goniometers and some computation programs of his laboratory. Part of the expenses of the present study were met by a grant from the Matsunaga Science Foundation, to which the author's thanks are due.
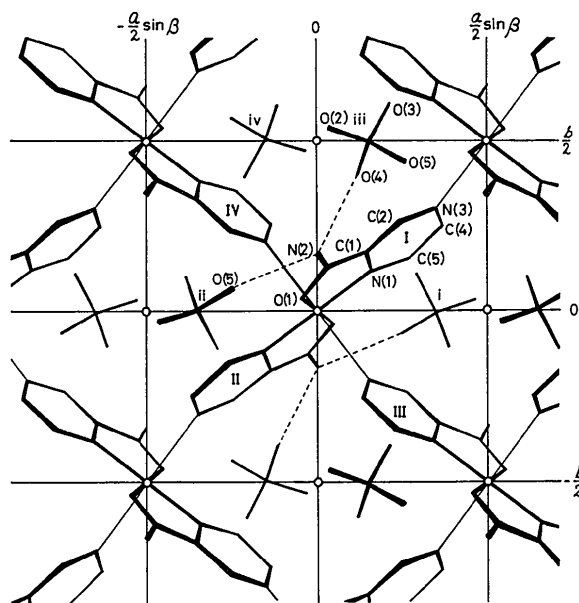

Fig. 3. Projection of the structure along the c axis. The molecules are numbered in a similar way as those in Fig. 2.

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The Crystal Structure of Phenyl Phosphorodiamidate

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Crystals of phenyl phosphorodiamidate, $C_6H_5O.PO(NH_2)_2$, are orthorhombic, $a=7.99$, $b=34.02$, $c=5.97$ Å, space group *Pbca*, 8 molecules in the unit cell. The crystal structure has been determined from X-ray diffractometer intensity data and refined by least squares to $R=0.045$ for 1457 reflexions. There is a significant difference between the lengths of the two P–N bonds (1.604, 1.628 Å), which results from the nitrogen atoms having different hydrogen-bond environments (respectively trigonal and tetrahedral). The shortness of the P–N bonds suggests that they have considerable π character. The P=O length is 1.482 Å and that of P–O(C_6H_5) 1.598 Å. A network of weak hydrogen bonds, NH$\cdots$O (lengths 2.93–3.08 Å) and NH$\cdots$N (3.20 Å), links the molecules in double sheets. The 'doubly bonded' oxygen atom forms three NH$\cdots$O bonds whose spatial arrangement resembles that in the phosphoric triamide and urea crystals.
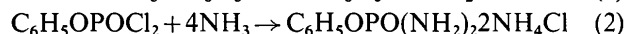
Introduction

Current theories of the bonding in cyclic phosphazenes and in phosphates (Craig & Paddock, 1962; Cruickshank, 1961a) allow for participation of all the atoms attached to phosphorus in molecular π-bond systems. Attached amino groups are considered to be involved as a result of donation of electrons from nitrogen to vacant $3d$ orbitals of phosphorus. This is supported

by the observation of short bonds between phosphorus and such groups in a number of amino-substituted cyclic phosphazenes, the exocyclic P–N bond length being 1.62–1.68 Å (see for example Ahmed & Pollard, 1972 or Bullen, 1962) as compared to the accepted length of a P–N single bond, 1.77 Å. In phosphoric triamide, $PO(NH_2)_3$, the P–N bonds are again short (Bullen, Stephens & Wade, 1969) and it has been estimated that they have about 30% π-bond order, a value

necessarily low because all three nitrogen atoms (and the oxygen) are competing to donate electrons to phosphorus. We have determined the crystal structure of phenyl phosphorodiamidate, $C_6H_5O.PO(NH_2)_2$, in order to find whether the P–N π-bond order is higher in a molecule which has fewer –NH_2 groups in competition.

