Solid-state Structure and Solution Conformation of 2,2,4,4,6,6,-Hexa(*p*-chlorophenoxo)cyclotri-λ^5-phosphazatriene. *X*-Ray and Dipole Moment Studies†

Giuliano Bandoli
Dipartimento di Scienze Farmaceutiche, Università di Padova, Via Marzolo 5, 35137 Padova, Italy
Umberto Casellato
Istituto di Chimica e Tecnologia dei Radioelementi C.N.R., Corso Stati Uniti, Area della Ricerca di Padova, 35100 Padova, Italy
Mario Gleria
Istituto di Fotochimica e Radiazioni d'Alta Energia, C.N.R., Via Romea 4, 35020 Legnaro (Padova), Italy
Antonio Grassi, Enzo Montoneri, and Giuseppe C. Pappalardo *
Dipartimento di Scienze Chimiche, II Cattedra di Chimica Generale, Facoltà di Farmacia, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

The crystal and molecular structure of $[NP(OC_6H_4Cl\text{-}p)_2]_3$ was determined by *X*-ray analysis. The dipole moments of this compound and its unsubstituted analogue $[NP(OC_6H_5)_2]_3$ were measured in benzene at 25 °C and interpreted in terms of the conformation in solution. Crystals of $[NP(OC_6H_4Cl\text{-}p)_2]_3$ are monoclinic with unit-cell dimensions $a = 17.804(6)$, $b = 7.656(3)$, $c = 27.951(9)$ Å, and $\beta = 91.68(7)°$; space group $P2_1/c$. The structure was determined from 2 418 three-dimensional counter data and refined to $R = 0.051$. The phosphazene ring is almost planar (maximum deviation 0.06 Å), and the mean bond distances and angles are P–N 1.575(5), P–O 1.579(5), and O–C 1.393(8) Å, P–N–P 122.5(3) and N–P–N 117.4(3)°. The conformations of the phenoxo-groups at P(3) are different from those at atoms P(1) and P(2) at which these groups adopt the same conformation. The measured dipole moment data for both compounds are in agreement with a C_3 symmetry conformation in which at each local O–P–O plane one phenoxo-group is rotated by *ca.* 40—50° from the *anti*-coplanar arrangement relative to this plane. These data also indicated that the conformation about the P–O bonds found in the crystal is not retained in solution.

The solid-state structure of hexaphenoxocyclotriphosphazene has been reported,[1] but no information is available on the solution conformations of aryloxophosphazenes. In this work we report the crystal and molecular structure of hexa(*p*-chlorophenoxo)cyclotriphosphazene $[NP(OC_6H_4Cl\text{-}p)_2]_3$ and the dipole moments of both this molecule and of hexaphenoxocyclotriphosphazene $[NP(OC_6H_5)_2]_3$. The dipole moment data are analysed and discussed in terms of the conformations about the P–O bonds.

Experimental

Samples.—Described methods [2–4] were used for the synthesis of $[NP(OC_6H_5)_2]_3$ (m.p. 115—116 °C) and $[NP(OC_6H_4Cl\text{-}p)_2]_3$ (m.p. 155—156 °C).

Crystallography.—*Crystal data.* $C_{36}H_{24}Cl_6N_3O_6P_3$, $M = 899.8$, monoclinic, $a = 17.804(6)$, $b = 7.656(3)$, $c = 27.951(9)$ Å, $\beta = 91.68(7)°$, $U = 3\,808.3(23)$ Å^3, $D_m = 1.56$ (by flotation in CCl_4–CS_2), $Z = 4$, $D_c = 1.569$ g cm^{-3}, $F(000) = 1\,824$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 5.6 cm^{-1}, space group $P2_1/c$.

The intensities of all reflections with $2\theta < 50°$ were measured on a Stoe-Siemens AED1 diffractometer. Of 3 112 independent reflections, 2 418 (78%) with $I > 3\sigma(I)$ were classified as observed and were used in the structure analysis.

Structure analysis. Refinement by minimization of the function $w\Delta F^2$ was terminated when the maximum and average shift-to-error ratios in positional parameters were <0.13 and <0.05. The carbon atoms were treated isotropically. Refinement was performed until convergence at $R = 0.051$ for the observed reflections. Final positional parameters for the non-hydrogen atoms are listed in Table 1, bond lengths and angles in Table 2. Computations were carried out with the use of the SHELX 86 program package.[5]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Dipole Moment Measurements.—The electric dipole moments (μ) were determined in benzene solution at 25 ± 0.01 °C using apparatus and techniques described previously.[6] The data required for the calculation of the values by the Guggenheim method [7] are reported in Table 3.

