

Table 5. Out-of-plane parameters for the C(sp<sup>2</sup>)-N(sp<sup>3</sup>) fragment (with e.s.d.'s in parentheses) for a selection of amidines

$\tau$ ,  $\chi_C$  and  $\chi_N$  are defined in the text.

Compound	$\tau$ (°)	$\chi_N$ (°)	$\chi_C$ (°)	$d_{CN}$ (Å)	Reference
(1) (Z)-2,6-cis-Dimethylpiperidyl-N-phenyl-2,2-dimethylpropionamidine	{ -87.2 -83.8 }	{ -47.6 -45.5 }	{ 1.6 3.2 }	{ 1.442 (5) 1.424 (5) }	(a)
(2) (E)-N,N'-Dicyclohexyl-4-morpholinecarboxamidine	34.6 (4)	50.2 (3)	1.2 (4)	1.414 (3)	(b)
(3) (E)-2,6-cis-Dimethylpiperidyl-N-phenylacetamidine	-9.8	-18.3	0.5	1.374 (3)	(a)
(4) 1,5,N(4),N(4)-Tetramethylcytosine	-1.5	-3.6	-0.6	1.348 (6)	(c)

References: (a) Gilli & Bertolasi (1979); (b) present work; (c) Dattagupta, Saenger, Bolewska & Kulakowska (1977).

The out-of-plane deformations of the C(sp<sup>2</sup>)-N(sp<sup>3</sup>) group (I) can be more properly described by the internal coordinates  $\tau$ , the mean twisting angle around the C-N bond, ranging from 0 (planar group) to 90° (when the two halves of the group are perpendicular), and  $\chi_N$  and  $\chi_C$ , respectively the out-of-plane bending angles of the N and C atoms, ranging from 0 (planar sp<sup>2</sup> atoms) to 60° (sp<sup>3</sup> atoms). These quantities are easily obtained as linear combinations of the torsion angles  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$  and  $\omega_4$  (see Table 4) (Winkler & Dunitz, 1971; Dunitz, 1979).<sup>\*</sup> Values of  $\tau$ ,  $\chi_C$ ,  $\chi_N$  and  $d_{CN}$  for the present molecule and some related amidine molecules are given in Table 5. The data show that  $\chi_C$  is always very small (0.5–3.2°) indicating that sp<sup>2</sup> carbon is resistant to out-of-plane bending. Conversely the observed range of  $\chi_N$  (3.6–50.2°) is much wider. The data agree in indicating the following scheme for the rotation around the C-N bond. The equilibrium geometry of the C(sp<sup>2</sup>)-N(sp<sup>3</sup>) group is planar (compound 4). Rotation of the amino group causes decoupling of the  $\pi$  system (II) and rehybridization of the nitrogen. For  $\tau = 34.6$  (4)°

$$* \tau = (\omega_1 + \omega_2)/2, \chi_C = \omega_1 - \omega_3 + \pi \text{ and } \chi_N = \omega_2 - \omega_3 + \pi.$$

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### 4,4,4',4',6,6,6',6'-Octachloro-2,2'-dimethyl-2,2'-bi(cyclotriphosphazene), C<sub>2</sub>H<sub>6</sub>Cl<sub>8</sub>N<sub>6</sub>P<sub>6</sub>

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**Abstract.**  $M_r = 583.58$ , orthorhombic,  $Pccn$ ,  $a = 2048$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.882$ ,  $D_x = 1.893$  Mg m<sup>-3</sup>, Mo K $\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 1.55$  mm<sup>-1</sup>,  $F(000) = 1144$ ,  $T = 294$  K,  $R = 0.041$  for 1432 unique reflections. The molecule lies on an inversion center with

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nitrogen is almost completely pyramidalized (compound 2). Further increment of  $\tau$  does not change the situation (two independent molecules of compound 1). This point of view is supported by the trend of  $d_{CN}$  distances, which is found to increase both with  $\tau$  and  $\chi_N$ . The shortest length of 1.348 (6) Å is observed for the planar compound (4) while the largest ones [1.442 (5) and 1.424 (5) Å] are associated with the both pyramidalized and twisted compound (1).