Experimental

Phenyl phosphorodiamidate was prepared by means of the reactions:

$$POCl_3 + C_6H_5OH \rightarrow C_6H_5OPOCl_2 + HCl \quad (1)$$
$$C_6H_5OPOCl_2 + 4NH_3 \rightarrow C_6H_5OPO(NH_2)_2 2NH_4Cl \quad (2)$$

and was purified by recrystallization from 95% ethanol (Brauer, 1963). Well developed orthorhombic bipyramidal crystals exhibiting the forms $\{100\}$, $\{010\}$, and $\{101\}$ were produced by slow evaporation of a solution in propan-2-ol. Unit-cell dimensions were obtained from precession photographs and diffractometer measurements. Crystal data are given in Table 1.

Table 1. Crystal data

Orthorhombic	$V = 1625$ Å³
$a = 7.992 (5)$ Å	$Z = 8$
$b = 34.02 (4)$	$D_m = 1.406$ g cm⁻³
$c = 5.97 (1)$	$D_c = 1.407$ g cm⁻³
λ(Mo $K\alpha$) = 0.7107 Å	$F(000) = 720$
μ(Mo $K\alpha$) = 3.3 cm⁻¹	Space group $Pbca$ (No. 61)

Systematic absences: $0kl$ when k is odd, $h0l$ when l is odd, and $hk0$ when h is odd.

X-ray intensities of the nine layers of reflexions $hk0$–8 were measured at 17–19°C on a Philips PAILRED diffractometer using monochromated Mo $K\alpha$ radiation. All reflexions with $\sin\theta/\lambda \leq 0.65$ Å⁻¹, and some with $\sin\theta/\lambda$ in the range 0.65–0.71 Å⁻¹, were measured. 1457 independent reflexions, for 90% of which two symmetry-related reflexions were measured and their intensities averaged, gave statistically significant intensities $[I > 2\sigma(I)]$. Intensities of $00l$ reflexions could not be measured as the crystal was aligned with its c axis parallel to the ω axis of the diffractometer. Corrections for Lorentz and polarization effects were applied but no absorption correction as the linear absorption coefficient is small (see Table 1).

The least-squares refinement was carried out at the Atlas Computer Laboratory, Chilton, using the 'X-ray' program package. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Structure determination

The positions of the phosphorus atoms were deduced from the three-dimensional Patterson function and the heavy-atom technique was applied to locate the oxygen, nitrogen and carbon atoms. The atomic positions were refined by least squares using isotropic temperature factors until R had dropped to 0.11. The hydrogen

atoms of the phenyl group were initially placed at calculated positions (assuming a C–H bond length of 1.08 Å) and those in the amino-groups were located from a difference-Fourier synthesis. With the hydrogen atoms inserted and assigned isotropic temperature factors 1 Å² greater than those of the atoms to which they are attached, the temperature factors of all other atoms were allowed to become anisotropic. The weighting scheme $w = (A/|F_o|)^2$ if $|F_o| > A$ and $w = (|F_o|/A)^2$ if $|F_o| \leq A$ was also introduced, the value of A being adjusted (final value 12 on absolute scale) until the average wA^2 for groups of reflexions was almost constant over the whole range of $|F_o|$. Four cycles of refinement were carried out with the hydrogen-atom parameters fixed and then a further four with the positional (but not thermal) parameters of the hydrogen atoms included as variables. The final R is 0.045 for 1457 reflexions and $R'[= (\sum wA^2/\sum w|F_o|^2)^{1/2}]$ is 0.054. In the last cycle of refinement all parameter changes, other than those of hydrogen atoms, were less (and many much less) than 0.18σ. The maximum hydrogen parameter change was 0.48σ.

The atomic coordinates and thermal vibration parameters are listed in Tables 2 and 3 (see Fig. 1 for the numbering of the atoms). Observed and calculated structure factors are given in Table 4. Bond lengths are listed in Table 5(a) and bond angles in Table 5(c), allowance being made for the accuracy of the unit-cell dimensions in the calculation of the estimated standard deviations. The orientation and magnitudes of the principal axes of the vibration ellipsoids (Table 6) were calculated from the thermal parameters. An analysis of the anisotropic thermal parameters in terms of a rigid-body motion for the phenoxy group gave the translational and librational tensors shown in Table 7.

