

and for all the facilities put at their disposal. They are also much indebted to Professor G. B. Carpenter for his helpful comments during the completion of the work. They also wish to thank the Brown University Computing Centre for providing them with ample time for the calculations.

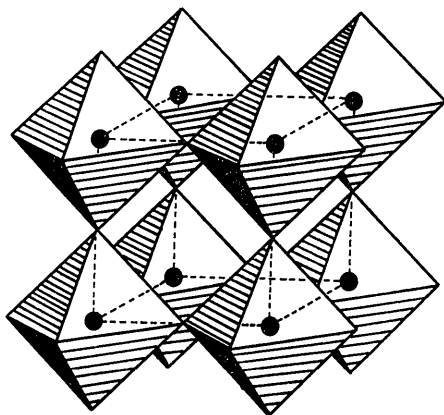


Fig. 4. The structure of  $\text{MoO}_{2.4}\text{F}_{0.6}$  showing a three-dimensional array of regular  $\text{MoX}_6$  octahedra sharing corners.

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## X-ray Crystallography of the Diphosphatriazines.

### I. The Crystal Structure of 6-Methyl-2,2,4,4-tetraphenyldiphospha-1,3,5-triazine

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The crystal structure of 6-methyl-2,2,4,4-tetraphenyldiphospha-1,3,5-triazine has been determined from Patterson and Fourier syntheses, and has been refined by least-squares to an  $R$  index of 0.067 for 4832 observed reflexions. The unit cell is triclinic,  $P\bar{1}$ , of dimensions  $a=13.585$ ,  $b=18.007$ ,  $c=10.838$  Å,  $\alpha=79.42$ ,  $\beta=112.97$ ,  $\gamma=109.58^\circ$ , and has two molecules in the asymmetric unit. The diphosphatriazine ring is non-planar, has a skewed boat form and approximate twofold symmetry, and its atoms are within  $-0.07$  and  $+0.10$  Å from the mean plane. The weighted mean bond lengths are: P-N in P-N-P segments, 1.597; P-N in P-N-C segments, 1.620; P-C, 1.801; N-C, 1.335; C-CH<sub>3</sub>, 1.508 Å. The weighted mean angles are: N-P-N, 116.5; P-N-P, 115.4; P-N-C, 119.9; N-C-N, 129.1; C-P-C, 105.4; N-C-CH<sub>3</sub>, 115.4°. One of the phenyl rings is disordered and has two possible orientations.

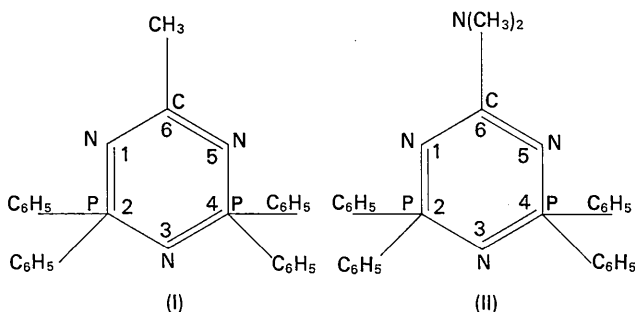
#### Introduction

The six-membered diphosphatriazine ring,  $\text{CP}_2\text{N}_3$ , is intermediate between the aromatic and planar triazine ring,  $\text{C}_3\text{N}_3$ , and the cyclotriphosphazene ring,  $\text{P}_3\text{N}_3$ ,

which has been found to be planar only in  $\text{F}_6\text{P}_3\text{N}_3$  and non-planar in other compounds by varying amounts depending on the ligands. In order to examine the planarity of the  $\text{CP}_2\text{N}_3$  ring, its bond lengths and valency angles and their dependence on the ligands, two compounds have been chosen for X-ray analysis, namely: (I) the 6-methyl-, and (II) the 6-dimethyl-

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amino- derivatives of 2,2,4,4-tetraphenyldiphosphat-1,3,5-triazine. The method of their preparation has been reported by Schmidpeter & Ebeling (1967).



