

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

*Acta Cryst.* (1971). B27, 172

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

By D. R. POLLARD\* AND F. R. AHMED

*Biochemistry Laboratory, National Research Council of Canada, Ottawa 7, Canada*

(Received 6 March 1970)

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 diphosphatriazine 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 diphosphatriazine 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.

### References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *World List of Crystallographic Computer Programs*. 2nd. ed. Appendix p. 52.
- AHMED, F. R., SINGH, P. & BARNES, W. H. (1969). *Acta Cryst.* B25, 316.
- BARNES, W. H. & AHMED, F. R. (1968). *Z. Kristallogr.* 127, 34.
- BLOW, D. M. (1960). *Acta Cryst.* 13, 168.
- BUERGER, M. J. (1957). *Z. Kristallogr.* 109, 42.
- DAVIS, R. J. (1961). *Miner. Mag.* 32, 817.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040.
- KARLE, I. L., DRAGONETTE, K. S. & BRENNER, S. A. (1965). *Acta Cryst.* 19, 713.
- LANCASTER, J. E. & STOICHEFF, B. P. (1956). *Canad. J. Phys.* 34, 1016.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- POLLARD, D. R. & AHMED, F. R. (1971). *Acta Cryst.* B27, 172.
- SCHMIDPETER, V. A. & EBELING, J. (1967). *Angew. Chem.* 79, 100.

\* National Research Council Postdoctorate Fellow.

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 diphosphatriazine 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

compound. The influence of the  $N(CH_3)_2$  group on the  $CP_2N_3$  ring can therefore be examined by comparing the results of parts I and II.

The diphosphatriazine ring,  $CP_2N_3$ , differs from the cyclotriphosphazene ring,  $P_3N_3$ , only in that one P atom has been replaced by a C atom, and thus both types of compound could be expected to show some similar properties. Some significant changes in the bond lengths and angles, however, should be observed. The inclusion of a C atom instead of a P atom in the ring alters the  $\pi$  bonding system to give more  $p\pi$  and less  $d\pi$  character and this could well influence the  $d\pi-p\pi$  bonding at the P-N-P segment.

### Crystal data

Crystals of 6-dimethylamino-2,2,4,4-tetraphenyldiphospha-1,3,5-triazine,  $C_{27}H_{26}N_4P_2$ , are monoclinic with the following unit-cell data:

$a$ 16.452 (0.004) Å	F.W. 468.46,
$b$ 9.415 (0.003)	$D_m$ 1.248 g.cm <sup>-3</sup> ,
$c$ 17.028 (0.004)	$D_x$ 1.249 g.cm <sup>-3</sup>
$\beta$ 109.21 (0.04)°	$\mu(Cu)$ 17.36 cm <sup>-1</sup> ,
$U$ 2490.7 Å <sup>3</sup> ,	$\mu(Mo)$ 2.01 cm <sup>-1</sup>
$Z$ 4	$F(000)$ 984

The density was measured by flotation in a mixture of carbon tetrachloride and toluene. Possible space groups are  $Cc$  and  $C2/c$  ( $hkl$  absent when  $h+k=2n+1$ , and  $h0l$  absent when  $l=2n+1$ ).  $C2/c$  is shown to be the probable space group with one half molecule per asymmetric unit (molecular symmetry, diad).

### Data collection

Preliminary examination of the crystals and determination of the space group were carried out by precession methods. The unit-cell constants and the reflexion intensities were measured on a Picker automatic 4-circle diffractometer with a scintillation counter. Cell dimensions were determined from  $2\theta$  values of high-order axial reflexions using a 1° take-off angle, narrow slit and Cu radiation ( $\lambda$ ;  $K\alpha_1=1.54050$ ,  $K\alpha_2=1.54434$  Å). Mo radiation (Nb filter) was adopted for the collection of the intensity data. The crystal was mounted with the  $b$  axis along the direction of the fibre. Integrated intensities were measured by the moving-crystal moving-counter method (Furnas, 1957) over scans of 1.6° for reflexions within  $2\theta=35^\circ$ , and 2.0° for high order reflexions up to  $2\theta=55^\circ$ . The background was measured at the beginning and end of each scan on the Laue streak through the reflexion. The intensity of the 004 reflexion was monitored at frequent intervals throughout the data collection and used for scaling the intensities. The strong reflexions were measured with a low current setting. Of the 2847 non equivalent lattice sites investigated (excluding those prohibited by the space group) 2407, representing 84% of the Cu sphere, were observed above an arbitrary

threshold. The  $1/Lp$  corrections were applied to the net counts (total - background) but absorption corrections were not considered necessary ( $\mu R \approx 0.04$ ).

