

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.

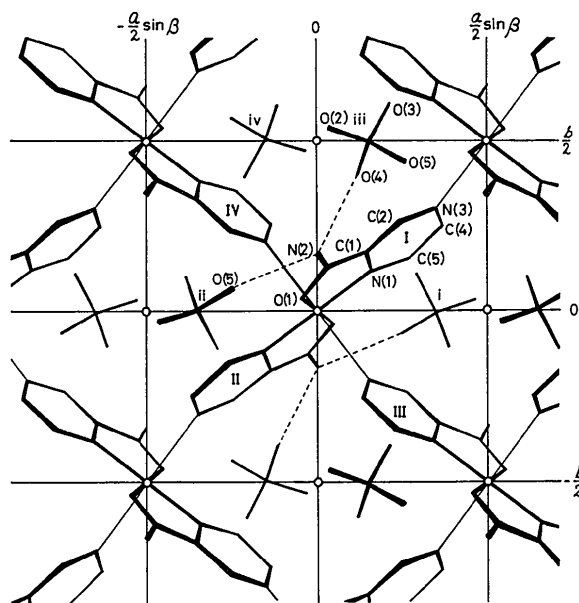


Fig. 3. Projection of the structure along the c axis. The molecules are numbered in a similar way as those in Fig. 2.

References

- BROWN, D. H., MACSWEEN, D. R., MERCER, M. & SHARP, D. W. A. (1971). *J. Chem. Soc. (A)*, pp. 1574–1576.
- BRUNTON, G. (1969). *Acta Cryst. B25*, 2161–2162.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- LEE, J. D., BROWN, D. S. & MELSOM, B. G. A. (1969). *Acta Cryst. B25*, 1378–1385.
- LONG, R. E., MADDOX, H. & TRUEBLOOD, K. N. (1969). *Acta Cryst. B25*, 2083–2094.
- MASUKO, A., NOMURA, T. & SAITO, Y. (1967). *Bull. Chem. Soc. Japan*, **40**, 511–515.
- NAWATA, Y., IWASAKI, H. & SAITO, Y. (1967). *Bull. Chem. Soc. Japan*, **40**, 515–521.
- RØ, G. & SØRUM, H. (1972). *Acta Cryst. B28*, 991–998.
- SEKIZAKI, M., MARUMO, F., YAMASAKI, K. & SAITO, Y. (1971). *Bull. Chem. Soc. Japan*, **44**, 1731–1734.
- SEKIZAKI, M., TANASE, M. & YAMASAKI, K. (1969). *Bull. Chem. Soc. Japan*, **42**, 399–404.
- SEKIZAKI, M. & YAMASAKI, K. (1969a). *Spectrochim. Acta* **25A**, 475–485.
- SEKIZAKI, M. & YAMASAKI, K. (1969b). *Rev. Chim. Minér.* **6**, 255–266.
- SEKIZAKI, M. & YAMASAKI, K. (1970). *Inorg. Chim. Acta*, **4**, 296–298.
- SIEGEL, S., TANI, B. & APPELMAN, E. (1969). *Inorg. Chem.* **8**, 1190–1191.
- TAKAKI, Y., SASADA, Y. & WATANABÉ, T. (1960). *Acta Cryst.* **13**, 693–702.
- TAKANO, T., SASADA, Y. & KAKUDO, M. (1966). *Acta Cryst.* **21**, 514–522.

Acta Cryst. (1973). **B29**, 331

The Crystal Structure of Phenyl Phosphorodiamidate

BY G. J. BULLEN AND P. E. DANN

Department of Chemistry, University of Essex, Colchester CO4 3SQ, England

(Received 24 October 1972; accepted 27 October 1972)

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

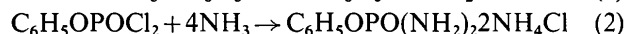
Current theories of the bonding in cyclic phosphazenes and in phosphates (Craig & Paddock, 1962; Cruickshank, 1961a) allow for participation of all the atoms attached to phosphorus in molecular π -bond systems. Attached amino groups are considered to be involved as a result of donation of electrons from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



