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Molecular Complexes. XII.* The Crystal and Molecular Structure of the 1:1 Complex of Triethyl Phosphate and Benzotrifurazan with Observations on the Structures of the Related Compounds, Trimethyl Phosphate Benzotrifurazan and Tri-isopropyl Phosphate Benzotrifurazan

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The crystal and molecular structure of the 1:1 molecular complex of triethyl phosphate with benzotrifurazan has been determined from three-dimensional data collected on a linear diffractometer at -120°C . The crystals are monoclinic $a = 7.702$, $b = 8.869$, $c = 13.131$ Å, $\gamma = 107.0^{\circ}$; space group $P2_1$. In the crystal the molecules form alternate stacks with the phosphoryl group almost coincident with the threefold axis of the benzotrifurazan molecule. The phosphoryl oxygen atom is 2.51 Å from the benzotrifurazan plane and 2.88 Å (mean) from the carbon atoms of the C_6 ring. The phosphate ester oxygen atoms are 3.05 Å (mean) from a second neighbouring benzotrifurazan molecule. The other complexes named in the title are believed to have similar structures.

Introduction

Benzotrifurazan is reduced (Bailey & Evans, 1967) by some trialkyl phosphites in benzene solution to give colourless crystalline products which are easily purified by sublimation but highly deliquescent. The chemical analyses are consistent with 1:1 complexes of the corresponding phosphate ester and benzotrifurazan. The infrared, visible and ultra-violet spectra are each the sum of the spectra of the components except that slight shifts (-20 cm^{-1}) are observed in the $\text{P}=\text{O}$ stretching frequency. Molecular weight determinations suggest that the component molecules stay associated in solution.

The structures of the trimethyl, triethyl and triisopropyl phosphate ester complexes with benzotrifurazan

have been investigated. The results for the triethyl phosphate complex, the only analysis that was successfully completed, have been reported briefly (Cameron & Prout, 1968).

Experimental

(i) Preparation

The complexes of $(\text{RO})_3\text{P}=\text{O}$ and benzotrifurazan ($\text{R} = \text{Me, Et, isopropyl}$) were prepared by the method described by Bailey & Evans (1967).

Crystals of the triethyl phosphate complex were grown to a size suitable for X-ray photography by alternately raising and lowering the temperature, between 5°C and room temperature, every few hours over a period of three months, of a saturated solution of the complex in 40/60 petroleum ether sealed in contact with a sample of small crystals.

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(ii) *X-ray photography at room temperature (22°C)*

The crystals of all three complexes are hygroscopic and when isolated on a glass fibre in air they decompose in less than two hours. Consequently all crystals were photographed sealed in glass capillaries. The unit-cell dimensions at room temperature were determined from calibrated zero-layer Weissenberg photographs.

X-ray intensities were estimated visually from multiple-film equi-inclination Weissenberg photographs, about the *a* axis only, for the trimethyl and triisopropyl complexes. (*0kl-6kl*) and about the *a* and *c* axes for the triethyl complex (*0kl-6kl*; *hk0-hk7*).

The X-ray intensities of the triethyl complex were placed upon a common scale (Rollett & Sparks, 1960) and the intensities of the other two complexes were scaled by their exposure times.

All three sets of data were corrected for Lorentz and polarization effects but not for absorption.

(iii) *X-ray diffractometry at low temperatures*

Some time after the room temperature measurements had been made, Professor D. C. Hodgkin, F.R.S. kindly loaned us her linear diffractometer for a limited time. The diffractometer was equipped with a low temperature device (designed by Viswamitra & Kannan, 1962, and later modified by ourselves) which permitted the crystal to be cooled to -160°C . At -120°C the temperature could be maintained for 12–24 hours before ice obscured the crystal from the primary X-ray beam; at lower temperatures the icing was much more rapid.

The crystal was mounted between glass springs in a glass capillary tube (Cameron, 1968*a*). This mounting allowed the glass capillary to expand and contract with the temperature change $+22^{\circ}\text{C}$ to -120°C without damaging the fragile crystals.

Before a set of three-dimensional data were collected several rows of reciprocal space were examined at 20°C intervals between $+20^{\circ}\text{C}$ and -140°C . It was found that considerable changes in the diffraction pattern occurred between $+20^{\circ}\text{C}$ and -60°C .