The X-ray analysis of compound (I) is described in the present paper (part I), and that of compound (II) is reported by Pollard & Ahmed (1970) as part II. The full comparison of the results is given in part II, but it is of interest to note here that crystals of compound (I) are triclinic,  $P\bar{1}$ , with two molecules in the asymmetric unit, while those of compound (II) are monoclinic,  $C2/c$ , with only one half molecule in the asymmetric unit.

### Experimental

#### Unit cell

Crystals of 6-methyl-2,2,4,4-tetraphenyldiphosphat-1,3,5-triazine are colourless triclinic prisms, and the one used for data collection was of dimensions  $0.23 \times 0.17 \times 0.27$  mm. Preliminary examination of the space group was carried out on a precession camera, with Cu radiation, according to the procedure described by Barnes & Ahmed (1968). Thus, from a set of zero-level precession photographs taken at  $10^\circ$  intervals over the range  $D=0$  to  $170^\circ$  with the crystal oriented at random, three suitable reciprocal axes were chosen and measured. After reduction of the unit cell by Buerger's (1957) algorithm and the procedure of Davis (1961), the reduced unit-cell was found to be triclinic of dimensions  $a'=10.843$ ,  $b'=12.972$ ,  $c'=9.271$  Å,  $\alpha'=106^\circ 53'$ ,  $\beta'=96^\circ 9'$ ,  $\gamma'=109^\circ 17'$ , and  $V'=1147.7$  Å<sup>3</sup>. In order to determine whether this reduced cell was primitive, the crystal was mounted on a 4-circle diffractometer, the reciprocal unit-cell parameters were measured with a narrow slit at a small take-off angle, and some of the lattice sites corresponding to halving of the reciprocal axes were scanned with an open counter window. This search showed a whole class of weak reflexions at the centres of the original  $b^*c^*$  net. The correct reduced primitive cell was, therefore, related to the original cell by the transformation  $\mathbf{a}^* = \frac{1}{2}(\mathbf{b}^* + \mathbf{c}^*)$ ,  $\mathbf{b}^* = \frac{1}{2}(-\mathbf{b}^* + \mathbf{c}^*)$ ,  $\mathbf{c}^* = \mathbf{c}^*$ ,  $V=2V'$ . The parameters of the reduced primitive cell as deduced from the diffractometer measurements (Cu radiation:  $\lambda$ ,  $K\alpha_1=1.54050$ ;  $K\alpha_2=1.54434$  Å) are given in Table 1. The crystal density was measured by flotation in aqueous potassium iodide solution.

Table 1. *Crystal data*

$a$	13.585 (0.004) Å	$C_{26}H_{23}N_3P_2$
$b$	18.007 (0.005)	M.W. 439.44 g.mole <sup>-1</sup>
$c$	10.838 (0.004)	Space group $P\bar{1}$
$\alpha$	$79.42$ (0.08) $^\circ$	$Z$ 4
$\beta$	$112.97$ (0.08)	$F(000)$ 920
$\gamma$	$109.58$ (0.08)	$\mu(\text{Cu})$ 18.4 cm <sup>-1</sup>
$U$	$2295.6$ Å <sup>3</sup>	$\mu(\text{Mo})$ 2.1 cm <sup>-1</sup>
$D_x$	1.271 g.cm <sup>-3</sup>	$D_m$ 1.277 g.cm <sup>-3</sup>

#### Intensity data

The intensity data were measured on a Picker automatic diffractometer with Mo radiation and Nb filters, using the  $\theta$ - $2\theta$  scan method. All the 10503 non-equivalent lattice sites within  $2\theta=55^\circ$  ( $\sin \theta/\lambda=0.649$ ) were scanned but only 4832 reflexions were observed above threshold. The intensities of the  $h+k=2n$  reflexions were relatively strong and 57% were observed, but the  $h+k=2n+1$  reflexions were much weaker and only 35% were observed. This uneven distribution of intensities was indicative that the two crystallographically independent molecules in the asymmetric part of the unit cell might be related by an approximate translation of  $\frac{1}{2}, \frac{1}{2}, 0$ , and this relation was confirmed later from the vector distribution in the Patterson map. The  $1\bar{1}0$  reflexion was measured at regular intervals during the data collection for scaling purposes. The very strong reflexions were measured separately at a low current setting. The net intensity counts were properly scaled and then corrected for the Lorentz and polarization effects but not for absorption which was considered to be negligible.

