C	5	-0.94146	-1.11554	0.00314
C	6	-1.43112	0.22673	0.18630
N	1	-1.22730	2.48992	-0.16995
N	2	1.93962	1.96526	-0.15493
N	3	2.77464	-0.19505	-0.17139
N	4	0.78890	-2.59766	0.29398
N	5	-1.50366	-2.31622	0.27195
N	6	-2.69098	0.72505	0.14691
O	5	-2.61941	2.16291	-0.02829
O	6	-0.44949	-3.32610	0.25798
O	7	3.16859	1.19306	-0.15425

Transformation matrix.

-0.6661	6.6967	-8.1965
..5786	-5.7000	-10.2225
7.8184	-2.1761	6.0828

APPENDIX VI

Published papers.

Investigation of the Reaction of Benztrifuroxan with Triphenylphosphine

By A. S. Bailey*, T. S. Cameron†, (Miss) J. M. Evans,*† and C. K. Prout†

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Investigation of the Reaction of Benztrifuroxan with Triphenylphosphine

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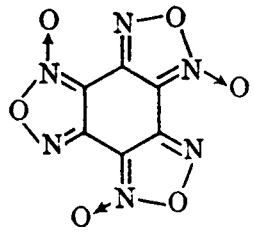
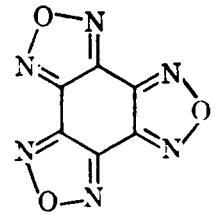
REDUCTION of benztrifuroxan (I) with trialkyl phosphites has been found to give crystalline 1 : 1 molecular complexes of benztrifurazan (II) with the corresponding trialkyl phosphates.[1]



(I)



(II)

In contrast, the reaction of benztrifuroxan (I) with triphenylphosphine is complex, and gives no benztrifurazan (II). The product is a mixture of triphenylphosphine oxide with a large number of coloured compounds, which are difficult to separate. Four of these, a dark green, a lighter green, a red, and a yellow compound, have been obtained as crystalline solids, and all contain nitrogen and phosphorus.

The physical data for the compounds gave little information. The compounds decomposed on analysis and in the inlet to the mass spectrometer. Spectroscopic data indicated the presence of P–Ph groups in all the compounds, and N–H or O–H groups in the red compound.

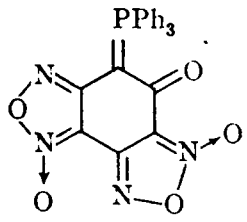
As only small quantities were available, it was decided to examine the compounds by *X*-ray crystallography. The structure analyses of the dark green and the red compounds are reported here.

Crystal data: *dark green compound*. Triclinic pinacoidal, $a = 15{\cdot}44$, $b = 11{\cdot}63$, $c = 10{\cdot}35$ Å; $\alpha = 114{\cdot}12°$, $\beta = 96{\cdot}63°$, $\gamma = 120{\cdot}63°$; *space group* $P\bar{1}$; Cu-K_α radiation $D_m = 1{\cdot}378$ g.cm.$^{-3}$, which gave an estimated molecular weight of 549 and two molecules per unit cell. From the structure analysis, the formula is $C_{30}H_{21}N_4O_5P$; $M = 548$; $Z = 2{\cdot}005$; $\mu = 13{\cdot}6$ cm.$^{-1}$ 2,500 independent reflections were measured visually from equi-inclination Weissenberg photographs.

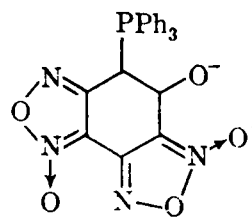
Crystal data: *red compound*. Triclinic pinacoidal; $a = 9{\cdot}59$, $b = 10{\cdot}82$, $c = 11{\cdot}81$ Å; $\alpha = 96{\cdot}70$, $\beta = 94{\cdot}90$, $\gamma = 90{\cdot}83$; space-group $P\bar{1}$; Cu-K_α radiation. $D_m = 1{\cdot}477$ g. cm.$^{-3}$, which gave an estimated molecular weight of 503 and two molecules per unit cell. From the structure analysis, the formula is $C_{24}H_{17}N_6O_5P$; $M = 502$; $Z = 2{\cdot}007$; $\mu = 15{\cdot}44$ cm.$^{-1}$ 3670 independent reflections were measured visually from equi-inclination Weissenberg photographs.

In both analyses, the positions of the phosphorus atom and three phenyl groups were established from a three-dimensional Patterson function "sharpened to point atoms at rest". The remaining atoms were located from a series of F_0 syntheses. The trial structures, with individual isotropic temperature-factors, were refined by a least-squares method that used a block-diagonal approximation to the full matrix with cross terms from atoms in chemically distinct units. The reliability factor R is 16% for both compounds, and the bond length e.s.d's are $\gtrsim 0{\cdot}02$ Å. Refinement is to be continued with anisotropic temperature-factors.