However, below -80°C the intensity pattern remained relatively constant. (Triethyl phosphate melts at -52°C). A selection of recorder traces of a typical row (*0k2*) are shown in Fig. 1. Although the relative intensities of reflexions are greatly changed, the reciprocal spacings remain almost constant.

A set of three-dimensional data was collected at -120°C about the *a* (*0kl-5kl*) and *c* (*hk0-hk9*) axes. The temperature of -120°C was chosen as the lowest that did not cause serious icing problems.

The diffractometer could not be used in its automatic mode without each reflexion being monitored by hand, and at the end of each row of reciprocal space it was necessary to check the setting of the crystal. Mo *K* α radiation was used but with only the β filter. The total length of time the instrument was available to us did not permit prolonging the data collection with the use of balanced filters. A number of high and

low angle reflexions were examined using balanced filters and the results suggested that the addition errors introduced into the data by the lack of balanced filters did not exceed 10% of the measured intensity.

The intensity measurements were corrected for Lorentz and polarization effects but not absorption or extinction and were then placed on a common scale (Hamilton, Rollett & Sparks, 1965).

Crystal data. – Trimethyl phosphate: benzotrifurazan $\text{C}_9\text{H}_9\text{N}_6\text{O}_7\text{P}$, M.W. 344.19; monoclinic, $a = 7.68 \pm 0.01$, $b = 7.77 \pm 0.01$, $c = 12.70 \pm 0.01$ Å, $\gamma = 107.3 \pm 0.5^{\circ}$, $U = 723.6$ Å³, $D_m = 1.52$ g.cm⁻³, $Z = 2$, $D_c = 1.578$ g.cm⁻³. Space group $P2_1$ (C_2^2 , No. 4) or $P2_1/m$ (C_{2h}^2 , No. 11), Cu *K* α radiation $\mu = 21.6$ cm⁻¹. Oscillation and Weissenberg photographs, 743 independent reflexions.

Crystal data. – Tri-isopropyl phosphate: benzotrifurazan $\text{C}_{15}\text{H}_{21}\text{N}_6\text{O}_7\text{P}$, M.W. 428.34; $a = 8.09 \pm 0.01$, $b = 9.32 \pm 0.01$, $c = 15.43 \pm 0.02$ Å, $\gamma = 104.5 \pm 0.5^{\circ}$, $U = 1126.3$ Å³, $D_m = 1.273$ g.cm⁻³, $Z = 2$, $D_c = 1.263$ g.cm⁻³. Space group $P2_1$ (C_2^2 , No. 4) or $P2_1/m$ (C_{2h}^2 , No. 11), Cu *K* α radiation $\mu = 15.1$ cm⁻¹. Oscillation and Weissenberg photographs, 602 independent reflexions.

Crystal data. – Triethyl phosphate: benzotrifurazan $\text{C}_{12}\text{H}_{15}\text{N}_6\text{O}_7\text{P}$, M.W. 386.26; monoclinic, at -120°C $a = 7.70 \pm 0.02$, $b = 8.87 \pm 0.02$, $c = 13.13 \pm 0.03$ Å, $\gamma = 107.0 \pm 0.5^{\circ}$, $U = 857.6$ Å³, Mo *K* α radiation, $\mu = 1.46$ cm⁻¹. Space group $P2_1$ (C_2^2 , No. 4) or $P2_1/m$ (C_{2h}^2 , No. 11), 959 independent reflexions were measured on a Hilger and Watts linear diffractometer. At $+22^{\circ}\text{C}$ $a = 7.84 \pm 0.01$, $b = 9.06 \pm 0.02$, $c = 13.30 \pm 0.02$ Å, $\gamma = 107.0 \pm 0.5^{\circ}$, $U = 903.4$ Å³, $D_m = 1.404$ g.cm⁻³; $Z = 2$, $D_c = 1.4199$ g.cm⁻³. Space group $P2_1$ (C_2^2 , No. 4) or $P2_1/m$ (C_{2h}^2 , No. 11). Cu *K* α radiation, $\mu = 17.78$ cm⁻¹. Oscillation and Weissenberg photographs; 509 independent reflexions.