#### Structure determination

From the distribution statistics of the normalized structure factors  $|E|$  and the theoretical values by Karle, Dragonette & Brenner (1965), shown in Table 2, the space group was accepted as  $P\bar{1}$ . An attempt at solving the structure automatically on the computer by the direct method of symbolic addition was unsuccessful, presumably since the reflexions with  $h+k=2n+1$  were very weak and the program was not designed to handle such special cases. The correct structure, however, was deduced from Patterson and Fourier syntheses.

Table 2. *Statistics of the normalized structure amplitudes*

	Observed $C_{26}H_{23}N_3P_2$	Theoretical $P\bar{1}$	
		$P\bar{1}$	$P1$
$\langle  E  \rangle$	0.793	0.798	0.886
$\langle  E ^2 \rangle$	1.001	1.000	1.000
$\langle  E^2 - 1  \rangle$	1.019	0.968	0.736
$ E  > 3$	0.8%	0.3%	0.01%
$ E  > 2$	4.8%	5%	1.8%
$ E  > 1$	29.8%	32%	37%

A sharpened Patterson function computed with  $|F_0^2|/Lp$  as amplitudes gave a strong peak at  $\frac{1}{2}, \frac{1}{2}, 0$  of height about half that of the origin peak, indicating

Table 3. Fractional coordinates, vibration tensor components ( $\text{\AA}^2$ ) for the expression  $T = \exp[-2\pi^2(U_{11}a^*h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$ , and their e.s.d.'s (all quantities  $\times 10^4$ )

Atoms C(14) to C(19) have 0.8 occupancy, and C(14)\* to C(19)\* 0.2 occupancy.