### Structure determination

A Wilson plot was prepared using the  $F_o^2$  data to determine the initial scale  $K$  and overall temperature factor  $B$ . In order to distinguish statistically between the space groups  $Cc$  and  $C2/c$ , the distribution statistics of the  $E$  amplitudes were evaluated and were found to be consistently closer to the theoretical values of a centrosymmetric structure calculated by Karle, Dragonette & Brenner (1965) as shown in Table 1. The structure was thus tentatively assumed to have space group  $C2/c$  with each molecule possessing exact twofold symmetry.

Table 1. Statistics of the normalized structure amplitudes

	Observed	Theoretical	
	$C_{27}H_{26}N_4P_2$	$C2/c$	$Cc$
$\langle  E  \rangle$	0.822	0.798	0.886
$\langle  E ^2 \rangle$	1.009	1.000	1.000
$\langle  E ^2 - 1 \rangle$	0.938	0.968	0.736
$\langle  E  \rangle_3$	0.18%	0.3%	0.01%
$\langle  E  \rangle_2$	3.76	5.0	1.8
$\langle  E  \rangle_1$	32.8	32.0	37.0

Two possible orientations of the diphosphatriazine ring,  $CP_2N_3$ , were deduced from a Patterson function, and the corresponding  $R$  values were 0.54 and 0.48. A three-dimensional electron density map, based on 78% of the structure factors with the lower  $R$  value, revealed the remainder of the molecule. The  $R$  index of this initial structure was 0.29. The structure was refined by successive cycles of block-diagonal least-squares employing observed reflexions and evaluating matrices of  $4 \times 4$  or  $9 \times 9$  per atom. Four cycles with isotropic thermal parameters and weights  $w=1/\{1+[(|F_o|-50)/45]^4\}$  reduced  $R$  to 0.13. Two further cycles with anisotropic thermal parameters gave an  $R$  index of 0.07. A difference electron-density distribution was then computed and the positions of all hydrogen atoms were deduced from it (peak values ranging from 0.30 to 0.52 e.Å<sup>-3</sup>). An additional five cycles of least-squares, utilizing the same weighting scheme, with the thermal parameters of the heavier atoms anisotropic and those of the hydrogen atoms isotropic gave an  $R$  value of 0.049. In the final cycle the average non-hydrogen atom parameter shift was  $0.1\sigma$  and  $0.05\sigma$  for positional and thermal parameters respectively. The final value of  $[\sum w\Delta^2/(m-n)]^{1/2}$  was 1.06. The atomic scattering factor curves used throughout the analysis were those of Hanson, Herman, Lea & Skillman (1964).

### Results

A perspective view of the molecule showing the numbering scheme adopted for the analysis is given in Fig.

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

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{23}$	$2U_{13}$	$2U_{12}$
N(1)	108(1)	4781(2)	6834(1)	660(11)	361(9)	493(5)	58(16)	462(18)	-31(18)
P(2)	152(1)	3080(1)	6768(1)	483(2)	339(2)	356(3)	3(5)	296(4)	-4(5)
N(3)	0	2175(2)	7500	765(18)	332(13)	415(13)	0	476(25)	0
C(6)	0	5396(3)	7500	357(13)	328(14)	512(16)	0	209(24)	0
N(7)	0	6844(3)	7500	517(15)	318(12)	689(17)	0	361(25)	0
C(8)	-608(1)	2561(2)	5782(1)	459(11)	442(11)	413(10)	3(18)	310(18)	-31(19)
C(9)	-1165(2)	3532(3)	5276(1)	802(18)	521(14)	523(13)	-3(22)	123(25)	39(26)
C(10)	-1762(2)	3098(3)	4523(2)	901(21)	714(18)	582(16)	113(29)	-114(28)	81(33)
C(11)	-1793(2)	1721(3)	4277(2)	703(17)	763(19)	554(14)	-179(28)	90(25)	-225(30)
C(12)	-1249(2)	748(3)	4774(2)	865(21)	570(17)	769(18)	-383(28)	32(32)	-104(29)
C(13)	-655(2)	1172(3)	5522(2)	747(18)	499(14)	693(17)	-139(26)	-81(28)	120(27)
C(14)	1183(1)	2602(2)	6688(1)	468(11)	471(12)	456(12)	-235(19)	234(19)	-43(19)
C(15)	1458(2)	3241(3)	6083(2)	688(16)	601(16)	836(18)	-479(28)	818(29)	-50(27)
C(16)	2256(2)	2910(3)	6024(2)	768(20)	868(22)	1144(25)	-499(38)	1144(38)	-324(34)
C(17)	2774(2)	1936(4)	6558(2)	494(15)	1147(26)	1098(24)	-934(43)	415(32)	-48(33)
C(18)	2512(2)	1299(4)	7151(2)	565(16)	1136(25)	718(18)	-472(35)	-158(28)	451(33)
C(19)	1716(2)	1625(3)	7224(1)	602(15)	780(18)	496(13)	-152(25)	87(23)	266(27)
C(20)	132(2)	7641(3)	6828(2)	753(17)	423(13)	578(21)	415(28)	557(32)	-71(26)

