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X-ray Crystallography of the Phenyltriphosphonitriles.
I. The Crystal Structure of 2,2-Diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene

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The crystal structure of 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene, $(C_6H_5)_2Cl_4P_3N_3$, has been determined from Patterson and Fourier syntheses using three-dimensional counter data. The parameters have been refined by differential and least-squares methods, and the hydrogen atoms have been located from difference maps. The R index is $0{\cdot}04_8$ for 2529 observed reflections. The space group is $P2_1/n$, and the cell constants are $a=10{\cdot}653$, $b=13{\cdot}223$, $c=12{\cdot}776$ Å, $\beta=94°54'$. The six-membered cyclotriphosphazatriene (cyclophosphazene) ring has a slight chair form with three pairs of P–N bonds of different lengths averaging 1·555, 1·578, 1·615 Å. The exocyclic bond angle C–P–C is larger than either of the Cl–P–Cl angles by about 4·1°, while the corresponding internal bond angle N–P–N is smaller than either of the other two N–P–N angles by about 4·5°. The P–N–P angles are 119·2°, 121·7°, and 122·4°. The mean C–C bond in each of the two phenyl rings is only 1·377 Å.

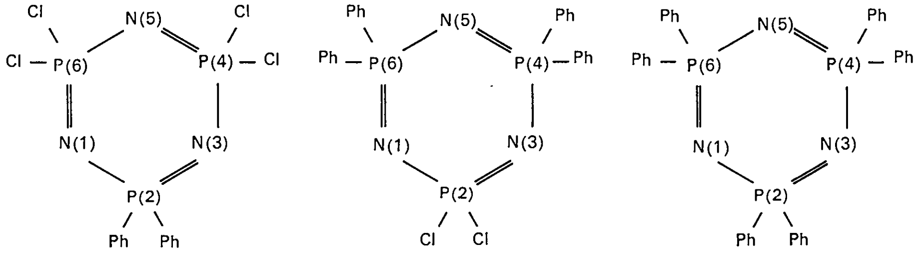
Introduction

The crystal structures of derivatives of cyclotriphosphazatriene (cyclophosphazene) have become of increasing importance in connection with chemical studies of the effect of the degree of electronegativity of the ligands on the stereochemistry of the cyclophosphazene ring and particularly the nature of the chemical bonds among the substituents and the phosphorus atoms and among the N–P bonds within the ring itself. The structure of the hexachloro derivative, $(NPCl_2)_3$, has been determined by Pompa & Ripamonti (1959) and refined by Giglio (1960), and has also been studied by Wilson & Carroll (1960). The structure of the hexabromo derivative, $(NPBr_2)_3$, has been described by Santis, Giglio & Ripamonti (1962), and an accurate analysis of the hexafluoro compound, $(NPF_2)_3$, has been reported by Dougill (1963). Shaw & Wells (1960) have prepared the three phenyl derivatives of cyclotriphosphazatriene shown schematically in Fig. 1: (I) the 2,2-diphenyl-4,4,6,6-tetrachloro, $(C_6H_5)_2Cl_4P_3N_3$, (II) the 2,2-dichloro-4,4,6,6-tetraphenyl, $Cl_2(C_6H_5)_4P_3N_3$, and (III) the hexaphenyl, $[(C_6H_5)_2PN]_3$.

The structures of the diphenyltetrachloro- and the dichlorotetraphenylcyclophosphazenes (Fig. 1, I and II) have now been determined in this laboratory. Because the electronegativity of the phenyl groups on the phosphorus atoms is less than that of the chlorine atoms, three types of P–N–P ring segments occur in these two molecules, depending upon whether the substituents on the two phosphorus atoms of the segment are four chlorine atoms, four phenyl groups, or two chlorine atoms and two phenyl groups. The investigation of the crystal structure of the diphenyltetrachloro derivative is described in the present paper, and that of the dichlorotetraphenyl derivative, together with some observations of disorder, twinning, and other phenomena in crystals of this compound will be reported in subsequent communications. A crystal structure study of hexaphenylcyclophosphazene (Fig. 1, III) is now in progress.