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	$V = 1625 \text{ \AA}^3$
$a = 7.992 (5) \text{ \AA}$	$Z = 8$
$b = 34.02 (4)$	$D_m = 1.406 \text{ g cm}^{-3}$
$c = 5.97 (1)$	$D_c = 1.407 \text{ g cm}^{-3}$
$\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$	$F(000) = 720$
$\mu(\text{Mo } K\alpha) = 3.3 \text{ cm}^{-1}$	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 $\sin \theta/\lambda \leq 0.65 \text{ \AA}^{-1}$, and some with $\sin \theta/\lambda$ in the range 0.65–0.71 \AA^{-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 \AA) and those in the amino-groups were located from a difference-Fourier synthesis. With the hydrogen atoms inserted and assigned isotropic temperature factors 1 \AA^2 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 $w\Delta^2$ 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 $R' [= (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2}]$ 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 coordinates with estimated standard deviations, and isotropic temperature factors for the hydrogen atoms*

	x/a	y/b	z/c	$B(\text{ \AA}^2)$
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 ($\text{\AA}^2, \times 10^4$) 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 ($\times 10$)

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c								
0	0	0	405	390	22	117	122	43	63	-75	8	144	143	0	987	-660	20	123	124	38	72	-75	23	87	86		
1	0	0	10	213	-206	21	138	-130	44	57	67	9	494	484	10	148	144	30	50	44	40	93	-63	24	99	95	
2	0	0	11	74	76	26	161	127	2	0	0	11	308	306	1	490	-190	12	660	-631	32	60	57	5	0	27	43
4	0	0	13	407	411	27	90	107	12	104	-101	14	62	50	14	62	50	14	122	-122	14	62	50	14	62	50	
6	0	0	14	286	270	29	54	64	1	724	-220	13	203	-193	3	127	-131	16	154	150	16	154	150	16	154	150	
8	0	0	15	451	451	30	51	-65	2	428	-524	15	767	737	3	234	-227	18	452	441	18	452	441	18	452	441	
10	0	0	15	137	134	31	54	74	3	517	514	15	105	-103	6	433	-334	20	244	224	36	51	60	2	76	-76	
12	0	0	17	263	-254	31	54	74	4	204	-200	17	94	-94	7	60	45	24	254	-254	37	101	-102	3	58	-47	
14	0	0	18	343	-345	32	54	74	5	249	-250	18	52	-61	8	128	-141	26	560	-600	40	127	-127	5	113	-117	
16	0	0	19	541	-544	33	54	74	6	900	-912	19	215	-218	9	247	254	28	104	98	45	45	45	6	107	100	
18	0	0	20	599	-594	34	54	74	7	79	77	22	180	-185	10	56	64	30	234	244	43	37	44	7	69	65	
20	0	0	21	453	-464	35	54	74	8	42	34	23	172	170	11	211	224	32	190	302	34	155	154	35	7	6	
22	0	0	22	114	-108	36	54	74	9	839	820	25	63	68	12	190	302	34	155	154	35	7	6	3	0	0	
24	0	0	23	371	-374	37	54	74	10	294	281	27	60	68	13	87	-84	36	90	97	3	0	0	10	151	144	
26	0	0	24	584	-584	38	54	74	11	103	100	30	63	65	14	116	324	38	47	50	9	572	-572	11	22	-35	
28	0	0	26	88	94	39	54	74	12	172	-175	31	71	-74	15	90	-103	40	151	-151	1	332	-332	12	89	-91	
30	0	0	27	202	214	40	54	74	13	410	-395	33	94	-100	16	49	-47	42	113	-112	3	174	-160	14	145	-147	
