Acta Cryst. (1979). B35, 1410–1413

Conformational Studies of the Triphenylphosphazenyl Side Chain in Cyclophosphazenes. I. Crystal and Molecular Structure of $N_3P_3Cl_5(NPPh_3)$

BY Y. SUDHAKARA BABU AND H. MANOHAR*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

AND T. STANLEY CAMERON†

Physical Science Department, The New University of Ulster, Coleraine, Co. Londonderry, N. Ireland

(*Received* 1 *December* 1978; *accepted* 27 *February* 1979)

Abstract

The title compound, $C_{18}H_{15}Cl_5N_4P_4$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 20{\cdot}14$ (2), $b = 8{\cdot}69$ (1), $c = 14{\cdot}92$ (2) Å, $\beta = 98{\cdot}8$ (3)°, $Z = 4$. The structure was determined from visual data and refined to $R = 0{\cdot}069$ for 1450 reflections. The cyclophosphazene ring is non-planar. The exocyclic $NPPh_3$ group exhibits type I conformation [R. A. Shaw (1975). *Pure Appl. Chem.* **44**, 317–341] in which the N–P bond is perpendicular to the adjacent P–Cl bond.

Introduction

Of late there has been considerable interest in the basicity studies of triphenylphosphazenyl derivatives of cyclophosphazenes. The pK_a' values of a series of compounds of the type $N_3P_3R_n(NPPh_3)_mCl_{6-n-m}$ [R = NMe_2, Ph and NH_2] have been measured (Nabi, Biddlestone & Shaw, 1975). An examination of these basicity values showed that they fell into two classes which were called type I and type II (Shaw, 1975, 1976). It was suggested that the difference in the behaviour of these two classes arises from the different sites of protonation. When the substituent on the P atom carrying the $NPPh_3$ group is Cl, the protonation site is endocyclic, while it is exocyclic when the substituent is Ph, NMe_2 or NH_2. These two types of behaviour were correlated with the conformation of the exocyclic $NPPh_3$ group. Shaw and co-workers proposed that type I should correspond to the conformation where the N–P bond of the substituent is perpendicular to the adjacent P–X bond (where X is the first atom of the other substituent on the same P atom), while in type II it is coplanar with the P–X bond. The first crystal structure to be solved in this series was that of $N_3P_3Cl_4Ph(NPPh_3)$ and it was shown to exhibit type II conformation (Biddlestone, Bullen, Dann & Shaw, 1974). We have taken up systematic crystallographic studies of triphenylphosphazenylcyclophosphazenes to study the conformational aspects of the exocyclic $NPPh_3$ group. We now report the structure of $N_3P_3Cl_5(NPPh_3)$. A preliminary communication has been published (Babu, Cameron, Krishnamurthy, Manohar & Shaw, 1976).

Experimental

Crystal data

$N_3P_3Cl_5(NPPh_3)$, monoclinic, $a = 20{\cdot}14$ (2), $b = 8{\cdot}69$ (1), $c = 14{\cdot}92$ (2) Å, $\beta = 98{\cdot}8$ (3)°, $V = 2580$ Å^3, $Z = 4$, $D_c = 1{\cdot}51$, $D_m = 1{\cdot}54$ Mg m^{-3}, $M_r = 591{\cdot}5$, m.p. = 488 K, space group $P2_1/n$, μ(Cu $K\alpha$) = 7·58 mm^{-1}.

The reaction of hexachlorocyclotri(phosphazatriene), $N_3P_3Cl_6$, with triphenylphosphazene, $HN{=}NPPh_3$, gives $N_3P_3Cl_5(NPPh_3)$. Needle-shaped crystals elongated along **b** were grown from a solution of light petroleum (Biddlestone & Shaw, 1973). A crystal with a nearly square cross-section of 0·25 mm was used for data collection. Intensities were collected by the Weissenberg technique for *hkl* reflections, $k = 0$ to 7, with Cu $K\alpha$ radiation. Intensities of 1450 independent reflections were measured visually.

Structure solution and refinement

The intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved with *MULTAN* (Main, Woolfson & Germain, 1971), adapted for the IBM 360/44 system by M. R. Narasimha Murthy and S. Rama Kumar. All the atoms except three C atoms of one phenyl ring could be identified from the E map calculated with the

* To whom correspondence should be addressed.

