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2,4,4,trans-6,8,8-Hexachloro-2,6-bis(*N*-methylanilino)-cyclo-tetraphosphazetetrane

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Abstract. $N_4P_4Cl_6[N(CH_3)(C_6H_5)]_2$, $M_r = 605$, monoclinic, $P2_1/n$, $a = 12.35$ (2), $b = 16.59$ (2), $c = 6.08$ (1) Å, $\beta = 93.23$ (30)°, $V = 1244$ Å³, $D_c = 1.615$ g cm⁻³, $Z = 2$, $\mu(Cu K\alpha) = 0.85$ cm⁻¹. The compound (m.p. 145°C) is the 2,trans-6 isomer. The P–N ring has a chair conformation. The final R was 0.084 for 1102 visually estimated reflections.

Introduction. The crystals were needles elongated along *c*. A crystal of radius 0.14 mm was used to collect

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Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	7936 (4)	647 (4)	5351 (13)
Cl(2)	6768 (5)	895 (4)	9635 (12)
Cl(3)	3896 (5)	1119 (4)	7819 (12)
P(1)	6478 (4)	488 (3)	6457 (11)
P(2)	4415 (4)	1108 (3)	4691 (10)
N(1)	5699 (13)	1074 (10)	5013 (32)
N(2)	3762 (16)	417 (10)	3323 (40)
N(3)	4047 (13)	1959 (9)	3487 (34)
C(1)	2921 (19)	2105 (14)	2655 (54)
C(2)	4720 (17)	2680 (12)	3878 (44)
C(3)	4633 (19)	3157 (13)	5755 (43)
C(4)	5243 (23)	3886 (15)	5965 (54)
C(5)	5872 (22)	4086 (15)	4304 (58)
C(6)	5949 (20)	3624 (16)	2502 (51)
C(7)	5372 (19)	2899 (14)	2260 (50)

intensities for reflections 0–7*kl* by the multiple-film Weissenberg technique with Cu $K\alpha$ radiation. 1102 intensities were estimated visually and corrected for absorption. The structure was solved by direct methods with *MULTAN* (Main, Woolfson & Germain, 1971) adapted for the IBM 360/44 system by M. R. Narasimha Murthy and S. Rama Kumar. The parameters were refined first isotropically and later anisotropically by block-diagonal least squares. A difference map failed to reveal the positions of the H atoms. Five H atoms of the phenyl ring were included at calculated positions but were not refined. The final R [$= \sum ||F_o| - |F_c|| / \sum |F_o|$] for the observed reflections is 0.084. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(a + |F_o| + c|F_o|^2)$ with $a = 9.0$ and $c = 0.035$ (Cruickshank, Bujosa, Lovell & Truter, 1961). Scattering factors were from Cromer & Waber (1965). The final atomic coordinates of the non-hydrogen atoms are given in Table 1.*

Discussion. The reaction of octachloro-cyclo-tetraphosphazetetrane, $N_4P_4Cl_8$, with *N*-methylaniline was studied by John, Moeller & Audrieth (1960), and a bis-*N*-methylanilino-hexachloro derivative, $N_4P_4Cl_6$ -(*NMePh*)₂ (m.p. 145°C), isolated. A reinvestigation of the reaction showed it to be far more complex and two isomers having m.p.'s of 145 and 105°C were obtained in comparable yields (Keat *et al.*, 1974). The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32821 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