Structure analysis

Absent X-ray spectra suggested space group $P2_1$ or $P2_1/m$ for all three complexes. $N(z)$ plots for each of the four sets of data were not conclusive but were more compatible with a centrosymmetric than with a non-centrosymmetric structure. Two formula units to the unit cell suggest space group $P2_1$, but it is possible to construct models of both molecules in any of the three complexes with symmetry m so that these molecules could use the mirror plane of space group $P2_1/m$. Instinctively space group $P2_1$ was preferred in spite of strong evidence favouring $P2_1/m$.

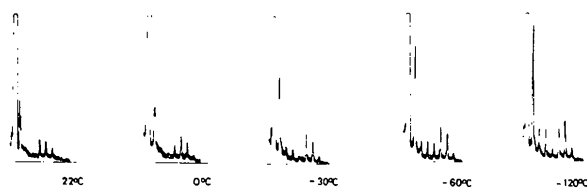


Fig. 1. Triethyl phosphate benzotrifurazan. Linear diffractometer recorder traces of the *0k2* row of reciprocal space at various temperatures.

Early work concentrated on the room temperature measurements of the three complexes, particularly the triethyl phosphate complex. Patterson functions sharpened to point atoms at rest and with other modification functions were computed for the three sets of data. The vector pattern about the origin in these Patterson functions was consistent with a benzotrifurazan molecule about the mirror plane of $P2_1/m$ and there was a short vector, perpendicular to the plane of the trifurazan vector system, which could be interpreted as one phosphorus-to-oxygen vector, but there was no sign of the other three vectors of the PO_4 tetrahedron. In a plane parallel to the benzotrifurazan vector system about the origin, but translated approximately $0.5a$, was a second vector system which could be interpreted as representing vectors from phosphorus atoms to the atoms of benzotrifurazan. The Harker section of each Patterson synthesis had a possible phosphorus-phosphorus vector and therefore trial structures were constructed with one P-O group and a benzotrifurazan molecule in space group $P2_1/m$; the P-O vector was along the normal that passed through the centroid of the benzotrifurazan plane.

The trial structures suggested that the trimethyl and triethyl phosphate complexes were isostructural and that the tri-isopropyl phosphate complex was similar but that it was rearranged slightly and expanded to accommodate the large isopropyl groups. Attempts were made to extend and refine the trial structures by all the usual methods (least-squares, difference synthesis, *etc.*) but at no time was it possible to deduce any convincing locations for the three alkoxy groups or to obtain R values below 35%. Several complete postulated structures in space groups $P2_1$ and $P2_1/m$ were also examined without any success. The X-ray diffraction patterns on the Weissenberg photographs showed considerable thermal diffuse scatter and a sharp temperature cut-off at a Bragg angle of about 40° . Photographs at $0^\circ C$ had less thermal diffuse scatter and reflexions with a Bragg angle greater than 40° appeared.

For the triethyl phosphate complex a Patterson function, sharpened to point atoms at rest was computed from the 959 measurements for the low temperature ($-120^\circ C$) data. This function had all the features of that calculated from the room temperature data but it was better resolved, and in addition there were indications of all four P-O vectors about the origin and about the phosphorus Harker vector. These vectors confirmed that the PO_4 group did not lie in the mirror plane of $P2_1/m$. An F_o synthesis was calculated in space group $P2_1$ phased on the positions of the atoms of the PO_4 group of the phosphate ester and the C_6N_6 group of benzotrifurazan. This gave possible positions of the nine remaining atoms. In the trial structure the positions of all the atoms except O(2), O(3), O(4), C(21) and C(22) are consistent with presence of a mirror plane that would have been expected had the space group been $P2_1/m$.

In these circumstances the normal matrix, calculated in least-squares refinement 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 seldom detected and the resulting parameter shifts are wildly inaccurate.

Therefore the trial structure, with individual isotropic temperature factors on all atoms, was refined by full-matrix least-squares with conditions of constraint imposed upon interatomic distances. These constraint conditions which were suggested by Waser (1963) and implemented in Oxford by Ford (1968) and Rollett (1970), are given by minimization of

$$\sum w'(d_{\text{obs}} - d_g)^2 + \sum w(F_o - F_c)^2$$

where $w' = \sum w^2(p - q)$ (e.s.d.), $(p - q)$ is the total number of independent observations and the estimated standard deviation is formally the expected standard deviation in the given bond length (d_g). The temperature factors of the benzotrifurazan molecule were constrained in a similar manner. After three cycles of refinement with weights (w) equal to unity, and subsequently three more cycles with the weights $w = \{1 + [(10|F_o| - 250)/250]^2\}^{-1}$ the R value was 14.7%.

