

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

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.

#### 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- tetraphenyldiphospha-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-tetraphenyldiphospha-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

\* National Research Council Postdoctorate Fellow,

present paper describes the structure of 6-dimethylamino-2,2,4,4-tetraphenyldiphospha-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 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,
<i>b</i> 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>
β 109·21 (0·04)°	$\mu$ (Cu) 17.36 cm <sup>-1</sup> ,
U 2490.7 Å <sup>3</sup> ,	$\mu(Mo) 2.01 \text{ cm}^{-1}$
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 4circle diffractometer with a scintillation counter. Cell dimensions were determined from  $2\theta$  values of highorder 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 movingcrystal moving-counter method (Furnas, 1957) over scans of  $1.6^{\circ}$  for reflexions within  $2\theta = 35^{\circ}$ , and  $2.0^{\circ}$ 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 ( $\mu R \simeq 0.04$ ).

#### 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<sub>2</sub>N<sub>3</sub>, 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 leastsquares employing observed reflexions and evaluating matrices of  $4 \times 4$  or  $9 \times 9$  per atom. Four cycles with isotropic thermal parameters and weights  $w = 1/\{1 + 1\}$  $[(|F_o| - 50)/45]^4$  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-3). An additional five cycles of leastsquares, utilizing the same weighting scheme, with the thermal parameters of the heavier atoms anisotropic and those of the hydrogen atoms isotropic gave an Rvalue of 0.049. In the final cycle the average nonhydrogen atom parameter shift was  $0.1\sigma$  and  $0.05\sigma$  for positional and thermal parameters respectively. The final value of  $\left[\sum w \Delta^2 / (m-n)\right]^{1/2}$  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 (Å<sup>2</sup>) for the expression  $T = exp \left[ -2\pi^2 (U_{11}a^{*2}h^2 + \cdots + 2U_{23}b^*c^*kl + \cdots) \right]$ , and their e.s.d.'s (all values × 10<sup>4</sup>)

	x	У	z	U 11	$U_{22}$	U 33	$2U_{23}$	2U <sub>13</sub>	$2U_{12}$
N(1)	108(1)	4781(2)	6834(1)	660(11)	361(9)	493(5)	58(16)	462(18)	-31(18)
N(3)	0	2175(2)	7500	765(18)	332(13)	415(13)	Ő	476(25)	0
C(6)	Ō	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)	<b>⊣</b> 79(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)	<b>978(21)</b>	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-tetraphenyldiphospha-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 leastsquares 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  $(\sigma = 0.04)$  Å.

Table 3. Fractional coordinates ( $\times 10^3$ ) and isotropic temperature factors (Å<sup>2</sup>) of the hydrogen atoms

	x	у	z	В
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.

ring. The two P–N bonds [P(2)–N(1), 1.608; P(2)–N(3), 1.597 Å] are significantly different when the t distribution is applied (t=3.9, P=0.01%), and this certainly indicates the effects of the different environments at N(1) and N(3). The C(6)–N(1) bond of 1.336 (0.002) Å is almost exactly the value expected in the case of approximate 1.5 double-bond order; a value of 1.338 Å was found for the similar bond in triazine (Lancaster & Stoicheff, 1956). Bond angles in the ring differ considerably from trigonal values (Fig. 2), especially the P-N-P and N-C-N angles (115.4 and 128.6° respectively). This distortion may have been caused by the presence of the two phosphorus atoms modifying the ring geometry. The mean value of the P-C bonds is 1.802 Å and the C-P-C angle is  $104.1^{\circ}$  which is significantly smaller than the tetrahedral angle of  $109.5^{\circ}$ .

In the dimethylamino group, bonds C(6)–N(7) and C(20–N(7) are of lengths 1.363 and 1.443 Å respectively, and are considerably shorter than the normal single bond value of 1.47 Å. The length of C(6)–N(7) in

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

\* Indicates unobserved reflexion and  $|F_{th}|$  in place of  $|F_o|$ .