Crystal data

Crystals of 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene are colourless, monoclinic prisms with $a=10{\cdot}653$, $b=13{\cdot}223$, $c=12{\cdot}776$ Å ($\sigma=0{\cdot}002$ Å in each case), $\beta=94°54'$ ($\sigma=3'$), $U=1793{\cdot}2$ Å^3, F.W. 430·99, D_m (flotation in aqueous potassium iodide solution) =



(I) (II) (III)

Fig. 1. Schematic diagram of the phenylchlorotriphosphonitriles.

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1·598 g.cm^{-3} at 21 °C, $Z=4$, $D_c=1{\cdot}596$ g.cm^{-3}, μ(Cu) = 82·7 cm^{-1}, μ(Mo) = 9·4 cm^{-1}, F(000) = 864.

The space group is $P2_1/n$ ($h0l$ absent when $h+l=2n+1$; $0k0$ absent when k odd).

Data collection

Preliminary examination of the crystals and the establishment of the space group were carried out by precession and Weissenberg methods. The unit cell constants and the reflection intensities were measured on a General Electric XRD-5 diffractometer with a scintillation counter. For the cell constants, Cu radiation (Ni filter) was employed (λ, $K\alpha_1=1{\cdot}54050$, $K\alpha_2=1{\cdot}54434$ Å) and the 2θ values for the high order axial reflections were measured at a take-off angle of 1° and with a 0·02° slit. Mo radiation (Zr filter) was adopted for the collection of the intensity data in order to reduce possible absorption errors. A nearly equidimensional crystal prism varying in linear dimensions from 0·21 to 0·27 mm was selected. It was mounted on a glass fibre with the b axis along the direction of the fibre. The integrated intensities were measured by the moving-crystal moving-counter method (Furnas, 1957) over scans of 2° in 2θ, a take-off angle of 2°, and an open counter window.

The sites of 4472 non-prohibited and non-equivalent reflections within $\sin\theta/\lambda \leq 0{\cdot}68$ were scanned; the background intensity was measured separately for each reflection on the streak through it and was deducted from the total integrated intensity. Only 2529 reflections (56·5% of those examined) gave a net count above an arbitrary significant level. The appropriate 1/Lp corrections were applied to the net intensity counts but, with Mo radiation, no corrections for absorption were considered necessary. The very strong and very weak reflections were measured twice. The intensity of the 200 reflection was recorded regularly at short time intervals to provide a standard for placing all the data on the same relative scale.

Structure analysis

The positions of the three phosphorus and four chlorine atoms were established unambiguously from a 3-D sharpened Patterson synthesis; the sharpening function was $2\sin 2\theta/(1+\cos^2 2\theta)$. Interpretation was simplified by assuming that the intramolecular P–P vectors form a nearly equilateral triangle (Fig. 1, I) of side 2·85 Å, and that the lengths of the P–Cl and Cl–Cl vectors are approximately 1·95 and 3·2 Å respectively. The R index, with only these atoms included, was 0·37, assuming B(P) = 3 Å^2 and B(Cl) = 4 Å^2. The nitrogen and carbon atoms were located from the first Fourier synthesis which was evaluated with 95% of the observed data. The electron-density maxima were 18 to 25 e.Å^{-3} for P, 20 to 23 e.Å^{-3} for Cl, 5 to 7 e.Å^{-3} for N, and 3 to 5 e.Å^{-3} for C, with a background within ± 1·6 e.Å^{-3}. The atomic positions obtained from the Fourier synthesis and refined by one differential synthesis reduced the R index to 0·17, assuming $B=2{\cdot}7$ to 3·5 Å^2 for the various atoms.

The first stage of refinement comprised four cycles of 'observed' and 'calculated' differential syntheses and two 3-D difference syntheses. The latter were employed for the location and refinement of the positions of the hydrogen atoms, and for an estimation of the thermal anisotropy of the other atoms. At this stage the R index for the observed data was 0·08. A second stage of refinement was carried out in four cycles of least squares with a program written by Mair (Ahmed, Gabe, Mair & Pippy, 1963) in which 3 × 3 and 6 × 6 block-diagonal matrices were formed for evaluation of the shifts in the positional and anisotropic thermal parameters, respectively. The parameters of the hydrogen atoms were excluded and a weighting function of the form $w=1/\{1+[(|F_o|-20)/60]^2\}$ was employed. The final R index for the observed data was 0·048.