A table of observed structure factors calculated from the atomic parameters in Table 1 has been deposited in the Radcliffe Science Library, Oxford (Cameron, 1968b).

Table 1. *Triethyl phosphate benzotrifurazan*
Atomic parameters ($\times 10^4$) with standard deviations
in parentheses ($-120^\circ C$).

	x/a	y/b	z/c	U_{iso}
P(1)	1515 (5)	645(4)	2515	298 (12)
O(1)	3421 (12)	759 (12)	2512 (19)	351 (27)
O(2)	196 (22)	-958 (16)	2168 (13)	623 (50)
O(3)	979 (23)	1847 (19)	1807 (13)	599 (47)
O(4)	710 (19)	953 (17)	3559 (10)	408 (37)
C(21)	541 (35)	-2458 (25)	1981 (12)	601 (67)
C(22)	839 (65)	-3285 (56)	2948 (30)	1317 (156)
C(31)	1738 (50)	1971 (39)	769 (23)	786 (105)
C(32)	2339 (47)	3718 (39)	712 (31)	909 (101)
C(41)	1921 (41)	1923 (33)	4359 (24)	650 (87)
C(42)	2760 (47)	3739 (37)	4316 (35)	737 (102)
C(1)	6360 (37)	-566 (16)	1989 (16)	395 (26)
C(2)	6659 (36)	851 (17)	1450 (15)	374 (26)
C(3)	7223 (31)	2342 (18)	1990 (14)	355 (28)
C(4)	7022 (33)	2374 (18)	3072 (14)	353 (27)
C(5)	6824 (34)	892 (17)	3629 (15)	337 (27)
C(6)	6276 (36)	-519 (16)	3099 (16)	370 (26)
N(1)	5943 (36)	-2044 (23)	1694 (18)	553 (33)
N(2)	6918 (37)	1167 (23)	453 (16)	534 (32)
N(3)	7467 (38)	3499 (19)	1319 (17)	515 (36)
N(4)	7561 (37)	3536 (19)	3733 (17)	520 (35)
N(5)	6828 (35)	1228 (22)	4622 (15)	497 (33)
N(6)	5904 (35)	-1959 (23)	3452 (17)	528 (33)
O(5)	5676 (20)	-2956 (15)	2581 (20)	668 (32)
O(6)	7379 (32)	2869 (21)	4706 (15)	631 (32)
O(7)	7252 (30)	2779 (22)	339 (15)	638 (32)

A similar constrained refinement with the atomic parameters of the low temperature structure and the structure amplitudes measured at room temper-

ature converged at an R value of 20%. The main features of the low temperature structure were unchanged and the final results closely resembled the trial models that originally had been suggested. The isotropic temperature factors at room temperature were much greater than those from the low temperature structure, particularly for those atoms at the periphery of the molecules. The observed structure amplitudes and the structure factors calculated from the atomic parameters at room temperature in Table 2 have also been deposited at the Radcliffe Science Library (Cameron, 1968c).

Table 2. *Triethyl phosphate benzotrifurazan*

Atomic parameters ($\times 10^4$) with standard deviations in parentheses (22°C).