K FB FC H= 0, L= 0 2 2889 -2979 4 341 306	x F0 FC 2 101 -109 4 137 133	K F0 F 5 446 46 7 214 -21 9 399 - 11 97 10	C K FO FC 5 3 58 -02 7 H= -1, L= 19	K FO FC 0 575 -554 2 209 205 4 557 -568 6 247 255	K FO BG 4 430 -22 H4 -2, La 1	K FO FC	FC FC 1 55 -49 3 40 23 5 400 17 7 47 -27	# FO FC H= -4, L= 7 2 710 -693	K FO FC 6 89 78 H= 4, L= 18	x FD FC 3 414 302 5 169 -172 7 548 553 9 343 -140	R FO FC 1 48 45 H+ -5, L= 18
6 480 502 8 315 -314 10 134 126 12 444 -12 H= 0, L= 1	0 230 -223 2 130 136	He 1, Le 1 36 L 3 43 9 5 367 - 37	1 99 101 9 3 65 -60 5 449 -2 5 H+ 1, L= 20	8 37* 16 10 121 -125 H* -2, L*	0 390 -4 2 400 -17 4 66 -48 6 58 39 He 2, Le 1	3 264 253 5 721 -325 7 8C3 822 9 377 -382 11 182 179	H= 3, [+ 18 1 474 0 3 43 63	6 533 -550 8 42 -8 10 414 13 H+ 4, L+ 8	0 430 -36 2 47 16 H= -4, L= 18 0 69 60	11 378 370 H= 5.L= 8 1 344 349 3 288 -289	1 48 -82 3 233 227 5 173 -160 7 59 60 He -5, [+ 19
2 108 101 4 441 458 6 524 -531 8 97 89 10 39 23 12 94 -104	1 914 -800 3 519 549 5 1115 -1103 7 101 76 9 147 157	9 95 8 H+ -1, L+ 1 704 -70	H1, L+ 20 9 1 76 73 3 136 -138	2 233 246 4 111 99 6 342 - 355 8 49 41 10 105 - 101 Ma 2, 14	2 109 -109 H= -2, L= 1 2 120 -124	1 38 49 3 291 -286 5 593 600 7 164 -173	1 H+ -3, [* 10 1 72* -11 3 136 134 5 88 -97	0 771 -771 2 342 345 4 115 -128 6 253 -262 8 190 196 10 92 -91	2 390 -25 4 90 -03 0 79 84 He -4, Le 19	5 153 157 7 370 -16 9 74 43	1 115 142 3 58 43 5 118 -108 He -5, Le 20
H= C, L= 2 C 1128 -979 2 602 617 4 642 -650	H= 1, L= 1 1082 989 3 796 -795 5 95 52	7 280 -29 0 111 10 11 48 -0 H= 1, L=	3 H+ -1, L+ 21 5 1 141 -132 1 H+ 2, L+ 0	2 445 427 4 260 -249 6 211 215 8 38* -30 10 97 85	H+ 2, L+ 21 0 140 -140 H+ -2, L+ 21	H+ -3, [+ 8 1 431 435 3 222 -237 5 258 245	1 75 62 3 444 -26 H+ -3, L+ 19	He -4, Le 8 0 107 84 2 441 -302 4 171 146 6 217 -231	H4, L- 20	3 110 -157 5 411 474 7 41 -44 9 39+ 30 11 103 86	1 56 54 3 97 -88 5 136 133 H= -5, (# 21
6 266 -274 8 165 174 10 132 -125 12 56 59 H= 0, L= 3	7 209 297 9 186 -172 11 193 180 n= -1, L+	1 268 -26 3 116 10 5 109 11 7 65 -6 9 87 -7	0 1435 1271 2 7 163 -165 5 4 985 954 6 28* -14 8 123 -116 1 10 161 148	H= -2, L= 2 192 182 4 128 -136 6 356 367	0 107 -101 2 99 66 4 440 -44 He -2, Le 2	7 82 67 9 79 -75 13 118 124 He 3, Le 9	1 65 75 3 41* 25 5 72 -71 H= -3, L= 20	8 88 96 10 109 -120 H- 4, L- 9 2 526 523	2 53 52 4 430 1 80 -4, 10 21 2 154 145	H+ 5, (+ 9 1 332 - 320 3 47 59 5 277 279 7 502 - 509	1 127 -115 3 444 50 H= 6, L= 0
2 1201 -1213 4 545 519 6 122 -121 8 98 -99 10 60 53 12 52 55	1 1472 1330 3 198 192 5 80 -113 7 223 221 9 145 -133 11 115 117	H= -1, L= 1 150 14 3 66 -5 5 61 -6 7 42 -4	12 86 -65 10 H= 2, L= 1 5 2 1402 -1413 4 416 432 13 339 -346	8 37* 2 10 42* 20 H= 2, L= 10 0 29* -9	2 125 127 H- 3, L- 0 1 907 -853	1 427 -420 3 77 95 5 51 46 7 319 -314 9 66 45	1 101 89 3 1e8 -155 H+ -3, L+ 21 1 113 -116	4 282 -274 6 380 384 8 95 -100 10 52 29	H+ 5, L+ 0 1 #54 -637 3 #2 95 5 559 -546	9 147 160 He -5, 1+ 9 1 35 -33 3 182 -182	2 493
H- 0, L- 4 0 293 269 2 806 828 4 540 -514	He 1, Le 2 1 81e 785 3 232 206 5 369 388 7 221 -211	4 57 -5 H= 1, L= 1 58 -10 3 118 11	a 119 92 10 63 74 11 12 147 -147 8 ma -2, La 1	4 146 131 6 127 113 8 398 17 10 438 10 H= -2, L= 10	5 431 -410 7 4C -20 9 181 187 11 209 -207 H- 3, 14	1 25* - 39 3 227 - 224 5 203 211 7 237 - 247 9 39 - 20	H+ 4, L+ 0 0 1558 1527 2 005 -075 4 070 002	2 380 373 4 160 -174 6 289 309 8 47 33 10 42* 14	9 74 87 11 216 -209 H+ 5, L+ 1	5 46 -44 7 41 14 9 97 -91 11 59 -62 He 5. Le 10	He 6, Le 1 2 620 -607 4 516 510 6 130 -128 8 366 -46 10 6-1