† Present address: Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

0567-7408/79/061410-04$01.00

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

	x	y	z
P(1)	−1378 (2)	4118 (4)	2858 (3)
P(2)	−449 (2)	2095 (4)	2292 (2)
P(3)	−744 (2)	2046 (4)	4079 (3)
N(1)	−919 (4)	3602 (13)	2142 (8)
N(2)	−1320 (6)	3294 (10)	3821 (8)
N(3)	−316 (6)	1479 (12)	3330 (7)
Cl(1)	−1010 (2)	406 (5)	1582 (3)
Cl(2)	−2375 (2)	4078 (6)	2307 (3)
Cl(3)	−1242 (2)	6352 (4)	3067 (3)
Cl(4)	−1201 (3)	291 (5)	4616 (3)
Cl(5)	−104 (3)	2763 (5)	5181 (3)
N(4)	225 (6)	2294 (10)	1841 (7)
P(4)	933 (2)	1433 (4)	1945 (3)
C(11)	1458 (8)	1843 (16)	3015 (10)
C(12)	1299 (9)	3058 (18)	3523 (11)
C(13)	2050 (9)	956 (18)	3356 (12)
C(14)	1712 (9)	3435 (23)	4374 (13)
C(15)	2306 (11)	2620 (28)	4686 (14)
C(16)	2466 (11)	1315 (31)	4187 (17)
C(21)	1374 (7)	2077 (14)	1018 (10)
C(22)	2077 (9)	1756 (19)	1025 (14)
C(23)	989 (8)	2831 (17)	255 (10)
C(24)	2374 (9)	2166 (20)	257 (13)
C(25)	1326 (10)	3234 (18)	−475 (9)
C(26)	2007 (10)	2962 (19)	−506 (13)
C(31)	862 (7)	−592 (15)	1843 (9)
C(32)	874 (7)	−1244 (17)	957 (10)
C(33)	750 (8)	−2840 (21)	885 (12)
C(34)	617 (9)	−3726 (18)	1615 (13)
C(35)	585 (10)	−3033 (20)	2446 (14)
C(36)	705 (9)	−1445 (20)	2607 (12)

set having the lowest Karle R value (28·6%). Least-squares refinement, followed by a Fourier synthesis, enabled the remaining atoms to be identified. In the initial stages the structure was refined by block-diagonal least-squares calculations with anisotropic temperature factors and Cruickshank, Bujosa, Lovell & Truter's (1961) weighting scheme, $w = 1/(11{\cdot}8 + 1{\cdot}0|F| + 0{\cdot}0081|F|^2)$. The last stages of refinement were by full-matrix least-squares calculation with the weighting scheme $w = K/(\sigma^2|F| + g|F|^2)$, where K and g were refined to fit the spread of $|F|$ values. The structure converged to a final $R = 0{\cdot}069$. H atoms were included at the positions deduced from molecular geometry, but were not refined. Scattering factors were from Cromer & Waber (1965) in the initial stages and subsequently from *International Tables for X-ray Crystallography* (1974). They were all corrected for the real part of the anomalous dispersion. The final atomic coordinates of non-hydrogen atoms are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and phenyl-ring dimensions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34246 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

Triphosphazatriene ring

A view of the molecule down **b** is shown in Fig. 1. Bond lengths and angles are given in Table 2. It is well known that the P—N distances in the phosphazene ring vary with the electronegativity of the substituents on the P atoms (Ahmed, Singh & Barnes, 1969; Wagner, 1971). In view of the presence of an electron-donating group like $NPPh_3$ in this compound, we expect three different P—N distances in the ring. In the P—N—P segments P(2)—N(3)—P(3) and P(2)—N(1)—P(1) the P atom [P(3) or P(1)] which carries the more electronegative substituents (Cl) competes more successfully for the electron density in the P—N—P system. Hence the P—N bond involving that P atom will have greater bond strength. In the remaining segment, P(3)—N(2)—P(1), both the P atoms have the same substituents and so the two P—N bonds in this segment should have equal strength. On this basis we expect P(2)—N(3) and P(2)—N(1) to be the longest, P(3)—N(3) and P(1)—N(1) the shortest bonds in the ring, and P(3)—N(2) and P(1)—N(2) to be intermediate in length. The presence of three different P—N bonds has been observed in similar trimeric structures like $N_3P_3Cl_4Ph(NPPh_3)$ and *gem*-$N_3P_3Cl_4Ph_2$ (Mani, Ahmed & Barnes, 1965). In the present structure, the distinction in bond lengths is not clear, presumably due to inaccuracies in the intensities. However, the mean of the P—N distances adjacent to the P atom carrying the $NPPh_3$ group is 1·617 (8) Å. The mean of P(3)—N(3) and P(1)—N(1) is 1·586 (8) Å and the average bond distance in the P(3)—N(2)—P(1) segment is 1·593 (8) Å. Thus the mean values of similar bonds suggest the above trend even though the high e.s.d.'s do not permit us to draw any firm conclusions.