1, where atom numbering has been chosen to correspond to the system used for 6-methyl-2,2,4,4-tetra-phenyldiphospha-1,3,5-triazine (part I of this series). Coordinates and anisotropic thermal parameters of the non-hydrogen atoms are given in Table 2 together with the standard deviations as obtained from the least-squares refinement. The positional and isotropic thermal parameters of the hydrogen atoms are given in Table 3 with each hydrogen atom having the same number as the C atom to which it is attached. The observed structure amplitudes and calculated structure factors based on the parameters in Tables 2 and 3 are listed in Table 4, and the agreement between  $|F_o|$  and  $|F_c|$  is summarized in Table 5. The bond lengths and bond angles, with their e.s.d.'s, are presented in Fig. 2. These results are based on the refined coordinates and do not include the corrections for thermal vibration. The C-H bond lengths have a mean value of 0.97 ( $\sigma=0.04$ )  $\text{\AA}$ .

Table 3. Fractional coordinates ( $\times 10^3$ ) and isotropic temperature factors ( $\text{\AA}^2$ ) of the hydrogen atoms

	x	y	z	B
H(9)	-113(2)	451(3)	547(2)	3.9(0.6)
H(10)	-215(2)	384(3)	413(2)	5.9(0.8)
H(11)	-222(2)	139(3)	372(2)	3.5(0.6)
H(12)	-128(2)	-21(3)	462(2)	4.5(0.7)
H(13)	-26(2)	52(3)	585(2)	4.4(0.7)
H(15)	106(2)	393(3)	570(2)	3.8(0.6)
H(16)	244(2)	340(3)	561(2)	6.1(0.9)
H(17)	333(2)	167(3)	648(2)	6.3(0.9)
H(18)	287(2)	59(3)	753(2)	5.1(0.8)
H(19)	150(2)	121(3)	764(2)	3.5(0.6)
H(20,1)	30(3)	700(5)	647(3)	10.2(1.2)
H(20,2)	60(2)	822(4)	703(2)	7.8(1.0)
H(20,3)	-34(3)	809(4)	654(2)	8.3(1.0)

## Discussion

### Bond lengths and angles

On account of the crystallographic diad axis through the molecule there are only three independent bonds and four independent angles in the diphosphatriazine

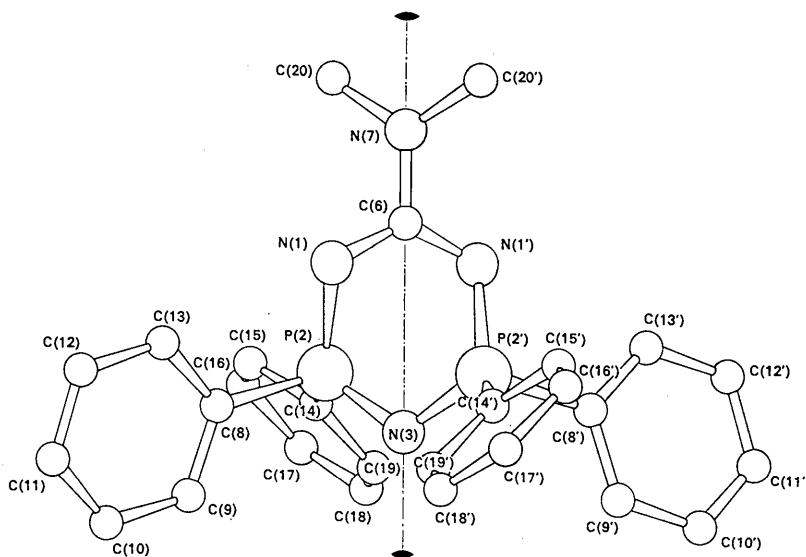


Fig. 1. Perspective view of the molecule.



