Solid State Structure of 2,2,4,4,6,6-Hexa(β-naphthyloxo)cyclophosphazatriene and Dipole Moments of Hexa(aryloxo)cyclophosphazatrienes

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Hexa(aryloxo)cyclophosphazatrienes, X-Ray, Solid State Structure, Dipole Moment

The crystal and molecular structure of $[NP(OC_{10}H_7)_2]_3$ was determined by X-ray analysis. The dipole moments of this compound and of the hexa(phenoxo)cyclotriphosphazatrienes of formula $[NP(OC_6H_3XX'Y)_2]_3$ (X = X' = H, Y = *p*-Br; X = *m*-CH_3, X' = H, Y = *p*-Cl; X = X' = *m*-CH_3, Y = *p*-Cl; X = X' = *m*-CH_3, Y = H; X = X' = H, Y = *p*-$CH(CH_3)_2$; X = X' = H, Y = *p*-$C(CH_3)_3$) were measured in benzene at 25 °C. Crystals of $[NP(OC_{10}H_7)_2]_3$ are monoclinic with unit cell dimensions a = 24.870(15), b = 7.712(8), c = 27.687(14) Å, β = 115.85(7)°; space group $P2_1/c$. The structure was refined to an agreement factor of 0.09. The phosphazene ring deviates (max. deviation 17°) from planarity, and mean distances (Å) and angles (°) are P–N 1.58(1), P–O 1.58(1), O–C 1.41(2); P–N–P 120(1), N–P–N 119(1), P–O–C 124(2). The conformations of the naphthyloxo groups at P(2) and P(3) are similar, and different from the group at P(1).

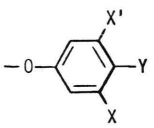
Dipole moment analysis showed that the solid state conformation changes in the solution state. The measured value was in agreement with a symmetric conformation in which at the O–P–O plane each naphthyloxo group is rotated by *ca.* 40–50° from the *anti*-coplanar arrangement relative to this plane. The dipole moment data for the *p*-substituted phenoxo derivatives agree with such a conformation, but the analysis of the dipole moment values of phosphazenes having phenoxo groups bearing more than one substituent group and *p*-$CH(CH_3)_2$ substituent failed to do so due to the inherent limitations of the method.

Introduction

Phosphazenes bearing aromatic substituents are ideal models to carry out electrophilic reactions for the synthesis of new phosphazene derivatives [1]. Our previous investigations on the sulphonation of linear and cyclic phenoxophosphazenes suggested that the conformational aspects [2] determine the selectivity in the substitution reaction at the aromatic ring. Studies on the structure and conformation of phosphazenes substituted with bulkier groups ($-NP(OAr)_2-$, with Ar = naphthyl or substituted phenyl) which may also undergo electrophilic substitution reactions, seemed a direct consequence of the above findings.

In this work we report the crystal and molecular structure of hexa(β-naphthyloxo)cyclotriphosphazatriene (**1**) and the dipole moments, in benzene solution, of this compounds as well as of the hexa(aryloxo)-cyclotriphosphazatrienes **2a–f.** The aryloxo group chemical structures are given below.

The crystal structures [3, 4] and the dipole moment data analysis [4] for hexa(phenoxo)cyclotriphosphazatriene $[NP(OC_6H_5)_2]_3$ and hexa(*p*-chlorophenoxo)cyclotriphosphazatriene $[NP(OC_6H_4Cl\text{-}p)_2]_3$ were reported previously.



2a	X = X' = H, Y = Br
2b	X = CH_3, X' = H, Y = Cl
2c	X = X' = CH_3, Y = Cl
2d	X = X' = CH_3, Y = H
2e	X = X' = H, Y = $CH(CH_3)_2$
2f	X = X' = H, Y = $C(CH_3)_3$

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Experimental

Samples. – The compounds **1** and **2a–f** were prepared by a general synthetic method described previously [5]. The synthesis of **1** and **2a** was reported also by other workers [6, 7]. The samples used for the experiments were crystallized twice from the appropriate solvent (**1,** m.p. 171–172 °C; **2a,** m.p. 176–177 °C; **2b,** m.p. 104–105 °C; **2c,** m.p. 186–187 °C; **2d,** m.p. 108–109 °C; **2e,** m.p. 72–73 °C; **2f,** m.p. 128–129 °C).