As a final check on the positional parameters, a fifth cycle of least squares and another differential synthesis were computed but the indicated shifts were small and randomly distributed. The average shifts in the bond lengths and angles were 0·002 Å and 0·1° respectively, with maxima of 0·010 Å for the C(4)–C(5) bond and 0·3° for the Cl(2)–P(4)–N(3) angle. A final difference synthesis was evaluated and some interesting features are pointed out later in a discussion of the structure. The atomic scattering-factor curves employed in the calculations were taken from *International Tables for X-ray Crystallography* (1962), and the hydrogen atoms were assumed to be isotropic with $B=4{\cdot}5$ Å^2.

Results

A perspective view of the molecule is shown in Fig. 2. The final coordinates of the P, N, Cl, and C atoms obtained from the fourth cycle of least squares are giv-

Table 1. *Fractional atomic coordinates*
(e.s.d.'s × 10^4 Å in parentheses)

Atom	x	y	z
N(1)	0·0388(43)	0·2016(48)	0·0693(47)
P(2)	0·1269(13)	0·2806(16)	0·1386(14)
N(3)	0·0760(46)	0·3125(54)	0·2493(48)
P(4)	−0·0426(14)	0·2634(16)	0·2910(16)
N(5)	−0·1263(44)	0·1884(53)	0·2186(49)
P(6)	−0·0747(13)	0·1479(16)	0·1144(16)
Cl(1)	0·0049(18)	0·1969(23)	0·4284(18)
Cl(2)	−0·1583(17)	0·3715(18)	0·3357(18)
Cl(3)	−0·2176(16)	0·1428(19)	0·0036(18)
Cl(4)	−0·0404(19)	−0·0006(17)	0·1346(20)
C(1)	0·2811(53)	0·2265(61)	0·1608(56)
C(2)	0·3075(60)	0·1330(66)	0·1201(64)
C(3)	0·4303(71)	0·0954(78)	0·1341(72)
C(4)	0·5228(65)	0·1492(89)	0·1878(77)
C(5)	0·4965(70)	0·2416(96)	0·2285(94)
C(6)	0·3757(64)	0·2814(77)	0·2137(78)
C(7)	0·1503(50)	0·3931(55)	0·0657(56)
C(8)	0·1924(65)	0·3862(60)	−0·0347(65)
C(9)	0·2221(70)	0·4719(66)	−0·0876(67)
C(10)	0·2095(65)	0·5662(67)	−0·0429(68)
C(11)	0·1646(78)	0·5734(66)	0·0529(76)
C(12)	0·1361(72)	0·4878(62)	0·1087(65)

Table 2. *Electron densities* (e.Å^{-3}), *principal curvatures* (e.Å^{-5}), *and anisotropic thermal parameters* ($\times 10^5$) *for the expression* $T = \exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)\}$

Atom	ϱ_o	ϱ_c	$-\varrho_o''$	$-\varrho_c''$	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
N(1)	10·1	10·2	81	82	650	523	568	−241	309	−277
P(2)	32·8	32·9	333	331	545	490	477	−158	270	−185
N(3)	8·9	8·9	67	68	703	769	570	−456	475	−564
P(4)	31·5	31·5	315	313	578	553	501	−102	282	−167
N(5)	9·5	9·5	75	76	585	671	692	−213	379	−350
P(6)	32·3	32·4	324	322	542	436	575	−126	125	−134
Cl(1)	23·3	23·3	197	195	1025	1075	732	505	−105	−214
Cl(2)	26·5	26·6	236	236	953	706	805	−286	570	134
Cl(3)	27·2	27·2	244	244	719	815	796	−321	−291	−151
Cl(4)	24·3	24·3	207	207	1316	459	1093	211	505	86
C(1)	8·9	8·8	80	80	632	585	543	154	121	−71
C(2)	7·4	7·4	58	59	850	640	664	87	183	267
C(3)	6·5	6·5	50	50	1086	908	778	360	333	768
C(4)	6·3	6·4	48	49	752	1241	949	824	170	638
C(5)	5·4	5·5	37	37	688	1196	1453	176	−451	−201
C(6)	6·5	6·6	50	50	699	821	1093	−193	−376	−142
C(7)	9·2	9·1	86	86	549	459	584	−146	270	−95
C(8)	7·7	7·8	66	67	1023	423	698	−64	330	187
C(9)	7·0	7·1	56	56	1181	566	705	67	425	186
C(10)	7·1	7·1	56	57	1031	569	772	194	−17	−17
C(11)	6·5	6·5	49	49	1528	431	955	−286	334	−83
C(12)	7·4	7·4	61	62	1396	470	656	−412	361	−185

