Crystal Structure and Molecular Mechanics, Dynamics and Quantum-mechanical *Ab Initio* Studies of 2,2,4,4,6,6-Hexakis(*p*-phenoxyphenoxy)-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-triene†

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Molecular mechanics modelling and molecular dynamic (MD) simulations have been carried out for $[NP(OC_6H_4OPh\text{-}p)_2]_3$. Force-field parameters developed for cyclotriphosphazenes gave calculated bond lengths and angles in agreement with the values determined by X-ray diffraction analysis of the crystal. Calculated and X-ray diffraction data for the torsional angles were in poor agreement due to crystal-packing forces determining the conformation in the solid. The MD simulation gave a nearly symmetric equilibrium conformation and showed that the fluxional mobility of the phenoxy groups increases on going from the P–O bonds of the phosphazene core to the external fragments of the molecule. The crystals were triclinic, space group $P\bar{1}$, with a = 15.345(2), b = 15.440(3), c = 15.999(3) Å, α = 80.43(1), β = 66.67(1), γ = 60.62(1)° and Z = 2, and the structure was refined to R = 0.057 and R' = 0.066. The force-field parameter set for MD well reproduces the energy difference between the solid and gas-phase conformations calculated by the *ab-initio* (STO-3G*) method. The calculated small energy differences between the molecular orbitals indicate a possible quasi-band structure for the bonding electrons. A perturbation of the electronic system localized on the atoms of the external phenyl groups can therefore propagate towards the P and N atoms of the cyclophosphazene ring.

The solid-state structures and conformations of hexa(aryloxy)-cyclotriphosphazenes bearing bulky aryloxy-groups have been previously studied by us using X-ray diffraction analysis.[1-3] These data thus refer to static structural and conformational properties in the solid. The conformational characteristics, molecular dynamics and intramolecular interactions of such compounds cannot be assessed unless theoretical force-field computational methods become applicable. At present molecular modelling and molecular dynamics force-field calculations useful for this task are unavailable because of the lack of force constants for N, P and O atoms. The application of these calculational techniques is also of importance when considering the potential inclusion ability of the compounds to form host–guest complexes. Recently force-field parameter sets have been developed by us[4] for linear and cyclic phosphazenes using *ab-initio* data.

In this work we have applied the parameter sets for modelling (MM2[5]) and for molecular dynamics (CharmM[6]) investigations to the cyclotriphosphazene $[NP(OC_6H_4OPh\text{-}p)_2]_3$ **1**. The single-crystal structure and *ab-initio* (STO-3G*) calculations on the electronic structure of **1** are also reported and discussed.

Experimental

Sample.—Compound **1** was synthesized according to the literature method.[7] Single crystals (m.p. 102 °C) suitable for X-ray diffraction study were grown by slow evaporation of tetrahydrofuran–methanol (1 : 1).

Structure Determination.—Accurate unit-cell parameters were determined by least-squares fit of the 2θ values measured on a Siemens R3m/V four-circle diffractometer for 50 independent reflections (2θ > 28°). Two reflections (231, 570) monitored every 100 showed no significant variations in intensities during the data collection. The crystal data, summary of data collection conditions and information on structure determination and refinement are given in Table 1. The hydrogen atoms were included in the analysis at calculated positions (C–H 0.96 Å) and assigned a variable overall isotropic thermal parameter. Final atomic positional parameters for the non-hydrogen atoms are given in Table 2, selected bond distances and angles in Table 3 and least-squares mean planes, dihedral angles and torsion angles in Table 4.

The major calculations were made using the Siemens SHELXTL PLUS package[8] and the molecular plots were prepared from the ORTEP[9] output.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Theoretical Calculations

The *ab-initio* (STO-3G* level) calculations were performed using the GAUSSIAN 92 package[10] for the molecule assumed as in the solid-state structure. Force-field molecular mechanics (MM2) and molecular dynamics (MD) calculations were performed with the interactive computer graphics MacroModel[11] and CharmM[12] programs, respectively. The MM2 and CharmM force constants required by the force-field methods were those calculated by us for phosphazenes.[4] The atomic charges required by CharmM were set at the values from *ab-initio* (4–31G* level) calculations for model compounds used

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI units employed: cal = 4.184 J, eV ≈ 1.60 × 10^{-19} J, dyn = 10^{-5} N, D ≈ 3.3 × 10^{-30} C m.