Crystallography. – Intensity data were recorded on a Stoe-Siemens (AED 1 System) automated four-circle diffractometer. The SHELXS-86 and SHELX-76 package [8] of computer programs was employed for the solution and refinement of the structure. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of a methanol-tetrahydrofuran (1:1) solution of compound **1.** A crystal had well developed (100), (010), and (001) faces with perpendicular distances between parallel faces of *ca.* 0.15, 0.30 and 0.20 mm, respectively, and was used for the data collection.

Crystal data. – $[NP(OC_{10}H_7)_2]_3$, M = 993.27, monoclinic, a = 24.870(15), b = 7.712(8), c = 27.687(14) Å, β = 115.85(7)°, U = 4478.9(4.6) Å^3, Z = 4, F(000) = 2064, D_c = 1.47 g cm^{-3}, space group $P2_1/c$, μ(Mo–Kα) = 1.4 cm^{-1}.

A total of 13006 ($\pm h$, $\pm k$, l) reflections were measured, by $\omega-2\vartheta$ scans within the limit $\sin\vartheta/\lambda \leq$ 0.595 Å^{-1} (2ϑ = 50°), using Mo–Kα radiation (λ = 0.7107 Å). The equivalent reflections were averaged (internal consistency R index of 4.3%) and of the remaining 6386 ($\pm h$, k, l) unique reflections only 2211 were considered observed [I > 3σ(I)] and were used for the structure analysis. The integrated intensities were corrected for Lorentz and polarization effects, but not for those of absorption.

Structure determination and refinement. – The structure was solved by direct methods and the best

Table I. Fractional atomic positional parameters.

Atom	*x*	*y*	*z*
N1	0.2667(5)	0.0674(16)	0.3582(5)
N2	0.2966(5)	−0.2710(18)	0.3740(5)
N3	0.1855(5)	−0.1835(18)	0.2983(4)
P1	0.3132(1)	−0.0774(6)	0.3882(1)
O1	0.3402(4)	−0.0532(16)	0.4521(4)
C1	0.3094(6)	−0.0193(21)	0.4820(6)
C2	0.3449(9)	0.0704(27)	0.5308(8)
C3	0.3165(8)	0.1157(24)	0.5625(7)
C4	0.2597(7)	0.0735(23)	0.5516(6)
C5	0.2328(8)	0.1253(24)	0.5853(7)
C6	0.1767(9)	0.0849(29)	0.5719(8)
C7	0.1397(9)	−0.0084(29)	0.5223(8)

Table I. (continuation)