Table 3. *Fractional coordinates of the hydrogen atoms and their observed electron densities* (e.Å^{-3})

Atom	x	y	z	ϱ_o
H(2)	0·237	0·097	0·063	0·58
H(3)	0·442	0·025	0·100	0·82
H(4)	0·620	0·127	0·193	0·45
H(5)	0·570	0·283	0·271	0·40
H(6)	0·357	0·353	0·253	0·39
H(8)	0·207	0·313	−0·066	0·42
H(9)	0·264	0·463	−0·162	0·45
H(10)	0·230	0·628	−0·092	0·48
H(11)	0·147	0·640	0·100	0·32
H(12)	0·102	0·496	0·183	0·50

Table 4. *Parameters of the principal axes of the ellipsoids of thermal vibration for the phosphorus and nitrogen atoms*

Atom	i	B_i(Å^2)	g_{i1}	g_{i2}	g_{i3}
N(1)	1	4·86	0·450	−0·663	0·634
	2	2·89	−0·175	0·591	0·769
	3	2·42	0·875	0·461	−0·072
P(2)	1	4·07	0·409	−0·736	0·572
	2	2·72	0·198	0·649	−0·749
	3	2·10	0·889	0·198	−0·334
N(3)	1	7·02	0·426	−0·782	0·490
	2	2·83	−0·169	−0·563	−0·821
	3	2·21	0·888	0·266	−0·297
P(4)	1	4·24	0·376	−0·825	0·454
	2	3·16	−0·312	−0·545	−0·802
	3	2·23	0·874	0·165	−0·381
N(5)	1	5·75	0·508	−0·431	0·786
	2	3·91	−0·001	0·999	0·044
	3	2·16	0·755	0·512	−0·344
P(6)	1	3·94	0·181	−0·450	0·887
	2	2·99	−0·426	0·762	0·449
	3	2·25	0·889	0·455	0·120

en in Table 1. Their e.s.d.'s were calculated with expression 6·4·3 (6) of *International Tables for X-ray Crystallography* (1959, p.330) and then increased by an arbitrary factor of 20% to allow for the excluded unobserved reflections. The observed and calculated electron densities, mean curvatures, and refined anisotropic thermal parameters are listed in Table 2. The positional parameters and electron-density maxima for the hydrogen atoms obtained from the second difference synthesis and without further refinement are shown in Table 3, where each hydrogen atom has been assigned the same number as the carbon atom to which it is attached. To illustrate the degree of thermal anisotropy of the P and N atoms of the cyclophosphazene ring, the parameters of their ellipsoids of thermal vibration, calculated by the method of Rollett & Davies (1955), are given in Table 4, where the direction cosines g_{ij} ($j = 1, 2, 3$) are referred to the reciprocal axes a^*, b^*, c^*, respectively.

The complete structure-factor table, based on the parameters listed in Tables 1, 2, and 3, has been de-

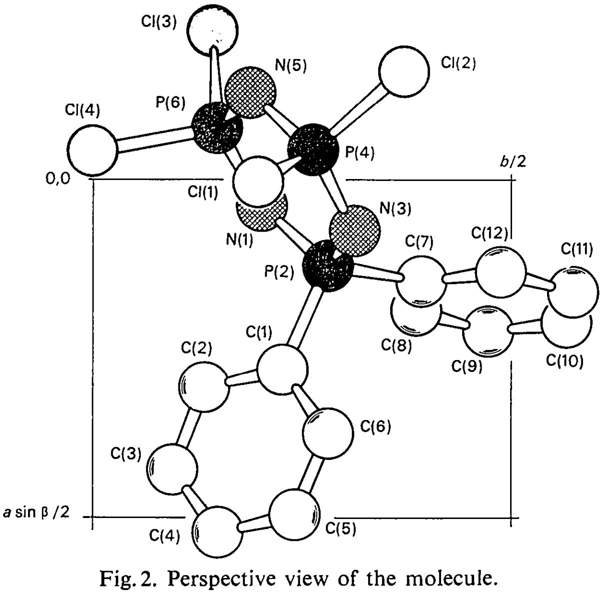


Fig. 2. Perspective view of the molecule.