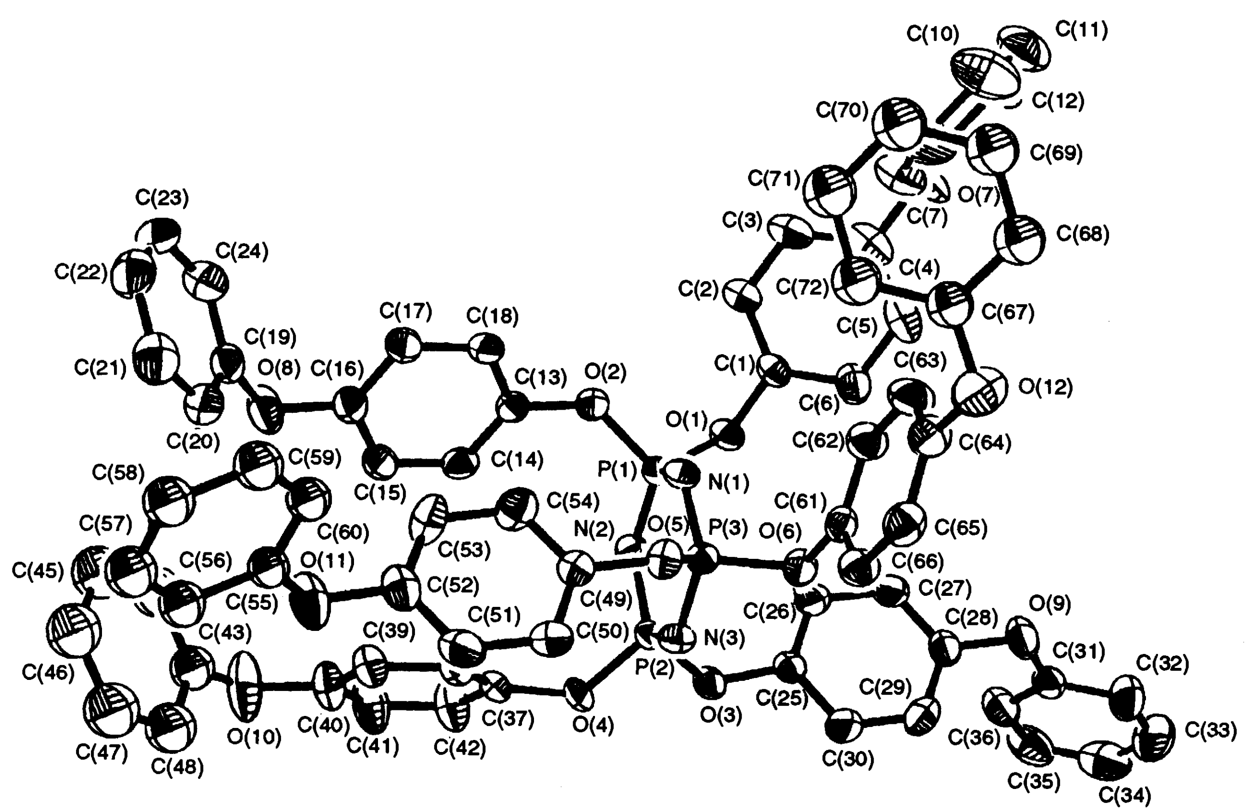

Fig. 1 An ORTEP view of the molecule **1** including the numbering scheme and the 50% probability thermal vibration ellipsoids of the non-hydrogen atoms

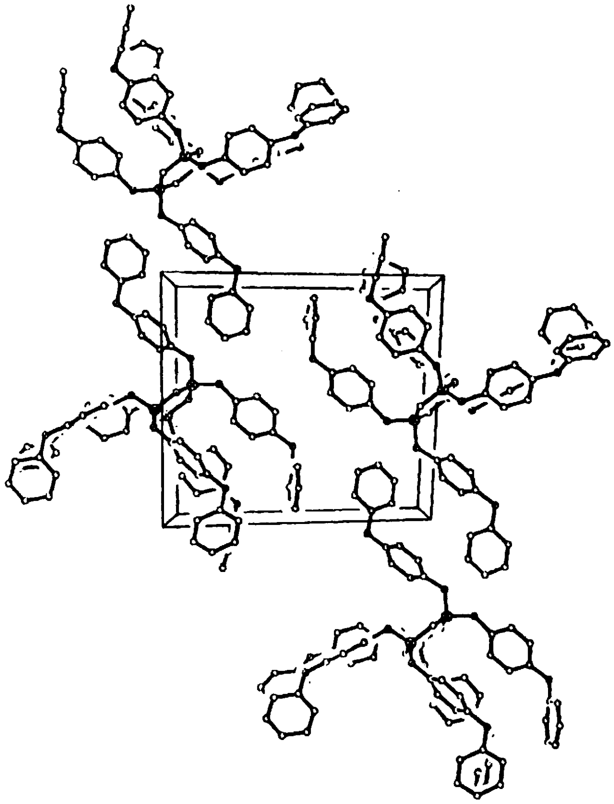

Fig. 2 The unit-cell contents

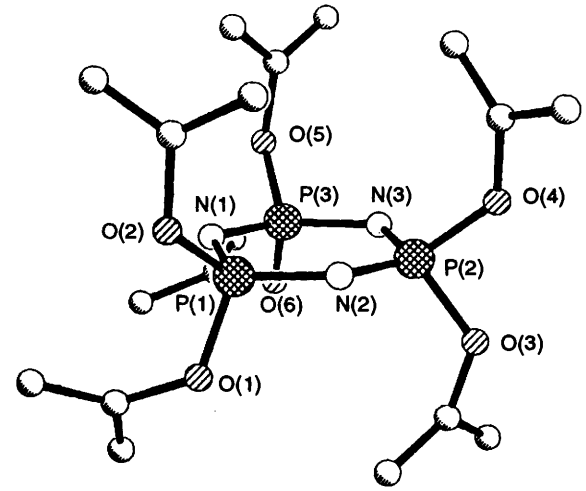

Fig. 3 A view of the 'inner core'