Results and Discussion

X-Ray Analysis.—The structure of $[NP(OC_6H_4Cl\text{-}p)_2]_3$ (Figure 1) does not show significant intermolecular interactions. The P–N bonds [from 1.566(7) to 1.589(7) Å] are equal (the difference is within 2σ). The N_3P_3 ring is close to planarity with N–P–N and P–N–P angles of 117.4(4) and 122.5(4)°, respectively. These features differ from those of other symmetrically substituted $(NPX_2)_3$ cyclotriphosphazatrienes.[8–14] The average dihedral angle between four of the phenyl groups and the N_3P_3 ring is 104.6°. The dihedral angles between N_3P_3 and phenyl groups bonded to O(2) and O(3) are 64.3 and 60.5°, respectively. The torsion angles of Ph–O at atoms P(1) and P(2) are similar. At P(3), while the relative *anti* orientation is retained, the deviation of the C–O bonds from coplanarity with

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: D ≈ 3.33 × 10^{-30} C m.

Table 1. Final positional parameters and standard deviations for $[NP(OC_6H_4Cl\text{-}p)_2]_3$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
P(1)	0.191 1(1)	0.262 4(3)	0.040 8(1)	C(10)	0.119 7(5)	0.105 2(13)	0.217 4(3)
P(2)	0.303 1(1)	0.293 7(3)	−0.024 5(1)	C(11)	0.191 9(5)	0.071 8(13)	0.207 6(3)
P(3)	0.247 8(1)	−0.033 1(3)	−0.001 8(1)	C(12)	0.221 0(5)	0.139 6(12)	0.165 5(3)
Cl(1)	−0.062 8(1)	0.285 7(4)	−0.146 6(1)	C(13)	0.318 8(4)	0.341 6(11)	−0.117 1(2)
Cl(2)	0.085 6(2)	0.035 1(5)	0.272 2(1)	C(14)	0.274 8(5)	0.268 7(13)	−0.152 4(3)
Cl(3)	0.415 4(2)	0.246 6(5)	−0.260 1(1)	C(15)	0.305 4(6)	0.235 3(15)	−0.196 9(3)
Cl(4)	0.567 5(1)	0.151 0(4)	0.153 7(1)	C(16)	0.378 3(5)	0.279 1(13)	−0.204 5(3)
Cl(5)	0.137 6(2)	−0.065 7(4)	−0.242 0(1)	C(17)	0.421 6(5)	0.355 4(14)	−0.169 8(3)
Cl(6)	0.364 2(2)	−0.257 3(5)	0.229 9(1)	C(18)	0.391 8(5)	0.384 0(13)	−0.124 8(3)
O(1)	0.108 7(3)	0.339 0(7)	0.035 1(1)	C(19)	0.428 6(4)	0.315 1(11)	0.026 5(2)
O(2)	0.208 0(3)	0.307 2(7)	0.095 1(1)	C(20)	0.494 1(5)	0.223 9(12)	0.020 1(3)
O(3)	0.285 6(3)	0.383 9(7)	−0.074 2(1)	C(21)	0.537 6(5)	0.174 3(12)	0.058 8(3)
O(4)	0.386 6(3)	0.363 4(7)	−0.014 3(1)	C(22)	0.514 4(5)	0.219 8(12)	0.104 0(3)
O(5)	0.205 6(3)	−0.160 1(8)	−0.037 8(2)	C(23)	0.448 9(4)	0.315 0(12)	0.110 0(3)
O(6)	0.292 1(3)	−0.181 2(7)	0.026 0(1)	C(24)	0.406 0(4)	0.364 7(11)	0.071 0(3)
N(1)	0.190 5(3)	0.057 7(8)	0.031 5(2)	C(25)	0.190 3(4)	−0.129 7(11)	−0.086 1(3)
N(3)	0.303 9(3)	0.087 7(9)	−0.029 2(2)	C(26)	0.128 6(5)	−0.035 2(13)	−0.100 8(3)
N(2)	0.247 6(3)	0.375 4(8)	0.011 8(2)	C(27)	0.112 8(5)	−0.014 0(13)	−0.148 9(3)
C(1)	0.068 7(4)	0.329 9(11)	−0.008 7(2)	C(28)	0.155 9(5)	−0.093 1(12)	−0.181 3(3)
C(2)	0.091 9(4)	0.425 1(11)	−0.048 0(2)	C(29)	0.218 3(5)	−0.191 0(12)	−0.166 9(3)
C(3)	0.050 7(5)	0.414 0(12)	−0.090 9(3)	C(30)	0.234 6(5)	−0.212 5(12)	−0.118 3(3)
C(4)	−0.013 4(4)	0.306 6(12)	−0.092 6(2)	C(31)	0.307 4(4)	−0.190 1(12)	0.074 9(2)
C(5)	−0.036 7(4)	0.219 2(12)	−0.053 5(3)	C(32)	0.371 7(5)	−0.117 0(12)	0.093 4(3)
C(6)	0.005 0(4)	0.227 9(12)	−0.010 9(2)	C(33)	0.389 7(5)	−0.138 9(13)	0.142 0(3)
C(7)	0.174 5(4)	0.230 2(11)	0.134 4(2)	C(34)	0.341 8(5)	−0.235 2(13)	0.169 3(3)
C(8)	0.101 3(5)	0.257 1(12)	0.144 3(3)	C(35)	0.276 2(5)	−0.306 9(12)	0.150 1(3)
C(9)	0.073 2(5)	0.193 4(13)	0.187 4(3)	C(36)	0.259 2(4)	−0.283 9(12)	0.102 9(2)