32	0	0	29	416	-414	41	54	74	14	160	-163	35	76	-75	17	58	-59	44	84	-84	4	224	-235	15	66	74	
34	0	0	30	199	-197	42	54	74	15	222	-222	37	80	74	18	95	-97	46	284	-284	5	224	-235	16	66	74	
36	0	0	31	131	-137	43	54	74	16	222	-222	39	83	79	19	139	-139	48	294	-291	18	159	-159	17	139	-151	
38	0	0	32	101	105	44	54	74	17	63	-68	21	144	144	20	144	144	50	304	-304	19	100	100	18	100	100	
40	0	0	33	144	-144	45	54	74	18	158	-152	22	144	144	21	144	144	52	314	-314	20	82	-82	19	82	-82	
42	0	0	34	152	-154	46	54	74	19	158	-152	23	144	144	22	144	144	54	324	-324	21	107	-107	20	107	-107	
44	0	0	35	158	-164	47	54	74	20	158	-152	24	144	144	23	144	144	56	334	-334	22	107	-107	21	107	-107	
46	0	0	36	158	-164	48	54	74	21	158	-152	25	144	144	24	144	144	58	344	-344	23	107	-107	22	107	-107	
2	0	0	41	63	-44	10	444	450	25	77	81	7	240	246	28	54	-50	6	244	-235	14	214	214	26	89	86	
0	1704	1704	0	0	0	12	564	558	26	52	-64	8	301	-304	30	83	79	8	314	324	18	124	-119	32	39	-71	
1	85	-191	0	396	-392	14	268	272	28	38	-48	9	31	-34	30	87	83	10	202	190	21	130	-129	34	30	-74	
2	84	-60	0	118	-114	18	117	-117	29	62	-68	10	241	240	32	87	83	10	202	190	21	130	-129	34	30	-74	
3	1704	-1362	1	394	-394	20	560	-457	30	143	147	12	504	506	33	131	-124	11	97	94	22	105	108	38	60	51	
4	473	-658	2	180	-192	27	67	-65	32	69	-57	13	46	-36	13	46	-36	12	143	-143	24	107	-107	39	62	54	
5	275	-294	3	528	-538	24	67	-71	33	104	-109	14	512	524	14	84	-68	14	167	-164	24	80	78	40	84	81	
6	515	-326	4	95	-84	24	104	-203	34	62	-64	15	200	-207	1	84	-68	15	69	-57	24	80	78	41	84	81	
7	411	373	5	723	-734	28	284	244	35	84	-85	18	200	-207	2	121	114	16	240	-240	26	114	114	42	84	81	
8	876	-844	6	41	90	10	174	-174	36	54	-54	19	385	-384	2	121	114	16	240	-240	26	114	114	43	84	81	
9	92	-90	7	700	-694	37	54	-54	37	20	213	-220	20	213	-220	3	51	-50	18	124	-114	31	43	40	2	27	-45
10	953	-745	8	105	102	38	54	-54	38	20	213	-220	21	213	-220	4	51	-50	19	124	-114	32	43	40	3	27	-45
11	284	-291	10	200	-203	39	54	-54	39	20	213	-220	22	213	-220	5	51	-50	20	124	-114	33	43	40	4	27	-45
12	174	-175	11	408	-414	40	54	-54	40	21	213	-220	23	213	-220	6	51	-50	21	124	-114	34	43	40	5	27	-45
13	507	-525	12	60	77	44	74	60	41	213	-220	24	213	-220	7	51	-50	22	124	-114	35	43	40	6	27	-45	
14	1650	1012	13	733	737	45	74	60	42	213	-220	25	213	-220	8	51	-50	23	124	-114	36	43	40	7	27	-45	
15	21	10	14	704	-704	46	74	60	43	213	-220	26	213	-220	9	51	-50	24	124	-114	37	43	40	8	27	-45	
16	710	704	15	354	354	47	74	60	44	213	-220	27	213	-220	10	51	-50	25	124	-114	38	43	40	9	27	-45	
17	233	204	17	175	-172	48	74	60	45	213	-220	28	213	-220	11	51	-50	26	124	-114	39	43	40	10	27	-45	
18	432	440	18	201	-200	49	74	60	46	213	-220	29	213	-220	12	51	-50	27	124	-114	40	43	40	11	27	-45	
19	752	-825	19	249	-245	50	74	60	47	213	-220	30	213	-220	13	51	-50	28	124	-114	41	43	40	12	27	-45	
20	414	416																									

CRYSTAL STRUCTURE OF PHENYL PHOSPHORODIAMIDATE

Table 4 (cont.)