in developing the force-field parameters: P, 1.955; N, −1.113; O(P), −0.797; O(C), −0.752; C(O), 0.376; C(H), −0.182; H, 0.182. The SHAKE protocol for simulation of C–H bonds was used for MD simulations of compound **1**. The MD simulations were run by starting from X-ray coordinates after a 10 ps equilibration at 298 K. Transients for 600 ps were usually collected.

All computations were done using Apollo HP-710, Digital VAX 3500 which controlled high-resolution Tektronix 4111 graphics, and Digital 'Alpha' workstations of the laboratory's network.

Results and Discussion

Crystal Structure Analysis.—The structure of compound **1** (Fig. 1) contains discrete, well separated molecules without any significant intermolecular contacts (Fig. 2), the shortest separation between non-hydrogen atoms being 3.4 Å. The N_3P_3 ring of the inner core (Fig. 3) adopts an approximately chair conformation with deviations from the mean plane up to ± 0.07 Å and torsion angles up to ± 15.7°. This situation parallels that of the parent compound 2,2,4,4,6,6-hexakis(dibenzofuran-2-yloxy)cyclotriphosphaza-1,3,5-triene **2** and superimposed

Table 1 Structure determination summary for compound **1**

Empirical Formula	$C_{72}H_{54}N_3O_{12}P_3$
M	1246.1
Colour, habit	Colourless, prismatic
Crystal size/mm	0.20 × 0.30 × 0.35
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	15.345(2)
b/Å	15.440(3)
c/Å	15.999(3)
α/°	80.43(1)
β/°	66.67(1)
γ/°	60.62(1)
U/Å^3	3031.3(9)
Z	2
D_c/Mg m^{-3}	1.365
μ/mm^{-1}	0.161
F(000)	1296
Radiation	Mo-Kα (λ = 0.710 73 Å)
T/K	294
Monochromator	Highly oriented graphite crystal
2θ range/°	3.5–50.0
Scan type	ω–2θ
Scan speed	Variable: 4.51–14.65° min^{-1} in ω
Scan range (ω)	0.60° plus Kα separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
hkl ranges	−18 to 16, −18 to 18, −19 to 0
Reflections collected	11 158
Independent reflections	10 741 (R_{int} = 0.0214)
Observed reflections	8064 [$F > 4.0\sigma(F)$]
Solution method	Heavy-atom methods
Refinement method	Full-matrix least squares
Quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0004F^2$
Number of parameters refined	762
Final R,R' (observed data)	0.0570, 0.0661
(all data)	0.0830, 0.0747
Goodness-of-fit	2.15
Largest, mean Δ/σ	0.154, 0.019
Data-to-parameter ratio	10.6:1
Largest difference peak, hole/e Å^{-3}	0.44, −0.42

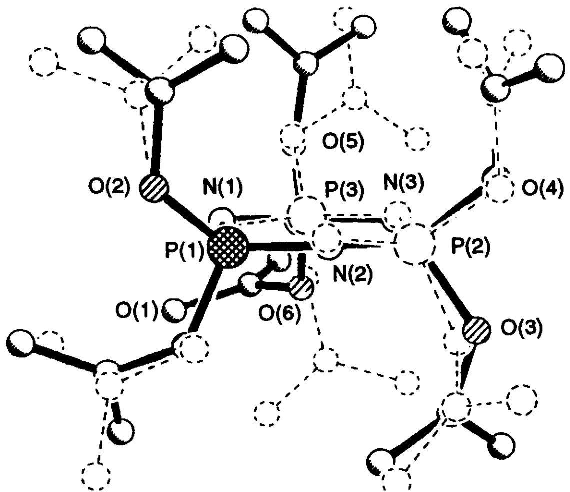

Fig. 4 Superimposition of the molecule **1** (full line) with the parent compound **2** (dashed line)

molecules **1** and **2** (Fig. 4) show that the weighted root-mean-square (r.m.s.) deviation[13] is 0.14 Å, when the fitting is performed on the $N_3P_3O_6$ skeleton [maximum deviation of 0.30 Å by O(3)]. The mean bond distances and angles (Table 3) are P–N 1.576(2), P–O 1.577(2), O–C 1.402(3) Å, P–N–P 122.3(2), N–P–N 116.8(2) and P–O–C 125.1(2)°, and they closely approach those of the parent compound. On the contrary, the overall conformations about the P–O bonds differ significantly, as shown by the two torsion angles C(25)–O(3)–P(2)–O(4) (−175.3 *vs.* 86.6°) and C(61)–O(6)–P(3)–O(5) (−40.8 *vs.* −82.1°).