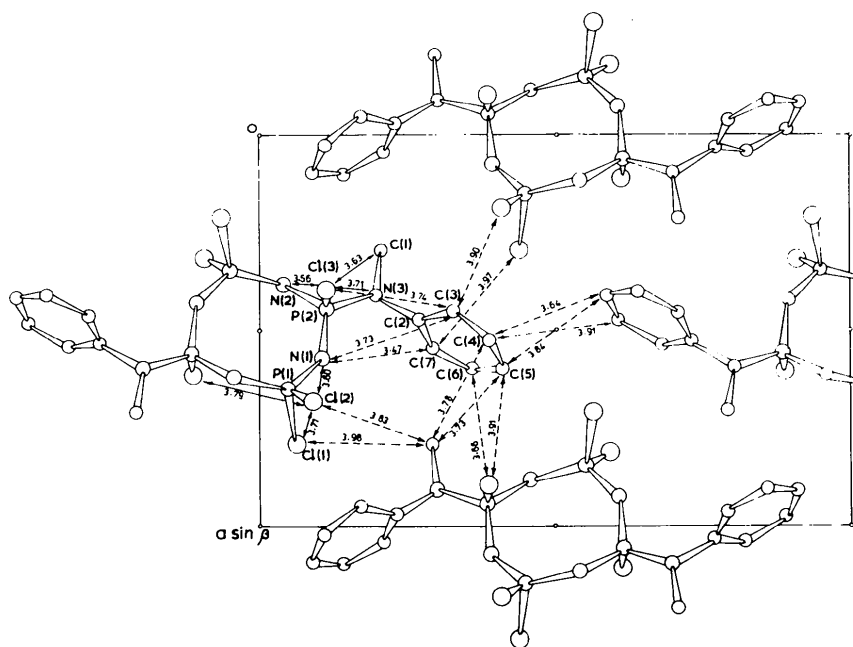


Fig. 1. The structure viewed down *c* and short intermolecular contacts ($<4 \text{ \AA}$). Distances (\AA) indicated by full lines are between molecules differing in height by one *c* lattice translation.

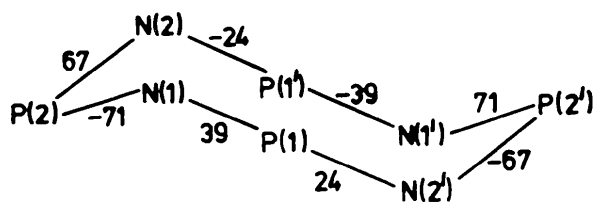


Fig. 2. Conformation and numbering of atoms of the ring, and torsion angles ($^\circ$).

Table 2. Bond distances (\AA) and angles ($^\circ$)

The standard deviations for bond lengths are P-Cl ~ 0.01 , P-N ~ 0.02 , N-C ~ 0.03 and C-C $\sim 0.04 \text{ \AA}$. For bond angles they are $\angle \text{ClPCl} \sim 0.5$, $\angle \text{NPN}$, $\angle \text{PNP}$, $\angle \text{ClPN}$, $\angle \text{PNC} \sim 1.0^\circ$ and $\angle \text{NCC}$, $\angle \text{CNC}$, $\angle \text{CCC} \sim 2-3^\circ$.

P(1)-N(1)	1.60	Cl(2)-P(1)-N(1)	113
P(1)-N(2')	1.54	Cl(2)-P(1)-N(2')	105
P(1)-Cl(1)	1.98	N(1)-P(2)-N(2')	121
P(1)-Cl(2)	2.06	Cl(3)-P(2)-N(3)	108
P(2)-N(1)	1.59	Cl(3)-P(2)-N(2)	108
P(2)-N(2)	1.61	Cl(3)-P(2)-N(1)	104
P(2)-N(3)	1.64	N(3)-P(2)-N(2)	105
P(2)-Cl(3)	2.04	N(3)-P(2)-N(1)	110
N(3)-C(1)	1.47	P(1)-N(1)-P(2)	131
N(3)-C(2)	1.47	P(2)-N(2)-P(1')	138
C(2)-C(3)	1.40	P(2)-N(3)-C(1)	122
C(3)-C(4)	1.43	C(1)-N(3)-C(2)	116
C(4)-C(5)	1.35	C(2)-N(3)-P(2)	119
C(5)-C(6)	1.35	C(7)-C(2)-C(3)	121
C(6)-C(7)	1.40	C(2)-C(3)-C(4)	119
C(7)-C(2)	1.36	C(3)-C(4)-C(5)	118
N(1)-P(1)-N(2)	122	C(4)-C(5)-C(6)	123
Cl(1)-P(1)-Cl(2)	99.3	C(5)-C(6)-C(7)	121
Cl(1)-P(1)-N(1)	105	C(6)-C(7)-C(2)	118
Cl(1)-P(1)-N(2')	110		

proton NMR spectrum of one isomer (m.p. 145°C) suggested a non-geminal disposition of the *N*-methylanilino groups. The ^{31}P NMR spectrum furnished little structural information and only a broad singlet was obtained (Sudheendra Rao, 1976). Consequently, an X-ray crystallographic study was undertaken.