Atom	*x*	*y*	*z*
C8	0.1632(7)	−0.0550(23)	0.4884(7)
C9	0.2257(7)	−0.0103(24)	0.5027(6)
C10	0.2502(7)	−0.0662(23)	0.4673(7)
O2	0.3707(4)	−0.0295(14)	0.3805(4)
C11	0.4225(7)	−0.1419(21)	0.3964(6)
C12	0.4581(7)	−0.1717(23)	0.4465(6)
C13	0.5077(7)	−0.2765(23)	0.4598(6)
C14	0.5490(8)	−0.3255(28)	0.5143(8)
C15	0.5951(8)	−0.4385(26)	0.5261(8)
C16	0.6012(8)	−0.5113(29)	0.4828(8)
C17	0.5668(7)	−0.4704(25)	0.4310(7)
C18	0.5173(7)	−0.3495(22)	0.4167(6)
C19	0.4789(7)	−0.3083(25)	0.3643(7)
C20	0.4315(7)	−0.2049(23)	0.3513(7)
P2	0.2363(2)	−0.3261(6)	0.3237(1)
O3	0.2479(4)	−0.4024(15)	0.2765(4)
C21	0.2990(7)	−0.4816(24)	0.2806(7)
C22	0.3338(7)	−0.5924(22)	0.3236(6)
C23	0.3859(8)	−0.6642(26)	0.3278(7)
C24	0.4049(7)	−0.6387(22)	0.2904(7)
C25	0.4577(9)	−0.7131(29)	0.2922(8)
C26	0.4750(9)	−0.6872(27)	0.2527(7)
C27	0.4388(9)	−0.5876(28)	0.2064(8)
C28	0.3863(7)	−0.5097(26)	0.2016(7)
C29	0.3705(7)	−0.5366(24)	0.2436(7)
C30	0.3160(7)	−0.4483(23)	0.2392(6)
O4	0.2090(4)	−0.4956(15)	0.3365(4)
C31	0.1864(6)	−0.4894(22)	0.3750(6)
C32	0.2200(8)	−0.5630(24)	0.4244(7)
C33	0.1981(8)	−0.5679(25)	0.4620(8)
C34	0.1423(7)	−0.5068(25)	0.4515(7)
C35	0.1148(9)	−0.5186(30)	0.4873(9)
C36	0.0589(9)	−0.4424(28)	0.4722(8)
C37	0.0270(9)	−0.3753(26)	0.4242(8)
C38	0.0491(8)	−0.3640(23)	0.3869(7)
C39	0.1062(7)	−0.4347(23)	0.3974(6)
C40	0.1313(6)	−0.4258(21)	0.3614(6)
P3	0.2014(2)	0.0153(6)	0.3133(1)
O5	0.1851(5)	0.1212(14)	0.2597(4)
C41	0.2040(7)	0.0539(24)	0.2211(7)
C42	0.2609(7)	0.0676(25)	0.2290(7)
C43	0.2785(7)	0.0062(25)	0.1907(7)
C44	0.3381(8)	0.0110(27)	0.1980(7)
C45	0.3508(9)	−0.0499(28)	0.1571(8)
C46	0.3083(8)	−0.1228(24)	0.1115(7)
C47	0.2519(8)	−0.1326(25)	0.1029(8)
C48	0.2337(7)	−0.0722(24)	0.1430(6)
C49	0.1728(8)	−0.0746(27)	0.1349(8)
C50	0.1591(8)	−0.0096(27)	0.1755(7)
O6	0.1573(4)	0.1041(15)	0.3322(4)
C51	0.0968(7)	0.0666(23)	0.3179(6)
C52	0.0765(7)	0.1178(21)	0.3552(6)
C53	0.0189(7)	0.0782(23)	0.3443(6)
C54	−0.0046(8)	0.1329(23)	0.3814(7)
C55	−0.0624(9)	0.0956(30)	0.3702(9)
C56	−0.1003(9)	0.0087(29)	0.3247(8)
C57	−0.0817(8)	−0.0447(27)	0.2869(8)
C58	−0.0206(7)	−0.0059(25)	0.2970(6)
C59	0.0016(8)	−0.0566(24)	0.2599(7)
C60	0.0604(7)	−0.0199(23)	0.2703(6)

Table II. Relevant bond distances (Å) (e.s.d. in parentheses) and angles (°) (mean e.s.d.: 1.5°) for $[NP(OC_{10}H_7)_2]_3$.

N(1)−P(1)	1.56(1)	P(1)−O(1)	1.60(1)	O(1)−C(1)	1.38(2)
P(1)−N(2)	1.55(2)	P(1)−O(2)	1.58(1)	O(2)−C(11)	1.45(2)
N(2)−P(2)	1.60(1)	P(2)−O(3)	1.57(2)	O(3)−C(21)	1.37(2)
P(2)−N(3)	1.59(1)	P(2)−O(4)	1.58(1)	O(4)−C(31)	1.41(2)
N(3)−P(3)	1.59(1)	P(3)−O(5)	1.58(1)	O(5)−C(41)	1.44(2)
P(3)−N(1)	1.61(1)	P(3)−O(6)	1.56(2)	O(6)−C(51)	1.41(2)

N(1)−P(1)−N(2)	120	N(3)−P(2)−O(4)	109
P(1)−N(2)−P(2)	121	O(3)−P(2)−O(4)	97
N(2)−P(2)−N(3)	118	N(3)−P(3)−O(5)	109
P(2)−N(3)−P(3)	119	N(3)−P(3)−O(6)	112
N(3)−P(3)−N(1)	120	N(1)−P(3)−O(5)	111
P(3)−N(1)−P(1)	120	N(1)−P(3)−O(6)	104
N(1)−P(1)−O(1)	111	O(5)−P(3)−O(6)	99
N(1)−P(1)−O(2)	105	P(1)−O(1)−C(1)	128
N(2)−P(1)−O(1)	109	P(1)−O(2)−C(11)	124
N(2)−P(1)−O(2)	110	P(2)−O(3)−C(21)	127
O(1)−P(1)−O(2)	99	P(2)−O(4)−C(31)	120
N(2)−P(2)−O(3)	113	P(3)−O(5)−C(41)	118
N(2)−P(2)−O(4)	111	P(3)−O(6)−C(51)	129
N(3)−P(2)−O(3)	107		

Table III. Some other geometrical data for $[NP(OC_{10}H_7)_2]_3$.