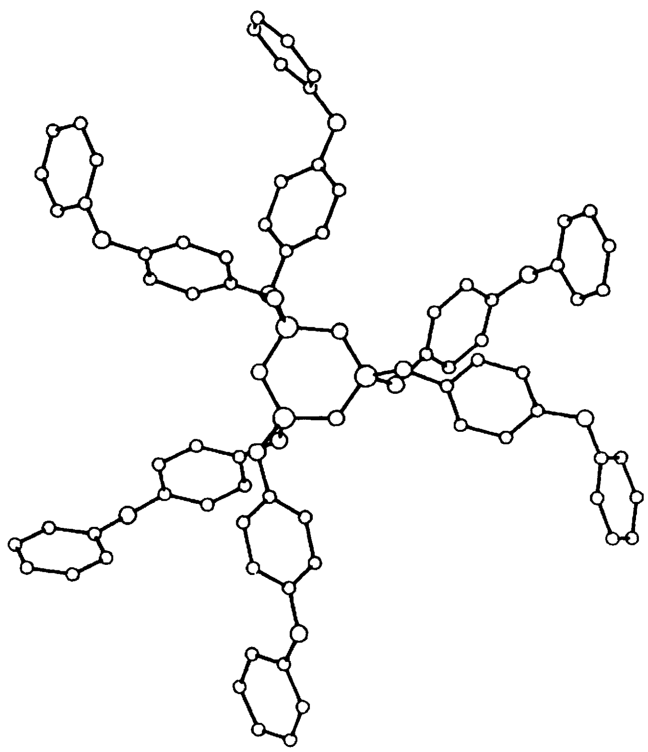

Fig. 5 Perspective view of compound **1** in the conformation from the simulation after averaging of atomic positions and subsequent minimization

The bond lengths and angles need no comment, apart from the surprisingly narrow (92.9°) O(3)–P(2)–O(4) angle.

Molecular Dynamics.—Time evolution of the N–P–O–C and P–O–C–C sets of torsion angles indicated that on the ps to ns time-scale at the junction of the phenoxy groups to the P atoms of the N_3P_3 ring the atoms scarcely moved. However, on passing to the external phenoxy groups, the involved atoms (torsion angles C–O–C–C and C–C–O–C) undergo torsional changes somewhat faster and wider. There are no long-lived transients, with the OPh moieties in continuous rapid movement on this time span. Interestingly, the time evolution of the angle between the phenyl ring planes at O(7), O(9), O(10) indicates that in the simulated molecule each C_6H_4OPh fragment interconverts, through fast concerted movements, between two conformations having the ring planes nearly perpendicular to each other.

The conformation of compound **1** in the crystal is significantly distorted on passing to the gas phase, as shown by the calculated torsional angles. This was expected, since for large molecules crystal-packing forces are expected to modify the molecule from its equilibrium gas-phase conformation (Fig. 5).

The CharmM parameters developed in the previous work[4] give results that are in good agreement with the experimental bond lengths and angles of the phosphazene ring in compound **1** (Table 5). In order to reproduce the extra-ring bond angles of **1** more accurately, the θ_0 (angle bending) values for the O–P–O

Table 2 Atomic coordinates (× 10^4)