Table 4 (cont.)

k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC	k	FO	FC										
4	97	-91	10	200	-186	1	83	-27	6	136	140	9	47	-43	1	326	-328	2	271	-275	6	88	-94	1	266	305	4	43	-7	1	266	305	4	43	-7	1	266	305	4	43	-7										
4	291	301	8	189	-186	7	41	-38	2	203	187	3	282	292	3	81	-99	4	133	165	6	33	-10	3	21	34	2	45	34	2	45	34	2	45	34	2	45	34	2	45	34	2	45	34							
8	144	153	2	77	82	11	56	14	11	113	123	11	94	-10	2	183	191	10	-10	-15	2	126	-135	5	171	174	5	31	-42	2	110	-108	4	96	-94	3	27	10	2	102	100	2	97	110							
8	152	152	2	77	82	11	56	14	11	113	123	11	94	-10	2	183	191	10	-10	-15	2	126	-135	5	171	174	5	31	-42	2	110	-108	4	96	-94	3	27	10	2	102	100	2	97	110							
6	51	88	2	80	47	1	36	-45	4	112	114	4	37	-35	5	67	-67	1	309	-13	0	145	161	0	74	-68	1	74	-68	0	899	-84	2	6	-80	0	899	-84	2	6	-80	0	899	-84	2	6	-80				
4	348	356	3	265	-320	3	295	373	6	105	109	6	105	-139	5	57	-54	4	140	-133	6	85	-28	2	205	212	2	281	-377	2	281	-377	2	281	-377	2	281	-377	2	281	-377	2	281	-377	2	281	-377				
6	73	72	9	45	104	9	142	-144	8	104	104	8	104	-112	10	83	-97	0	40	-38	0	184	-158	0	107	-105	6	110	-112	6	110	-112	6	110	-112	6	110	-112	6	110	-112	6	110	-112	6	110	-112	6	110	-112	
10	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31			
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31
8	135	-132	8	112	-112	2	291	-287	0	231	-223	1	207	227	1	242	-246	10	14	5	4	189	-139	1	111	104	8	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31	2	360	-31

particular is indicative of considerable double-bond character. The Me-N-Me angle of 117.3 (0.2)° is comparable with angles of 116 (1.0)° found in other approximately planar dimethylamino groups (Bullen, 1962). In the phenyl rings the mean C-C bond is 1.378 Å which is shorter than the value of 1.394 Å (Sutton, 1965) for aromatic C-C bonds. This difference can probably be attributed to the omission of thermal vibration corrections in the analysis. All intermolecular distances are greater than the sum of the corresponding atomic van der Waals radii (Pauling, 1960); the

shortest distances are: C...N, 3.483; C...C, 3.521; N...H, 2.728; C...H, 3.137; and H...H, 2.515 Å. None of the P atoms is less than 4.0 Å from any atom on a neighbouring molecule.

### Ring planarity

The equations for the unweighted mean planes calculated by the method of Blow (1960), and referred to orthogonal axes, X' along **a**, Y' along **b**, and Z' along **c\*** (where X', Y' and Z' are in Å) are as follows:

Table 4 (cont.)

K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC	K	FC	FC																																										
** -13.1	1.46	-76	** -14.1	2.80	80	** -15.1	0.475	449	** -16.1	2.761	260	** -17.1	2.180	-107	** -18.1	0.95	-92	** -19.1	4.153	127	** -20.1	1.432	-137	** -21.1	3.444	-23	** -22.1	1.1	1	** -23.1	3.88	36	** -24.1	3.39	50	** -25.1	2.88	56	** -26.1	2.37	62	** -27.1	1.86	67	** -28.1	1.35	71	** -29.1	0.84	74	** -30.1	0.33	76	** -31.1	0.1	77	** -32.1	0.1	77	** -33.1	0.1	77	** -34.1	0.1	77	** -35.1	0.1	77	** -36.1	0.1	77	** -37.1	0.1	77	** -38.1	0.1	77	** -39.1	0.1	77	** -40.1	0.1	77