Molecule I	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{23}$	$2U_{13}$	$2U_{12}$
N(1)	415(4)	4388(3)	2213(5)	789(36)	382(26)	499(30)	167(44)	611(54)	490(49)
N(2)	864(1)	3675(1)	2097(1)	566(9)	357(7)	294(7)	35(11)	325(13)	341(13)
N(3)	956(4)	2018(3)	3322(4)	499(24)	499(24)	374(25)	115(62)	647(72)	573(68)
N(4)	446(1)	3072(1)	4387(1)	482(9)	350(7)	346(7)	97(12)	368(13)	359(12)
N(5)	-189(4)	3741(3)	4C57(5)	611(31)	539(31)	469(29)	80(47)	392(49)	546(50)
C(6)	-82(5)	4308(3)	3C54(5)	626(31)	333(28)	-423(32)	-56(47)	264(55)	-400(52)
C(7)	-598(6)	4951(4)	3010(7)	1108(58)	607(42)	694(45)	355(7C)	952(87)	1021(82)
C(8)	2170(5)	4073(3)	1861(5)	659(38)	337(28)	311(28)	-6(44)	328(54)	268(51)
C(9)	2435(6)	4816(4)	1208(8)	815(46)	539(41)	863(54)	135(74)	751(85)	-431(73)
C(10)	340(7)	1032(8)	974(10)	974(50)	491(42)	1089(64)	453(84)	1072(102)	145(79)
C(11)	4220(6)	4680(4)	1519(7)	728(48)	620(45)	794(51)	-101(75)	661(80)	74(74)
C(12)	3972(5)	3975(4)	2187(7)	430(41)	712(45)	607(42)	120(69)	582(69)	427(69)
C(13)	2450(5)	3674(3)	2370(6)	652(42)	500(36)	479(36)	91(57)	462(53)	442(64)
C(14)	-108(6)	3221(4)	5501(7)	506(44)	-101(39)	456(41)	75(63)	277(63)	263(66)
C(15)	-659(8)	3658(5)	-505(8)	646(52)	613(54)	490(47)	-31(80)	112(78)	539(64)
C(16)	-1418(7)	5324(5)	-1673(8)	653(52)	830(55)	414(44)	-56(85)	118(77)	659(64)
C(17)	1592(8)	2546(6)	-1811(8)	952(68)	825(65)	392(48)	-359(89)	139(89)	-111(104)
C(18)	-981(9)	2131(5)	-848(9)	1362(87)	485(49)	545(55)	-237(84)	255(110)	178(104)
C(19)	-231(9)	2467(5)	361(9)	1371(87)	485(49)	545(55)	-103(85)	183(110)	87(111)
C(20)	-501(5)	2139(3)	4634(6)	480(34)	471(33)	487(35)	43(55)	343(56)	366(54)
C(21)	-1304(5)	2077(4)	5134(7)	641(41)	487(36)	828(48)	27(67)	81(75)	325(64)
C(22)	-2044(6)	1394(4)	5323(8)	738(50)	606(44)	1196(63)	-56(85)	1040(66)	299(72)
C(23)	-1958(6)	672(4)	4928(8)	551(47)	555(42)	1152(60)	-116(85)	786(91)	14(72)
C(24)	-1155(6)	731(4)	4503(8)	892(52)	461(39)	974(59)	-295(75)	647(90)	360(73)
C(25)	-430(5)	1455(4)	4298(7)	704(44)	510(38)	788(49)	-26(68)	590(77)	374(66)
C(26)	1534(5)	322(3)	4001(5)	568(35)	309(28)	416(31)	-11(64)	394(63)	170(69)
C(27)	2632(5)	3379(4)	6171(6)	482(36)	671(42)	561(39)	-345(64)	385(60)	150(62)
C(28)	3468(5)	3520(5)	7427(7)	493(39)	1055(6C)	664(46)	-635(83)	321(68)	189(76)
C(29)	3199(6)	3525(5)	7970(7)	850(37)	747(40)	718(44)	-730(81)	234(65)	52(85)
C(30)	2113(6)	340(4)	8374(6)	884(51)	979(55)	435(37)	-373(73)	609(72)	449(85)
C(31)	1281(5)	3254(4)	7131(6)	665(43)	805(46)	453(37)	-335(67)	453(65)	460(72)
C(32)	-115(2)	3222(3)	505(2)	427(17)	427(17)	320(15)	112(54)	641(294)	530(27)
C(33)	-380(26)	3650(22)	-548(32)	4864(194)	972(280)	716(207)	322(385)	1060(343)	277(179)
C(34)	-1093(30)	3288(27)	-1746(35)	873(246)	1621(386)	377(216)	550(458)	833(380)	1181(506)
C(35)	-1842(32)	2584(23)	-1746(42)	849(276)	6105(619)	1060(296)	282(437)	-280(348)	351(144)
C(36)	-1708(31)	2090(22)	-575(40)	725(254)	276(243)	1070(279)	-112(420)	512(470)	162(388)
C(37)	-830(28)	2450(21)	620(34)	532(221)	866(253)	588(215)	-132(369)	338(346)	462(378)