posited in the Library of the National Research Council, Ottawa. A summary of the agreement between $|F_o|$ and $|F_c|$ (Ahmed & Barnes, 1963) is presented in Table 5, where it may be noted that only one observed reflection of medium intensity and only five unobserved reflections, out of 4472 examined, show relatively high discrepancies. The bond lengths and bond angles, not corrected for thermal vibrations, and their e.s.d.'s (*International Tables*, 1959, p.331) are recorded in Fig. 3. The C–H bonds have a mean value of 1·075 Å ($\sigma =$ 0·021 Å).

Table 5. *Agreement summary*

2529 observed reflections ($4{\cdot}9 \le |F_o| \le 192{\cdot}7$)
$R = 0{\cdot}048$

Category	Limits	Number
1	$\|\Delta F\| \le 1{\cdot}0\|F_{\text{th}}\|$, or $\|\Delta F\|/\|F_o\| \le 0{\cdot}10$	2522
2	$1{\cdot}0\|F_{\text{th}}\| < \|\Delta F\| \le 2{\cdot}0\|F_{\text{th}}\|$, or $0{\cdot}10 < \|\Delta F\|/\|F_o\| \le 0{\cdot}15$	6
3	$2{\cdot}0\|F_{\text{th}}\| < \|\Delta F\| \le 3{\cdot}0\|F_{\text{th}}\|$, or $0{\cdot}15 < \|\Delta F\|/\|F_o\| \le 0{\cdot}20$	1
	1943 unobserved reflections ($\|F_c\|_{\text{max.}} = 12{\cdot}9$)	
1	$\|F_c\| \le 1{\cdot}0\|F_{\text{th}}\|$	1738
2	$1{\cdot}0\|F_{\text{th}}\| < \|F_c\| \le 1{\cdot}5\|F_{\text{th}}\|$	200
3	$1{\cdot}5\|F_{\text{th}}\| < \|F_c\| \le 2{\cdot}0\|F_{\text{th}}\|$	5

$|F_{\text{th}}| =$ threshold amplitude $= 2{\cdot}5$ to $7{\cdot}7$.

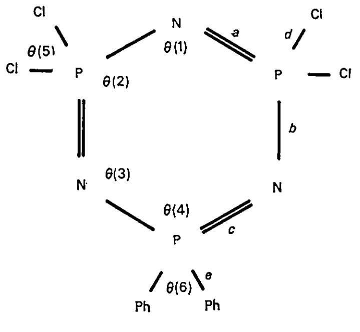
Discussion

Bond lengths and angles

The mean values of the chemically equivalent bonds and angles, the maximum deviations from the means, and the corresponding r.m.s. standard deviations are listed in Table 6.

Table 6. *Mean values for the chemically equivalent bonds* (Å) *and angles* (°), *maximum deviations from the means, and r.m.s. standard deviations*

Bond	Type	Mean	Deviation	σ(r.m.s.)
P–N	*a*	1·578	0·001	0·005
P–N	*b*	1·555	0·000	0·005
P–N	*c*	1·615	0·002	0·005
P–Cl	*d*	1·998	0·012	0·002
P–C	*e*	1·788	0·004	0·006
Angle				
P–N–P	θ(1)	119·2	—	0·3
N–P–N	θ(2)	119·7	0·0	0·3
P–N–P	θ(3)	122·0	0·3	0·3
N–P–N	θ(4)	115·2	—	0·2
Cl–P–Cl	θ(5)	100·3	0·1	0·1
C–P–C	θ(6)	104·4	—	0·3