Table 2. Fractional atomic co ordinates with estimated standard deviations, and isotropic temperature factors for the hydrogen atoms

	x/a	y/b	z/c	$B(Å^2)$
P	0.55260 (7)	0.06065 (2)	0.45479 (10)	—
O(1)	0.3812 (2)	0.05294 (5)	0.5389 (3)	—
O(2)	0.6248 (2)	0.10170 (5)	0.5391 (3)	—
N(1)	0.5532 (3)	0.05874 (8)	0.1864 (3)	—
N(2)	0.7077 (2)	0.03389 (6)	0.5438 (4)	—
C(1)	0.5399 (3)	0.13739 (7)	0.5158 (4)	—
C(2)	0.5805 (4)	0.16107 (9)	0.3366 (6)	—
C(3)	0.5079 (5)	0.19814 (10)	0.3245 (6)	—
C(4)	0.3984 (4)	0.21050 (8)	0.4859 (7)	—
C(5)	0.3576 (4)	0.18630 (9)	0.6627 (6)	—
C(6)	0.4301 (4)	0.14901 (8)	0.6782 (5)	—
H(2)*	0.657 (6)	0.152 (1)	0.225 (7)	5.1
H(3)	0.545 (5)	0.216 (1)	0.195 (8)	6.2
H(4)	0.354 (6)	0.236 (1)	0.477 (8)	5.9
H(5)	0.262 (5)	0.195 (1)	0.780 (8)	5.7
H(6)	0.407 (6)	0.131 (1)	0.793 (8)	5.0
H(11)	0.452 (6)	0.054 (1)	0.095 (8)	5.0
H(12)	0.645 (6)	0.059 (1)	0.115 (8)	5.0
H(21)	0.689 (4)	0.009 (1)	0.524 (6)	3.8
H(22)	0.749 (5)	0.040 (1)	0.674 (6)	3.8

* Atom H(i) is attached to C(i); atoms H(ij) are attached to N(i).

The orthogonal axial system for the analysis has its origin at the phosphorus atom, the x axis passing through the centroid of the phenoxy group, and the z axis perpendicular to the plane containing the centroid and the atoms P and O(2). Since the off-diagonal terms of the ω tensor are small in comparison with their standard deviations, the librations can be discussed in terms of oscillations about the three group axes. The largest oscillation, with r.m.s. amplitude 6·3°, is understandably about the x axis since it will be easier for the phenoxy group to oscillate about its length than about other axes. Bond lengths corrected

Table 3. *Components of thermal vibration tensors* (Å^2, $\times 10^4$) *and their estimated standard deviations*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	251 (3)	360 (3)	300 (3)	−32 (2)	0 (3)	−3 (3)
O(1)	296 (8)	494 (9)	371 (8)	−54 (7)	67 (8)	−10 (8)
O(2)	390 (9)	365 (8)	592 (11)	−43 (7)	−108 (9)	−23 (9)
N(1)	299 (9)	867 (17)	321 (10)	−21 (12)	−4 (10)	18 (11)
N(2)	346 (10)	420 (10)	363 (10)	−3 (8)	−47 (10)	3 (10)
C(1)	347 (12)	366 (10)	504 (15)	−52 (9)	−57 (11)	−30 (9)
C(2)	542 (17)	545 (16)	588 (20)	−12 (13)	29 (14)	85 (14)
C(3)	712 (20)	555 (17)	749 (23)	−21 (16)	3 (19)	172 (16)
C(4)	619 (18)	402 (13)	911 (30)	−16 (13)	−106 (18)	−4 (15)
C(5)	576 (18)	473 (15)	812 (24)	−35 (13)	84 (18)	−149 (15)
C(6)	563 (17)	439 (13)	606 (19)	−91 (12)	71 (15)	−52 (12)

Table 4. *Observed and calculated structure factors* ($\times 10$)

Table 4 (cont.)