k			l			m			n			o			p			q			r			s			t			u			v			w			x			y			z																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
k	l	m	n	o	p	q	r	s	t	u	v	w	x	y	z	aa	ab	ac	ad	ae	af	ag	ah	ai	aj	ak	al	am	an	ao	ap	aq	ar	as	at	au	av	aw	ax	ay	az	ba	bb	bc	bd	be	bf	bg	bh	bi	bj	bk	bl	bm	bn	bo	bp	bq	br	bs	bt	bu	bv	bw	bx	by	bz	ca	cb	cc	cd	ce	cf	cg	ch	ci	cj	ck	cl	cm	cn	co	cp	cq	cr	cs	ct	cu	cv	cw	cx	cy	cz	da	db	dc	dd	de	df	dg	dh	di	dj	dk	dl	dm	dn	do	dp	dq	dr	ds	dt	du	dv	dw	dx	dy	dz	ea	eb	ec	ed	ee	ef	eg	eh	ei	ej	ek	el	em	en	eo	ep	eq	er	es	et	eu	ev	ew	ex	ey	ez	fa	fb	fc	fd	fe	ff	fg	fh	fi	fj	fk	fl	fm	fn	fo	fp	fq	fr	fs	ft	fu	fv	fw	fx	fy	fz	ga	gb	gc	gd	ge	gf	gg	gh	gi	gj	gk	gl	gm	gn	go	gp	gq	gr	gs	gt	gu	gv	gw	gx	gy	gz	ha	hb	hc	hd	he	hf	hg	hh	hi	hj	hk	hl	hm	hn	ho	hp	hq	hr	hs	ht	hu	hv	hw	hx	hy	hz	ia	ib	ic	id	ie	if	ig	ih	ii	ij	ik	il	im	in	io	ip	iq	ir	is	it	iu	iv	iw	ix	iy	iz	ja	jb	jc	jd	je	jf	jj	jk	jl	jm	jn	jo	jp	jq	jr	js	jt	ju	kv	kw	kx	ky	kz	la	lb	lc	ld	le	lf	lg	lh	li	lj	lk	ll	lm	ln	lo	lp	lq	lr	ls	lt	lu	lv	lw	lx	ly	lz	ma	mb	mc	md	me	mf	mg	mh	mi	mj	mk	ml	mm	mn	mo	mp	mq	mr	ms	mt	mu	mv	mw	mx	my	mz	na	nb	nc	nd	ne	nf	ng	nh	ni	nj	nk	nl	nm	nn	no	np	nq	nr	ns	nt	nu	nv	nw	nx	ny	nz	oa	ob	oc	od	oe	of	og	oh	oi	oj	ok	ol	om	on	oo	op	oq	or	os	ot	ou	ov	ow	ox	oy	oz	pa	pb	pc	pd	pe	pf	pg	ph	pi	pj	pk	pl	pm	pn	po	pp	pq	pr	ps	pt	pu	pv	pw	px	py	pz	qa	qb	qc	qd	qe	qf	qg	qh	qi	qj	qk	ql	qm	qn	qo	qp	qq	qr	qs	qt	qu	qv	qw	qx	qy	qz	ra	rb	rc	rd	re	rf	rg	rh	ri	rj	rk	rl	rm	rn	ro	rp	rq	rr	rs	rt	ru	rv	rw	rx	ry	rz	sa	sb	sc	sd	se	sf	sg	sh	si	sj	sk	sl	sm	sn	so	sp	sq	sr	ss	st	su	sv	sw	sx	sy	sz	ta	tb	tc	td	te	tf	tg	th	ti	tj	tk	tl	tm	tn	to	tp	tq	tr	ts	tt	tu	tv	tw	tx	ty	tz	ua	ub	uc	ud	ue	uf	ug	uh	ui	uj	uk	ul	um	un	uo	up	uq	ur	us	ut	uu	uv	uw	ux	uy	uz	va	vb	vc	vd	ve	vf	vg	vh	vi	vj	vk	vl	vm	vn	vo	vp	vq	vr	vs	vt	vu	vv	vw	vx	vy	vz	wa	wb	wc	wd	we	wf	wg	wh	wi	wj	wk	wl	wm	wn	wo	wp	wq	wr	ws	wt	wu	wv	ww	wx	wy	wz	xa	xb	xc	xd	xe	xf	xg	xh	xi	xj	xk	xl	xm	xn	xo	xp	xq	xr	xs	xt	xu	xv	xw	xa	xb	xc	xd	xe	xf	xg	xh	xi	xj	xk	xl	xm	xn	xo	xp	xq	xr	xs	xt	xu	xv	xw	ya	yb	yc	yd	ye	yf	yg	yh	yi	yj	yk	yl	ym	yn	yo	yp	yq	yr	ys	yt	yu	yv	yw	ya	yb	yc	yd	ye	yf	yg	yh	yi	yj	yk	yl	ym	yn	yo	yp	yq	yr	ys	yt	yu	yv	yw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr	zs	zt	zu	zv	zw	za	zb	zc	zd	ze	zf	zg	zh	zi	zj	zk	zl	zm	zn	zo	zp	zq	zr</