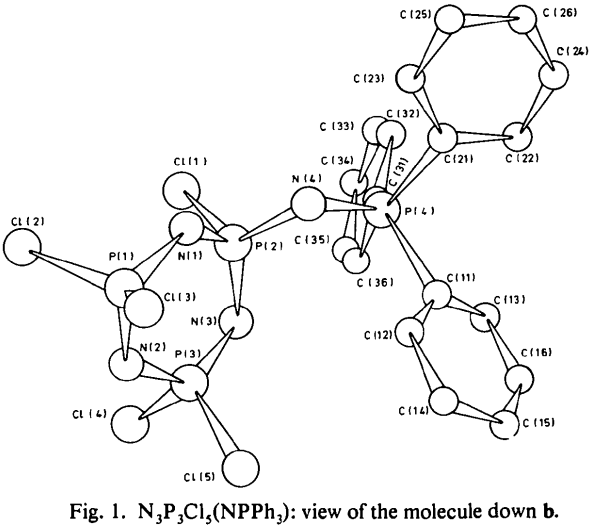

Fig. 1. $N_3P_3Cl_5(NPPh_3)$: view of the molecule down **b**.

Table 2. *Bond distances* (Å) *and angles* (°)

The e.s.d.'s for bond lengths are P–Cl ~0·005, P–N ~0·012, P–C ~0·01 Å; for bond angles they are ∠ClPCl 0·3, ∠NPN, ∠PNP, ∠NPC, ∠NPCl 0·6–0·8° and ∠CPC 0·6–0·7°.

P(1)–N(1)	1·582	P(3)–N(2)	1·593
P(1)–N(2)	1·594	P(3)–N(3)	1·590
P(1)–Cl(2)	2·050	P(3)–Cl(4)	2·010
P(1)–Cl(3)	1·979	P(3)–Cl(5)	2·025
P(2)–N(1)	1·611	P(4)–N(4)	1·597
P(2)–N(3)	1·622	P(4)–C(11)	1·81
P(2)–Cl(1)	2·046	P(4)–C(21)	1·84
P(2)–N(4)	1·614	P(4)–C(31)	1·77
N(1)–P(1)–N(2)	120·8	N(2)–P(3)–Cl(5)	109·6
N(1)–P(1)–Cl(2)	111·2	N(3)–P(3)–Cl(4)	112·0
N(1)–P(1)–Cl(3)	107·6	N(3)–P(3)–Cl(5)	108·6
N(2)–P(1)–Cl(2)	106·6	Cl(4)–P(3)–Cl(5)	100·5
N(2)–P(1)–Cl(3)	108·0	P(1)–N(1)–P(2)	121·8
Cl(2)–P(1)–Cl(3)	100·5	P(1)–N(2)–P(3)	118·2
N(1)–P(2)–N(3)	114·2	P(2)–N(3)–P(3)	122·7
N(1)–P(2)–Cl(1)	104·2	P(2)–N(4)–P(4)	134·8
N(1)–P(2)–N(4)	111·6	N(4)–P(4)–C(11)	112·8
N(3)–P(2)–Cl(1)	104·8	N(4)–P(4)–C(21)	108·1
N(3)–P(2)–N(4)	114·0	N(4)–P(4)–C(31)	113·5
Cl(1)–P(2)–N(4)	107·0	C(11)–P(4)–C(21)	108·6
N(2)–P(3)–N(3)	119·7	C(11)–P(4)–C(31)	107·4
N(2)–P(3)–Cl(4)	104·6	C(21)–P(4)–C(31)	106·2

In each geminal PCl_2 group, P–Cl distances are unequal. Similar differences in geminal P–Cl distances have been observed in *gem*-$N_3P_3Ph_2Cl_4$ (Mani, Ahmed & Barnes, 1965) and $N_3P_3Cl_4Ph(NPPh_3)$ (Biddlestone, Bullen, Dann & Shaw, 1974). The two exocyclic P–N distances are equal within experimental error and are similar to those of the ring indicating delocalization of electrons in the exocyclic P–N–P segment. The P–C distances are unexceptional.

The average endocyclic angle at P(1) and P(3) is 120·3° and the corresponding exocyclic angle is 100·5°. These values are similar to the 118·4 and 101·3° in $N_3P_3Cl_6$ (Bullen, 1971). Around P(2), however, the bonds approach tetrahedral geometry, the endocyclic angle decreasing to 114·2° and the exocyclic angle increasing to 107·0°. This is due to the presence of the electron-donating group, $NPPh_3$. As in $N_3P_3Cl_4Ph(NPPh_3)$, the triphosphazatriene ring is non-planar; P(2) to which the triphenylphosphazenyl group is attached is 0·23 Å out of the plane formed by the other five atoms. The non-planarity of the triphosphazatriene ring appears to be due to the short intramolecular contact which P(2) makes with C(31) [P(2)···C(31) = 3·65 Å].