Molecule II	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{23}$	$2U_{13}$	$2U_{12}$
N(1)	511(4)	9326(3)	2232(5)	1069(44)	497(31)	410(29)	96(47)	674(59)	533(60)
N(2)	5558(1)	8627(1)	2104(1)	675(10)	343(7)	351(8)	56(12)	484(15)	217(14)
N(3)	5695(1)	7974(3)	333(4)	620(31)	430(28)	457(28)	67(47)	346(46)	346(46)
N(4)	5201(1)	8026(1)	445(1)	437(8)	336(7)	288(7)	12(11)	248(12)	248(12)
N(5)	4535(4)	8680(2)	4096(4)	6C4(3C)	382(25)	431(27)	90(41)	466(46)	387(44)
C(6)	4636(5)	9251(3)	3137(5)	699(49)	428(35)	-735(56)	508(37)	259(62)	359(62)
C(7)	4133(6)	9086(4)	3048(5)	992(57)	514(41)	725(48)	158(71)	591(85)	704(79)
C(8)	6878(5)	9092(4)	1862(6)	762(44)	485(35)	419(33)	-163(54)	571(61)	81(62)
C(9)	7093(8)	9822(4)	1217(9)	1333(76)	603(49)	982(66)	291(93)	1124(118)	142(96)
C(10)	8118(8)	10137(5)	1017(10)	1603(87)	927(65)	1317(83)	-156(118)	1966(148)	-991(120)
C(11)	8904(7)	9731(6)	1485(9)	902(62)	1588(92)	1083(72)	-1367(132)	1188(114)	-1093(117)
C(12)	8682(6)	9017(5)	2135(8)	748(54)	1235(73)	830(59)	-713(104)	795(94)	-461(98)
C(13)	767(6)	8691(4)	2324(7)	608(64)	828(61)	429(44)	-21(75)	64(72)	81(75)
C(14)	4597(6)	8161(4)	575(7)	729(52)	463(42)	313(37)	73(62)	453(71)	400(75)
C(15)	4493(7)	8620(6)	-641(8)	760(58)	917(74)	525(52)	218(99)	650(92)	411(105)
C(16)	3886(8)	8249(5)	-1835(9)	856(67)	1432(103)	592(62)	-415(126)	338(105)	850(105)
C(17)	2931(8)	7486(6)	-1750(11)	7C7(67)	909(78)	608(76)	73(122)	-21(110)	188(114)
C(18)	3060(8)	7090(6)	-580(10)	798(65)	809(71)	714(64)	-197(107)	326(102)	-411(106)
C(19)	3950(8)	7422(5)	608(9)	931(65)	523(54)	567(55)	108(87)	383(96)	276(94)
C(20)	4278(4)	7075(3)	4668(5)	447(30)	338(28)	250(25)	-28(42)	105(43)	231(46)
C(21)	3477(5)	7013(3)	5222(6)	527(36)	394(32)	623(40)	-63(56)	502(62)	133(53)
C(22)	2777(5)	6271(4)	5430(7)	649(43)	501(36)	742(47)	113(60)	655(73)	153(64)
C(23)	2858(5)	5605(4)	5127(7)	696(44)	469(38)	699(46)	107(66)	451(75)	173(65)
C(24)	3684(6)	5658(3)	4594(7)	767(46)	402(35)	709(46)	-79(62)	529(74)	221(64)
C(25)	4373(5)	6398(3)	4359(6)	662(40)	452(31)	523(37)	191(56)	365(62)	446(60)
C(26)	6290(4)	8235(3)	4024(5)	485(32)	347(28)	392(30)	24(46)	244(50)	392(49)
C(27)	7405(5)	8489(3)	6074(6)	585(39)	492(35)	557(38)	-151(57)	386(62)	178(60)
C(28)	8274(5)	8702(4)	7265(7)	514(40)	873(54)	779(50)	-486(82)	339(72)	265(73)
C(29)	8061(6)	8436(4)	8420(7)	614(46)	872(61)	658(61)	-586(79)	55(70)	463(77)
C(30)	6990(6)	8377(4)	8393(6)	868(52)	923(54)	457(38)	-296(73)	324(72)	729(85)
C(31)	6104(5)	8181(4)	7185(6)	645(40)	658(41)	427(35)	-14(59)	411(61)	523(65)
C(32)	4621(23)	8173(17)	573(29)	400(173)	436(167)	472(175)	56(27)	345(134)	345(134)
C(33)	3890(31)	8500(22)	-360(38)	1360(267)	941(256)	1165(260)	-1085(411)	-646(410)	1530(432)
C(34)	3238(28)	8235(25)	-1669(33)	747(217)	1534(343)	699(197)	-496(414)	-205(326)	1463(452)
C(35)	3075(30)	7400(24)	-1702(32)	822(255)	1260(288)	345(186)	-1085(388)	-43(358)	0(400)
C(36)	3930(32)	7130(18)	-951(35)	1197(287)	421(171)	518(219)	-105(368)	-85(388)	443(359)
C(37)	4740(31)	7510(20)	203(34)	1219(286)	597(221)	553(215)	30(349)	-272(387)	1098(438)

that the two non-equivalent molecules are in fact related by an approximate translation of  $\frac{1}{2}, \frac{1}{2}, 0$ . Several plausible partial structures were tried before all the non-hydrogen atoms were located. For the structure accepted, the  $R$  index for the observed data was 0.35.