for the effect of these molecular oscillations (Cruickshank, 1956, 1961*b*) 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)		
P—N(1)	1.604 (3)	N(1)—H(11)	0.98 (5)
P—N(2)	1.628 (2)	N(1)—H(12)	0.85 (5)
		N(2)—H(21)	0.87 (4)
		N(2)—H(22)	0.87 (4)
C(1)—C(2)	1.379 (4)	C(2)—H(2)	0.96 (5)
C(2)—C(3)	1.390 (5)	C(3)—H(3)	1.03 (5)
C(3)—C(4)	1.368 (5)	C(4)—H(4)	0.94 (5)
C(4)—C(5)	1.378 (5)	C(5)—H(5)	1.08 (4)
C(5)—C(6)	1.398 (4)	C(6)—H(6)	0.94 (4)
C(6)—C(1)	1.366 (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)	P—N(2)—H(21)	112 (2)
O(2)—P—N(2)	96.4 (1)	P—N(2)—H(22)	116 (3)
N(1)—P—N(2)	107.6 (1)	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(1)—C(2)—C(3)	118.2 (3)	C(4)—C(3)—H(3)	122 (3)
C(2)—C(3)—C(4)	120.6 (3)	C(3)—C(4)—H(4)	119 (3)
C(3)—C(4)—C(5)	120.5 (3)	C(5)—C(4)—H(4)	120 (3)
C(4)—C(5)—C(6)	119.6 (3)	C(4)—C(5)—H(5)	120 (2)
C(5)—C(6)—C(1)	118.8 (3)	C(6)—C(5)—H(5)	120 (2)
C(6)—C(1)—C(2)	122.2 (3)	C(5)—C(6)—H(6)	124 (3)
		C(1)—C(6)—H(6)	117 (3)

An attempt to make a similar rigid-body vibration analysis for the tetrahedral PO₂N₂ 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(NH₂)₃ is reduced to three in C₆H₅OPO(NH₂)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

		<i>a</i>	<i>b</i>	<i>c</i>		<i>a</i>	<i>b</i>	<i>c</i>
P	0.192	105°	15°	88°	C(1)	0.229	74°	85°
	0.173	89	92	2		0.202	126	37
	0.156	15	75	91		0.169	41	54
O(1)	0.226	107	21	78	C(2)	0.256	98	126
	0.199	114	108	30		0.235	22	111
	0.158	30	80	62		0.217	69	44
O(2)	0.253	67	89	23	C(3)	0.291	87	120
	0.201	125	39	76		0.267	6	92
	0.174	45	51	108		0.213	86	30
N(1)	0.295	92	3	92	C(4)	0.307	72	90
	0.179	81	88	9		0.242	19	95
	0.173	9	88	99		0.200	85	5
N(2)	0.205	99	14	101	C(5)	0.299	106	70
	0.200	52	76	42		0.234	16	86
	0.175	40	90	130		0.204	89	20
					C(6)	0.264	52	111
				0.229		50	105	
				0.197		64	27	

Table 7. *Translational* (T , Å²) and *librational* (ω , deg²) tensors for the phenoxy-group

See text for definition of the axial system

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

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

Atom A	Atom B	Transform of atom A	
N(1)–H(12)···O(1)		$-\frac{1}{2} + x, y, \frac{1}{2} - z$	2.95 Å
N(2)–H(21)···O(1)		$1 - x, -y, 1 - z$	3.08
N(2)–H(22)···O(1)		$-\frac{1}{2} + x, y, 1\frac{1}{2} - z$	2.93
N(1)–H(11)···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 $-OC_6H_5$ 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, 1961*a*) 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)···O(1) 3.40 Å, C(2)···N(1) 3.60 Å. The shortest intermolecular contacts between phenoxy-groups are (a) within a hydrogen-bonded sheet: C···O 3.38 Å, C···C 3.59 Å; (b) between the sheets: C···C 3.81 Å.