The hydrogen-bond system in the crystal. For clarity only the NH···O bonds (shown as broken lines) are inserted in left-hand half of the diagram, and only the NH···N bonds in the right-hand half. The hydrogen atoms of the phenyl are omitted.

for the effect of these molecular oscillations (Cruickshank, 1956, 1961b) are given in Table 5(b).

Table 5. *Bond lengths (Å) and bond angles (°) with estimated standard deviations*

(a) Bond lengths from the least-squares refinement

P–O(1)	1·482 (2)	C(1)–O(2)	1·398 (3)
P–O(2)	1·593 (2)		
		N(1)–H(11)	0·98 (5)
P–N(1)	1·604 (3)	N(1)–H(12)	0·85 (5)
P–N(2)	1·628 (2)	N(2)–H(21)	0·87 (4)
		N(2)–H(22)	0·87 (4)
C(1)–C(2)	1·379 (4)		
C(2)–C(3)	1·390 (5)	C(2)–H(2)	0·96 (5)
C(3)–C(4)	1·368 (5)	C(3)–H(3)	1·03 (5)
C(4)–C(5)	1·378 (5)	C(4)–H(4)	0·94 (5)
C(5)–C(6)	1·398 (4)	C(5)–H(5)	1·08 (4)
C(6)–C(1)	1·366 (4)	C(6)–H(6)	0·94 (4)

(b) Corrected for molecular oscillations

P–O(2)	1·598 (2)	C(1)–O(2)	1·400 (3)
C(1)–C(2)	1·387 (4)	C(4)–C(5)	1·386 (5)
C(2)–C(3)	1·392 (5)	C(5)–C(6)	1·400 (4)
C(3)–C(4)	1·376 (5)	C(6)–C(1)	1·374 (4)
		Mean C——C	1·386 (10)

(c) Bond angles

O(1)–P–O(2)	112·5 (1)	P——N(1)–H(11)	124 (3)
O(1)–P–N(1)	109·5 (1)	P——N(1)–H(12)	120 (3)
O(1)–P–N(2)	119·6 (1)	H(11)–N(1)–H(12)	115 (4)
O(2)–P–N(1)	110·5 (1)		
O(2)–P–N(2)	96·4 (1)	P——N(2)–H(21)	112 (2)
N(1)–P–N(2)	107·6 (1)	P——N(2)–H(22)	116 (3)
		H(21)–N(2)–H(22)	115 (4)
P–O(2)–C(1)	123·7 (2)		
		C(1)–C(2)–H(2)	120 (3)
O(2)–C(1)–C(2)	118·1 (2)	C(3)–C(2)–H(2)	121 (3)
O(2)–C(1)–C(6)	119·5 (2)	C(2)–C(3)–H(3)	117 (3)
		C(4)–C(3)–H(3)	122 (3)
C(1)–C(2)–C(3)	118·2 (3)	C(3)–C(4)–H(4)	119 (3)
C(2)–C(3)–C(4)	120·6 (3)	C(5)–C(4)–H(4)	120 (3)
C(3)–C(4)–C(5)	120·5 (3)	C(4)–C(5)–H(5)	120 (2)
C(4)–C(5)–C(6)	119·6 (3)	C(6)–C(5)–H(5)	120 (2)
C(5)–C(6)–C(1)	118·8 (3)	C(5)–C(6)–H(6)	124 (3)
C(6)–C(1)–C(2)	122·2 (3)	C(1)–C(6)–H(6)	117 (3)

An attempt to make a similar rigid-body vibration analysis for the tetrahedral PO_2N_2 group was unsuccessful in that the components of the librational tensor so produced had standard deviations too large for the results to be reliable. This may be because the different hydrogen-bond environments of the oxygen and nitrogen atoms (see discussion below) prevent the group behaving as a rigid body. The P=O and P–N bond lengths cannot therefore be corrected for librational error. The only bond which may be seriously affected by this omission is P–N(1). Atom N(1) has a large vibration (r.m.s. amplitude 0·295 Å, see Table 6) perpendicular to the P–N(1)–H(11)–H(12) plane which could be attributed either to a libration or to translational motion permitted by the atom's planar hydrogen-bond environment.