The molecular structure of the dark green compound (Figure 1) may be formulated as (III) or (IV).



(III)



(IV)

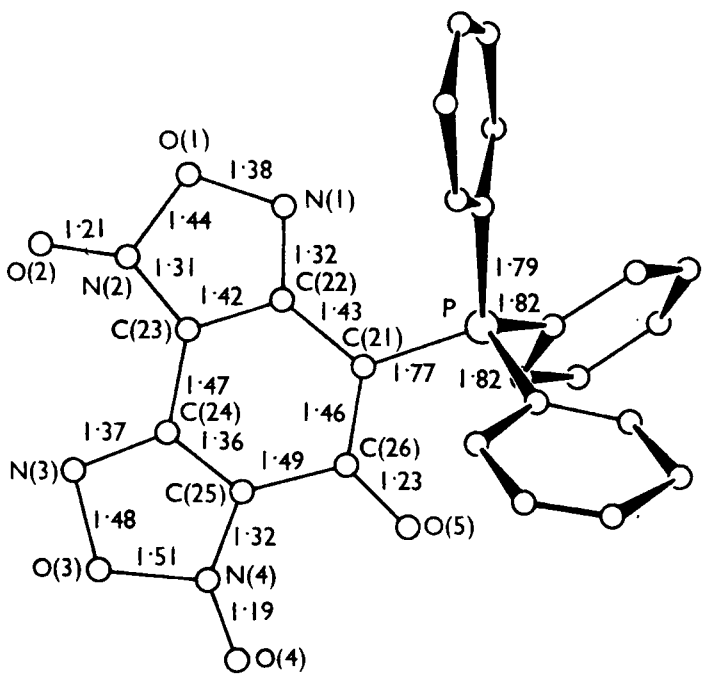
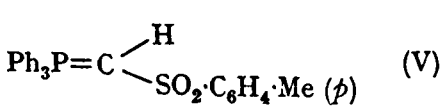


FIGURE 1.

The dark green compound (III) *projected perpendicular to the least-squares best plane of the carbon ring of the benztrifuroxan fragment. The interatomic distances are in Å units.*

The interatomic distances in the phenyl groups are in the range of accepted values, and those in the furoxan rings agree with the values recently published for benztrifuroxan.[2] The P–C bond lengths vary between 1·77 and 1·82 Å; these are similar to the P–C lengths in structure (V),[3]



(V)

except that in contrast to the latter, no one length is significantly shorter than any other. The bond lengths in the C(21)–C(26)–O(5) system are very similar to those in the quinones.[4] The correct representation for the compound is probably (III) ⟷ (IV). The crystals contain two molecules of benzene of crystallisation in each unit cell.

The dark green compound is probably formed by an aromatic substitution by triphenylphosphine. Similar reactions have been reported for 2,5-dichloro-*p*-benzoquinone[5] and recently for *o*-dinitrobenzene.[6]

The red compound (Figure 2) is a hydrogen-bonded complex of triphenylphosphine oxide and an unusual difurazan (VI).

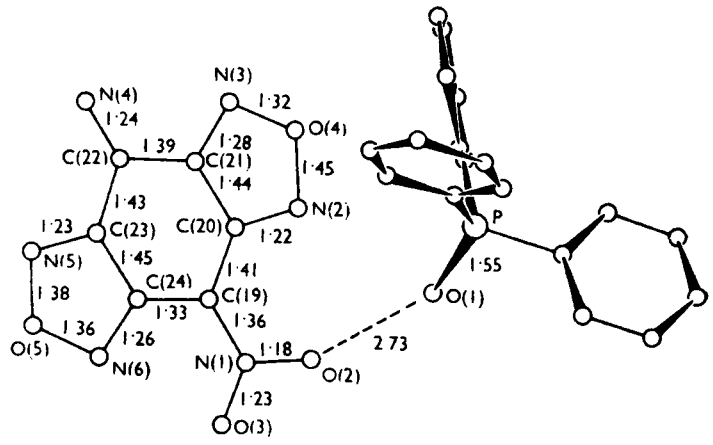
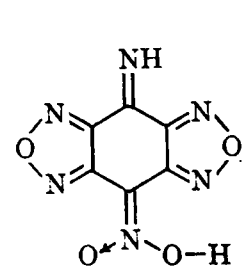


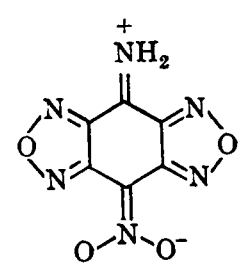
FIGURE 2.