	x/a	y/b	z/c	U_{iso}
P(1)	1632 (13)	804 (13)	2515	621 (36)
O(1)	3474 (25)	802 (35)	2516 (43)	946 (96)
O(2)	234 (32)	-799 (25)	2501 (29)	841 (99)
O(3)	1066 (43)	2057 (36)	1871 (32)	1007 (107)
O(4)	778 (41)	1184 (37)	3520 (19)	867 (101)
C(21)	539 (67)	-2335 (45)	1993 (50)	1059 (176)
C(22)	918 (113)	-3352 (102)	2866 (57)	1785 (304)
C(31)	1740 (143)	2008 (97)	827 (53)	1700 (371)
C(32)	2465 (114)	3786 (92)	665 (72)	1547 (280)
C(41)	1952 (104)	1785 (94)	4412 (51)	1658 (273)
C(42)	2863 (139)	3567 (99)	4384 (101)	2036 (368)
C(1)	6088 (55)	-654 (28)	2045 (29)	789 (65)
C(2)	6854 (59)	760 (29)	1490 (29)	798 (65)
C(3)	7361 (52)	2269 (31)	2044 (26)	794 (64)
C(4)	6348 (57)	2234 (32)	3092 (27)	783 (64)
C(5)	6615 (67)	772 (30)	3679 (28)	779 (64)
C(6)	6504 (56)	-636 (28)	3145 (29)	784 (64)
N(1)	5754 (71)	-2137 (43)	1725 (34)	1127 (70)
N(2)	6771 (79)	1064 (46)	511 (30)	1115 (69)
N(3)	7322 (77)	3390 (35)	1358 (35)	1102 (70)
N(4)	7719 (72)	3415 (32)	3717 (38)	1115 (70)
N(5)	6984 (80)	1169 (46)	4653 (30)	1128 (69)
N(6)	6012 (73)	-2124 (41)	3459 (34)	1129 (69)
O(5)	5585 (43)	-3126 (27)	2588 (42)	1307 (75)
O(6)	7426 (77)	2846 (47)	4730 (31)	1313 (75)
O(7)	7246 (67)	2723 (47)	368 (30)	1311 (75)

Results and discussion

(1) Structure of triethyl phosphate:benzotrifurazan at -120°C

Fig. 2 shows the projections of the crystal structure down the a and b axes. Fig. 3 gives the bonded distances and interbond angles with standard deviations. In the crystal, the benzotrifurazan molecules and the phosphate ester form alternating stacks parallel to a (Fig. 2). There is no close contact between atoms in adjacent stacks, but within stacks, the $\text{P}=\text{O}$ bond is almost coincident with the threefold axis of the nearest benzotrifurazan molecule [Fig. 4(a)]. The oxygen atom O(1) is only 2.51 Å from the plane of the molecule, 2.88 Å (mean) from the six carbon atoms of the trifurazan molecule, and the $\text{C}\cdots\text{O}$ vectors make angles of 150° (mean) with the axis of the phosphoryl bond.

The carbon-oxygen contact distances (2.88 Å) are significantly shorter than the sum of the contact radii (3.1 Å) (Bolton, 1964a) but are very similar to those found in crystals where there is a specific $\text{C}\cdots\text{O}$ interaction (Bolton, 1964a). These crystals, alloxan (Bolton, 1964b), barbituric acid (Bolton, 1963) chloranil (Chu, Jeffrey & Sakurai, 1962) and parabanic acid (Davies & Blum, 1955), contain molecules with a number of highly polar carbonyl groups whose full hydrogen bonding potential cannot be satisfied. In these crystals the $\text{C}\cdots\text{O}$ contact vector, mean length 2.83 Å, makes angles of 155° (mean) with the axes of the interacting carbonyl groups. In the phosphate ester complex the environment is very similar; a highly polar phosphoryl group interacts with the carbon atoms of $\text{C}=\text{N}$ -systems the polarity of which are increased by the oxygen atoms bonded to the nitrogen atoms.

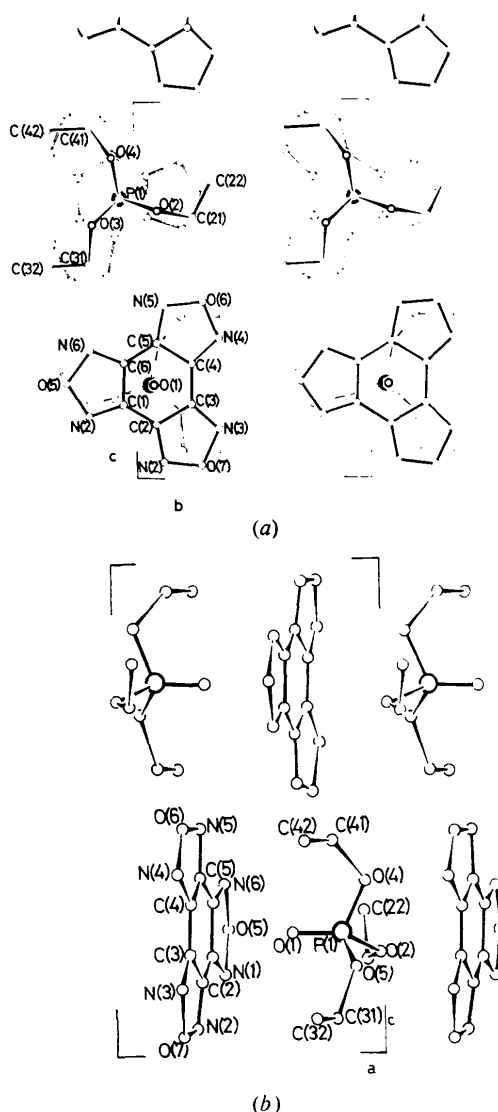


Fig. 2. Triethylphosphate benzotrifurazan. The crystal structure projected (a) down a and (b) down b .