The contents of the unit cell viewed down *c* are shown in Fig. 1. The two molecules in the cell occupy centres of symmetry; consequently, the compound is the *2,trans-6* isomer. The four P atoms are coplanar. N(1), N(2), N(1') and N(2') (Fig. 2) deviate from this plane by 0.48 , 0.35 , -0.48 and -0.35 \AA respectively. Thus the phosphazene ring has a chair conformation, as in the *T* form of $\text{N}_4\text{P}_4\text{Cl}_8$ (Wagner & Vos, 1968), $\text{N}_4\text{P}_4\text{Cl}_4\text{Ph}_4$ (Bullen, Mallinson & Burr, 1969), the β -*trans* isomer of $\text{N}_4\text{P}_4(\text{NHMe})_4\text{Ph}_4$ (Bullen & Mallinson, 1972) and the *2,trans-6* isomer of $\text{N}_4\text{P}_4\text{Cl}_6(\text{NMe}_2)_2$ (Bullen & Dann, 1973). The ring has approximate C_{2h} ($2/m$) symmetry with the diad axis passing through P(1)-P(1'). The torsion angles in the ring are shown in Fig. 2.

Bond lengths and angles are given in Table 2. These are in reasonable agreement with those found in other structures, e.g. *2,trans-6* $\text{N}_4\text{P}_4\text{Cl}_6(\text{NMe}_2)_2$ (Bullen & Dann, 1973), with which the present structure has many points of similarity. A detailed discussion of these values is, however, not presented in view of their large e.s.d.'s. C(1), C(2), N(3) and P(2) of the methylanilino group are almost planar, N(3) being out of the plane of the other three by 0.16 \AA . The plane through N(3), C(1) and C(2) is orientated approximately symmetrically with respect to the ring, the two torsion angles

Cl(3)—P(2)—N(3)—C(1) and Cl(3)—P(2)—N(3)—C(2) being -77 and $+83^\circ$ respectively. This is probably due to the equalization of the non-bonded contacts between the Cl and C atoms: Cl(3)···C(1) and Cl(3)···C(2) are 3.68 and 3.71 Å respectively. Of the non-geminal substituents the Cl atoms are axial and the bulkier NMePh groups equatorial. The molecule thus has an extended conformation and lies along **b**. These features have been observed for other structures (Bullen & Tucker, 1972; Bullen & Dann, 1973).

Intermolecular contacts <4.0 Å are indicated in Fig. 1. The orientation of the phenyl ring is apparently decided by the close contacts between the phenyl C atoms on the one hand and Cl(1), Cl(2), Cl(3) and the methyl C(1) of neighbouring molecules on the other. There are also short contacts between atoms of phenyl rings related by a centre of symmetry and between N(1) and Cl(3) and the phenyl C(3) and C(7), respectively, belonging to the same molecule.

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Diphényl-4,5 Méthoxycarbonyl-5 Pyrazoline-2 (*E*)

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Abstract. C₁₇H₁₆N₂O₂, monoclinic, $P2_1$, $a = 14.395$ (4), $b = 5.695$ (2), $c = 8.826$ (3) Å, $\beta = 103.06$ (2)°, $Z = 2$. The structure was solved by direct methods. $R = 0.038$ for 1104 observed reflexions. The 2-pyrazoline ring is in an envelope conformation (folding angle: 31°).

Introduction. La présente étude fait partie d'un ensemble de recherches sur les pyrazolines menées conjointement au Laboratoire de Chimie Quantique de l'Université de Louvain, sous la direction du Professeur G. Leroy, et dans notre propre laboratoire.

Le spectre de diffraction a été relevé sur un diffractomètre Picker, à quatre cercles commandé par cartes

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perforées. Les intensités de 1163 réflexions indépendantes ont été mesurées en balayage $\omega-2\theta$ jusqu'à une valeur de $2\theta_{\max} = 110^\circ$; radiation incidente: Cu $K\alpha$ ($\lambda = 1.5418$ Å). 1104 de ces réflexions ont été considérées comme observées, le critère de rejet étant: $I < 2.5\sigma(I)$. La structure a été résolue par application des programmes du système *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) et affinée par moindres carrés selon les programmes de Ahmed, Hall, Pippy & Huber (1966) jusqu'à une valeur de $R = 0.038$ pour l'ensemble des réflexions observées. Les positions de 13 atomes d'hydrogène ont été trouvées sur une série de Fourier-différence. Seuls les hydrogènes du groupe-méthyle n'ont pu être repérés.