(i) Least squares mean planes and deviations (Å) of relevant atoms

Plane	Deviations
(A) C(1···10)	P(1) 0.64, O(1) 0.05, O(2) 0.93
(B) C(11···20)	P(1) 1.31, O(1) 0.16, O(2) 0.08
(C) C(21···30)	P(2) −0.78, O(3) −0.04, O(4) 0.41
(D) C(31···40)	P(2) −1.18, O(3) −0.46, O(4) 0.10
(E) C(41···50)	P(3) −1.30, O(5) 0.01, O(6) −0.91
(F) C(51···60)	P(3) −0.54, O(5) 0.78, O(6) −0.04
(G) N(1), N(2), N(3), P(1), P(2), P(3)	N(1) 0.07, N(2) −0.12, N(3) −0.10, P(1) 0.00, P(2) 0.03, P(3) 0.00

(ii) Dihedral angles (°)

(G)−(A)	68	(G)−(B)	121	(G)−(C)	91	(G)−(D)	94
(G)−(E)	65	(G)−(F)	69	(A)−(E)	7	(A)−(F)	1
(E)−(F)	7	(B)−(C)	30	(B)−(D)	28	(C)−(D)	10

(iii) Torsion angles (°)

C(1)−O(1)−P(1)−O(2)	156	O(1)−P(1)−O(2)−C(11)	73
C(21)−O(3)−P(2)−O(4)	−90	O(3)−P(2)−O(4)−C(31)	−175
C(41)−O(5)−P(3)−O(6)	−164	O(5)−P(3)−O(6)−C(51)	85
N(1)−P(1)−N(2)−P(2)	9	P(1)−O(2)−C(11)−C(20)	114
P(1)−N(2)−P(2)−N(3)	−17	P(2)−O(3)−C(21)−C(22)	37
N(2)−P(2)−N(3)−P(3)	15	P(2)−O(3)−C(21)−C(30)	−143
P(2)−N(3)−P(3)−N(1)	−6	P(2)−O(4)−C(31)−C(32)	−105
N(3)−P(3)−N(1)−P(1)	−2	P(2)−O(4)−C(31)−C(40)	80
P(3)−N(1)−P(1)−N(2)	1	P(3)−O(5)−C(41)−C(42)	−76
P(1)−O(1)−C(1)−C(2)	−153	P(3)−O(5)−C(41)−C(50)	109
P(1)−O(1)−C(1)−C(10)	27	P(3)−O(6)−C(51)−C(60)	−22

E map revealed the positions of all 72 nonhydrogen atoms. Full-matrix least-squares refinement, with anisotropic thermal parameters assigned only to P, O and N atoms, converged with a reliability index *R*, defined as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, of 0.09 for 349 variables. The function minimized was $\Sigma w(\Delta F)^2$, where w = 1 was assigned to each reflection. The final difference map was featureless, the maximum peak height being 0.5 $e\text{Å}^{-3}$.

Final atomic positional co-ordinates, with e.s.d.s in parentheses, are listed in Table I. The most important bond lengths and angles are contained in