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#### References

- BENT, H. A. (1960). *J. Chem. Educ.* **37**, 616–624.  
 BENT, H. A. (1961). *Chem. Rev.* **61**, 275–311.  
 BERTOLASI, V., BELLUCCI, F., FERRETTI, V. & GILLI, G. (1984). *Acta Cryst.* **A40**, C107.  
 BROWN, K. L., DAMM, L., DUNITZ, J. D., ESCHENMOSER, A., HOBI, R. & KRATKY, C. (1978). *Helv. Chim. Acta*, **61**, 3108–3135.  
 CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.  
 DATTAGUPTA, J. K., SAENGER, W., BOLEWSKA, K. & KULAKOWSKA, I. (1977). *Acta Cryst.* **B33**, 85–89.  
 DUNITZ, J. D. (1979). In *X-ray Analysis and the Structure of Organic Molecules*. Ithaca: Cornell Univ. Press.  
 FRENZ, B. A. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 44–71. Delft Univ. Press.  
 GILLI, G. & BERTOLASI, V. (1979). *J. Am. Chem. Soc.* **101**, 7704–7711.  
 GILLI, G. & BERTOLASI, V. (1981). *Acta Cryst.* **A37**, C85.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1981). *MULTAN81. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.  
 WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

a *trans* configuration for the two methyl groups. The phosphazene ring is slightly puckered because of steric repulsion between ring atoms and the methyl group on the other ring. The N—P bonds are alternately long and short, which leads to distortions in the endocyclic bond angles.

**Introduction.** The reactivity of bi(cyclotriphosphazenes) toward nucleophilic P—P bond cleavage is critically dependent on the organic substituents attached to the linkage phosphorus atoms (Allcock, Connolly & Harris, 1982). Here we report the structure of  $[\text{N}_3\text{P}_3\text{Cl}_4\text{CH}_3]_2$ . This study was carried out in an attempt to understand the reactivity of the P—P bond in terms of the structure of the bi(cyclotriphosphazene).

**Experimental.**  $[\text{N}_3\text{P}_3\text{Cl}_4\text{CH}_3]_2$  prepared by reaction of  $(\text{NPCl}_2)_3$  with  $\text{CH}_3\text{MgCl}$  (Allcock, Desorcie & Harris, 1983); colorless crystals grown from dichloromethane/hexane (70/30) solution, m.p. 477–478 K;  $D_m$  by flotation in tetrachloromethane/iodoethane; rectangular shaped piece (0.25 × 0.32 × 0.48 mm) cut from larger crystal; Enraf–Nonius CAD-4 diffractometer; 25 reflections with  $9.7 \leq \theta \leq 11.9^\circ$  used for measuring lattice parameters; data corrected for Lorentz and polarization factors but not for absorption since  $\psi$  scans indicated that absorption was not severe;  $\theta/2\theta$  scan technique; max.  $(\sin\theta)/\lambda = 0.4812 \text{ \AA}^{-1}$ ;  $3.0 \leq 2\theta \leq 40.0^\circ$ ;  $0 \leq h \leq 21$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 7$ ; 3 standard reflections (12,2,0; 732 and 552), intensity variation 1.4%, anisotropic-drift corrections random and varied from 0.965 to 1.059; 1687 reflections measured, 1432 unique, no equivalent reflections collected; 294 unobserved with  $I < 2\sigma(I)$ ;  $I = [\text{SC} - 2(B_1 + B_2)]T_R$ , where SC = scan count,  $B_1$ ,  $B_2$  = background counts at each end of scan,  $T_R = 2\theta$  scan rate;  $\sigma(I) = T_R[\text{SC} + 4(B_1 + B_2) + (0.025I)^2]^{1/2}$ . Structure solved by direct methods with all nonhydrogen atoms refined anisotropically; \*  $F^2$  magnitudes used in least-squares refinement; H atoms located from difference electron density Fourier maps and refined with  $B_{\text{iso}}$  fixed at  $5.0 \text{ \AA}^2$ ; 109 parameters refined;  $R = 0.041$ ,  $wR = 0.042$ ,  $w = 1/\sigma(F_o)^2$ ,  $S = 1.882$ ;  $w$  calculated by non-Poisson distribution;  $\Delta/\sigma = 0.08$ ; max. and min. height in final difference Fourier synthesis  $\pm 0.18 \text{ e \AA}^{-3}$ ; atomic scattering factors from Cromer & Waber (1974, Table 2.2B) and anomalous-dispersion correction coefficients from Cromer & Waber (1974, Table 2.3.1); computer programs: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *SDP* (Frenz & Okaya, 1980), *ORTEPII* (Johnson, 1976).