We are indebted to the University of Essex Computing Centre and the Atlas Computer Laboratory, Chilton for the use of their facilities, Mr N. Lewis for the preparation of diagrams, the Science Research Council for the award of a research studentship (to P. E. D.), and the Department of Physical Chemistry, University of Cambridge for its hospitality (to G. J. B.) while this paper was being prepared.

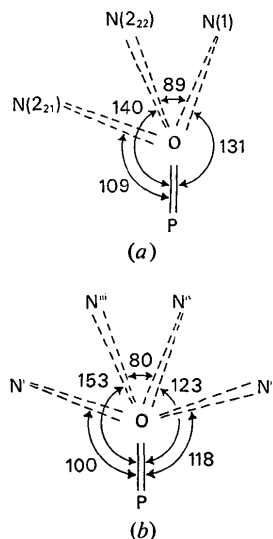


Fig. 2. Angles (°) between the $NH \cdots O$ bonds meeting at one oxygen atom. (a) $C_6H_5OPO(NH_2)_2$. The nitrogen atoms are those whose coordinates are given in Table 8; the subscripts 21 and 22 show which hydrogen atom is involved in the bond. The angle between the $P=O \cdots N(2_{21})$ and the $N(2_{22}) \cdots O \cdots N(1)$ 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 <i>et al.</i> , 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.

References

- AHMED, F. R. & POLLARD, D. R. (1972). *Acta Cryst.* **B28**, 513-519.
 BRAUER, G. (1963). *Handbook of Preparative Inorganic Chemistry*. Vol. 1, 2nd ed., p. 582. London: Academic Press.
 BULLEN, G. J. (1962). *J. Chem. Soc.* pp. 3193-3203.
 BULLEN, G. J., STEPHENS, F. S. & WADE, R. J. (1969). *J. Chem. Soc.* pp. 1804-1812.

- CORBRIDGE, D. E. C. (1966). *Topics in Phosphorus Chemistry*. Vol. 3, p. 218. New York: Interscience.
 CRAIG, D. P. & PADDOCK, N. L. (1962). *J. Chem. Soc.* pp. 4118-4133.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757-758.
 CRUICKSHANK, D. W. J. (1961a). *J. Chem. Soc.* pp. 5486-5504.
 CRUICKSHANK, D. W. J. (1961b). *Acta Cryst.* **14**, 896-897.
 DOUGILL, M. W. (1961). *J. Chem. Soc.* pp. 5471-5479.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 203. Birmingham: Kynoch Press.

Acta Cryst. (1973). **B29**, 337

The Crystal Structure of Pentamethylbenzotrichloride

BY N. C. BAENZIGER AND R. J. SCHULTZ

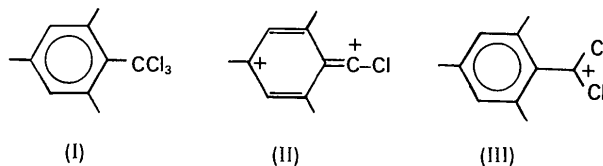
Department of Chemistry, University of Iowa, Iowa City, Iowa 52240 U.S.A.

(Received 30 June 1972; accepted 27 October 1972)

The crystal structure of pentamethylbenzotrichloride [(CH₃)₅C₆CCl₃] 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 C₆(CH₃)₅-fragment of the molecule shows significant deviations from planarity with the methyl group *ortho* to the -CCl₃ group forced 0.3 Å out of the plane. The carbon atom of the -CCl₃ 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 polymethylbenzotrichlorides (I), and Hart & Fleming (1962) reported the preparation of such a salt of pentamethylbenzotrichloride. 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 pentamethylbenzotrichloride 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.



Experimental

Pentamethylbenzotrichloride, (CH₃)₅C₆CCl₃, (PMBTC), was prepared according to the method of Hart & Fish (1958). Colorless crystals of symmetry