Conformation of the exocyclic $NPPh_3$ *group*

The torsion angles P(4)–N(4)–P(2)–N(3), P(4)–N(4)–P(2)–N(1) and P(4)–N(4)–P(2)–Cl(1) are 34 (1), 164 (1) and −83 (1)° respectively. The triphenylphosphazenyl substituent thus exhibits type I conformation. This is in contrast to the conformation in $N_3P_3Cl_4Ph(NPPh_3)$ where the $NPPh_3$ group exhibits type II conformation. The difference in the conformations of the $NPPh_3$ group in $N_3P_3Cl_5(NPPh_3)$ and $N_3P_3Cl_4Ph(NPPh_3)$ may be due to electronic factors. The greater electronegativity of Cl(1) in the former compared with the phenyl group in the latter would cause electron transfer from the adjacent N(1), N(3) and N(4) into the P–N π-bond system. The exocyclic N(4) is in a favourable position to contribute electrons if the torsion angle P(4)–N(4)–P(2)–Cl(1) is 90°. In this position the p_z orbital of N(4) can overlap effectively with the d_{z^2} orbital of P(2).

Packing

The packing of molecules in the cell is shown in Fig. 2. Intermolecular contacts <4·0 Å likely to determine the packing are shown in the figure and are listed in Table 3. The molecules are arranged in rows parallel to [100]. Cl(3) and one of the phenyl rings in each molecule of the row project into the neighbouring rows. There are short intermolecular contacts within each row and between neighbouring rows. The orientation

Table 3. *Intermolecular contacts* <3·9 Å

Contact	Symmetry code	Distance (Å)	Contact	Symmetry code	Distance (Å)
N(1)–C(25)	(I)	3·71 (2)	N(2)–C(24)	(II)	3·66 (2)
Cl(2)–C(26)	(I)	3·87 (1)	N(2)–C(26)	(II)	3·82 (2)
Cl(3)–C(25)	(I)	3·86 (1)	Cl(4)–C(24)	(II)	3·86 (1)
Cl(5)–C(35)	(I)	3·82 (2)	Cl(4)–C(26)	(II)	3·89 (1)
Cl(5)–C(36)	(I)	3·86 (1)	Cl(2)–Cl(3)	(III)	3·634 (5)
Cl(3)–Cl(5)	(I)	3·552 (5)	Cl(2)–Cl(4)	(III)	3·880 (5)
Cl(1)–C(25)	(I)	3·58 (1)	C(14)–C(22)	(III)	3·88 (2)
Cl(1)–C(26)	(I)	3·77 (1)	C(14)–C(24)	(III)	3·73 (2)
Cl(4)–C(13)	(I)	3·85 (1)	C(16)–C(33)	(III)	3·68 (2)
Cl(4)–C(14)	(I)	3·78 (2)	C(16)–C(24)	(III)	3·70 (2)
Cl(4)–C(15)	(I)	3·63 (2)	C(23)–C(34)	(IV)	3·75 (2)
Cl(4)–C(16)	(I)	3·61 (2)	N(4)–C(34)	(IV)	3·57 (2)
Cl(4)–Cl(5)	(I)	3·715 (5)			
C(23)–C(33)	(I)	3·65 (2)			

Symmetry code: (I) $-x,-y,-z$; (II) $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; (III) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; (IV) $x, 1+y, z$.

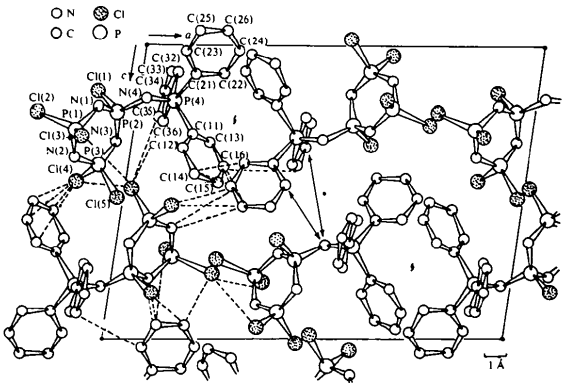

Fig. 2. The crystal structure viewed down **b**.

of the phenyl rings is determined by the close contacts they make with atoms in adjacent molecules.