There appear to be three different types of P–N bond of mean lengths 1·555, 1·578, and 1·615 Å in the cyclophosphazene ring. There are two bonds of each type, but the three types are significantly different from one another on the basis of the present analysis, σ(P–N) = 0·005 Å. The two P–N bonds of length 1·578Å occur in the P(4)–N(5)–P(6) segment which has two chlorine atoms attached to each of P(4) and P(6). The length of these two bonds is very close to the mean value of 1·577 Å obtained by averaging the results of Wilson & Carroll (1960), and of Giglio (1960) for the P–N bonds in $(NPCl_2)_3$. In each of the other two segments, P(2)–N(3)–P(4) and P(2)–N(1)–P(6), where the ligands are two phenyl rings at P(2) and two chlorine atoms at P(4) and at P(6), the P(4)–N(3) and P(6)–N(1) bonds are 0·06 Å shorter than the P(2)–N(3) and P(2)–N(1) bonds. In view of the higher electronegativity of the chlorine atoms compared with that of the phenyl groups these results are in agreement with the theoretical expectation that the bond strength and the total additional bond energy should increase with increasing electronegativity of the ligand (Paddock, 1964). At each of P(4) and P(6), the mean exocyclic angle Cl–P–Cl is $100{\cdot}3_5$° and the mean internal angle N–P–N is $119{\cdot}7_5$°, while at P(2) the exocyclic angle C–P–C is 104·4° and the internal angle is only 115·2°. Thus an increase of about 4·1° in the exocyclic angle at P(2) over those at P(4) and P(6) has been compensated for by a decrease of about 4·5° in the corresponding internal angle.

The mean value for the four P–Cl bonds is 1·998 Å but the maximum deviation from this mean is only 0·012 Å which is about six times the e.s.d.'s for these bonds. This suggests that the four P–Cl bonds probably are not of equal length. It is also of interest to note that the two longest P–Cl bonds [P(4)–Cl(2) and P(6)–Cl(4)] are involved in the two smallest Cl–P–N angles (106·9° ± 0·3°) in the molecule.

In each of the two phenyl rings, the mean C–C bond is 1·377 Å which is considerably shorter than the normal value of 1·394 Å (Sutton, 1965) for an aromatic C–C bond. As mentioned previously, the bond lengths have not been corrected for thermal vibrations and consequently a small proportion of this difference may be attributed to this intentional omission.

Finally it should be mentioned that all intermolecular distances are greater than the van der Waals contacts calculated from the radii of the atoms involved (Pauling, 1960, p.260).

Planarity of the rings

The equations for the three mean planes through the cyclophosphazene, phenyl I [C(1) to C(6)] and phenyl II [(C(7) to C(12)] rings, referred to the orthogonal axes, $x' = x + z\cos\beta$, $y' = y$, $z' = z\sin\beta$, are as follows:

Phosphazene:

$$0{\cdot}5137x' - 0{\cdot}7339y' + 0{\cdot}4444z' + 1{\cdot}3386 = 0 \qquad (1)$$

Phenyl I:

$$0{\cdot}2909x' + 0{\cdot}4326y' - 0{\cdot}8534z' - 0{\cdot}3740 = 0 \qquad (2)$$