6 290 18 8 340 14 10 58 -60 H- 0, L- 5 2 811 792	9 36 -33 11 177 164 He -1. Le 2 1 1105 1054	5 179 -17 7 141 144 9 42* 3 H1, L-	2 325 -315 4 573 581 6 207 -206 8 85 -93 11 10 394 -19 12 74 -82	0 230 -222 2 224 220 4 82 87 6 74 -56 8 360 -25	1 769 -736 3 726 -217 5 59 -69 7 484 493 9 328 -327	11 #1 -5# H= 3, L= 10 1 266 -209 3 175 165	6 320 319 8 274 -275 10 283 259 H- 4, L+ 1	H= 4, L= 10 0 240 207 2 44 -37 4 67 -58 0 124 133	3 159 143 5 280 -273 7 566 566 9 352 -366 11 143 189	1 53 -38 3 71 55 5 147 -143 7 39+ 16 9 43+ -18	H+ -0, L+ 1 2 220 -6 4 118 -100 6 123 -143
4 520 -516 6 448 455 8 90 -74 10 43 53 H= 0, L= 6	5 75 79 7 31+ 23 9 107 -132 11 136 139	3 251 25 5 186 -184 7 87 98 9 92 94	Han 2, La 2 0 2200 -2275 2 1143 1149 4 810 -821 12 6 457 -459	He 2. Le 11 2 267 -259 4 122 120 6 67 -65	He -3, (- 1 1069 1034 3 173 170 5 45 23	7 65 76 9 42* -26 H= -3, L= 10	4 57 63 6 224 - 279 8 72 71 10 39+ 3	H+ -4, (+ 10 C 202 -182 2 101 97 4 75 89	H= -5, (* 1 1 277 -267 3 66 -59 5 32 -23 7 75 71 9 66 -77	He -5, [= 10 1 153 140 3 269 -241 5 137 134 7 45 -21 9 62 -68	6 85 87 10 40+ 62 H= 6, L+ 2 C 10C3 -1019 2 196 215
0 204 218 2 45 -80 4 333 329 6 94 99 8 142 -144 10 112 118	1 1339 -1335 3 201 184 5 215 212 7 214 -224 9 159 156 11 424 -24	1 103 -101 5 53 41 5 84 -81 7 104 90 9 430 -11	0 193 -196 12 56 28 H+ -2, L= 2	H = -2, L = 11 2 126 130 4 317 -118	7 122 129 9 165 -163 11 175 161 H- 3, t- 2	3 130 -118 5 32 31 7 26 -12 9 80 -97 H= 3, L= 11	2 187 206 4 409 420 6 323 -333 8 34* -28 10 43 52	e 148 -205 8 219 215 10 54 -44 H= 4, L= 11	11 136 125 H+ 5, L+ 2 1 037 027 3 140 -158	H* 5, L* 11 1 124 115 3 80 85 5 374 2	4 197 -219 6 367 -366 8 251 252 10 177 -163 He -6, Le 2
He 0, Le 7 2 856 -642 4 209 204 6 506 -506	He -1, L 1 1 2180 22CE 3 28 -35 5 55 -43 5 55 -43	He -1, Le 1 1 263 -261 3 358 364 5 334 -356 7 80 93	2 2 31 53 6 626 -636 6 114 -127 8 161 166 10 124 -123 12 92 81	6 186 189 8 399 7 10 104 -88 H= 2, L= 12	3 937 -930 5 671 549 7 114 141 9 136 -137 11 175 169	1 150 -145 3 240 238 5 99 81 7 67 -76 9 50 41	H= 4, L= 2 C 1581 -1578 2 123 -95 4 178 -170	4 41 -42 6 171 -176 8 55 48 H* -4, L* 11	7 98 98 9 124 -135 11 136 136 H+ -5, L+ 2	9 44+ -35 ++ -5, (+ 1) 1 85 67 3 62 -49	0 1229 -1196 2 366 340 4 345 -351 6 132 140 8 90 -87 10 44 45
10 51 -6 H+ 0, L+ 8 0 1032 -1048 2 477 484	9 108 108 11 74 -09 H- 1, L- 4 1 049 446	H= 1, L= 1 1 438 645 3 204 -215 9 106 -100	3 2 943 895 4 704 -709 6 43 27 8 70 46	2 311 -325 4 51 70 6 193 185 8 90 -96 M= -2, L= 12	1 512 515 3 200 -215 5 415 407 7 93 106 9 137 -139	1 645 -644 3 121 123 5 260 263 7 139 -140 9 125 112	# 321 324 10 174 -103 H= -4, L= 2 0 3167 -3327	4 34 13 6 35 -29 8 42 43 10 75 -102 m- 4, L= 12	1 184 180 3 110 -106 5 330 328 7 128 134 9 131 -141 11 42 47	5 274 276 7 221 -219 9 146 149 H= 5-1= 121	H= 6, L= 3 2 25* -13 4 52 -52 6 328 330 8 150 114