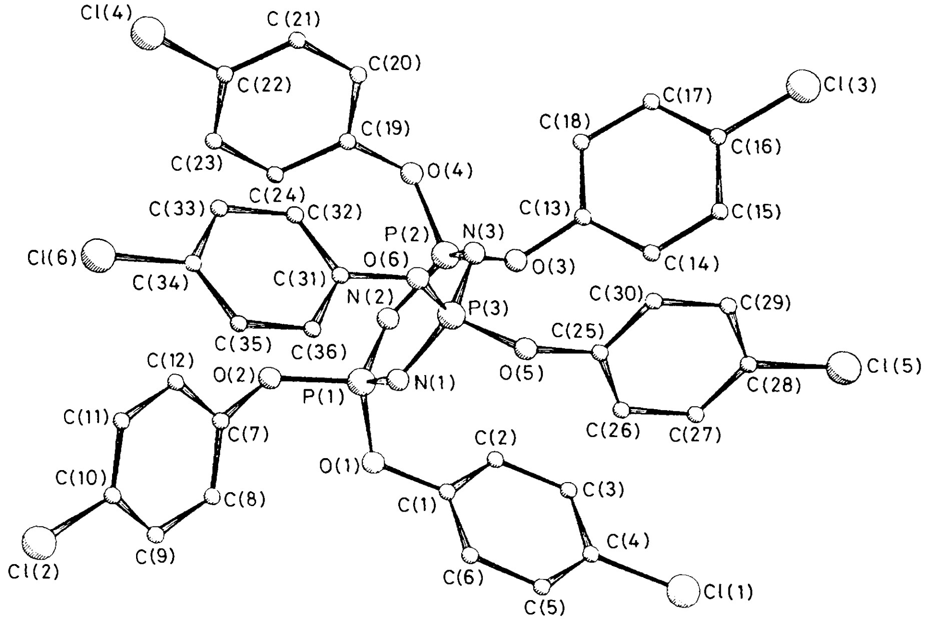

Figure 1. Perspective of 2,2,4,4,6,6-hexa(*p*-chlorophenoxo)cyclotriphosphazatriene with the atom numbering

respect to the O–P–O plane is more significant (*ca.* 90°). These orientations of the *p*-chlorophenoxo-groups differ from those observed in the phenoxo analogue (Figure 2), presumably due to different inter- and intra-molecular effects operating in the crystals.

Dipole Moment Analysis.—Theoretical dipole moments ($\mu_{calc.}$) for the possible conformations denoted by the angles ω_1,ω_2; ω'_1,ω'_2; and ω''_1,ω''_2 (Figure 3) were calculated through vector addition of bond moments ($\mu_{Ph-O} = 1.04$, $\mu_{Ph-Cl} = 1.57$ D).[15] In the assumed symmetric frame of the planar N_3P_3 ring, the resultant of the three fixed P–O bond moments was zero. Clear disagreement was found between experimental ($\mu_{exptl.}$) and $\mu_{calc.}$ {0.62 and 0.39 D for $[NP(OC_6H_5)_2]_3$ and $[NP(OC_6H_4Cl\text{-}p)_2]_3$, respectively} for the angles corresponding to the conformations in the solid state that, on this basis, can be