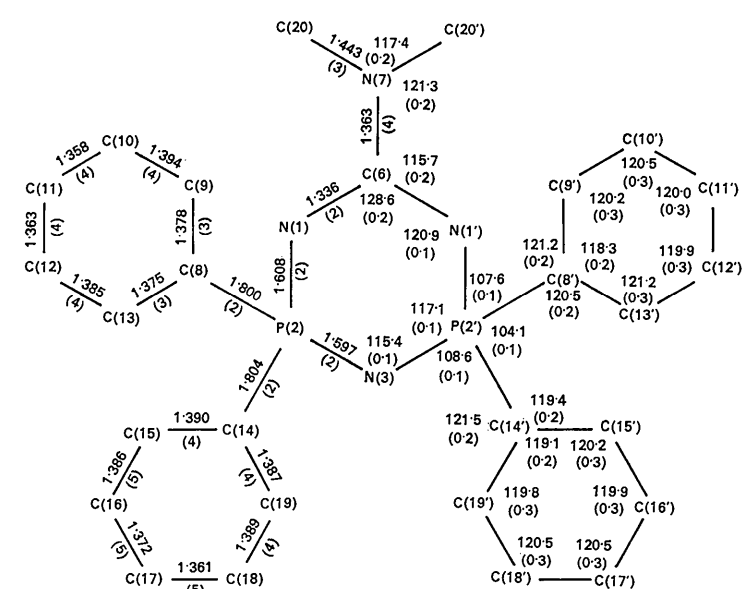
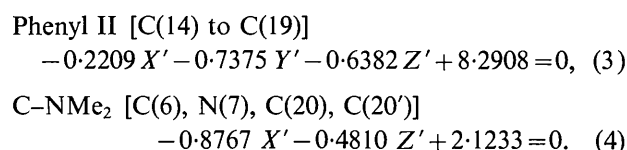
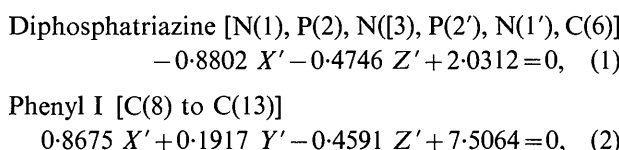


Fig. 2. Bond lengths (Å) and valency angles (°); e.s.d.'s in parentheses. E.s.d.'s of bond lengths are × 10<sup>3</sup>.

The corresponding  $\chi^2$  values are 2754, 5.9, 3.7 and 0 respectively, and thus only the atoms of the diphosphatriazine ring deviate significantly from planarity while the six C atoms of each phenyl ring are coplanar within the accuracy of the analysis.

A projection of the molecule (excluding hydrogen atoms) along the normal to plane (1) with the perpendicular distances of the atoms from this plane is shown in Fig. 3. N(1) is at 0.024 Å from the mean plane and P(2) is at -0.021 Å on the opposite side. This arrangement gives a skewed boat conformation for the diphosphatriazine ring and can best be considered as a rotation of the P(2)-N(3)-P(2') segment around the twofold axis away from the N(1)-C(6)-N(1') segment by about 2.0°. The dimethylamino group lies almost in the mean plane of the diphosphatriazine ring with C(20) at a distance of only 0.009 Å from it. This atom, C(20), is considerably further from the plane of the N(1)-C(6)-N(1') segment where it is off the plane by 0.034 Å. The conformation of the dimethylamino group thus adopted indicates strong  $\pi$ -bond character of the C(6)-N(7) bond resulting from the near alignment and consequent overlap of the appropriate orbitals. It is

of interest to note that of the methyl hydrogen atoms H(20,1) is only 0.15 Å away from the mean plane of the diphosphatriazine ring and at a very short distance of 2.24 (0.04) Å from N(1), whereas the H atoms of the phenyl rings are no closer than 2.55 (0.03) Å from the N atoms of the CP<sub>2</sub>N<sub>3</sub> ring [Pauling (1960) gives the corresponding sum of the van der Waals radii as 2.7 Å]. Thus N(1) and H(20,1) appear to adopt some form of preferential alignment. The dihedral angles between the diphosphatriazine ring and phenyl groups I and II are 56.9 and 60.2°, and that between the two independent phenyl rings is 87.7°.