After four cycles of isotropic block-diagonal least-squares the  $R$  index was reduced to 0.14, and after two more cycles with anisotropic thermal parameters, it was reduced to 0.12. About 1200 reflexions with low net counts were remeasured for better statistics, and

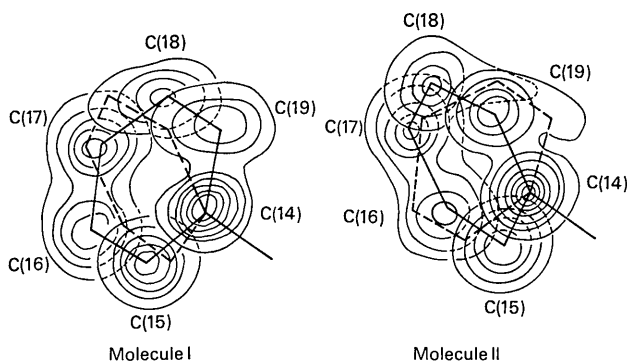


Fig. 1. Electron density of the disordered phenyl ring in molecules I and II. The contours start at  $1 \text{ e.}\text{\AA}^{-3}$ , then at intervals of  $1 \text{ e.}\text{\AA}^{-3}$ . The rings drawn in solid lines are for the 0.8 occupancy, and those in broken lines are for the 0.2 occupancy.

Table 4. Fractional coordinates ( $\times 10^3$ ) of the H atoms as deduced from the final difference map

	x	y	z		x	y	z
H(9)	176	502	80	H(9)	650	1012	80
H(10)	366	558	61	H(10)	853	1063	77
H(11)	562	489	142	H(11)	967	995	138
H(12)	449	366	262	H(12)	930	870	258
H(13)	263	311	277	H(13)	748	810	268
H(15)	-48	430	-61	H(15)	489	927	-52
H(16)	-181	369	-256	H(16)	340	872	-268
H(17)	-225	245	-258	H(17)	237	729	-271
H(18)	-106	165	-83	H(18)	260	648	-138
H(19)	26	224	77	H(19)	390	695	138
H(21)	-140	257	548	H(21)	343	751	548
H(22)	-280	134	548	H(22)	210	628	570
H(23)	-250	22	520	H(23)	231	514	520
H(24)	-119	24	416	H(24)	271	517	434
H(25)	15	142	406	H(25)	496	640	419
H(27)	272	349	524	H(27)	765	850	541
H(28)	420	359	739	H(28)	903	886	723
H(29)	377	374	924	H(29)	870	874	920
H(30)	188	340	914	H(30)	684	836	920
H(31)	47	317	705	H(31)	532	810	702
H(7,1)	-10	536	274	H(7,1)	341	969	262
H(7,2)	-73	493	370	H(7,2)	457	1034	274
H(7,3)	-99	501	203	H(7,3)	440	1003	385









Owing to the disorder of atoms C(14) to C(19) and the difficulty in deriving the exact atomic positions in such cases, the C-C bond lengths of this phenyl ring show rather high discrepancies. In the other phenyl rings, the C-C bond lengths are in the range 1.346–1.406 Å, and their weighted mean is 1.379 ( $\sigma_{w,m}=0.002$ ) Å. At least part of the difference between this mean value and the normal value of 1.394 Å must be due to the omission of the corrections for thermal vibration. Further discussion of the bond lengths and angles and their relation to other compounds will be given in part II.