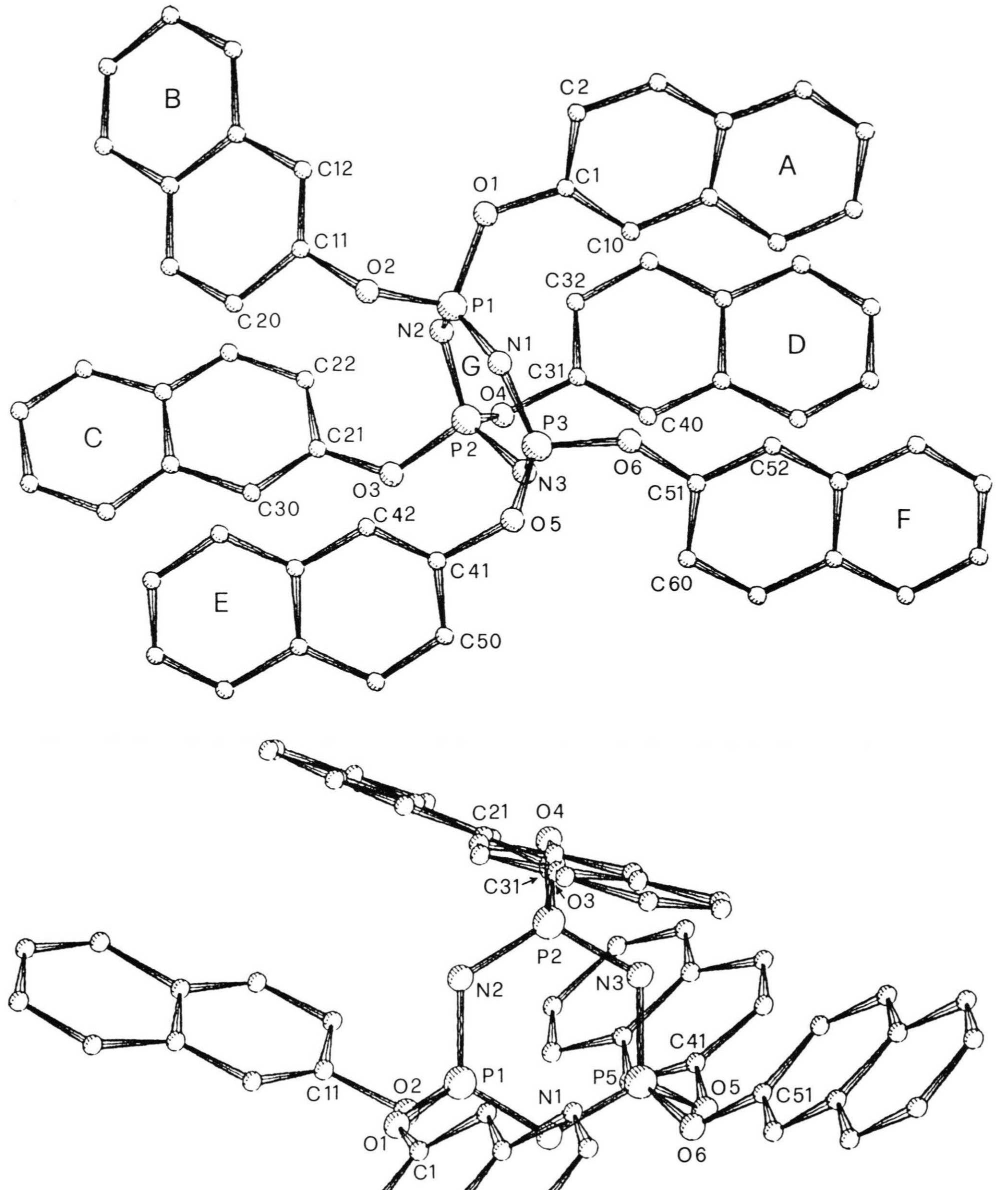

Fig. 1. Perspective views of 2,2,4,4,6,6-hexa(β-naphthyloxo)cyclotri-λ^5-phosphazatriene (**1**) in the solid with numbering of atoms.

Table II, while Table III lists some other geometrical data. The molecular structure with atom labelling is shown in Fig. 1.

The atomic thermal parameters as well as the structure factor tables are given in the Supplementary Material.

Dipole moment measurements. – The electric dipole moments (μ, Debyes) were determined in benzene solution at 25±0.1° using apparatus and techniques described previously [9]. The data required for the calculation of the μ values by the Guggenheim method [10] are reported in Table IV.