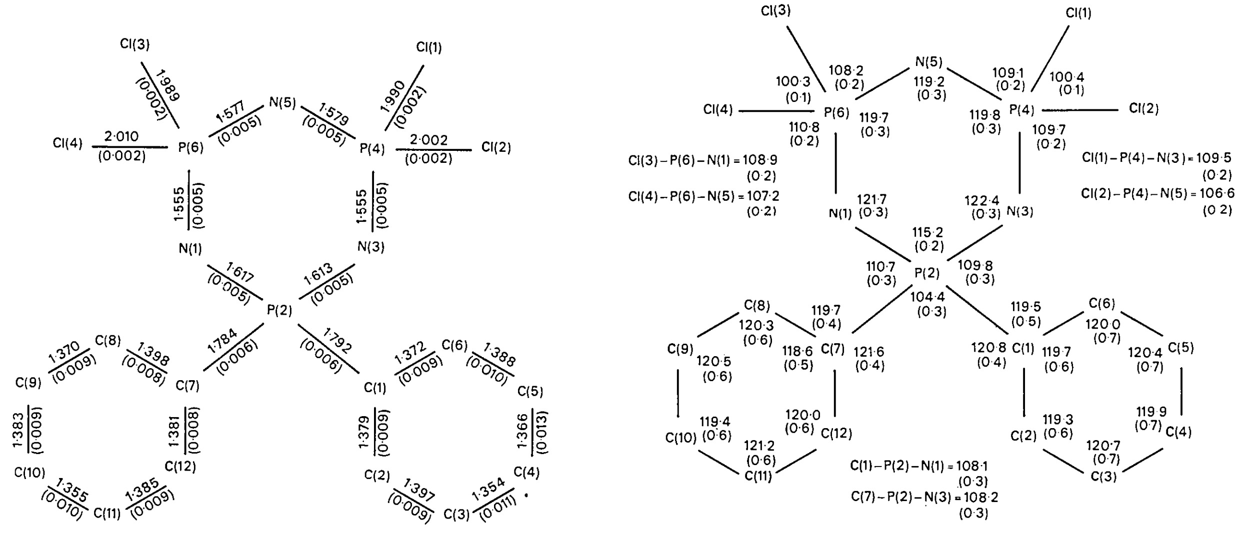


Fig. 3. Bond lengths (Å) and bond angles (°); e.s.d.'s in parentheses.

Phenyl II:

$$0{\cdot}9084x' - 0{\cdot}0448y' + 0{\cdot}4158z' - 1{\cdot}4939 = 0 \quad (3)$$

These equations were derived by Blow's method (1960) and are nearly the same as those calculated by the method of least-squares. A projection of the molecule (excluding the hydrogen atoms) along the normal to plane (1), showing the perpendicular distances of the atoms from the plane, is presented in Fig. 4. The cyclophosphazene ring is definitely non-planar, because $\chi^2 = 3340$ and for $\nu = 3$, $P \ll 0{\cdot}001$, and it has a slight chair form with a maximum deviation of $\pm 0{\cdot}078$ Å from the mean plane. Both phenyl rings are planar; for phenyl I, $\chi^2 = 4{\cdot}4$ and $P > 0{\cdot}05$, and for phenyl II, $\chi^2 = 13{\cdot}3$ and $P > 0{\cdot}001$.

Residual electron-density distribution

The final difference synthesis, evaluated at $R = 0{\cdot}05$ and with all atoms removed, showed a residual electron-density within $\pm 0{\cdot}3$ e.Å^{-3} near the atomic positions and an almost flat background elsewhere. Three sections through the planes of the rings are shown in Fig. 5. An interesting feature is the marked similarity among the residual electron densities on chemically equivalent bonds, indicating that they are not merely the result of random experimental errors but may in fact represent a feature of the bond system in the molecule. The values are as high as 0·25 e.Å^{-3} on P(6)–N(1) and P(4)–N(3), between 0·10 and 0·20 e.Å^{-3} on P(2)–N(1) and P(2)–N(3), and between 0·15 and 0·25 e.Å^{-3} on P(2)–C(1) and P(2)–C(7). The maxima on the P–N bonds occur at about 0·6 Å from N(1) and N(3), which supports the possibility of increased delocalization of lone pairs of electrons on the nitrogen atoms (Craig & Paddock, 1962).

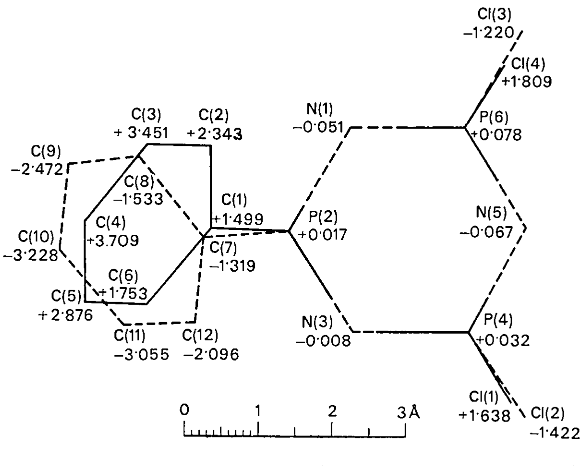


Fig.4. The mean plane of the cyclophosphazene ring showing the perpendicular distances (Å) of the atoms from it.