The hydrogen bonded complex found in the red compound (VI) *projected perpendicular to the least-squares best plane of the bentrifuroxan fragment. The interatomic distances are in Å units.*

The interatomic distances in the triphenylphosphine oxide are similar to those of triphenylphosphine;[7] the P=O distance is 1·55 Å. The bond lengths in the furazan rings, which are very different from those reported in a two-dimensional analysis of benzofurazan,[8] are consistent with double bonds between carbon and nitrogen and single bonds between nitrogen and oxygen. The C–C bonds in the furazan rings correspond to the



(VI)



(VII)

"single" bonds in quinones[4] and the C–C bond in dimethylglyoxime.[9] The C–N bond lengths not in the furazan rings are in agreement with structure (VI) rather than its tautomer(VII). The short

O–O contact (2·73 Å) between the phosphoryl and nitro-groups is presumed to be a hydrogen bond.

Other physical data indicated that the compound can exist in the tautomeric form (VII) in solution.

(*Received, August 18th,* 1966; *Com.* 614.)

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Further Investigation of the Reaction of Benztrifuroxan with Triphenylphosphine

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IT has been reported[1,2] that amongst the products of the reaction of triphenylphosphine with benztrifuroxan (I) in toluene is a high-melting yellow crystalline solid. The structure of this compound has been determined.

Crystal data: triclinic needles, $a = 8{\cdot}864$, $b = 13{\cdot}502$, $c = 25{\cdot}534$ Å; $\alpha = 97{\cdot}92°$, $\beta = 99{\cdot}13°$, $\gamma = 111{\cdot}47°$; Cu-K_α radiation, $\mu = 11{\cdot}28$ cm.$^{-1}$; $D_m = 1{\cdot}2975$ g.cm.$^{-3}$, D_c for $2(C_{60}H_{45}N_6O_6P_3),CH_3C_6H_5$, 1·30049 cm.$^{-3}$. Space group $P\bar{1}$, 6218 independent reflections were measured visually from equi-inclination Weissenberg photographs.

The positions of the three phosphorus atoms were unambiguously established from a three-dimensional Patterson function "sharpened to point atoms at rest." The 75 light atom positions were located from an F_0 synthesis phased on the three phosphorus positions. The trial structure, with individual isotropic temperature factors, was refined by a method of least-squares that used a block diagonal approximation to the full matrix with cross terms from atoms in chemically distinct units. A difference synthesis calculated when the reliability factor R was 20% showed that the crystals contained a clathrate toluene molecule at sites disordered about a centre of symmetry.

The R factor is now 16%, the bond length e.s.d.'s are $\gtrsim 0{\cdot}02$ Å and the refinement is continuing.

The molecular structure (Figure) may be formulated as (II).

The interatomic distances in the phenyl groups are in the range of accepted values, and the temperature factors for the atoms in the central ring, are similar to the temperature factors of both, the nitrogen atoms bonded to the ring and the carbon atoms bonded to the phosphorus.