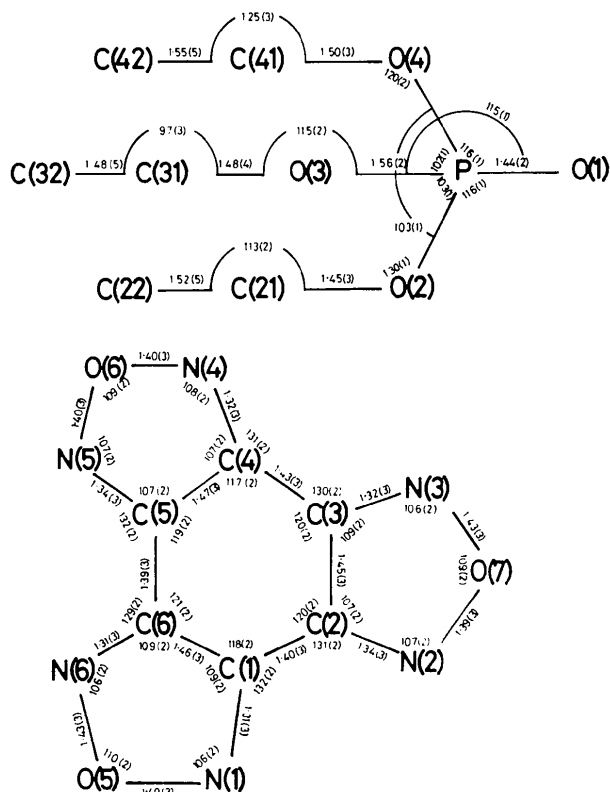


Fig. 3. Triethylphosphate:benzotrifurazan bonded distances and interbond angles, with standard deviations in parentheses.

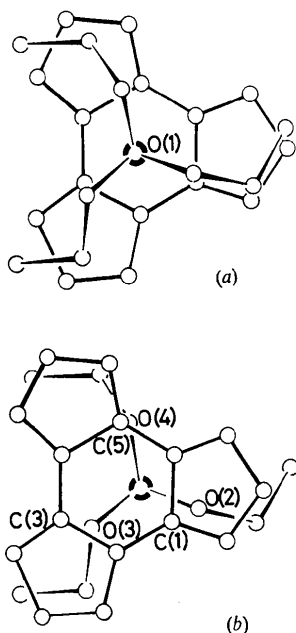


Fig. 4. Triethyl phosphate:benzotrifurazan. Projection on to the least-squares best plane of the benzotrifurazan molecule of a triethyl phosphate molecule with (a) the phosphoryl group directed towards the benzotrifurazan, (b) the phosphoryl group directed away from the benzotrifurazan molecule. The equation to the plane is $7.691x - 2.127y - 0.001z = 4.984$ with respect to the orthogonal axes a, b^*, c .

Formally there is the possibility that this is an electron donor-acceptor complex with the phosphoryl oxygen atoms acting as an n -donor and the benzotrifurazan as a π^* -acceptor. However the absence of any identified charge transfer band in the spectrum together with the marked similarity of the $C \cdots O$ interaction to those reviewed by Bolton (1964*a*) leads the authors to believe that this complex is polarization bonded, with dipole-dipole interactions. It is the first occasion that such a type of interaction has been reported in a molecular complex, although polarization bonded dipole induced dipole complexes, tetramethyluracil:pyrene, 3,4-benzopyrene and coronene (Liquori, Damiani, Giglio & Ripamonti, 1967) are known.

The dipole-dipole interaction is consistent with the observed shift of -20 cm^{-1} in the $P=O$ stretching frequency when the ester complexes in solution with benzotrifurazan. The three ester oxygen atoms O(2), O(3) and O(4) are 3.08, 3.11 and 2.97 Å respectively from carbon atoms C(1), C(3) and C(5) of a second benzotrifurazan molecule [Fig. 4(b)]. These distances are not significantly different from the sums of the contact radii.