Atom	x	y	z	Atom	x	y	z
P(1)	1 497(1)	4 495(1)	282(1)	C(28)	−902(3)	8 733(2)	1 635(2)
P(2)	2 252(1)	5 787(1)	−716(1)	C(29)	1(3)	8 854(3)	1 163(3)
P(3)	2 945(1)	4 756(1)	678(1)	C(30)	804(3)	8 230(3)	438(2)
O(1)	286(1)	5 006(1)	954(1)	C(31)	−2 340(3)	10 330(2)	2 222(2)
O(2)	1 546(2)	3 536(1)	3(1)	C(32)	−2 785(3)	11 018(3)	2 904(3)
O(3)	1 488(2)	6 945(1)	−622(1)	C(33)	−3 447(4)	11 997(3)	2 782(4)
O(4)	2 889(2)	5 828(2)	−1 754(1)	C(34)	−3 658(3)	12 281(3)	1 994(4)
O(5)	4 115(2)	3 991(1)	660(1)	C(35)	−3 213(3)	11 590(3)	1 331(3)
O(6)	2 536(2)	5 384(1)	1 561(1)	C(36)	−2 547(3)	10 608(3)	1 435(2)
O(7)	−1 265(2)	3 835(2)	4 454(2)	C(37)	3 576(2)	5 076(2)	−2 431(2)
O(8)	5 030(2)	662(2)	−2 551(2)	C(38)	4 451(3)	4 241(2)	−2 363(2)
O(9)	−1 715(2)	9 354(2)	2 383(1)	C(39)	5 143(3)	3 563(3)	−3 099(2)
O(10)	5 554(2)	3 142(2)	−4 658(2)	C(40)	4 932(3)	3 757(3)	−3 887(2)
O(11)	7 503(2)	1 430(2)	−2 175(2)	C(41)	4 049(3)	4 607(3)	−3 948(2)
O(12)	3 410(3)	3 739(2)	4 657(2)	C(42)	3 377(3)	5 271(3)	−3 227(2)
N(1)	2 289(2)	4 187(2)	802(2)	C(43)	6 467(3)	2 277(3)	−4 676(2)
N(2)	1 612(2)	5 192(2)	−550(2)	C(44)	6 435(4)	1 399(4)	−4 568(3)
N(3)	2 986(2)	5 475(2)	−141(2)	C(45)	7 336(5)	545(4)	−4 640(3)
C(1)	−64(2)	4 673(2)	1 838(2)	C(46)	8 288(5)	543(4)	−4 823(3)
C(2)	−150(3)	3 816(3)	1 970(2)	C(47)	8 309(4)	1 423(5)	−4 922(3)
C(3)	−522(3)	3 520(3)	2 849(3)	C(48)	7 399(4)	2 296(3)	−4 861(3)
C(4)	−815(3)	4 100(3)	3 569(2)	C(49)	4 945(2)	3 342(2)	−68(2)
C(5)	−746(3)	4 953(3)	3 439(2)	C(50)	5 875(2)	3 418(2)	−430(2)
C(6)	−362(3)	5 258(3)	2 557(2)	C(51)	6 736(3)	2 762(3)	−1 121(2)
C(7)	−608(3)	3 304(3)	4 936(2)	C(52)	6 653(3)	2 052(2)	−1 442(2)
C(8)	479(3)	2 911(3)	4 576(3)	C(53)	5 727(3)	1 974(3)	−1 077(3)
C(9)	1 068(4)	2 372(4)	5 110(3)	C(54)	4 854(3)	2 622(3)	−370(3)
C(10)	559(5)	2 238(4)	6 011(3)	C(55)	8 303(2)	571(2)	−2 000(2)
C(11)	−526(4)	2 628(3)	6 359(3)	C(56)	9 254(3)	136(3)	−2 723(3)
C(12)	−1 122(3)	3 165(3)	5 838(2)	C(57)	10 090(3)	−735(3)	−2 603(3)
C(13)	2 462(2)	2 805(2)	−632(2)	C(58)	9 978(3)	−1 166(3)	−1 772(3)
C(14)	2 804(3)	3 026(2)	−1 544(2)	C(59)	9 028(3)	−733(3)	−1 061(3)
C(15)	3 678(3)	2 278(2)	−2 154(2)	C(60)	8 180(3)	142(2)	−1 161(2)
C(16)	4 174(3)	1 338(2)	−1 870(2)	C(61)	2 765(2)	4 939(2)	2 348(2)
C(17)	3 824(3)	1 114(2)	−957(2)	C(62)	2 132(3)	4 555(2)	2 965(2)
C(18)	2 955(3)	1 870(2)	−343(2)	C(63)	2 354(3)	4 143(3)	3 738(2)
C(19)	5 738(3)	−253(2)	−2 332(2)	C(64)	3 177(3)	4 130(3)	3 878(2)
C(20)	6 721(3)	−398(3)	−2 420(2)	C(65)	3 802(3)	4 532(2)	3 268(2)
C(21)	7 462(3)	−1 326(3)	−2 286(3)	C(66)	3 579(3)	4 946(2)	2 489(2)
C(22)	7 235(4)	−2 090(3)	−2 074(3)	C(67)	3 501(3)	2 813(3)	4 888(2)
C(23)	6 254(4)	−1 948(3)	−1 996(3)	C(68)	3 136(3)	2 643(3)	5 806(3)
C(24)	5 485(3)	−1 021(3)	−2 125(2)	C(69)	3 222(3)	1 722(3)	6 073(3)
C(25)	707(2)	7 489(2)	184(2)	C(70)	3 660(3)	979(3)	5 461(3)
C(26)	−176(2)	7 353(2)	649(2)	C(71)	4 052(3)	1 146(3)	4 540(3)
C(27)	−988(3)	7 985(2)	1 387(2)	C(72)	3 970(3)	2 061(3)	4 263(3)

Table 3 Selected bond lengths (Å) and angles (°)