The P=N bond lengths vary between 1·54 and

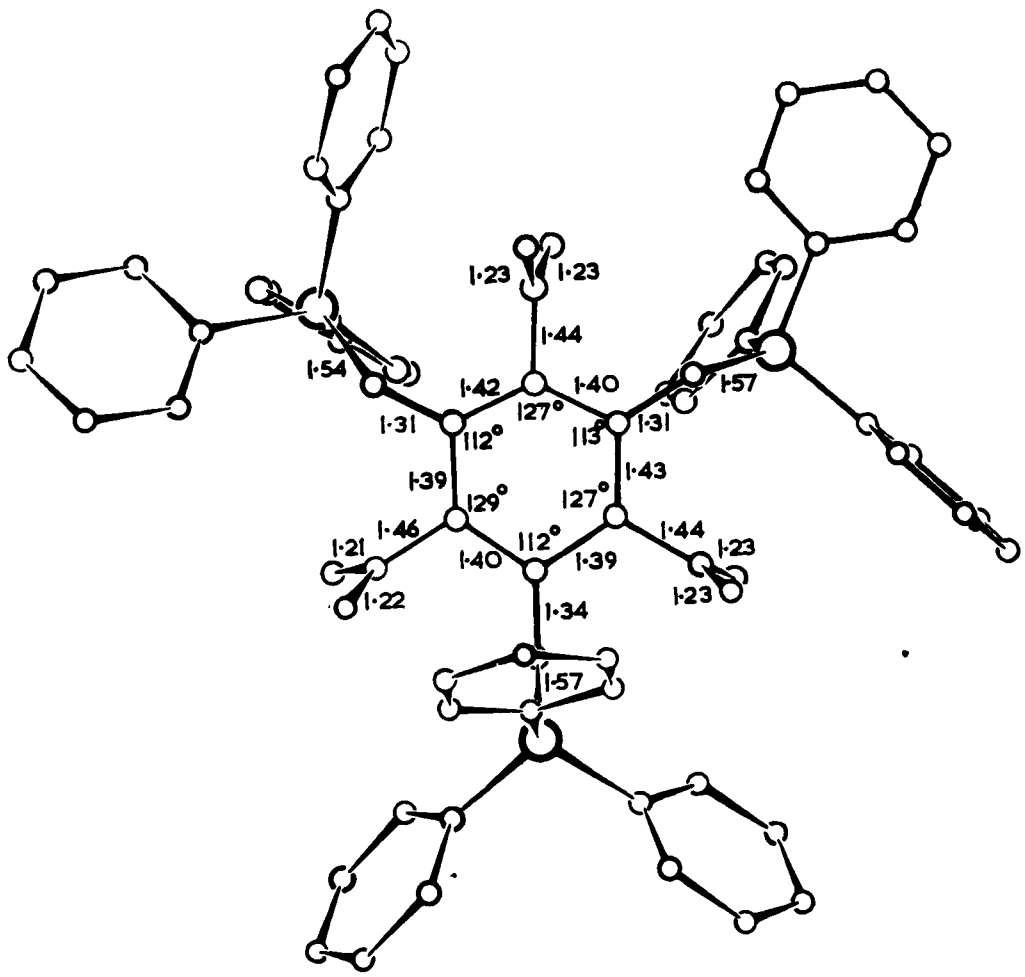

FIGURE. *Yellow compound* (II) *projected perpendicular to the least-squares best plane of the central carbon ring. The interatomic distances are in Å units.*

1·57 Å and compare with an average phosphorus to nitrogen distance of 1·59 Å in $(PNCl_2)_3$,[3] and of 1·62 Å at the phosphorus atom bonded to the phenyl groups in *gem*-$P_3N_3Cl_4Ph_2$.[4]

The average angle in the C–N=P system is 137° and is distorted from the 120° of sp^2 hybridization by a $p\pi$–$d\pi$ interaction between the nitrogen lone pair and an available *d* orbital on phosphorus, which would tend to give a linear system.[5] There is also some delocalization of the ring system over this nitrogen,[6] as the C–N distances are intermediate in value between 1·43 Å for C–N[7] and 1·24 Å for C=N.[1]

The planes through the nitro-groups are almost at right-angles to the plane of the central C_6 ring and these groups make no abnormally short contacts to the other substituents; the central ring, however, is considerably distorted. This effect has been observed in other atomatic nitro-compounds.[8] It has been suggested[9] that the distortion is caused by repulsions of the σ-bonding electrons and not by π-bond interactions.

The yellow compound, which may be considered as a stable Wittig intermediate, is important in the understanding of the complex reactions of triphenylphosphine with benztrifuroxan.

(*Received, March 29th*, 1967; *Com.* 296.)

(I)

(II)

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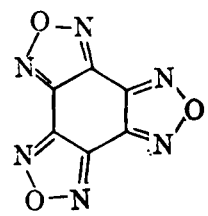
Crystal and Molecular Structure of the 1:1 Complex of Benzotrifurazan and Triethyl Phosphate

By T. S. CAMERON and C. K. PROUT*

(*Chemical Crystallography Laboratory, South Parks Road, Oxford*)

BENZOTRIFUROXAN is reduced in good yield to the corresponding trifurazan by trialkyl phosphites; the product is isolated as a colourless crystalline 1:1 complex of benzotrifurazan (I) and the trialkyl phosphate.[1] Molecular weight determinations suggest that the component molecules of this complex remain associated in solution.[2]



(I)

The three-dimensional *X*-ray diffraction patterns for the trimethyl, triethyl, and tri-isopropyl phosphate complexes have been observed photographically at 20°. All show thermal diffuse scatter and a sharp temperature cut off at a Bragg angle of ≈40°. The diffraction patterns have so far defied detailed interpretation.

The triethyl phosphate complex has been examined at low temperature. On cooling the crystals, the number of observed *X*-ray reflections increases and their relative intensities are greatly altered without change in space group or significant change in cell dimensions. The most significant alterations in intensity occur above the melting point of triethyl phosphate (−52°).

Crystal data (at −120°): monoclinic needles, $a = 7{\cdot}702$, $b = 8{\cdot}869$, $c = 13{\cdot}131$ Å; $\alpha = \beta = 90°$, $\gamma = 107{\cdot}0°$; $D_m = 1{\cdot}4040$ g. cm.$^{-3}$ (at 20°), D_c for $2(C_{12}H_{15}N_6O_7P)$, 1·4137 g. cm.$^{-3}$; Mo-K_α radiation $\mu = 1{\cdot}460$ cm.$^{-1}$; space group $P2_1$, 1030 independent reflections were measured on a Hilger and Watts linear diffractometer.

The structure was determined from a 'sharpened'

Patterson function and F_0 syntheses using the 'heavy-atom method'. Because of the approximate mirror plane at $Z = \frac{1}{4}$ (Figure 1) the structure was refined with constraints.[3,4] With individual isotropic temperature factors the reliability factor R is now 15% and the refinement is continuing.