#### Residual electron density

The final difference synthesis, computed at  $R=0.05$  and with all atoms removed, showed residual electron density within  $\pm 0.35 \text{ e.}\text{Å}^{-3}$  near atomic sites and was almost featureless elsewhere. The section through the mean plane of the diphosphatriazine ring and a second section 0.7 Å from the ring are shown in Fig. 4. Some negative regions are associated with the P atoms and most of the maxima occur approximately midway between atomic sites. The peak heights are 0.32 e.Å<sup>-3</sup>

Table 5. Agreement summary

2407 observed reflexions ( $2.1 \leq  F_o  \leq 316.7$ )			
$R=0.049$			
Category	Limits		Number
1	$ \Delta F  \leq 1.0 F_{th} $ , or $ \Delta F / F_o  \leq 0.10$		2377
2	$1.0 F_{th}  <  \Delta F  \leq 2.0 F_{th} $ , or $0.10 <  \Delta F / F_o  \leq 0.15$		28
3	$2.0 F_{th}  <  \Delta F  \leq 3.0 F_{th} $ , or $0.15 <  \Delta F / F_o  \leq 0.20$		2
440 unobserved reflexions ( $ F_{cmax}  = 6.28$ )			
1	$ F_c  \leq 1.0 F_{th} $		399
2	$1.0 F_{th}  <  F_c  \leq 1.5 F_{th} $		38
3	$1.5 F_{th}  <  F_c  \leq 2.0 F_{th} $		3

$|F_{th}| = \text{threshold amplitude} = 2.03 \text{ to } 4.44.$

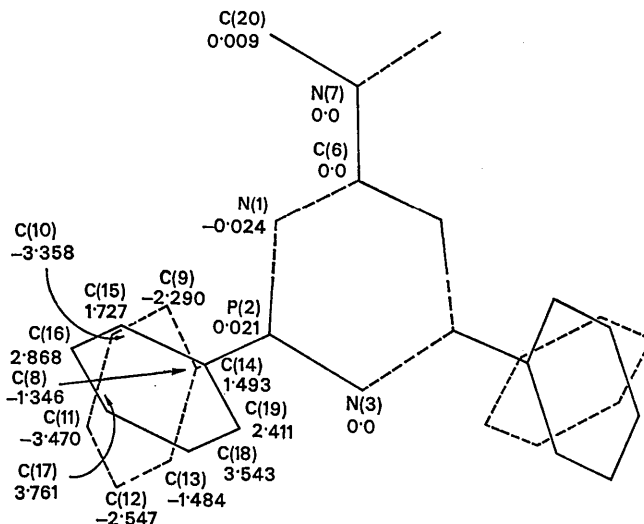


Fig. 3. Projection of the molecule onto the mean plane of the CP<sub>2</sub>N<sub>3</sub> ring, and distances (Å) of the atoms from it.

on P(2)–N(1),  $0.13 \text{ e.}\text{\AA}^{-3}$  on N(1)–C(6),  $0.15 \text{ e.}\text{\AA}^{-3}$  on P(2)–N(3) and between  $0.20$  and  $0.35 \text{ e.}\text{\AA}^{-3}$  on P(2)–C(8) and P(2)–C(14). The residual peak on the P(2)–N(1) bond occurs about  $0.7 \text{ \AA}$  from N(1); the residual distribution at the N atoms may be indicative of delocalization of the lone pair of electrons of each of these atoms (Craig & Paddock, 1962).

#### Comparison of the 6-methyl and 6-dimethylamino compounds

For this discussion the 6-methyl compound, part I of this series, will be referred to as phos. I and the 6-dimethylamino compound as phos. II, and, as described in the *Introduction*, the diphosphatriazine ring

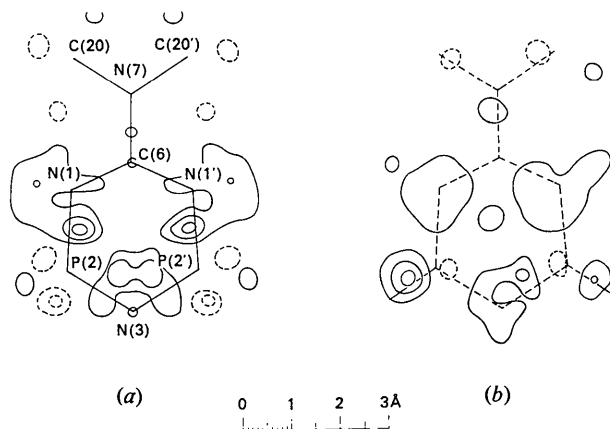


Fig. 4. Residual electron-density distribution (a) in the plane of the  $\text{CP}_2\text{N}_3$  ring and (b)  $0.7 \text{ \AA}$  away from it; first contour at  $\pm 0.1 \text{ e.}\text{\AA}^{-3}$ , then at intervals of  $\pm 0.1 \text{ e.}\text{\AA}^{-3}$ .