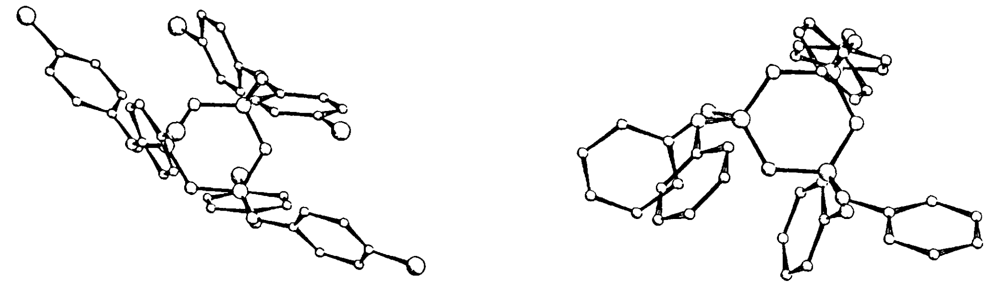

Figure 2. Comparison of the conformations of 2,2,4,4,6,6-hexa(*p*-chlorophenoxo) (left) and 2,2,4,4,6,6-hexaphenoxo-cyclotriphosphazatriene (right) in the solid, as viewed along the perpendicular to the N_3P_3 plane

Table 2. Interatomic distances (Å) and angles (°)

P(1)–N(1)	1.589(7)	Cl(1)–C(4)	1.732(9)
P(1)–N(2)	1.570(7)	Cl(2)–C(10)	1.747(10)
P(2)–N(2)	1.568(7)	Cl(3)–C(16)	1.725(10)
P(2)–N(3)	1.583(7)	Cl(4)–C(22)	1.740(9)
P(3)–N(1)	1.566(7)	Cl(5)–C(28)	1.731(10)
P(3)–N(3)	1.576(7)	Cl(6)–C(34)	1.736(9)
P(1)–O(1)	1.584(6)	O(1)–C(1)	1.400(9)
P(1)–O(2)	1.576(6)	O(2)–C(7)	1.396(9)
P(2)–O(3)	1.575(6)	O(3)–C(13)	1.390(10)
P(2)–O(4)	1.596(6)	O(4)–C(19)	1.396(9)
P(3)–O(5)	1.573(7)	O(5)–C(25)	1.390(10)
P(3)–O(6)	1.575(6)	O(6)–C(31)	1.387(9)
C–C mean	1.38	C–H mean	1.09
N(1)–P(1)–N(2)	117.4(4)	O(5)–P(3)–N(3)	110.6(4)
O(2)–P(1)–N(2)	105.8(4)	O(5)–P(3)–N(1)	110.4(4)
O(2)–P(1)–N(1)	111.9(3)	O(5)–P(3)–O(6)	95.5(4)
O(1)–P(1)–N(2)	110.4(4)	P(1)–O(1)–C(1)	121.1(5)
O(1)–P(1)–N(1)	110.3(4)	P(1)–O(2)–C(7)	126.3(5)
O(1)–P(1)–O(2)	99.6(3)	P(2)–O(3)–C(13)	125.6(5)
N(2)–P(2)–N(3)	117.3(4)	P(2)–O(4)–C(19)	122.1(5)
O(4)–P(2)–N(2)	110.7(4)	P(3)–O(5)–C(25)	126.4(6)
O(4)–P(2)–N(3)	109.7(4)	P(3)–O(6)–C(31)	127.2(6)
O(3)–P(2)–N(2)	106.5(4)	P(1)–N(1)–P(3)	122.3(4)
O(3)–P(2)–N(3)	111.4(4)	P(2)–N(3)–P(3)	122.5(5)
O(3)–P(2)–O(4)	99.8(3)	P(1)–N(2)–P(2)	122.7(4)
N(1)–P(3)–N(3)	117.4(4)	O–C–C mean	119.1(6)
O(6)–P(3)–N(3)	110.3(4)	Cl–C–C mean	119.2(5)
O(6)–P(3)–N(1)	110.5(3)	C–C–C mean	120.0(6)
P(1)–O(1)–C(1)–C(2)	−67.34	P(1)–O(2)–C(7)–C(8)	−69.14
P(1)–O(1)–C(1)–C(6)	114.48	P(1)–O(2)–C(7)–C(12)	117.17
P(2)–O(3)–C(13)–C(14)	113.06	P(2)–O(4)–C(19)–C(20)	117.67
P(2)–O(3)–C(13)–C(18)	−71.73	P(2)–O(4)–C(19)–C(24)	−65.02
P(3)–O(5)–C(25)–C(26)	−83.74	P(3)–O(6)–C(31)–C(32)	−89.89
P(3)–O(5)–C(25)–C(30)	102.76	P(3)–O(6)–C(31)–C(36)	94.60