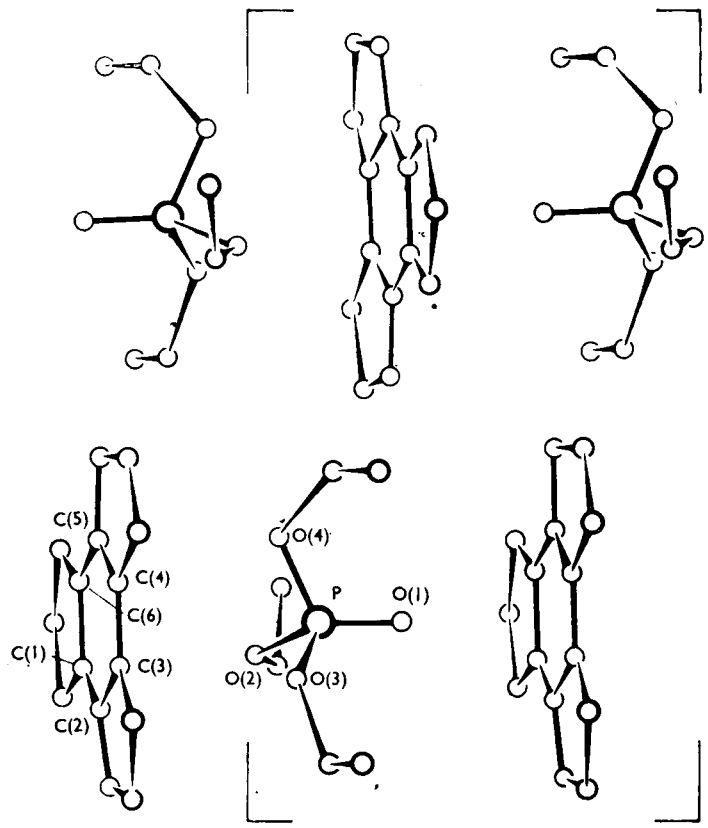


FIGURE 1.

The structure is shown projected perpendicular to [0 1 0] in Figure 1, and projected on to the least-squares best plane of benzotrifurazan in Figure 2.

The phosphate ester and the benzotrifurazan molecules form alternating stacks parallel to *a*. There are no close contacts between atoms in adjacent stacks, but within the stacks the P=O bond is almost co-incident with the three-fold axis of the nearest benzotrifurazan molecule and the oxygen atom 0(1) is only 2·49 Å from the plane of this molecule. The oxygen atoms 0(2), 0(3), and 0(4) are respectively 3·08, 3·11, and 2·97 Å from carbon atoms C(1), C(3), and C(5) of a second benzotrifurazan molecule (Figure 2b). The close approach of oxygen atom 0(1) to the plane of the C_6 ring suggests a specific interaction between the ring π-electron system and this phosphate ester oxygen. Shifts of the order 20 cm.$^{-1}$ have been observed in the P=O stretching frequency. However the visible and u.v. spectrum of the complex is the sum of the spectra of the components and there is no spectroscopic evidence for intramolecular charge transfer. The benzene–iodine complex has a formally similar structure.[5]