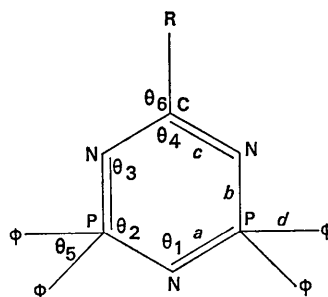
in phos. I should be considered as the normal case. For convenience the mean bond lengths and angles of phos. I and phos. II, and the probability of their equivalence, are summarized in Table 6. The only significant changes in the bond lengths and internal angles of the diphosphatriazine ring, resulting from the different substituents  $R$ , occur in the P–N–C segments where in phos. II the P–N bond shows a decrease of  $0.012 \text{ \AA}$  and the P–N–C angle an increase of  $1.0^\circ$  from those in phos. I. The dimensions of the P–N–P segment are identical in the two structures: P–N =  $1.597 \text{ \AA}$  and angle P–N–P =  $115.4^\circ$ . Similar bond lengths but different angles were found in hexaphenyltriposponitrile reported by Ahmed, Singh & Barnes (1969): P–N =  $1.597 \text{ \AA}$ , P–N–P =  $122.1^\circ$ . Likewise, the N–C–N segments in phos. I and phos. II are nearly identical: C–N =  $1.336 \text{ \AA}$  and N–C–N =  $128.9^\circ$ , while the corresponding values given by Lancaster & Stoicheff (1956) for s-triazine are  $1.338 \text{ \AA}$  and  $127^\circ$ .

As shown in Fig. 5, the diphosphatriazine rings of phos. I and phos. II adopt similar skewed boat conformations, with that of phos. II much less pronounced than phos. I. The ring atoms are within  $-0.075$  and  $0.100 \text{ \AA}$  from their mean plane in phos. I compared with  $-0.021$  and  $0.024 \text{ \AA}$  in phos. II, and the corresponding dihedral angles between the relevant P–N–P and N–C–N segments are about  $8.5^\circ$  in phos. I and only  $2.0^\circ$  in phos. II. The overall picture is now of two relatively independent segments, P–N–P and N–C–N, which interact to a greater or lesser extent through the P–N bonds joining them depending on the substituent at C(6). In phos. II the dimethylamino group lies in the mean plane of the diphosphatriazine ring and this, together with a shortening of the C–N bond linking

Table 6. Summary of the agreement between similar bonds and angles in the two diphosphatriazine molecules

E.s.d.'s refer to the last significant digits.

Type	6-Methyl	6-Dimethylamino	$t$	$P$ limits
P–N	$1.597 (3) \text{ \AA}$	$1.597 (2) \text{ \AA}$	0	1.0
P–N	$1.620 (3)$	$1.608 (2)$	3.33	< 0.001
C–N	$1.335 (4)$	$1.336 (2)$	0.22	> 0.50
P–C	$1.801 (2)$	$1.802 (2)$	0.35	> 0.50
P–N–P	$115.4 (2)^\circ$	$115.4 (1)^\circ$	0	1.0
N–P–N	$116.5 (2)$	$117.1 (1)$	2.68	0.01–0.001
P–N–C	$119.9 (2)$	$120.9 (1)$	4.47	< 0.001
N–C–N	$129.1 (4)$	$128.6 (2)$	1.12	0.5–0.1
C–P–C	$105.4 (2)$	$104.1 (1)$	5.81	< 0.001
N–C–R	$115.4 (3)$	$115.7 (2)$	0.83	0.5–0.1