P(1)–N(1)	1.581(3)	O(2)–C(13)	1.406(3)
P(1)–N(2)	1.576(2)	P(2)–O(3)	1.576(2)
N(2)–P(2)	1.575(4)	O(3)–C(25)	1.396(3)
P(2)–N(3)	1.578(3)	P(2)–O(4)	1.567(2)
P(3)–N(3)	1.573(2)	O(4)–C(37)	1.395(3)
P(3)–N(1)	1.571(3)	P(3)–O(5)	1.584(2)
P(1)–O(1)	1.579(2)	O(5)–C(49)	1.394(3)
O(1)–C(1)	1.406(3)	P(3)–O(6)	1.577(2)
P(1)–O(2)	1.577(3)	O(6)–C(61)	1.416(4)
N(1)–P(1)–N(2)	117.1(2)	O(3)–P(2)–N(2)	111.5(1)
P(1)–N(2)–P(2)	122.3(2)	O(4)–P(2)–N(2)	112.0(2)
N(2)–P(2)–N(3)	116.2(1)	O(3)–P(2)–N(3)	110.6(1)
P(2)–N(3)–P(3)	123.1(2)	O(4)–P(2)–N(3)	111.2(1)
N(1)–P(3)–N(3)	117.0(2)	P(2)–O(3)–C(25)	126.2(2)
P(1)–N(1)–P(3)	121.6(2)	P(2)–O(4)–C(37)	130.8(2)
O(1)–P(1)–N(1)	111.3(1)	O(5)–P(3)–N(3)	111.1(1)
O(2)–P(1)–N(1)	109.7(1)	O(6)–P(3)–N(3)	106.8(1)
O(1)–P(1)–N(2)	107.6(1)	O(5)–P(3)–N(1)	109.9(1)
O(2)–P(1)–N(2)	111.1(1)	O(6)–P(3)–N(1)	112.1(1)
P(1)–O(1)–C(1)	122.7(2)	P(3)–O(5)–C(49)	125.2(2)
P(1)–O(2)–C(13)	123.5(2)	P(3)–O(6)–C(61)	122.4(2)
O(1)–P(1)–O(2)	98.5(1)	O(5)–P(3)–O(6)	98.4(1)
O(3)–P(2)–O(4)	92.9(1)		

and P–O–C bond angles were modified to 90° (with the Urey–Bradley bond stretching term $l_0 = 2.3$ Å) and to 125° (with $l_0 = 2.58$ Å), respectively (Table 6). This was necessary since in larger molecules the bulky substituents borne by the P–O fragment are expected to deform the equilibrium bond angles assumed in the small and less-hindered model compound used for developing force constants. The structural features in addition to the smaller values of the bending force constants make these fragments external to the rigid ring more susceptible to such deformation.

Owing to the quite distinct conformations assumed by the symmetric molecule **1** in the two aggregation states, there cannot be unequivocal correspondence of the numbering schemes of the same atoms in the crystal and in the gas phase. When comparing the bond lengths and angles of the simulated structure to the experimental data, the values of each set of data for the same type of bond distance or angle can be interchanged in the sequence of figures to match more correctly the experimental data along the sequence. Accordingly, the comparison in Table 5 between the mean values of calculated and experimental geometric data and average percent error values shows that the developed set of parameters for CharmM reproduces quite satisfactorily the structure of **1**.

Table 4 Least-squares mean planes, dihedral and torsion angles

Plane	Atoms defining plane	Deviations/Å
1	C(1)–C(6), O(1), O(7)	O(1) −0.04, O(7) −0.05, P(1) 1.19
2	C(13)–C(18), O(2), O(8)	O(2) −0.04, O(8) −0.02, P(1) 1.13
3	C(25)–C(30), O(3), O(9)	O(3) −0.08, O(9) −0.03, P(2) 0.96
4	C(37)–C(42), O(4), O(10)	O(4) 0.05, O(10) 0.02, P(2) −0.82
5	C(49)–C(54), O(5), O(11)	O(5) 0.01, O(11) −0.03, P(3) −1.08
6	C(61)–C(66), O(6), O(12)	O(6) 0.01, O(12) 0.01, P(3) −1.28
7	N(1)–N(3), P(1)–P(3)	N(1) 0.06, N(2) 0.06, N(3) 0.03, P(1) −0.07, P(2) −0.04, P(3) −0.04

Dihedral angles (°) between mean planes

1–7	55.0	5–7	82.3	5–6	106.4	5–3	7.7
2–7	92.3	6–7	163.5	1–3	42.4	6–3	108.1
3–7	78.7	1–2	45.1	2–3	66.8	2–5	73.2
4–7	86.0	3–4	98.2				

Torsion angles (°)