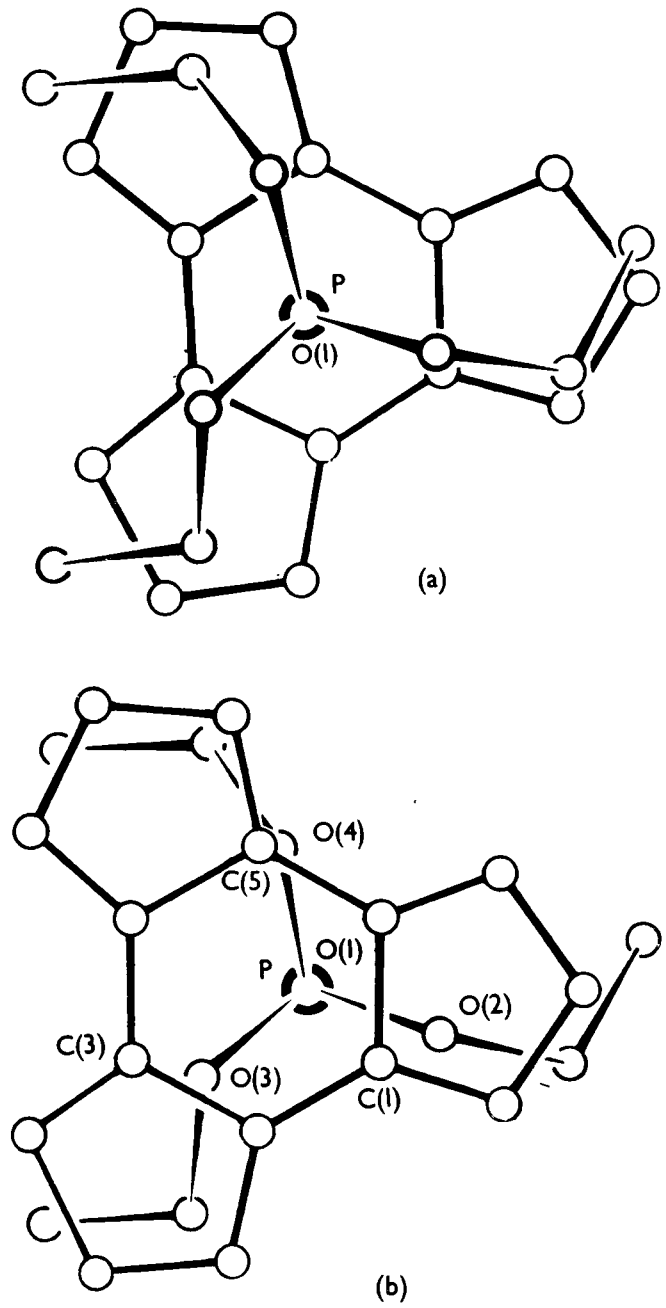


FIGURE 2.

In the benzotrifurazan molecule the intra-heterocyclic and extra-heterocyclic C–C bonds were constrained by analogy to benzotrifuroxan[6] to be 1·43 and 1·44 Å respectively with standard deviations of 0·03 Å, but despite this constraint, at the end of the present refinement, the average values of these bond lengths are 1·46 and 1·41 Å respectively. The C=N bond lengths were constrained to be 1·33 Å with a standard deviation of 0·03 Å and have remained at this value. The average N–O bond length is 1·40 Å. This is

another example of the π character of a multicyclic conjugated system collecting on the periphery of the rings.[7]

The bond lengths in the phosphate ester, P=O of 1·45 Å and the mean value for P–O of 1·56 Å are in good agreement with those found in triphenyl phosphate.[8]

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A Novel Phosphorus-containing Eight-membered Heterocycle

By Miss C. Y. Cheng and R. A. Shaw*
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A Novel Phosphorus-containing Eight-membered Heterocycle

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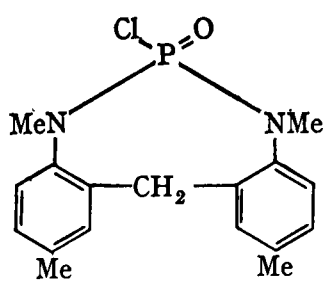
and T. S. CAMERON and C. K. PROUT*

(*Chemical Crystallography Laboratory, South Parks Road, Oxford*)

IN our studies on neutral ambident nucleophiles,[1] we have investigated the reactions of *NN*-dialkylanilines and related compounds with phosphorus halides. We report an unusual reaction leading to a novel phosphorus-containing eight-membered heterocycle.

When phosphorus oxychloride reacts at 130° with *NN*-dimethyl-4-toluidine, the major product, m.p. 170—171°, has a composition (elemental analysis) and molecular weight (mass spectrometry) corresponding to $C_{17}H_{20}ClN_2OP$. Its ^1H n.m.r. spectrum, measured on a Varian HA 100 spectrometer (at 35°), has four features: (i) a broad signal centred at τ 2·94; (ii) an AB quartet at τ 5·99; (iii) two very broad featureless humps of approximately equal intensity, at about τ 6·97 and 7·69, the latter being partially obscured by (iv) a slightly broadened singlet at τ 7·74. Integration showed these signals to be in the ratio 6 : 2 : 6 : 6. The whole spectrum is somewhat temperature dependent, and this is most marked for the two signals at τ 6·97 and 7·69. At temperatures of 0° and below, each of these has become a sharp doublet of separation 10·6 Hz compatible with the assignment $J_{P\text{-}N\text{-}C\text{-}H}$. At 50—55° the two signals have coalesced and at higher temperatures this broad hump at about τ 7·26, resolves into one doublet of separation 10·6 Hz. At low temperature, the singlet (iv) at τ 7·74 (C–CH_3) has resolved into two slightly broadened singlets [overlapping in part, the high-field signals from (iii)] and the absorption (i) at τ 2·94 (aromatic protons) has become more complex. The AB quartet (ii) (CH_2) changed little over the temperature range −60 to 140° (−60 to 55° in $CDCl_3$, 20 to 140° in $PhNO_2$). Hydrolytic degradation yielded the diamine, $CH_2(C_6H_3Me{\cdot}NHMe)_2$, m.p. 84—85°.

The structure most compatible with the above findings is shown below:



An *X*-ray crystallographic investigation gave the following results: crystal data: triclinic, $a = 9{\cdot}151$, $b = 9{\cdot}610$, $c = 13{\cdot}801$ Å; $\alpha = 96{\cdot}10°$, $\beta = 126{\cdot}12°$, $\gamma = 106{\cdot}25°$; $D_m = 1{\cdot}294$, D_c for 2 ($C_{17}H_{20}ClN_2OP$), 1·304 g. cm.$^{-3}$. Space group $P\bar{1}$, Cu-K_α-radiation, $\mu = 22{\cdot}14$ cm.$^{-1}$; 2696 independent reflections were visually estimated from equi-inclination Weissenburg photographs.