them, indicates considerable  $\pi$ -orbital overlap, whereas the  $sp^3$  hybridized state of the methyl group in phos. I forbids this. It appears then that the ring geometry is determined by the degree with which the substituent group can interact to give  $\pi$ -orbital overlap at C(6) with corresponding enhanced delocalization of the  $\pi$ -electron systems and associated greater ring planarity. The relevant orbitals of the P and N atoms will then overlap more efficiently in phos. II leading to increased type (b) P-N bond strength and shorter bond distance than in phos. I (1.620 Å in phos. I and 1.608 Å in phos. II). The exocyclic C-P-C angle is significantly different in phos. I and phos. II as are the dihedral angles between pairs of phenyl groups on each P atom (69.2–75.6° for phos. I and 87.7° for phos. II); this is most likely caused by weak intramolecular interactions between the N atoms of the diphosphatriazine rings and the nearest H atoms of the phenyl rings. Dihedral angles between the diphosphatriazine rings and attached phenyl groups in phos. I vary from 40.5 to 77.7° and in phos. II are 60.2 and 56.9°. No preferred orientation of phenyl to diphosphatriazine can be found and thus little or no exocyclic  $\pi$ -orbital overlap of the type discussed by Paddock (1964) can be present. The mean P-C bonds of 1.801 and 1.802 Å (for phos. I and phos. II respectively) do however show a decrease from the single P-C bond value of 1.84 Å given by Sutton (1965). This has been noticed in other ring phosphorus compounds and does in fact agree well with the results quoted by Ahmed, Singh & Barnes (1969).

### Conclusions

In both molecules the diphosphatriazine ring has a skewed boat conformation, with the two phosphorus atoms situated on opposite sides of the plane of the N-C-N segment. Substitution of the dimethylamino group in place of the methyl group at C(6) has the effect of reducing the degree of puckering of the diphosphatriazine ring and this is accomplished through small changes in the P-N-C and N-P-N angles. This flattening of the ring is indicative of some gain in its resonance energy, and the gain appears to strengthen the P-N bond in the P-N-C segments as indicated by the slight shortening of its length from 1.620 to 1.608 Å. The substitution, however, has no effect on the geometry of the N-C-N or P-N-P segments. The bonds in these segments maintain the same lengths as in *s*-triazine and hexaphenylphosphazene respectively, but the interbond angles show an increase of 1.8° in N-C-N and a decrease of 2.4° in P-N-P.

Crystals for the present investigation were supplied by Dr V. A. Schmidpeter who also aroused our interest in the problem. The calculations involved in

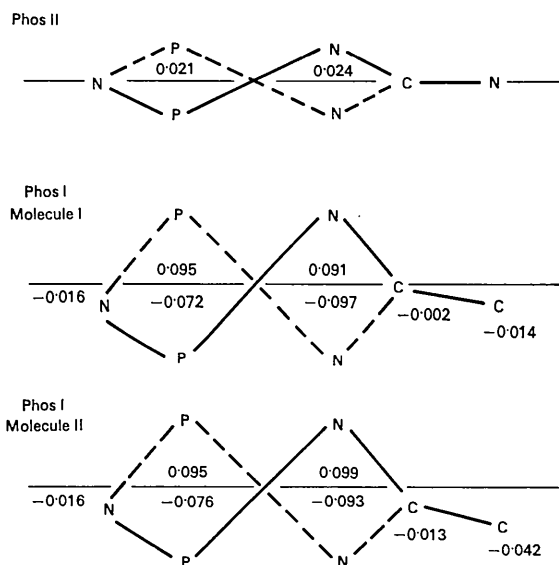


Fig. 5. Schematic side view of the diphosphatriazine rings, with the vertical deviations (Å) exaggerated.

the analysis were carried out on an IBM 360 computer employing the programs of Ahmed, Hall, Pippy & Huber (1966). Grateful acknowledgement is made to Mrs M. E. Pippy for assistance in the data preparation, and to the staff of the N.R.C. Computation Centre for their cooperation.

### References

- AHMED, F. R. & POLLARD, D. R. (1971). *Acta Cryst.* **B27**, 163.  
 AHMED, F. R., SINGH, P. & BARNES, W. H. (1969). *Acta Cryst.* **B25**, 316.  
 AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *World List of Crystallographic Computer Programs*. 2nd ed. Appendix p. 52.  
 BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.  
 BULLEN, G. J. (1962). *J. Chem. Soc.* p. 3193.  
 CRAIG, D. P. & PADDOCK, N. L. (1962). *J. Chem. Soc.* p. 4188.  
 FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.  
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.  
 KARLE, I. L., DRAGONETTE, K. S. & BRENNER, S. A. (1965). *Acta Cryst.* **19**, 713.  
 LANCASTER, J. E. & STOICHEFF, B. P. (1956). *Canad. J. Phys.* **34**, 1016.  
 PADDOCK, N. L. (1964). *Quart. Revs.* **18** (2), 168.  
 PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 93. Ithaca: Cornell Univ. Press.  
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration of Molecules and Ions*. Supplement 1956–1959. London: The Chemical Society.