* 218 -220 e 133 -144 \$ 370 18 10 137 -113 H= 0, 1= *	3 797 -802 3 218 231 7 172 -161 9 107 97 11 420 29 H1, L- 4	7 100 105 9 115 -100 Her -1, Le 1 1 368 374 3 349 -355	10 390 22 H= -2, L= 3 2 425 410 4 460 438 6 355 -316	0 775 804 2 363 -371 4 304 321 6 36 -34 8 156 -155 10 98 89	11 63 56 H= 3, L= 3 1 212 209 3 328 -33 5 120 -110	He 3, Le 12 1 200 -105 3 300 306 5 134 -143	2 528 531 4 144 130 6 255 -253 8 156 168 10 55 -45	0 60 77 2 344 -26 4 364 38 6 118 110 8 148 -150	H* 5, L# 3 1 603 -500 3 116 113 5 247 274 7 149 -136	3 102 83 9 64 -62 7 58 -66 He -4, Le 17	10 51 -40 N+ -6, L+ 3 2 537 -538 4 255 300
2 347 369 + 303 -517 6 494 499 8 50 -43 10 46 41	1 53 -44 3 149 189 5 103 92 7 235 -222 9 85 79	9 300 199 7 204 199 9 110 -110 H= 1, L= 1	8 344 0 10 394 -42 12 444 24 4 He 24 L- 4	H= 2, 1= 13 2 136 -138 4 206 196 6 125 -125	7 35 4 9 64 41 11 71 -56 He -3, (- )	9 55 44 H= -3, L= 12 1 120 -127 3 193 197	2 66 57 4 62 -70 6 71 54 8 65 79 10 78 -72	H -4, (- 12 0 848 881 2 314 -312 4 39 47 6 257 272	11 141 -142 He -5, Le 3 1 673 -671 3 133 120	7 155 159 5 200 -311 7 110 117 9 65 75	6 354 -347 6 354 -7 10 96 109 H- 6, [+ 4 0 523 516
0 217 -214 2 112 110 4 53 66 53 45 8 38 1	H= 1, L= 9 1 200 -8 1 200 -8 5 123 -122	3 161 -170 5 108 305 7 30 -33 80 -1, Lo 1	0 717 710 2 51192 4 317 337 6 147 -145 8 161 162 4 10 59 -65	8 620 -7 He -2, Le 13 2 156 -149 6 161 157 6 125 -115	1 1016 975 3 327 322 5 26 -5 7 31* 13 9 5* 40 11 56 -53	5 380 -400 7 65 60 9 99 109 H+ 3, L+ 13	H4, L- 3 2 148 154 4 96 76 6 229 -234 4 14	8 230 -239 10 133 125 H- 4, L+ 13 2 364 13	5 133 132 7 115 114 9 102 -00 11 115 108 No 5, to 4	1 65 61 3 37* 29 5 73 -78 7 138 129	2 111 -92 • 256 255 • 64 -59 8 93 -84 10 49 63
10 +3+ -13 H= 0, L= 11 2 162 -147 4 115 -112	7 525 -534 9 303 504 11 95 -97 Me -1, L= 5	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	H= -2, L= 4 0 63 -47 2 84 87 4 113 -63 6 206 194	8 410 18 He 2, L- 14 0 593 -590 2 171 161	H- 3. L= 4 1 745 -720 3 384 382 5 278 -276 7 90 86	3 36 19 5 88 -80 7 132 137 H+ -3, L= 13	10 58 -35 He 4, Le 4 0 1352 1323 2 760 -722	6 44 -36 8 43 2 He -4, Le 13 2 175 -163	1 117 110 3 347 -334 5 211 -206 7 102 100 9 119 115 11 70 -74	1 388 400 3 182 -185 5 50 47 7 168 168 9 164 -162	0 73 -85 2 367 -341 4 158 167 6 53 -55 8 82 74
8 394 -5 10 444 -20 H= 0, t= 12 0 503 515	3 76 92 5 76 61 7 466 -482 9 188 198 11 96 -97	1 292 -285 3 94 89 5 39* 25 7 145 -137	10 50 70 12 63 42 H= 2, L= 5 2 956 947	6 134 -130 8 146 146 H= -2, L= 14 0 579 -592	11 434 -23 H= -3, t= 4 1 61 49 3 349 -354	1 261 268 3 145 -153 5 354 35 7 219 214 9 176 -178 He 3, 14 14	4 224 216 6 67 73 8 364 -5 10 404 38 H4, L4 4	4 309 303 6 222 -218 8 51 47 H+ 4, L= 14	H= -5, L= 4 1 307 -330 3 351 -361 5 630 619 2 112 -104	H= 5, L= 14 1 192 192 3 208 -208 5 252 245 7 55 -13	10 131 -127 H+ 6, L+ 5 2 208 207 4 172 -182
2 382 -380 4 372 385 6 364 -4 8 132 -126 10 56 35 H= C, L= 13	He 1, Le 6 1 808 -783 3 780 796 5 459 -456 7 330 -5 9 380 4	Re -1, Le 1 1 61 -56 3 70 -67 5 42 51 7 123 -124	5 4 798 -805 6 340 326 8 92 104 10 400 -31 H= -2, L= 5	2 243 245 4 69 -76 6 272 -273 8 169 172 H- 2. L= 15	5 398 388 7 130 -127 9 84 88 11 624 0 H- 3. L+ 5	1 53 47 3 37* 0 5 211 217 7 113 -115	0 2159 -2257 2 850 874 9 56 -39 6 79 -84 8 92 79 10 71 -77	2 124 117 4 101 -88 6 141 -136 He -4, Le 14	9 37+ -1 11 89 82 H+ 5, L= 5 1 25+ -1	H* -5, (* 1*) 1 255 258 3 146 -145 5 243 243	8 38 -37 10 50 -40 H= -8, L= 5 2 794 790