Discussion

Hydrogen bonding

All the hydrogen atoms are involved in a hydrogen-bond system which links the molecules in double sheets (Fig. 1). Each oxygen atom forms three NH···O bonds (Table 8) whose spatial disposition resembles that of the NH···O bonds in phosphoric triamide (Fig. 2) and urea. The grouping of four hydrogen bonds present in $PO(NH_2)_3$ is reduced to three in $C_6H_5OPO(NH_2)_2$ because fewer NH groups are available and the space at one side of the P=O bond is occupied by the phenyl group (Fig. 1). In addition to the NH···O bonds there is just one NH···N bond per molecule (Table 8). As a result, the environments of N(1) and N(2) are dissimilar, N(2) forming hydrogen bonds to two oxygen atoms and another nitrogen while N(1) forms hydrogen bonds to only one oxygen atom and a nitrogen. The environment of N(2) is distorted tetrahedral but that of N(1) is very close to trigonal planar [see angles in Table 5(c)]. A similar situation occurs in phosphoric triamide where one nitrogen atom forms fewer hydrogen bonds than the other two (Bullen, Stephens & Wade, 1969).

Table 6. *Root-mean-square amplitudes of thermal vibration (Å) along the principal axes of the vibration ellipsoids*

The direction of each principal axis is specified by the angles it makes with the crystallographic axes

		a	b	c			a	b	c
P	0·192	105°	15°	88°	C(1)	0·229	74°	85°	17°
	0·173	89	92	2		0·202	126	37	84
	0·156	15	75	91		0·169	41	54	106
O(1)	0·226	107	21	78	C(2)	0·256	98	126	37
	0·199	114	108	30		0·235	22	111	96
	0·158	30	80	62		0·217	69	44	53
O(2)	0·253	67	89	23	C(3)	0·291	87	120	31
	0·201	125	39	76		0·267	6	92	95
	0·174	45	51	108		0·213	86	30	60
N(1)	0·295	92	3	92	C(4)	0·307	72	90	18
	0·179	81	88	9		0·242	19	95	108
	0·173	9	88	99		0·200	85	5	91
N(2)	0·205	99	14	101	C(5)	0·299	106	70	26
	0·200	52	76	42		0·234	16	86	75
	0·175	40	90	130		0·204	89	20	110
					C(6)	0·264	52	111	134
						0·229	50	105	44
						0·197	64	27	94

Table 7. *Translational* (**T**, Å^2) *and librational* (ω, deg^2) *tensors for the phenoxy-group*

See text for definition of the axial system

$$\mathbf{T} = \begin{pmatrix} 0.043\ (2) & -0.002\ (2) & 0.003\ (2) \\ & 0.030\ (3) & 0.001\ (3) \\ & & 0.038\ (3) \end{pmatrix} \qquad \omega = \begin{pmatrix} 39\ (8) & 0\ (2) & 0.6\ (8) \\ & 5.3\ (7) & -1.0\ (6) \\ & & 3.6\ (6) \end{pmatrix}$$

Table 8. NH$\cdots$O *and* NH$\cdots$N *hydrogen-bond distances*

Atom A	Atom B	Transform of atom A			
N(1)-H(12)$\cdots$O(1)		$-\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$	2.95 Å
N(2)-H(21)$\cdots$O(1)		$1-x$,	$-y$,	$1-z$	3.08
N(2)-H(22)$\cdots$O(1)		$-\frac{1}{2}+x$,	y,	$1\frac{1}{2}-z$	2.93
N(1)-H(11)$\cdots$N(2)		$\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$	3.20