#### Planarity of the rings

The unweighted mean planes of the rings calculated by the method of Blow (1960), and referred to the orthogonal set of axes,  $X'$  along  $a$ ,  $Y'$  in the  $ab$  plane,

and  $Z'$  along  $c^*$ , where  $X'$ ,  $Y'$  and  $Z'$  are in Å, are listed in Table 8. The  $\chi^2$  values for the mean planes of the two diphosphatriazine rings,  $CP_2N_3$ , are extremely high, indicating that these rings are definitely non-planar. They adopt a skewed boat conformation with the opposite bonds N(1)–P(2) and N(5)–P(4) being skew instead of parallel as in the case of a regular boat form. This results in approximate twofold symmetry for the ring about the N(3)···C(6) diagonal. The deviations of the ring atoms from their mean planes are shown in the projections in Fig. 4, and are in the range  $-0.075$  to  $+0.100$  Å. In each molecule, atoms N(1), N(5), C(6) and C(7) are coplanar (to within  $\pm 0.003$  Å), but the P atoms are about  $+0.18$  and  $-0.20$  Å off that plane. The  $\chi^2$  values of the phenyl rings indicate that they are planar except for the disordered ring, but in view of its disorder it is more

Table 7. Range and weighted mean values of chemically equivalent bonds and angles

	No.	Range	Weighted	$\sigma_{w,m}$	$\chi^2$	P limits
P–N*	4	1.589–1.604 Å	1.597 Å	0.003 Å	7.96	0.05–0.01
P–N†	4	1.616–1.627	1.620	0.003	1.91	0.95–0.50
C–N	4	1.334–1.338	1.335	0.004	0.13	0.99–0.95
P–C	8	1.790–1.816	1.801	0.002	13.36	0.10–0.05
C–CH <sub>3</sub>	2	1.506–1.510	1.508	0.007	0.07	0.95–0.50
P–N–P	2	115.4–115.5°	115.4°	0.2°	0.11	0.95–0.50
N–P–N	4	116.1–117.0	116.5	0.2	4.67	0.20–0.10
P–N–C	4	119.4–120.3	119.9	0.2	3.68	0.30–0.20
N–C–N	2	129.0–129.2	129.1	0.4	0.06	0.95–0.50
C–P–C	4	104.1–106.6	105.4	0.2	37.02	$\angle 0.01$
N–C–CH <sub>3</sub>	4	114.8–116.0	115.4	0.3	3.16	0.50–0.30

\* In P–N–P segments.

† In P–N–C segments.

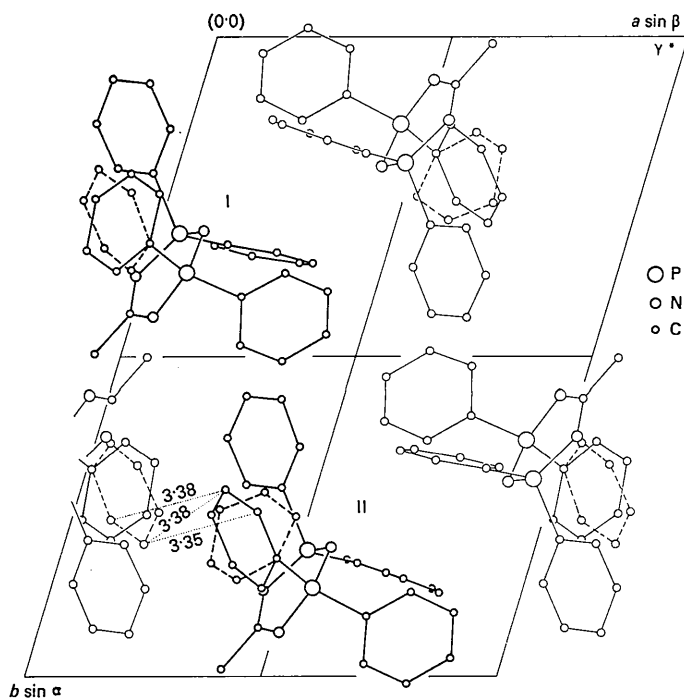


Fig. 2. A projection of the unit-cell contents along the  $c$  axis.