The 20 light-atom positions were located from an F_0 synthesis phased on the phosphorus and chlorine atom positions established from a Patterson function sharpened to "point atoms at rest." The trial structure, with individual isotropic temperature factors, was refined by least squares. The *R* factor is now 12·9% and the refinement is continuing.

The structure suggested by the physico-chemical measurements is confirmed. Some interesting features emerge from the *X*-ray determination. The P–N bond lengths (*cf.* Figure) of 1·64 and 1·65 Å are longer than those in some cyclophosphazenes, *e.g.*, 1·58 Å for $N_3P_3Cl_6$,[2] and for $N_4P_4(NMe_2)_8$,[3] but the same length as that in 1-(2′,2′,2′-triphenylphosphazen-1′-yl)-2-nitrosobenzdifurazan.[4]

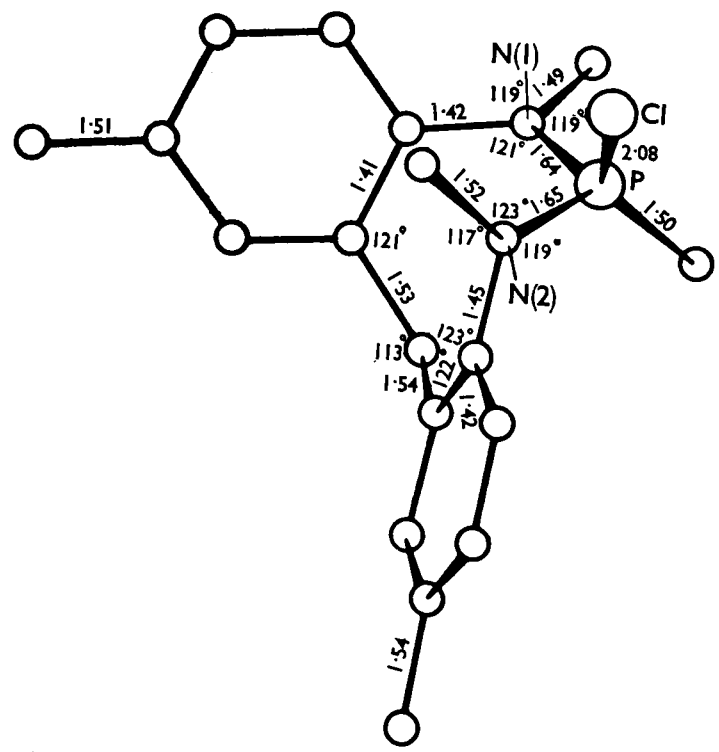


FIGURE. *Structure projected onto the least-squares best plane through the benzene ring bonded to N(1). The interatomic distances are in* Å *units.*

The nitrogen atoms deviate by only 0·01 [N(1)] and 0·08 [N(2)] Å from the plane of the three atoms bonded to them, indicating a contribution from a π-bond involving the lone-pair of electrons on the nitrogen atoms. The C–N bond lengths and the orientation of the trigonal planes containing the nitrogen atoms are inconsistent with strong delocalisation to the benzene rings, whilst the sp^2-hybridisation of the nitrogen atoms and the P–N bond lengths are in keeping with some p_π–d_π bonding involving the phosphorus atom.

The eight-membered ring containing the phosphorus atom has a distorted chair configuration (*cf.* Figure), and the two *N*-methyl groups can be seen to be non-equivalent due to differences in the local environment of the ring.

The temperature-dependence of the ^{1}H n.m.r. spectrum and, in particular, the appearance below 50°, of two signals arising from the *N*-methyl groups, show that the non-equivalence of these groups persists in solution. It is not yet clear whether this is due to the same causes as in the crystal or to the synchronous inversion at two non-planar nitrogen atoms.[5]

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ABSTRACT

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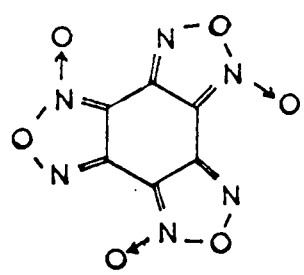
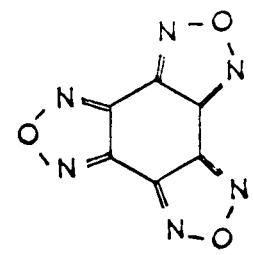
The reduction of benzotrifuroxan(I) by triethyl phosphite gives a crystalline 1:1 molecular complex of benzotrifurazan(II) with triethyl phosphate ester.