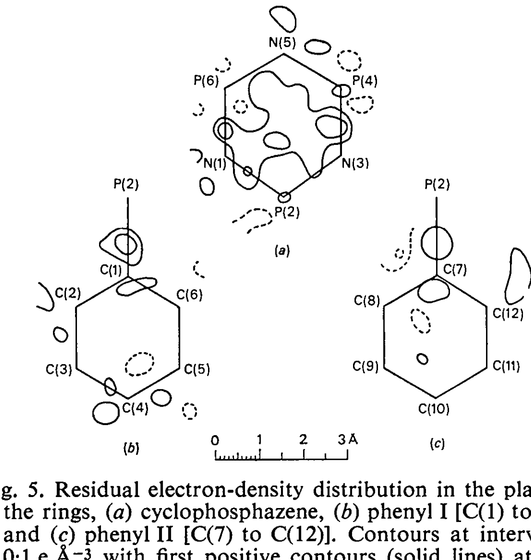


Fig. 5. Residual electron-density distribution in the planes of the rings, (*a*) cyclophosphazene, (*b*) phenyl I [C(1) to C(6)], and (*c*) phenyl II [C(7) to C(12)]. Contours at intervals of 0·1 e.Å^{-3} with first positive contours (solid lines) at +0·1 e.Å^{-3}, and first negative contours (broken lines) at −0·1 e.Å^{-3}.

All the computations were carried out on an IBM 1620 computer with a unified set of crystallographic programs developed by Ahmed, Gabe, Mair & Pippy (1963). The authors are indebted to Dr R. A. Shaw of Birkbeck College, London for stimulating their interest in the problem and for supplying the specimens. Grateful acknowledgement is made to Mrs M. E. Pippy for assistance with the computations, and to the staff of the N. R. C. Computation Centre for their cooperation.

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The Crystal Structure of Succinic Anhydride

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The crystal structure of succinic anhydride, $(CH_2CO)_2O$, which is isomorphous with maleic anhydride, has been determined and refined with the use of three-dimensional X-ray data. The crystals are orthorhombic with cell dimensions $a = 6{\cdot}963$, $b = 11{\cdot}710$, $c = 5{\cdot}402$ Å. The space group is $P2_12_12_1$. The molecular arrangement is similar to that of maleic anhydride.

The thermal vibrations of the molecule are discussed.

Introduction

The structure of maleic anhydride has recently been published by Marsh, Ubell & Wilcox (1962). Lonsdale, (1939), referring to unpublished work by Monvoisin, states that maleic and succinic anhydride are isomorphous although the latter substance has two more hydrogen atoms in the molecule and the corresponding acids have different configurations. It appeared therefore of particular interest to compare the structures of succinic anhydride and maleic anhydride, and a detailed structure determination of succinic anhydride was undertaken.

Experimental

Crystal data

Succinic anhydride $(CH_2CO)_2O$
M.W. 100·08
Orthorhombic
$a = 6{\cdot}963 \pm 0{\cdot}015$ Å
$b = 11{\cdot}71 \pm 0{\cdot}04$
$c = 5{\cdot}402 \pm 0{\cdot}010$

(The errors given are three times the standard errors of averages).

Density (calculated, $Z = 4$) 1·509 g.cm^{-3}
Density (measures) 1·505 g.cm^{-3} (S.T.P.)

Total number of electrons per unit cell $= F(000) = 208$

Systematic absences:
$h00$: $h = 2n + 1$
$0k0$: $k = 2n + 1$
$00l$: $l = 2n + 1$
Space group: $P2_12_12_1$
Molecular symmetry: none.

Description of crystals

Crystals were grown from a hot solution of commercial succinic anhydride and chloroform. Most crystals were needle-shaped, but for the X-ray work two almost equidimensional crystals of $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}45$ mm^3 and $0{\cdot}54 \times 0{\cdot}61 \times 0{\cdot}67$ mm^3 respectively were found. They were somewhat hygroscopic, and were therefore coated with collodion, which proved sufficient protec-