N(1)–P(1)–N(2)–P(2)	−15.7	P(1)–O(1)–C(1)–C(2)	−73.9	C(1)–O(1)–P(1)–O(2)	75.3	P(2)–O(4)–C(37)–C(38)	−54.8
P(1)–N(2)–P(2)–N(3)	13.1	P(1)–O(1)–C(1)–C(6)	109.1	O(1)–P(1)–O(2)–C(13)	177.7	P(2)–O(4)–C(37)–C(42)	131.3
N(2)–P(2)–N(3)–P(3)	−10.8	P(1)–O(2)–C(13)–C(14)	−68.2	C(25)–O(3)–P(2)–O(4)	−175.3	P(3)–O(5)–C(49)–C(50)	122.0
P(2)–N(3)–P(3)–N(1)	11.1	P(1)–O(2)–C(13)–C(18)	116.0	O(3)–P(2)–O(4)–C(37)	−163.6	P(3)–O(5)–C(49)–C(54)	−61.9
N(3)–P(3)–N(1)–P(1)	−13.5	P(2)–O(3)–C(25)–C(26)	−65.7	C(49)–O(5)–P(3)–O(6)	−168.1	P(3)–O(6)–C(61)–C(62)	−83.3
P(3)–N(1)–P(1)–N(2)	15.8	P(2)–O(3)–C(25)–C(30)	120.7	O(5)–P(3)–O(6)–C(61)	−40.8	P(3)–O(6)–C(61)–C(66)	99.7

Table 5 Mean values of calculated and experimental bond lengths (Å) and angles (°) and percent differences (%) from the mean experimental values

	MM2		MD		
		%		%	Exptl.
P–N	1.571	0.3	1.569	0.4	1.576
P–O	1.559	1.2	1.552	1.7	1.577
O–C	1.405[a]	0.2	1.386	1.1	1.402
N–P–N	114.70	1.8	117.02	0.2	116.77
P–N–P	125.10	2.3	122.08	0.2	122.33
O–P–N	110.80	0.4	109.95	0.4	110.41
C–O–P	123.60[b]	1.2	124.50	0.5	125.13
O–P–O	97.36[b]	0.8	98.07	1.52	96.6

[a] Extra-ring bond length value calculated using the original MM2 parameter adjusted by modifying the equilibrium value l_0 to 1.41 Å to reproduce better the experimental mean value. [b] Extra-ring bond angle value calculated using the original MM2 parameter adjusted by modifying the equilibrium value θ_0 (128.0 and 94.0° for C–O–P and O–P–O respectively) to reproduce better the experimental mean value.

MM2 *Modelling*.—The MM2 calculated structure is in reasonably good agreement with the experimental structure (Table 5). Although the crystal structure coordinates were employed as starting point for the MM2 modelling, the resulting MM2-minimized conformation significantly differs from that in the solid state. This was expected considering that intermolecular association (CH $\cdots$ π-aryl ring hydrogen bonds between phenyl rings) in the unit cell (Fig. 2) could be involved in determining the conformation found in the solid state. As one might also anticipate for a large and relatively flexible molecule, the MM2 minimum-energy conformation was a local minimum so that it does not reproduce the conformation found in MD simulation.

The MM2 force constants derived to model cyclophosphazene molecules (Table 6) give quite acceptable geometries for the N_3P_3 ring and for the rest of molecule **1** (Table 5). The effects of crystal-packing forces are unknown in detail and they might be the origin of the small differences (average values $\leqslant 2\%$) between some of the calculated O–P–O and P–O–C bond angles with respect to the experimental.

Ab-initio *Calculations*.—The *ab-initio* calculated total energies of compound **1** in the conformation found in the solid and in that resulting from MD simulations showed that the latter is energetically favoured by a large amount (557.51 kcal mol^{-1}) with respect to the former. A check made by comparing the CharmM-calculated single-point energy for **1** in the crystal state with that calculated by MD at equilibrium showed a difference of 400 kcal mol^{-1} in the favour of the latter. These data indicate the reliability of the MD results and CharmM-related force-field parameters as well as the occurrence in the crystal of packing forces which can result in distortion of the molecule from its equilibrium structure and conformation.

Results from *ab-initio* studies of the bonding of compound **1** in both the crystalline and gas-phase conformations are summarized in Fig. 6 which shows the calculated molecular orbital (MO) energy levels. The conformational change does not yield significant differences between the levels. In both cases band portions can be located in which the separation between the levels is of the order of magnitude of 0.1 eV and thus comparable to the mean value of the thermal energy. The highest-occupied band calculated for the molecule in the gas-phase equilibrium conformation shows a difference in the energy levels as a consequence of the conformational change. This implies that the energy of these orbitals, to which contribute the P and, to a larger extent, N atoms of the ring, may fluctuate giving rise to a continuous band.

Analysis of the coefficients showed that the atomic orbitals of the P and N atoms contribute to MOs that are not sequentially ordered with respect to each other on the energy scale. The small energy difference between MO levels indicates an approximate band structure owing to the conformational movements of the molecule which determine fluctuations and then a continuum of MO energies. Such a bonding feature implies that perturbations of the peripheral phenyl groups can easily be transmitted to the cyclotriphosphazene core of the molecule.