\* Lists of structure factors, anisotropic thermal parameters, least-squares planes and bond lengths and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39913 (17 pp.). Copies can be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters

$B_{\text{eq}} = \frac{2}{3}\pi^2 \sum_i \sum_j |U_{ij}(a_i^* a_j^*) \mathbf{a}_i \cdot \mathbf{a}_j|$ . The hydrogen atoms were assigned a  $B_{\text{iso}}$  of  $5.0 \text{ \AA}^2$ .

	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
Cl(1)	0.7884 (1)	-0.0441 (1)	0.2096 (2)	4.9
Cl(2)	0.8535 (1)	-0.2401 (1)	0.0271 (2)	5.4
Cl(3)	0.8935 (1)	0.0414 (1)	-0.4489 (2)	5.0
Cl(4)	0.8265 (1)	0.2209 (1)	-0.2374 (2)	5.1
P(1)	0.9619 (1)	0.0512 (1)	0.0448 (2)	2.3
P(2)	0.8558 (1)	-0.0704 (1)	0.0510 (2)	2.8
P(3)	0.8771 (1)	0.0826 (1)	-0.2065 (2)	2.9
N(1)	0.9157 (1)	-0.0338 (3)	0.1375 (4)	2.5
N(2)	0.8388 (2)	-0.0168 (4)	-0.1264 (5)	3.8
N(3)	0.9363 (2)	0.1196 (3)	-0.1175 (5)	2.8
C	0.9932 (2)	0.1486 (4)	0.1951 (7)	3.8
H(1)	0.961 (2)	0.195 (4)	0.241 (6)	
H(2)	1.012 (2)	0.113 (4)	0.285 (6)	
H(3)	1.024 (2)	0.193 (4)	0.146 (6)	

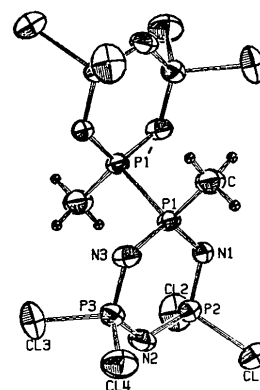


Fig. 1. Perspective view of  $[\text{N}_3\text{P}_3\text{Cl}_4\text{CH}_3]_2$ .

**Discussion.** Atomic positional parameters are listed in Table 1. An ORTEP drawing with the atom-numbering system is shown in Fig. 1. The molecule contains a mean P—Cl bond length of  $1.987 (3) \text{ \AA}$  and a mean exocyclic Cl—P—Cl bond angle of  $100.8 (1)^\circ$ . These are similar to those reported for  $(\text{NPCl}_2)_3$  (Bullen, 1971). The P(1)—C bond length of  $1.781 (4) \text{ \AA}$  and the exocyclic P(1)—P(1)—C bond angle of  $104.6 (2)^\circ$  are consistent with those found for  $[\text{N}_3\text{P}_3(\text{C}_6\text{H}_5)_4\text{CH}_3]_2$  (Ahmed, 1976).

The bridging phosphorus atoms are separated by  $2.200 (1) \text{ \AA}$ . This is not significantly different from the value of  $2.208 (3) \text{ \AA}$  reported for  $[\text{N}_3\text{P}_3\text{Cl}_4\text{C}_6\text{H}_5]_2$  (Zoer & Wagner, 1972). Hence, the susceptibility of these compounds to nucleophilic cleavage does not appear to be due to steric lengthening of the P—P bond. Instead, the electronic nature of the organic substituents probably exerts a greater effect (Allcock, Connolly & Harris, 1982).

The phosphazene rings of  $[\text{N}_3\text{P}_3\text{Cl}_4\text{CH}_3]_2$  are slightly puckered with P(1) positioned  $0.214 (1) \text{ \AA}$  above the plane of the other ring atoms. The largest deviation

from planarity for the other ring atoms is shown by N(2) and is 0.035 (4) Å. This distortion is ascribed to steric repulsions between the phosphazene ring atoms and the methyl group attached to the other ring.