Table 3. Parameters for the calculation of dipole moments for cyclotriphosphazenes in benzene solution at 25 °C

Compound	$\Sigma(\varepsilon_{12} - \varepsilon_{10})/\Sigma w_2$	$\Sigma(n_{12}^2 - n_{10}^2)/\Sigma w_2$	μ/D
$[NP(OC_6H_5)_2]_3$	1.54	0.399	2.70
$[NP(OC_6H_4Cl\text{-}p)_2]_3$	0.37	0.188	1.24

* Symbols are as given in ref. 6.

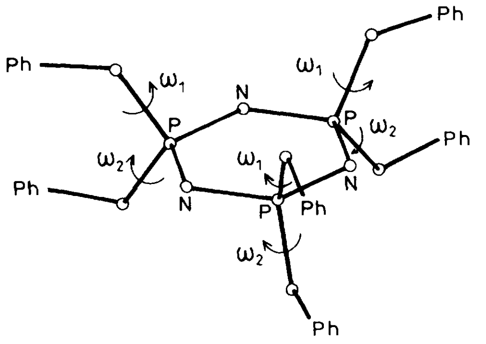

Figure 3. Perspective of the cyclophosphazatriene molecule in the assumed starting conformation 0,0°. Positive rotations are taken as anticlockwise along each O–P bond (looking from O to P). Each set of three phenoxo groups placed on each face of the N_3P_3 plane was considered to undergo simultaneous conrotatory torsions ($\omega_1 = \omega_1' = \omega_1''$; $\omega_2 = \omega_2' = \omega_2''$) for independent rotations of the two sets. The triads of rotational angles could be thus denoted as ω_1,ω_2

reasonably excluded in solution. A search of the conformations compatible with the $\mu_{exptl.}$ values was made by assuming that C_3 symmetry is retained by rotations about P–O bonds (see Figure 3). Among the conformations for which $\mu_{calc.} = \mu_{exptl.}$, those with angles 0,130—140° were chosen on the basis of steric effects. The conformation 0,130° proposed in solution for the *p*-chlorophenoxo compound resembles the conformations found in the crystal, while this is not the case for the unsubstituted analogues, due to different intermolecular effects in the solid. In solution, where almost exclusively intramolecular effects operate, the same relative orientations of phenoxo-groups were expected for the two cyclophosphazenes. This appears verified, the difference between the ω_2 values (130 and 140°) being negligible and within the approximation limits of the approach. The above results indicate that steric, more than electronic effects, are the conformation-determining factors *in solution* for both cyclophosphazenes dealt with.

References

1 W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 1971, 169.
2 H. R. Allcock, 'Phosphorus-Nitrogen Compounds,' Academic Press, New York, 1972.
3 H. R. Allcock, K. L. Kugel, and K. J. Valan, *Inorg. Chem.*, 1966, **5**, 1709.
4 R. L. Dieck and M. A. Selvosky, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 313.
5 G. M. Sheldrick, in 'Crystallographic Computing 3,' eds. G. M. Sheldrick, C. Krüger, and R. Goddard, Oxford University Press, 1985, pp. 175—189.
6 G. C. Pappalardo and S. Pistarà, *J. Chem. Eng. Data*, 1972, **17**, 2.
7 F. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.
8 M. W. Dougill, *J. Chem. Soc.*, 1963, 3211.
9 G. J. Bullen, *J. Chem. Soc. A*, 1971, 1450.
10 H. Zoer and A. J. Wagner, *Acta Crystallogr., Sect. B*, 1970, **26**, 1812.

11 F. R. Ahmed, P. Singh, and W. H. Barnes, *Acta Crystallogr., Sect. B*, 1969, **25**, 316.

12 S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1973, **51**, 1295.

13 R. J. Ritchie, T. J. Fuller, and H. R. Allcock, *Inorg. Chem.*, 1980, **19**, 3842.

14 T. S. Cameron, J. F. Labarre, and M. Graffeuil, *Acta Crystallogr., Sect. B*, 1982, **38**, 2000.

15 C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.

Received 3rd February 1988; *Paper* 8/00552D