2 404 -457 4 335 324 6 107 -101 8 414 34	11 03 -40 He -1, Le 6 1 21 -10 3 103 199	H= 1, L+ 1 1 181 -172 3 112 106 5 177 -175 7 55 45	6 2 333 334 4 143 -147 6 611 620 8 191 -172 10 43 31	2 370 5 6 152 -126 6 222 200 H= -2, L= 15	1 07 81 3 753 -728 5 509 518 7 434 -434 9 00 97 11 67 -71	1 219 217 3 340 7 5 131 131 7 47 -40 9 440 -25	N= 4, L= 5 2 232 214 4 251 246 6 00 54 8 364 15	2 178 180 4 240 -250 6 162 -150 8 162 164 H- 4, L+ 15	3 27 -21 5 162 176 7 246 -255 9 46 50 11 94 -81 H= -5, t= 5	7 36 -58 9 43 -19 H- 5, L- 15 1 147 -154 3 95 91	* 861 -883 6 599 615 8 90 89 10 404 -*3
0 541 -541 2 199 207 4 134 -150 6 148 -145 6 161 162	7 136 142 9 121 -116 11 120 -114 He 1, Le 7	H+ -1, L+ 1 1 36+ -35 3 133 -127 5 43 -36 7 47 -20	0 607 611 2 225 -250 4 107 -91 6 326 328 8 82 -48	4 150 -146 6 88 91 8 81 71 H= 2, 1- 16	H+ -3, L= 5 1 44 -60 3 317 325 5 83 -75 7 415 -621	H= 3, L= 15 1 200 -258 3 148 151 5 44 35 7 101 -103	10 414 -2 He -4, Le 5 2 1319 1322 4 680 -683	2 225 232 4 163 -190 6 120 119 H+ -4, L+ 15	1 786 -631 3 477 -464 5 353 345 7 524 -539 9 182 184	5 424 19 He -5, Le 15 1 142 -144 3 116 120	0 33* -3 2 114 100 4 136 139 6 216 -230 8 64 63 10 106 86
H* 0, L* 15 2 91 92 4 164 -171 6 109 107	1 671 659 3 243 -249 5 35 -29 7 405 399 9 137 -128 11 192 179	H= 1, L= 1 1 46 40 3 51 -66 5 56 49	7 10 144 121 H= -2, L+ 6 0 1101 1107 2 320 -335	0 465 448 2 237 -236 4 134 133 6 81 65 H= -2, L= 16	9 142 130 11 163 -154 H= 3, L= 6 1 219 -192	H= -3, (= 15 1 103 -102 3 71 -47. 5 100 102	8 354 19 10 40+ -52 H# 4, L# 6 0 603 622	2 145 140 4 61 -58 6 89 86 8 50 -24 H= 4, L= 16	H= 5, 1= 0 1 200 - 30 3 130 147 5 342 - 350	7 117 -105 ** 5, 1* 18 1 113 -113 5 79 93	H+ -0, L= 0 0 046 045 2 336 -308 4 296 301 0 195 199
H+ 0, L= 16 0 152 141 2 50 -32 4 150 142	H1, L- 7 1 273 207 3 502 440 5 292 -294 7 431 440	H= -1, L= 1 1 59 -66 3 46 -37 5 55 29 7 44 -16	7 6 312 314 8 322 -333 10 203 202 H= 2, L= 7	0 207 198 2 92 83 4 384 -23 6 75 90 8 92 -83	5 396 -395 7 251 235 9 46 23 11 115 -112 K= -3, 1= 6	n= 3, L= 16 1 155 -149 3 107 97 5 128 -131	2 327 -327 + 153 -159 6 367 370 8 133 -136 10 144 145 He -4, Le 6	0 313 300 2 141 -140 4 126 123 6 44 44	7 151 153 9 40+ -7 H= -5, L= 6 1 780 -782 3 514 549	3 105 -106 45, [. 16 1 119 -170 3 3711 41	8 85 -106 10 144 138 H= 0, L= 7 2 356 -346
0	<pre>4 106 -96 11 100 158 H= 1, L= 8 1 181 190 3 209 -214</pre>	H= 1, L= 1 1 54 3 3 95 88 5 105 -87	2 769 -735 4 761 767 6 843 -848 8 69 69 10 414 39 He -7, 14 7	He 2, Le 17 7 400 11 4 420 -2 6 444 18 He -2, Le 17	1 401 -393 3 119 128 5 336 -347 7 189 180 9 110 -97	H= -3, L= 16 1 60 -65 3 370 -26 5 106 -108	0 122 -116 2 47 -87 4 262 263 6 359 373 8 248 -249	0 237 241 2 43 21 4 36* -1 6 74 91 8 52 -39	5 489 -506 7 85 76 9 70 82 11 172 -172 He 5, Le 7	7 08 -59 ** 5, 10 17 1 53 32 3 58 -11	e 306 -309 8 394 20 10 434 -23 He -e, 1+ 7
H* 0, L= 18 0 64 00 2 75 -87 4 420 -40	5 458 470 7 127 -125 9 43 40 11 86 80 He -1, Le 8	H= -1, L= 14 1 40* 33 3 57 56 5 87 -79	2 878 -872 4 814 821 6 623 -643 8 42 -11 10 40* 16	2 139 148 • 117 -128 • +2+ 20 H+ 2, L= 18	H- 3, L- 7 1 945 936 3 52 68 5 191 -204	H= 3, L= 17 1 216 206 3 79 -83 5 43 13	He 4, Le 7 2 120 -127 4 408 409 6 537 -525	H- 4, (+ 17 2 53 -66 4 61 82 H4, (+ 17	1 108 107 3 102 91 5 99 100 7 302 302 9 167 -171	14 -5, Le 17 1 72 -66 3 51 57 5 54 29 7 96 -5	2 012 -013 4 283 201 6 472 -480 8 73 01 10 55 -51
0 440 42 H- 0, L- 19	1 201 266 3 26* -21	1 207 204	m- 2, L- 0	0 101 -97 2 42• -9	7 418 422 9 222 -214 11 169 157	** -3, 1* 17	10 424 32	2 127 120	H5, L- 7	** 5, 1+ 18	0 225 -230 2 204 210

