Crystal and Molecular Structure of 1,3-(Di-t-butyl)-2,4-dichlorodiazadiphosphetidine

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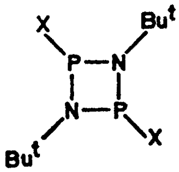
Summary X-ray analysis of $(Me_3CNPCl)_2$ establishes that the $(N-P)_2$ ring is slightly puckered; the exocyclic P–Cl bonds are unexpectedly long; and there are significant differences in the co-ordination of the chemically equivalent nitrogen atoms.

RECENTLY syntheses of diazadiphosphetidine compounds (I) have been developed.[1,2] The existence of the unusual ring system, containing formally single bonds between nitrogen and tervalent phosphorus, has been confirmed by the ^{19}F n.m.r. spectrum of (Ia).[2] A single crystal X-ray analysis of (Ib) has now been carried out, mainly in order to determine the conformation of the four-membered ring.



(I)

a; X = F

b; X = Cl

Crystal data: $C_8H_{18}Cl_2N_2P_2$; $M = 275{\cdot}1$, orthorhombic, $a = 15{\cdot}818(7)$, $b = 15{\cdot}742(6)$, $c = 11{\cdot}608(6)$ Å; $D_m = 1{\cdot}22(2)$, $Z = 8$, $D_c = 1{\cdot}264$; Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}4$ cm^{-1}, space group *Pbca*.

The intensities of all independent reflections with $\theta \leqslant 25°$ were measured on an Hilger and Watts four circle diffractometer, using Mo radiation. The structure was solved by direct methods. Least-squares refinement of the positional and anisotropic thermal parameters of all atoms except hydrogen converged with $R = 0{\cdot}098$ over 926 observed intensities.

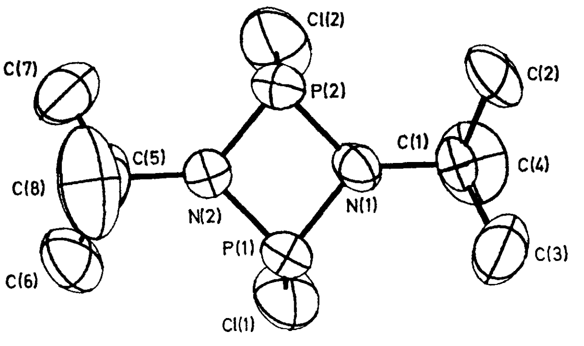


FIGURE. *The molecule viewed down the normal to the* (N–P)$_2$ *ring plane*

The molecular structure of the compound is shown in the Figure. There are no significant differences between chemically equivalent bond lengths (Table). The mean N–C and C–C distances are close to expected values. The mean length of the formally single P–N bonds lies in the range 1·63—1·69 Å commonly found[3-5] for such bonds in molecules where the nitrogen lone pair is believed to participate in p_π–d_π bonding, and is in goood agreement with the corresponding distance of 1·69(3) Å in Me_2NPCl_2.[3] The mean P–Cl distance of 2·105(9) Å differs significantly from the value of 2·039(2) Å found in PCl_3,[6] and is close to that of 2·083(5) Å in Me_2NPCl_2.[3] Correction of the P–Cl distances for the effects of thermal motion, on the assumption that the chlorine atoms ride on the phosphorus atoms, increases the mean to 2·149(9) Å. Substitution of chlorine by nitrogen in PCl_3 thus appears to be accompanied by a substantial weakening of the remaining P–Cl bonds. This can be explained, on the assumption that nitrogen engages more readily in p_π–d_π bonding with phosphorus than does chlorine, in terms either of a direct competition of nitrogen and chlorine for the available phosphorus 3*d* orbitals, or of a decrease in chlorine 3*s* character in the P–Cl bonding orbital as negative charge accumulates on phosphorus.

TABLE

Mean bond lengths (Å) *and interbond angles* (°)

P–Cl	2·105(9)	N–P–N	82·5(3)
P–N	1·689(5)	P–N–P	97·3(4)
N–C	1·498(12)	Cl–P–N	103·3(4)
C–C	1·564(9)	N–C–C	107·2(9)
		C–C–C	111·6(12)

The molecule has a non-crystallographic mirror plane normal to the (N–P)$_2$ ring and containing N(1) and N(2). The ring is slightly puckered, successive atoms being alternatively 0·045 Å above and below the mean plane of the ring. The chlorine atoms are mutually *cis* and on the same side of the ring as the nitrogen atoms.

The nitrogen atoms show important differences in their co-ordination. N(1) lies 0·006 Å from the plane defined by P(1), P(2), and C(1), whereas the corresponding value for N(2) is 0·247 Å. The mean exocyclic C–N–P angles, 131·2(7)° for N(1) and 127·9(6) for N(2), differ slightly, and C(1) lies 0·15 Å from the mean plane of the ring on the same side as the chlorine atoms, while C(5) lies 0·41 Å on the opposite side. The equivalence of the P–N distances despite these differences suggests that in this system the p_π–d_π overlap is not very sensitive to deviations of the bonds involving nitrogen from coplanarity.

The contributions to the molecular energy from angle strain and the non-bonded N · · · N and P · · · P repulsions are slightly increased by the adoption of a non-planar conformation. However, this is offset by a small decrease in the energy of torsional (Pitzer) strain.

(*Received, August 25th,* 1971; *Com.* 1491.)

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