(I)



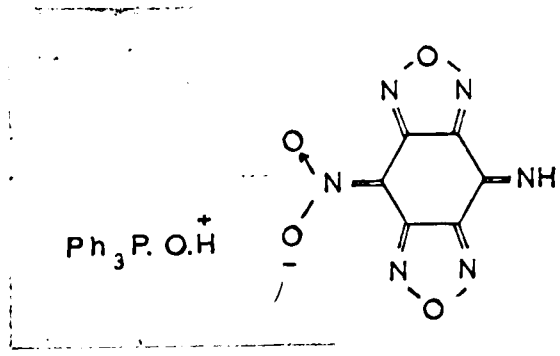
(II)

The structure of the complex (at -120°C.) was solved by X-ray crystallography and the molecules were found to be associated by a weak 'polar' interaction between the phosphoryl (P=O) bond of the phosphate and the molecular system of benzotrifurazan. The phosphoryl bond was almost coincident with the three-fold axis of the heterocycle.

The reaction of triphenyl phosphine with benzotrifuroxan was very complex and the product contained a large number of coloured compounds but no benzotrifurazan. Five crystalline compounds were isolated in small yield: a red, a light green, a yellow, a darker green and traces of a blue compound. Analysis of the first four showed that they contained both nitrogen and phosphorus but the physical data for the compounds gave little further information.

The structures of all five compounds have been solved by X-ray crystallography.

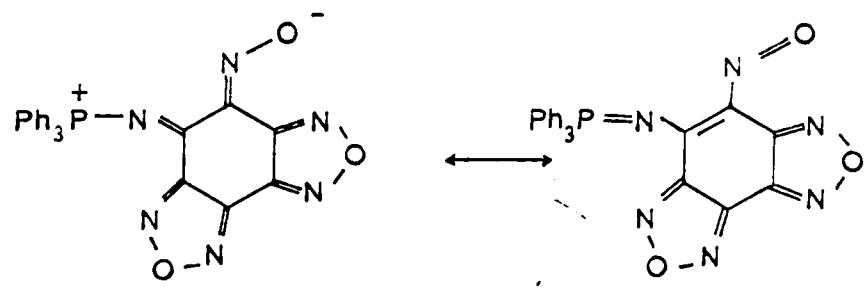
The red compound is a molecular complex of an <u>aci</u>- nitro- benzo-difurazan, associated as an ion pair with protonated triphenyl phosphine oxide(III). There is also a close approach of the planes



(III)

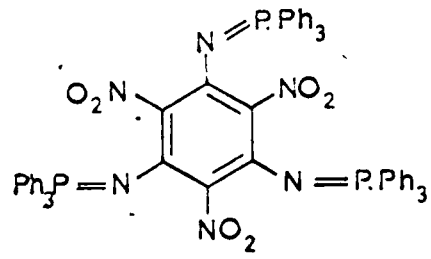
through two difurazan molecules and the red colour is thought to result from charge transfer between these two molecules.

The light green compound is a triphenylphosphine-nitroso-benzo-difurazan and is best represented as (IV). The colour is attributed to the aromatic nitroso chromophore.



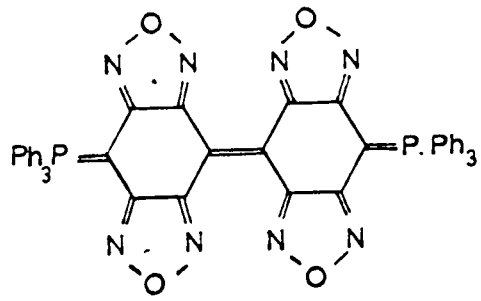
(IV)

The yellow compound is a <u>sym</u>-triphosphazine-trinitrobenzene and is represented as (V). The central C_6 ring is distorted from a regular hexagon by the nitro groups bonded to it, and the planes of these nitro groups are almost perpendicular to the planes of the central ring.



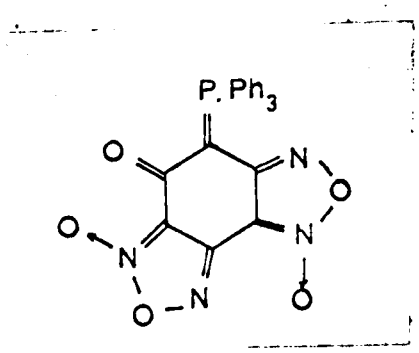
(V)

The blue compound is an unusual diphosphorane (VI). The central C_6 rings are deformed into boat conformations without completely destroying the associated π system and the geometry of the compound is that expected for an overcrowded aromatic molecule.



(VI)

The structure of the dark green compound (VII) was determined by Miss J. M. Evans (Oxford University).



(VII)

The reaction mechanisms for the reduction of benzotrifuroxan by triphenyl phosphine and by trialkyl phosphites is discussed within the context of the general reactions of P(III) compounds, and possible methods are suggested for the formation of the red, light green and yellow compounds and for the phosphate ester complex.