Table IV. Parameters for the calculation of dipole moments for hexa(aryloxo)cyclotriphosphazatrienes 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)
1	1.62	0.669	2.95
2a	0.44	0.317	1.14
2b	0.50	0.258	1.47
2c	0.37	0.149	1.48
2d	1.60	0.166	3.37
2e	1.76	0.156	3.74
2f	1.34	0.220	3.26

Results and Discussion

X-ray analysis. – The structure of $[NP(OC_{10}H_7)_2]_3$ contains discrete molecules without any significant intermolecular interaction. Two perspective views of the molecule are shown in Fig. 1. The N_3P_3 ring deviates slightly from planarity (up to 0.12 Å for N(2) atom and to 17° for P(1)–N(2)–P(2)–N(3) torsion angle, as reported in Table III) and such deviation is rather common in symmetrically substituted phosphazenes of the type $(NPX_2)_3$. The mean bond distances and angles are: P–N 1.58(1), P–O 1.58(1), O–C 1.41(2) Å; P–N–P 120(1), N–P–N 119(1) and P–O–C 124(2)° (Table II). Comparison of the relevant data of **1** with those of the parent $(NPX_2)_3$ compounds does not deserve any comment and, in any event, the differences should not be regarded as being chemically significant because of the low accuracy of the structure determination (see Experimental). In particular, the O–C bond distances range from 1.37 to 1.45 Å, the difference being greater than 3σ.

As to the conformation about P–O bonds, the following features are noteworthy: i) at the P(1) site, the P(1)–O(1)–C(1) plane is almost coplanar with the O(2)–P(1)–O(1) one (O(1)–C(1)/O(2)–P(1) bonds in relative *anti* arrangement), while the P(1)–O(2)–C(11) plane deviates by 17° from the orthogonality with respect to this plane (O(2)–C(11)/O(1)–P(1) in *syn* position); ii) at P(2), the P(2)–O(4)–C(31) plane is coplanar with O(3)–P(2)–O(4) (O(4)–C(31)/O(3)–P(2) bonds in *anti* position, O(4)–C(31) bond pointing towards the N_3P_3 ring), while the P(2)–O(3)–C(21) plane is virtually perpendicular to the pertinent O–P–O plane; iii) the conformational arrangement at P(3) recalls that at P(2), only the relative orientations of P–O bonds with respect to the N_3P_3 plane being inverted relative to P(2). Namely, the P(3)–O(5)–C(41) plane is coplanar with O–P–O (O(5)–C(41)/O(6)–P(3) bond in *anti* arrangement), whereas the P(3)–O(6)–C(51) plane is nearly perpendicular (85°) to this plane.

There is a significant difference in the solid-state conformation of **1** and its phenoxo [3] and *p*-chlorophenoxo [4] parent compounds. An easy comparison can be made by simultaneous inspection of Fig. 2 and of the Fig. 3 of ref. [4], which show the molecular projections along the perpendicular to the mean N_3P_3 plane. The phenyloxo derivatives adopt overall conformations in which the P-substituent groups do not cover the view of the N_3P_3 ring "area", while in **1** the bulkier naphthyloxo groups determine such steric interactions that a naphthyloxo moiety (that designed E in Fig. 1) partially overlaps the N_3P_3 ring area.

Five (A, C, D, E, F mean planes of Fig. 1 and Table III) of the six naphthyloxo groups are arranged in such a way that the dihedral angle between their planes and the N_3P_3 ring (G) range from 65 to 94°, while the remaining dihedral angle between B and G is 121°; the two naphthyloxo groups at P(2) (C, D) and P(3) (E, F) are nearly coplanar (dihedral angle of 10 and 7°, respectively), while the dihedral angle for the two moieties at P(1) (A, B) is 127°. The resulting orientation makes the three A, E and F planes coplanar and, on the other hand, the B, C and D planes only approximately coplanar.

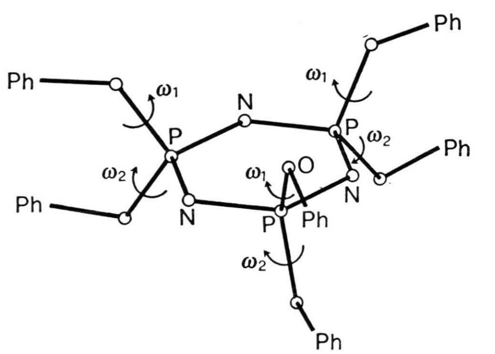

Fig. 2. Perspective view of an hexa(aryloxo)cyclotriphosphazatriene molecule in the assumed "starting" conformation 0°, 0° for dipole moments data analysis. Positive rotations are denoted by the arrows (anticlockwise along O–P bond looking from O to P atom).