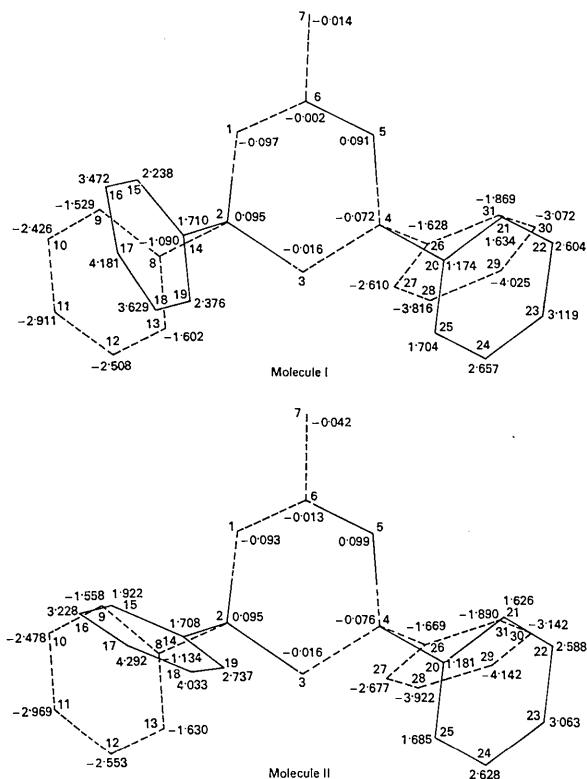


Fig. 4. Projections of the two molecules onto the mean planes of the  $CP_2N_3$  rings, and deviations of the atoms from them.

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## X-ray Crystallography of the Diposphatriazines. II. The Crystal Structure of 6-Dimethylamino-2,2,4,4-tetraphenyldisphospha-1,3,5-triazine

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The crystal structure of 6-dimethylamino-2,2,4,4-tetraphenyldisphospha-1,3,5-triazine has been determined from Patterson, Fourier and difference syntheses, and has been refined by least-squares to an  $R$  index of 0.049 for 2407 observed reflexions. The unit cell is monoclinic,  $C2/c$ , with constants  $a = 16.452$ ,  $b = 9.415$ ,  $c = 17.028$  Å,  $\beta = 109.21^\circ$ , and has one half molecule per asymmetric unit. The diposphatriazine ring is non-planar, has a skewed boat conformation and its atoms are within  $\pm 0.024$  Å of the mean plane. The bond lengths are: P-N in the P-N-P segment, 1.597; P-N in the P-N-C segment, 1.608; P-C, 1.802; N-C in ring, 1.336; C-N(CH<sub>3</sub>)<sub>2</sub>, 1.363 Å. The valency angles are: N-P-N, 117.1; P-N-P, 115.4; P-N-C, 120.9; N-C-N in ring, 128.6°; C-P-C, 104.1; N-C-N(CH<sub>3</sub>)<sub>2</sub>, 115.7°. The dimethylamino group is planar and lies in the mean plane of the diposphatriazine ring.

### Introduction

The crystal structure of 6-methyl-2,2,4,4-tetraphenyldisphospha-1,3,5-triazine,  $C_{26}H_{23}N_3P_2$ , has been reported by Ahmed & Pollard (1971) as part I of this series. The

The crystals were kindly supplied by Dr V. A. Schmidpeter of the University of Munich. The calculations were carried out on an IBM 360 system with programs by Ahmed, Hall, Pippy & Huber (1966). Grateful acknowledgement is made to those mentioned, and to Mrs M.E. Pippy for the preparation of computer input data.

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present paper describes the structure of 6-dimethylamino-2,2,4,4-tetraphenyldisphospha-1,3,5-triazine,  $C_{27}H_{26}N_4P_2$ , given as formula (II) in part I. In the 6-methyl compound, the diposphatriazine ring may be regarded as normal since very little influence of the methyl substituent on the ring structure is to be expected, but this is not the case in the 6-dimethylamino

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