Table 4 (cont.)

<pre>     K</pre>		M       1       2			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1         1	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10         -10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

particular is indicative of considerable double-bond character. The Me–N–Me angle of  $117\cdot3$   $(0\cdot2)^{\circ}$  is comparable with angles of 116  $(1\cdot0)^{\circ}$  found in other approximately planar dimethylamino groups (Bullen, 1962). In the phenyl rings the mean C–C bond is  $1\cdot378$  Å which is shorter than the value of  $1\cdot394$  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:  $C \cdots N$ , 3.483;  $C \cdots C$ , 3.521;  $N \cdots H$ , 2.728;  $C \cdots H$ , 3.137; and  $H \cdots H$ , 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 FQ FC	x ** **	K *C *C	1 " " "	× ** **	1		* FC FC	K FO FC	* *C *C	* ** **	1 * *C *
1 69 -50	5 80 80	H+ -14, L+	* 0 473 449 2 220 -205		5 186 -147	2 100 108	He -10, Le 10	1 11 15		; 2: 23	H+ -20, L+
152 -147	H+ -13, L+ 19	2 116 10	6 157 143 6 131 -123	4. 15. 1.	HE -15+ LE L	6 58 -51 8 444 48	2 49 -02	5 410 -5	2 64 47	19. (- 1	2 68 50
9 43• 3 H• 13, 1•	1 38 -15 3 30 31 5 41 -17	8 153 15	H+ -14, 1+ 11	1 17 -94	1 91 63 1 350 -11 5 40 -40	H- 16. 1- 5	H+ -10, 1+ 17	H17, L- 8	H16, L- 3	3 67 -43	0 434 39
1 168 -110	7 440 33 He -13, Le 10	H. 14, 1.4	5 2 78 -74 4 10- 93 6 81 -76	5 128 -120 He -15, Le -	7 68 70 H 14, 1 - 11	2 424 -40	2 1C1 102 4 121 -119	1 76 -63 3 131 133 5 101 -100	2 117 -122 4 155 154 6 154 -159	1 42 - 34	2 70 -74 H+ -20, 1+
1 129 130	1 39+ 3 3 140 -131	: 30 -5	H+ -14, L+ 14	1 70 61	1 39+ 28	2 210 221	H+ -16. L+ 18	H -17, L 9	18.1- 4	3 43• 28 H• 19, L• 2	2 91 -100
1 15 -17	H+ -13, L+ 11	H14, L. 2 219 21	5 0 217 -215 2 38 -1 4 40• -10	5 114 106	5 424 10	4 184 -178 4 188 179 5 8 449 -19	2 444 -49	1 40 65	0 105 108 2 74 -03	1 62 41	H20. 1.
1 117 144 5 36* 18 7 60 56	1 133 -123	4 140 -151 6 151 16 8 474 4	6 90 -38	** 15. L* * 5 1 40* -3	1 119 99 3 41+ -39	H- 10, L- 0	H= 17. (= 0	* 46 -40 7 166 107	18, L · ·	He - 19, Le 2	2 68 66 He -20, Le
9 430 9 He 13. Le 1	5 83 83 He -13, 14 18	H= 14, 14	6 2 92 -82	3 41+ -0 5 43+ -28	5 420 - 34		3 -20 -37	H17. 1- 10-	2 172 171 4 110 -99	1 60 PC	2 94 88
1 108 107	1 82 -79	C 114 -13 2 47 6	6 43 -42 He 14, 14 14	H= -15, L= -	3 140 -140			3 131 -151	··· ·]8. (* · ·	1 228 235	H2C. L.
5 126 129	5 103 -153	6 51 14 1 He - 14, 14	0 10 -41 0 2 78 60	3 97 -108 5 66 55 7 228 -229	5 111 102 He -15, 1 - 1	0 1/0 -10 2 370 22 4 17 11	3 61 -59 5 434 16	······································	2 104 89	5 444 10 He -19, Le 4	2 57 72
1 104 -143	1 147 151	0 154 12	a 100 -85	- 15. 1	1 41 -73	: 23 3	He -17, 1 = 1	3 103 100 5 424 -9	18. 1. 6	1 +1+ 35 3 80 -78	H= -20, 1=
5 135 -124 7 54 AQ 9 64 60	H13. L- 20	6 143 14 6 429 -4	2 179 173		5 88 77	n= 10, 1. 7	3 69 -49 5 70 71	H17. L. 12	0 58 55 2 40° -10 8 41° -1	5 94 83	2 43• 17 4 68 -53
** 17, 1*	3 27 -23	** 14. 14	7 4 184 -173	H+ -15, 1+ 0	1 66 -01	H. 16. L. 7	H- 17, L- 2	1 41+ 30 1 95 -99	6 55 46 H18,14 7	1 71 -86	He -20, 1+
1 43 -45	- 14. L- C	2 44 -3; 4 59 44 6 82 -61	0 133 133	1 68 -66 3 36 15 5 64 -47	40 -15. 10 10	2 130 -131 6 67 65 6 119 -116	3 56 -53 5 99 92	H+ -17, L+ 13	2 44 -23	5 440 - 3 110 - 15, 10 - 6	2 100 -114