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Table 6 The MM2 and CharmM parameter sets for hexa(aryloxy)cyclophosphazatrienes[a]

Parameter[b]	l_0/Å	k_s/mdyn Å^{-1}		μ/D
(*a*) MM2				
P–N	1.615	8.430		4.33
P–O	1.580	8.300		3.13
	θ_0/°	k_b/mdyn Å rad^{-2}		
N–P–N	127.18	1.180		
P–N–P	163.00	0.516		
N–P–O	112.30	1.170		
	V_1/kcal mol^{-1}	V_2/kcal mol^{-1}		V_3/kcal mol^{-1}
N–P–N–P	−17.996	−0.123		−0.043
O–P–N–P	3.462	−0.313		0.055
C–O–P–N	5.400	0.192		0.772
Atom type: P, 25; N, 9; O, 6; C, 2				
	l_0/Å	k_s/kcal mol^{-1} Å^{-2}		
(*b*) CharmM				
P–N	1.610	401.15		
P–O	1.600	346.72		
O–C	1.415	291.75		
	θ_0/°	k_b/kcal mol^{-1} deg^{-2}	l_0/Å	k_{UB}/kcal mol^{-1} Å^{-2}
N–P–N	127.00	29.40	2.80	76.55
P–N–P	137.00	61.66	3.0	158.94
N–P–O	108.00	41.65	2.65	55.45
O–P–O	90.00	40.00	2.30	59.69
P–O–C	125.25	9.49	2.58	94.25
	k_φ/kcal mol^{-1}	*n*		φ_0/°
N–P–N–P	9.88	1		180.0
	−0.64	2		180.0
	0.20	3		180.0
O–P–N–P	1.73	1		0.0
	0.16	2		0.0
	0.03	3		0.0
C–O–P–N	2.70	1		0.0
	−0.10	2		0.0
	0.39	3		0.0
C–O–P–O	6.10	1		180.0
	1.95	2		180.0
	0.24	3		180.0

[a] The P–N bond denotes the delocalized bond of the cyclotriphosphazene ring. [b] Bond stretching l_0 and k_s, bond movement μ, angle bending θ_0 and k_b, torsional V_1–V_3, Urey–Bradley stretching l_0 and k_{UB} and torsional k_0, *n* and φ_0 parameters.

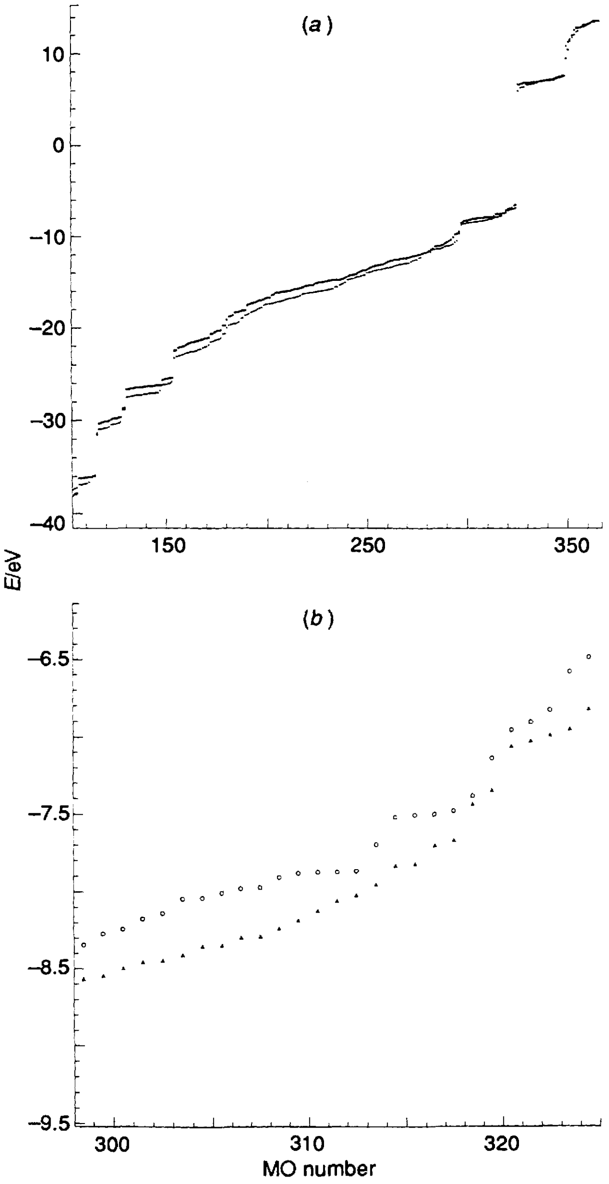

Fig. 6 (*a*) *Ab-initio* (STO-3G*) calculated MO energy levels of compound **1** in the crystal (lower) and in the equilibrium (upper) conformations. (*b*) Enlarged portion of (*a*) showing the highest-occupied band in the crystal (▲) and in the gas-phase (○) conformations

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