Dipole moments analysis. – The interpretation of μ_{exp} values (Table IV) for **1** and **2a–f** molecules was made by comparison with theoretical dipole moments (μ_{calcd}) calculated, through vector addition of the component bond moments, for the possible conformations denoted by the torsional angles ω_1, ω_2; ω'_1, ω'_2; ω''_1, ω''_2 about P–O bonds (Fig. 2). In the assumed symmetric frame of planar N_3P_3 ring, the resultant of the three fixed P–O bond moments was zero. The solid state bond angles of **1** and its phenoxo parent compound [3] as well as a planar N_3P_3 ring were used as geometric parameters in the vectorial additive scheme for **1** and **2a–f** compounds, respectively. Literature bond moments [11] were assumed.

μ_{exp} for **1** (2.95 D) was found in a very significant disagreement with μ_{calcd} (0.99 D) for the angle combinations corresponding to the conformation in the solid state. This latter is therefore not retained in the solution state.

The search of the conformations compatible with μ_{exp}'s of **1** and **2a–f** was then initiated under the assumption that C_3 symmetry is retained by rotations about P–O bonds. Therefore each set of three P–O fragments placed on each face of the N_3P_3 plane was considered to undergo simultaneous conrotatory torsions (i.e., $\omega_1 = \omega'_1 = \omega''_1$; $\omega_2 = \omega'_2 = \omega''_2$) for independent rotations of the two sets (Fig. 2). The triads of rotational angles could thus be denoted as ω_1, ω_2. The starting conformation $\omega_1 = \omega_2 = 0°$ was that having the C_{Ph}–O–P–O–C_{Ph} atoms coplanar (this plane being perpendicular to the N_3P_3 plane) and C_{Ph}–O bonds in *syn* arrangement to each other. The use of the whole set of six independent variables in the computation of μ_{calcd} values was avoided due to the rather time-consuming computer process as well as to the infinite combinations of angles attainable for which $\mu_{calcd} = \mu_{exp}$ and which correspond to sterically hindered conformations.

The equation was then deduced that calculates the total moment μ_{calcd} as a function of ω_1, ω_2. These angles were independently varied from 0 to 360° by increments of 0.1° by means of a computerized procedure run on a VAX 11/750 system. The results of the calculations were summarized graphically in contour maps of iso-moment curves.

In the case of **1** the condition $\mu_{exp} = \mu_{calcd}$ was verified by angle pair combinations ranging from 0°, 150° to 25°, 180°. Since the conformations having ω_2 near to 180° are sterically hindered, a choice could be made in favour of the conformation 0°, 150° that is energetically preferred among those that lie on the contour $\mu_{exp} = \mu_{calcd}$. This conformation was in good agreement with the one found for the analogous phenoxo compound [4].

Preliminary μ_{calcd} values were calculated for **2a, 2d** and **2f** in the conformation corresponding to that found [4] for the analogous *p*-chlorophenoxo in the solid state. Such a possibility was ruled out on the basis of considerable differences between the μ_{exp} and μ_{calcd} values (ranging from 1.5 to 2 D, and therefore of an order of magnitude greater than the accuracy of the approach).

The computerized search indicated that the μ_{exp} values of **2a, 2d** and **2f** were compatible with μ_{calcd} for conformations 0°, 140°; 0°, 130° and 0°, 120°, respectively. This is in good agreement with previous findings for *p*-chlorophenoxo analogue [4] and reasonably indicates that steric more than electronic effects due to the different *p*-substituent are the conformation-determining factors.

In the case of **2b** and **2c** in which the phenoxo groups contain more than one polar substituent the vectorial additive scheme of group moments could not be applied. This is because the inductive and mesomeric effects which considerably affect the degree of polarization of bonds lead to appreciable changes in the group moments that, accordingly, cannot be deduced from dipole moments of molecules with only one polar group. The analysis of μ_{exp} values of **2b** and **2c** was therefore impossible. In the case of **2f** the analysis was also impossible because the direction of action of the component group moment of the *p*-substituent could not be safely located.

The following main facts appear established therefore by this work: i) the exocyclic conformation of hexa(β-naphthyloxo)cyclotriphosphazatriene **1** changes on going from the solid to the solution phases; ii) the same relative orientations of phenoxo groups occur for *p*-substituted phenoxo compounds as solutes, thus indicating that similar steric intramolecular effects operate to determine the conformation; iii) separate effects (crystal packing) can be the conformation determining factors in the solid state.

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