··· -13, L.	2 35 -38	m14, L+	, 4 430 -10	· · · · · · · ·	1 105 94	8 444 -1	-17, 1- 2	3 42 -12	6 44.0 1 H18, 1.0 8	1 3: 2	He -20, 1-
1 314 11	8 434 -43 He 14, Le 1	2 34 56	2 114 -111	1 74 00		C 120 -110	3 133 134 5 116 -111 7 444 28	P+ -17, L+ 14	0 157 146	5 440 2 He - 19, 10 2	4 137 128
7 40* 11 9 109 -101	2 139 -131	8 -2* 10 H+ 14, 1*	8 0 440 -44	H - 15. (* )	7 70 -44	H10.1. 8	H. 17, 1. 3	3 70 64	4 45 47 6 48 37	1 60 -93	0 1+8 -138
H= 13, L= 10	6 99 -61 8 439 -16	0 414 24	2 48 19	1 86 81	- 16.1.	2 274 7	1 92 -91 3 429 -3	H17, L- 15	-18, L= 9	5 440 - 59 Ma - 10 - 10 - 10	He -70.10 1
9 142 143	-1+, L= 1 2 15 41	- 54 41 He -144 14	1 58 -51	3 38 45 7 62 54	2 30 - 10	na -10, 10 9	HP -17, LP 3	3 50 -49	4 100 117 6 52 -34	1 24	2 55 48
1 140 144	• 10• -109 • 123 121	0 50 44	5 59 -01 7 42+ -33	H= 15, 1= 4	H16, L. 1	2 65 -52	1 141 141 3 394 -20	H17. L. 16		5 81 -85	C 80 84
201 208	H= 14, 14 3	40 -7 6 15 13	H- 15, L- 1		2 174 135	* -1e, L* 10	3 35 33	3 135 -136	2 150 140	1 106 106	
- 13, 1+ 13	0 334 -345 2 137 138	H- 14, 1-	0 5 64 -50	1 15 -12	H. 16. L. 1	0 310 - 140	1 . 10 - 15	1 131 -120	H18. L. 11	5 56 -37	2 440 21
1 58 7C 3 81 -80	6 147 -146 6 138 133	2 123 127	-15, (- 1	5 75 30	C 151 -172 2 47 64	e 67 -95	-17, L+ 4	H17. (- 18	2 63 62 6 319 -102	1 100 101	c
He -13, 1+ 11	ו -1•, •• 3	He -14, Le	9 1 195 -186 3 370 -20	H. 15. L. S	e ac -90	2 122 119	1 76 67	1 57 -31	H18. L. 12	5 128 125	H4 -21. C4
3 109 1C8 5 38 19	2 152 -168	6 394 -11	7 143 -137	15, 1	C 162 1-0	e 150 134	7 102 -88	0 223 230	2 115 -108	1 107 -111	He -21, Le
· 13, t- 13	8 424 10	H- 14, 1- 1	0 1 223 230	1 105 92	4 190 -12 6 81 65	0 362 361	1 84 86	4 5 66	H18. (* 1)	······································	1 84 -71
1 440 32	2 230 233	0 70 71 2 83 -7	5 126 131	3 116 111	H= 16.1.	2 160 -166 4 129 114 6 63 62	He -17, 10 5	2 424 -14		1 78 -66 3 43 36	3 52 25
1 249 -248	6 167 -156 6 50 64 8 52 -16	** -1*, 1* 1	0 ×+ -15, L+ 2	1 59 67	6 73 57	H+ -1e, L+ 1)	1 142 -148 3 60 41	4 434 -12 He -18, 14 1	0 424 5	H19, L- 13	Ha -21, LA
3 150 155 5 159 -159 7 42• -4		2 114 10	1 35* -19 3 159 157 5 1*1 -148	3 85 -73 5 214 200 7 80 -79	H16, L.	2 50 -77 4 45 46 0 43* -17	5 41* -18 7 117 -123	2 95 105	2 50 -58	1 57 -21 3 44 -17	1 83 -75 He -21, Le 1
m1), L. 11	2 218 -206 4 240 253 4 337 -314	8 119 105	H= 15. L= 1	H15. L. 11	2 183 -163 4 152 157 6 181 -179	H10, L. 14	1 440 9	M+ 18, L+ 7	H+ -18, L+ 15 2 80 -69	H+ -19, L+ 34 3 47 25	1 79 -67
1 36• 24 3 17• 9 5 43 -56	8 60 41   14, 1- 4	He -14, Le 1	1 1 38+ 36	1 303 -315 3 129 121 5 40* 36	H- 16. L- 4	2 65 -35	H17, 1. 0	0 150 -148 2 78 67 4 88 -75	4 84 74 H= -18, L+ 16	3 65 54 He -19, Le 15	1 79 61
7 153 145	2	6 116 -110 6 74 00 8 44* -24	5 56 41 7 130 -133	7 110 -110	0 290 293 2 91 -79 6 429 -4	0 44 -3 He -10, L+ 15	1 42 -39 3 76 80 5 73 -69	** -18, 1. 2	0 141 -140	1 144 147	21, 1- 1
1 107 109	1	In14, 1- 1	, He -15. Le 1	1 199 -178	1	1 2 101 - 100	7 48 -19	2 104 -101	H- 19.1- 0	Me 20.1. 0	1 66 60