The mean P–N bond distance at P(1) of 1.608 (3) Å is longer than those adjacent to the PCl<sub>2</sub> units. Of the latter, the mean P–N bond distance closest to the P–P bridge is 1.562 (3) Å while the other is 1.572 (3) Å. This alternation in longer and shorter P–N bonds has been detected for other geminally substituted cyclo-triphosphazenes and has been attributed to the influence by the less electronegative substituents at P(1) on the  $\pi$  bonding in the ring (Mani, Ahmed & Barnes, 1965; Craig & Paddock, 1962).

The unequal bond lengths within the six-membered ring lead to corresponding distortions of the endocyclic bond angles from 120°. The largest deviation is at P(1) where the N(1)–P(1)–N(3) bond angle is narrowed to 115.8 (1)°. Both steric and electronic arguments have been used to explain this effect (Allcock, Connolly & Whittle, 1983; Ritchie, Harris & Allcock, 1980).

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#### References

- AHMED, F. R. (1976). *Acta Cryst.* **B32**, 3078–3083.  
 ALLCOCK, H. R., CONNOLLY, M. S. & HARRIS, P. J. (1982). *J. Am. Chem. Soc.* **104**, 2482–2490.  
 ALLCOCK, H. R., CONNOLLY, M. S. & WHITTLE, R. R. (1983). *Organometallics*, **2**, 1514–1523.  
 ALLCOCK, H. R., DESORCIE, J. L. & HARRIS, P. J. (1983). *J. Am. Chem. Soc.* **105**, 2814–2819.  
 BULLEN, G. J. (1971). *J. Chem. Soc. A*, pp. 1450–1453.  
 CRAIG, D. P. & PADDOCK, N. L. (1962). *J. Chem. Soc.* pp. 4118–4133.  
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 FRENZ, B. A. & OKAYA, Y. (1980). *Enraf-Nonius Structure Determination Package (SDP)*. Enraf-Nonius, Delft.  
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain-la-Neuve, Belgium.  
 MANI, N. V., AHMED, F. R. & BARNES, W. H. (1965). *Acta Cryst.* **19**, 693–698.  
 RITCHIE, R. J., HARRIS, P. J. & ALLCOCK, H. R. (1980). *Inorg. Chem.* **19**, 2483–2486.  
 ZOER, H. & WAGNER, A. J. (1972). *Cryst. Struct. Commun.* **1**, 17–21.

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## Structure of (RS–SR)-Ethyl 2,5-Dioxo-4-phenyl-3-pyrrolidinecarboxylate, C<sub>13</sub>H<sub>13</sub>NO<sub>4</sub>

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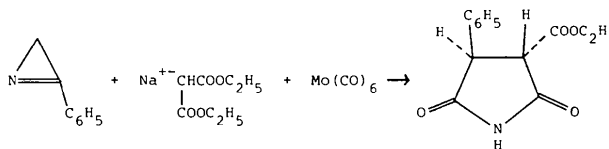
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**Abstract.**  $M_r = 247.25$ , monoclinic,  $P2_1/n$ ,  $a = 15.286$  (3),  $b = 5.377$  (2),  $c = 16.218$  (4) Å,  $\beta = 109.72$  (2)°,  $V = 1254.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.309$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha_1) = 0.70930$  Å,  $\mu = 0.091$  mm<sup>-1</sup>,  $F(000) = 520$ ,  $T = 291$  K,  $R = 0.046$  for 1130 observed reflexions. The analysis shows the compound to be a *trans*-substituted succinimide, hydrogen-bonded into one-dimensional chains [N(H)⋯O = 2.870 (4) Å] running in the **b** direction. The five-membered ring is in an envelope conformation with the phenyl-substituted carbon atom lying 0.224 (3) Å out of the least-squares plane through the other four atoms.

**Introduction.** We recently published a preliminary report on work performed on the molybdenum carbonyl induced reaction of azirines with carbanions derived from  $\beta$ -dicarbonyl compounds (Alper, Mahatantila, Einstein & Willis, 1984). The following reaction was found to take place.



An X-ray structure analysis performed to establish the identity of the product is reported here.

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