Bond lengths and bond angles

The bond lengths in $C_6H_5OPO(NH_2)_2$ are compared in Table 9 with those in $PO(NH_2)_3$ and $(C_6H_5O)_3PO$. As in $PO(NH_2)_3$, P-N$_{trig}$ is significantly shorter than P-N$_{tet}$, showing that where the trigonal environment of the nitrogen atom is not disturbed by hydrogen bonding the P-N bond acquires greater π character. Both the P-N bonds are substantially shorter than those in $PO(NH_2)_3$, implying a higher bond order. Since nitrogen is a better electron donor than oxygen, replacement of an -NH$_2$ group by -OC$_6$H$_5$ has allowed the remaining nitrogen atoms to donate to phosphorus more effectively. For this reason one might expect the P-N bond to be shorter still in a molecule of type $(RO)_2PONH_2$. The shorter P=O in $C_6H_5OPO(NH_2)_2$, as compared to $PO(NH_2)_3$, arises from the same effect, which becomes even more pronounced in $(C_6H_5O)_3PO$ from which the nitrogen atoms have been eliminated completely. This progressive shortening of the P=O bond is also found in the series $PO_4^{3-}-P_2O_7^{4-}-(PO_3^-)_\infty-P_4O_{10}$ (Cruickshank, 1961a) showing that π systems analogous to those in phosphates are also produced by donation of electrons from nitrogen to phosphorus. Indeed in $C_6H_5OPO(NH_2)_2$ the bond P-N(1) is very nearly as short as the ring bonds in some cyclic phosphazenes (e.g. $N_4P_4Me_8$ 1.596 Å, Dougill, 1961) suggesting that its π-bond order is in the region of 40-50%.

The P-O length and P-O-C angle in $C_6H_5OPO(NH_2)_2$ are of similar size to those in $(C_6H_5O)_3PO$ and are consistent with the bond P-O(2) possessing some π character (cf. the Schomaker-Stevenson estimate for a single P-O, 1.71 Å). A further test for participation of the oxygen and nitrogen atoms in the π system with phosphorus is that the orientation of the $2p$ orbitals on these atoms must follow a consistent pattern. The P-O(2)-C(1) plane is parallel (within 2°) to the N(2)-P-O(2) plane so that, taking the bisector of the N(2)-P-O(2) angle as the axis of quantization (z), the $2p$ orbital on O(2) will mate almost perfectly with the $3d_{x^2-y^2}$ orbital on phosphorus. If the $2p$ orbital on N(1) is to overlap with this same $3d$ orbital, the P-N(1)-H(11)-H(12) plane must also be parallel to the axis of quantization. This condition is satisfied quite well, the

angle between the plane and the axis being less than 7°. Unfortunately the same test cannot be applied to N(2) because it is in a tetrahedral, rather than a trigonal, environment.

The six carbon atoms of the phenyl group are coplanar (maximum deviation from their mean plane 0.004 Å) but O(2) is displaced by 0.128 Å from their plane. The phenyl ring makes an angle of 85° with the P-O(2)-C(1) plane. There is thus no overlap between its π system and the $2p$ orbital on O(2). This orientation results in the two sides of the ring making similar intramolecular contacts with the phosphorodiamidate group: C(6)$\cdots$O(1) 3.40 Å, C(2)$\cdots$N(1) 3.60 Å. The shortest intermolecular contacts between phenoxy-groups are (*a*) within a hydrogen-bonded sheet: C$\cdots$O 3.38 Å, C$\cdots$C 3.59 Å; (*b*) between the sheets: C$\cdots$C 3.81 Å.
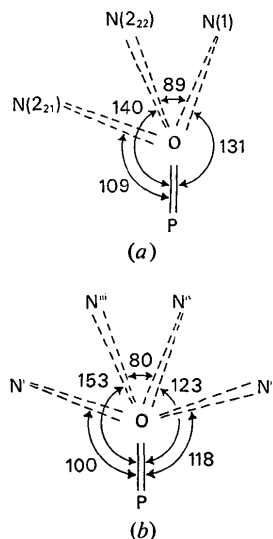
Fig. 2. Angles (°) between the NH$\cdots$O bonds meeting at one oxygen atom. (*a*) $C_6H_5OPO(NH_2)_2$. The nitrogen atoms are those whose coordinates are given in Table 8; the subscripts 21 and 22 show which hydrogen atom is involved in the bond. The angle between the P=O$\cdots$N(2$_{21}$) and the N(2$_{22}$)$\cdots$O$\cdots$N(1) planes is 87°. (*b*) $PO(NH_2)_3$. The angle between the N$^i\cdots$O$\cdots$N^{ii} and N$^{iii}\cdots$O$\cdots$N^{iv} planes is 86°.