We thank Professor R. A. Shaw for suggesting the problem and for valuable comments, Dr S. S. Krishnamurthy for the crystals and Professors C. C. Patel and A. R. Vasudeva Murthy for their interest.

References

AHMED, F. R., SINGH, P. & BARNES, W. H. (1969). *Acta Cryst.* B**25**, 316–328.

BABU, Y. S., CAMERON, T. S., KRISHNAMURTHY, S. S., MANOHAR, H. & SHAW, R. A. (1976). *Z. Naturforsch. Teil B*, **31**, 999–1000.

BIDDLESTONE, M., BULLEN, G. J., DANN, P. E. & SHAW, R. A. (1974). *Chem. Commun.* pp. 56–57.

BIDDLESTONE, M. & SHAW, R. A. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2740–2747.

BULLEN, G. J. (1971). *J. Chem. Soc. A*, pp. 1450–1453.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. Oxford: Pergamon Press.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 101. Birmingham: Kynoch Press.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN*. Univ. of York, England.

MANI, N. V., AHMED, F. R. & BARNES, W. H. (1965). *Acta Cryst.* **19**, 693–698.

NABI, S. N., BIDDLESTONE, M. & SHAW, R. A. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2634–2638.

SHAW, R. A. (1975). *Pure Appl. Chem.* **44**, 317–341.

SHAW, R. A. (1976). *Z. Naturforsch. Teil B*, **31**, 641–667.

WAGNER, A. J. (1971). *J. Inorg. Nucl. Chem.* **33**, 3988–3989.

Acta Cryst. (1979). B**35**, 1413–1419

The Crystal and Molecular Structures of Three Cyclopolymethylenetetrazole Compounds

BY DONALD L. WARD, KWO-TSAIR WEI, ALFRED J. SMETANA AND ALEXANDER I. POPOV

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, *USA*

(*Received* 11 *September* 1978; *accepted* 30 *January* 1979)

Abstract

Trimethylenetetrazole (I), $C_4H_6N_4$, crystallizes in the monoclinic system, space group $P2_1/n$, with a = 7·758 (5), b = 10·367 (6), c = 6·694 (2) Å, β = 102·02 (4)°, 292 K, D_x = 1·389 Mg m^{-3}, Z = 4. Pentamethylenetetrazole (II), $C_6H_{10}N_4$, crystallizes in the monoclinic system, space group $P2_1/n$, with a = 13·310 (6), b = 8·409 (3), c = 6·589 (2) Å, β = 94·72 (3)°, 297 K, D_x = 1·249 Mg m^{-3}, Z = 4. 8-*tert*-Butylpentamethylenetetrazole (III), $C_{10}H_{18}N_4$, crystallizes in the monoclinic system, space group $P2_1/c$, with a = 12·881 (4), b = 6·614 (2), c = 14·132 (6) Å, β = 111·52 (2)°, 291 K, D_x = 1·152 Mg m^{-3}, Z = 4. The X-ray intensities were measured with a Picker FACS-I automatic diffractometer, Mo $K\alpha$ radiation, and θ–2θ scans: (I) 1213 unique data for $2\theta \leq 55°$ (638 observed); (II) 1693 unique data for $2\theta \leq 55°$ (887 observed); (III) 1980 unique data for $2\theta \leq 50°$ (1245 observed). The parameters were refined by full-matrix least squares to a final R of (I) 0·053, (II) 0·055, (III) 0·043. The atoms N(1) and C(5) of the tetrazole ring are disordered in all three structures; they were refined as composite 'NC' atoms consisting of $\frac{1}{2}$N + $\frac{1}{2}$C in their scattering factors. The unusual aqueous solubility of (II) is discussed in relation to the crystal structure. Differences are noted in the molecular structures of complexed and free ligand (II).

Introduction

Cyclopolymethylenetetrazoles are noted for their strong stimulating activity on the central nervous system. In sufficient doses they are capable of inducing epileptic convulsions. The activity increases with the length of the hydrocarbon chain and varies from 1000 mg kg^{-1} for trimethylenetetrazole to 30 mg kg^{-1} for heptamethylenetetrazole (Stone, 1970).

As expected, the aqueous solubility decreases with increasing length of the hydrocarbon chain; trimethylenetetrazole (I) is soluble to the extent of 1·4 molal while the solubility of heptamethylenetetrazole is 0·18 molal. A glaring exception is pentamethylenetetrazole (II) which is soluble to the extent of 5·0 molal (Baum, 1976).

Crystallographic studies of the pentamethylenetetrazole (II) complex with iodine chloride (Baenziger,

0567-7408/79/061413-07$01.00