From the formula for constrained refinement, the weight given to any constraint depends on $\sum w\Delta^2$. As the refinement of a structure converges, $\sum w\Delta^2$ decreases and the effect of the constraint condition upon the atomic positional parameters correspondingly decreases. Consequently the bond lengths derived from the final positional parameters, do not depend entirely on the value (d_g) but tend to the true measured value for the structure.

The crystal structures of triethyl phosphate and benzotrifurazan are not yet known. For the ester, d_g was given the value 1.43 Å for the $P=O$ and 1.56 Å for bridging $P-O$ distances by analogy with the structure of $(\text{PhO})_3\text{PO}$ (Svetich & Caughlan, 1965). The final observed distances were not significantly different from these values. For the $C-O$ and $C-C$ bonds (*Interatomic Distances*, 1965) the value of d_g was set at 1.47 Å for $C-O$ bonds by analogy with epoxides and $C-C$ at 1.54 Å, the length of an sp^3-sp^3 single bond. The corresponding mean lengths after refinement are 1.48 and 1.52 Å but the spread of values was large. The interbond angles of the phosphate ester were in good agreement with those observed in $(\text{PhO})_3\text{PO}$ but the angles at the carbon and oxygen atoms are less reasonable (Fig. 3). A difference Fourier synthesis indicates that there may be some disorder in the positions of these light atoms. 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 (Table 1). Carbon atom C(22) lies between atoms C(32') and C(42') of the ester molecule 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 and 3.27 Å from oxygen atoms in adja-

cent trifurazan molecules (Fig. 2) and, held by polar interactions, are thought to be less free to vibrate.

Values of d_g for the various bond types in the benzotrifurazan molecule were obtained by analogy from the structure of benzotrifuroxan (Cady, Larson & Cromer, 1966). Interatomic distances between non-bonded atoms were also specified but these latter restrictions do not impose planarity. Table 3 gives the values of d_g and the mean refined bond lengths and angles in the heterocycle.

Table 3. *Bond lengths and angles*

	Bond	d_g	Refined length
In the furazan ring	C-C	1.43 Å	1.46 Å
Between furazan rings	C-C	1.44	1.41
	C-N	1.33	1.33
	N-O	1.40	1.41
	Angle	Implied	Refined
	C-C-C	120°	119
	C-N-O	107	107
	N-O-N	110	109
In the furazan rings	C-C-N	108	108

The C=N and N-O bond lengths hardly changed from the given values during refinement, but there is a striking change in the C-C bond lengths. Contrary to expectation, after refinement the longer bonds appeared within the furazan rings. These distances, which may not be significant, are consistent with the principle that the π character of a multi-cyclic conjugated system, collects, whenever possible on the periphery of the ring (Coulson & Streitweisser, 1965).

The benzotrifurazan molecule after refinement was not planar. The maximum and mean deviations of the atoms of the molecule from the plane of the C₆ ring 0.09 and 0.05 Å, but non-planarity is thought to be of doubtful significance.

(ii) *The structure of triethyl phosphate benzotrifurazan at 22°C*

Comparison of the parameters in Tables 1 and 2 show that the structures of this complex are essentially the same at 22°C and -120°C, but the temperature factors of the peripheral atoms at both molecules of the complex are very high at 22°C. Those of the ethyl groups of the phosphate ester are so large that the atoms must be 'smeared out' over a large volume, due either to disorder or partial rotation about the P=O axis. We suggest that at 22°C, 70° above the melting point of triethyl phosphate, only the two atoms of the P=O group of the phosphate ester have definite positions and that the rest of the molecule executing large oscillations about the bond axis behaves in a manner similar to a molecule in a plastic crystal. It is only below the melting point of triethyl phosphate that the

whole of this molecule in the complex is restricted to a definite site.

(iii) *Trimethyl and tri-isopropyl phosphate benzotrifurazan complexes at 20°C*

The Patterson functions of these crystals at 20°C show that they have similar features to the triethyl phosphate complex, the stack of planar furazan molecules alternating with phosphate esters, and the phosphoryl bond lying along the threefold axis of the furazan. Again the alkoxy groups are not visible, indicating the plastic crystal behaviour of the phosphate ester.

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