Table 9. *Comparison with related molecules*

	PO(NH$_2$)$_3$ (Bullen *et al.*, 1969)	C$_6$H$_5$OPO(NH$_2$)$_2$ (This work)	(C$_6$H$_5$O)$_3$PO (Corbridge, 1966)
P=O	1·510 Å	1·482 Å	1·43 Å
P–N$_{tet}$*	1·658, 1·661	1·628	–
P–N$_{trig}$	1·648	1·604	–
P–O	–	1·598	1·55–1·60
C–O	–	1·400	1·39–1·43
P–O–C	–	123·7°	123–125°

* The subscripts 'tet' and 'trig' signify atoms in tetrahedral and trigonal hydrogen-bond environments.

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The Crystal Structure of Pentamethylbenzotrichloride

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The crystal structure of pentamethylbenzotrichloride [(CH$_3$)$_5$C$_6$CCl$_3$] at 143°K was determined from densitometer measurements of photographic precession camera data (1035 independent reflections). The orthorhombic unit-cell dimensions are $a = 19·133$ (3), $b = 11·898$ (4), $c = 10·666$ (1) Å, space group = *Pbca*, $Z = 8$, $D_c = 1·45$ g cm^{-3}, $D_m = 1·32$ (2) (by flotation). The structure was solved by the symbolic-addition method and refined by the full-matrix least-squares method to $R = 8·6\%$. The C$_6$(CH$_3$)$_5$-fragment of the molecule shows significant deviations from planarity with the methyl group *ortho* to the –CCl$_3$ group forced 0·3 Å out of the plane. The carbon atom of the –CCl$_3$ group is displaced 0·4 Å out of the plane in the opposite direction. The average C–Cl bond length of 1·796 (11) Å is longer than the typical C–Cl bond length of 1·76 Å.

Hart & Fish (1958, 1962) proposed the formation of dications (II) by the loss of two chlorine atoms from the trichloromethyl group of various polymethyl-benzotrichlorides (I), and Hart & Fleming (1962) reported the preparation of such a salt of pentamethyl-benzotrichloride. Gillespie & Robinson (1964, 1965) and others (Deno, Friedman & Mockus, 1964; Robinson & Ciruna, 1964) proposed that the monocation (III) was formed instead and contended that the experimental observations of Hart & Fish were consistent with this model. The formation of the dication has never been repeated by other workers, but, in any event, the formation of even the monocation species is undoubtedly aided by overcrowding in the trichloromethyl group. The crystal structure of pentamethyl benzotrichloride has been carried out to determine the extent of this distortion in the parent molecule due to the interaction of the bulky methyl and trichloromethyl groups.

(I)   (II)   (III)
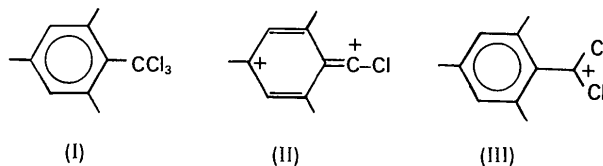
Experimental

Pentamethylbenzotrichloride, (CH$_3$)$_5$C$_6$CCl$_3$, (PMBTC), was prepared according to the method of Hart & Fish (1958). Colorless crystals of symmetry