Diphosphatriazine [N(1), P(2), N([3), P(2'), N(1'), C(6)] -0.8802 X' - 0.4746 Z' + 2.0312 = 0, (1) Phenyl II [C(14) to C(19)] -0.2209 X' - 0.7375 Y' - 0.6382 Z' + 8.2908 = 0, (3)

Phenyl I [C(8) to C(13)]

0.8675 X' + 0.1917 Y' - 0.4591 Z' + 7.5064 = 0, (2)

 $C-NMe_2$  [C(6), N(7), C(20), C(20')]

-0.8767 X' - 0.4810 Z' + 2.1233 = 0.(4)



Fig. 2. Bond lengths (Å) and valency angles (°);  $\epsilon$ .s.d.'s in parentheses. E.s.d.'s of bond lengths are  $\times 10^3$ .

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=0.05and with all atoms removed, showed residual electron density within  $\pm 0.35$  e.Å<sup>-3</sup> 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 $(2 \cdot 1 \le  F_o  \le 316 \cdot 7)$
R=0.049

Category	Limits	Number
1 2 3	$\begin{split}  \Delta F  &\leq 1.0  F_{\rm th} , \text{ or }  \Delta F  /  F_o  &\leq 0.10\\ 1.0  F_{\rm th}  &<  \Delta F  &\leq 2.0  F_{\rm th} , \text{ or } 0.10 <  \Delta F  /  F_o  &\leq 0.15\\ 2.0  F_{\rm th}  &<  \Delta F  &\leq 3.0  F_{\rm th} , \text{ or } 0.15 <  \Delta F  /  F_o  &\leq 0.20 \end{split}$	2377 28 2
	440 unobserved reflexions ( $ F_{cmax}  = 6.28$ )	
1	$ F_c  \leq 1.0 F_{\rm th} $	399
2	$1.0 F_{\rm th}  <  F_c  \le 1.5 F_{\rm th} $	38
3	$1.5 F_{\rm th}  <  F_c  \le 2.0 F_{\rm th} $	3

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



Fig. 3. Projection of the molecule onto the mean plane of the  $CP_2N_3$  ring, and distances (Å) of the atoms from it.

on P(2)–N(1), 0·13 e.Å<sup>-3</sup> on N(1)–C(6), 0·15 e.Å<sup>-3</sup> on P(2)–N(3) and between 0·20 and 0·35 e.Å<sup>-3</sup> on P(2)–C(8) and P(2)–C(14). The residual peak on the P(2)–N(1) bond occurs about 0·7 Å 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 6dimethylamino 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 CP<sub>2</sub>N<sub>3</sub> ring and (b) 0.7 Å away from it; first contour at  $\pm 0.1$  e.Å<sup>-3</sup>, then at intervals of  $\pm 0.1$  e.Å<sup>-3</sup>.

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 Å and the P-N-C angle an increase of 1.0° from those in phos. I. The dimensions of the P-N-P segment are identical in the two structures: P-N = 1.597 Å and angle  $P-N-P=115.4^{\circ}$ . Similar bond lengths but different angles were found in hexaphenyltriphosphonitrile reported by Ahmed, Singh & Barnes (1969): P-N = 1.597 Å,  $P-N-P = 122.1^{\circ}$ . Likewise, the N-C-N segments in phos. I and phos. II are nearly identical: C-N = 1.336 Å and  $N-C-N = 128.9^{\circ}$ , while the corresponding values given by Lancaster & Stoicheff (1956) for s-triazine are 1.338 Å and 127°.

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 Å from their mean plane in phos. I compared with -0.021 and 0.024 Å 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	e last significant digits.		
	Type	6-Methyl	6-Dimethylamino	t	P limits
P-N	a	1·597 (3) Å	1·597 (2) Å	0	1.0
P-N	Ь	1.620 (3)	1.608 (2)	3.33	< 0.001
C-N	С	1.335 (4)	1.336 (2)	0.22	>0.20
P-C	d	1.801 (2)	1.802 (2)	0.35	>0.20
P-N-P	$\theta_1$	115·4 (2)°	115·4 (1)°	0	1.0
N-P-N	$\hat{\theta_2}$	116.5 (2)	117.1 (1)	2.68	0.01-0.001
P-N-C	$\theta_{3}$	119.9 (2)	120.9 (1)	4.47	< 0.001
N-C-N	$\tilde{\theta_A}$	129.1 (4)	128.6 (2)	1.12	0.2-0.1
C-P-C	$\theta_{s}$	105.4 (2)	104.1 (1)	5.81	< 0.001
N-C-R	$\theta_{6}$	115.4 (3)	115.7 (2)	0.83	0.2-0.1



them, indicates considerable  $\pi$ -orbital overlap, whereas the sp<sup>3</sup> 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  $87.7^{\circ}$  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  $2.4^{\circ}$  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.

180