Crystal and Molecular Structure of Hexadeca(dimethylamino)cyclo-octaphosphazene

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Crystals of the title compound are monoclinic, a = 17.383(5), b = 24.167(7), c = 14.637(6) Å, β = 111.16(2)°, space group $C2/c$. The structure was determined by direct methods from diffractometer X-ray data and refined by full-matrix least-squares methods to R 0.048 for 1 920 observed reflexions. The molecule occupies a crystallographic centre of symmetry. Mean endo- and exo-cyclic P–N bond lengths are 1.548(9) and 1.651(7) Å. P–N–P angles range from 145.9(4) to 170.2(5)°, mean 156.5°, and endocyclic N–P–N angles range from 114.8(3) to 119.2(3)°, mean 116.8°. Three exocyclic N–P–N angles are nearly equal, mean 101.5(7)°, the fourth being significantly larger, 106.1(3)°. Mean N–C is 1.43(2) Å, and mean C–N–C angle 113.9(8)°. The molecular conformation is very similar to that of $[NP(OMe)_2]_8$; structural comparisons are also made with the dimethylamides $[NP(NMe_2)_2]_{3,4,6}$.

DIMETHYLAMINOPHOSPHAZENES $N_nP_n(NPMe_2)_{2n}$ have been isolated up to $n = 9$,[1] and several complexes with transition metals have been prepared.[2] The crystal structures of the neutral tri-,[3] tetra-,[4] and hexa-meric [5] compounds have been reported, as well as those of $[N_3P_3(NMe_2)_6H]^+{}_2[Mo_6O_{19}]^{2-}$,[6] $[N_3P_3(NMe_2)_6H_2]^{2+}$-$[CoCl_4]^{2-}$,[7] and the complexes $[N_4P_4(NMe_2)_8{\cdot}W(CO)_4]$,[8] $[N_6P_6(NMe_2)_{12}CuCl]^+[CuCl_2]^-$,[9] and $[N_6P_6(NMe_2)_{12}$-$CoCl]^+{}_2[Co_2Cl_6]^{2-}$.[10] Some insight into the nature of the bonding in these compounds is provided by a study of the structures of the parent compounds and the changes induced in them by reaction with acceptors, and also by comparisons between the dimethylamino- and methoxy-phosphazenes. The present structure determination of $N_8P_8(NMe_2)_{16}$ extends the range of comparison, and serves as the starting point for the analysis of the molecular structures of its complexes.

EXPERIMENTAL

Crystals of the title compound [1] were obtained from light petroleum as colourless plates. A crystal *ca.* 0.5 × 0.1 × 0.5 mm was sealed in a thin-walled glass capillary tube.

Crystal Data.—$C_{32}H_{96}N_{24}P_8$, M = 1 065.08, Monoclinic, a = 17.383(5), b = 24.167(7), c = 14.637(6) Å, β = 111.16(2)°, U = 5 734(3) Å^3, Z = 4, D_c = 1.233 6(8), $F(000)$ = 2 304. Space group $C2/c$ (No. 15). Mo-K_α radiation, λ = 0.71069 Å; μ(Mo-K_α) = 2.9 cm^{-1}.

Unit-cell parameters were obtained by least-squares refinement of 17 $\sin^2\theta(hkl)$ values measured on a General Electric XRD 6 diffractometer. Intensity data were measured on a Datex-automated General Electric XRD 6 diffractometer with zirconium-filtered Mo-K_α radiation. All reflexions with 2θ(Mo-K_α) < 45° were measured by use of a θ–2θ scan at 2° min^{-1} in 2θ over a range in 2θ of (1.80 + 0.86 tan θ)°. 20 s Background counts were taken on either side of every scan. A check reflexion, monitored every 30 reflexions, was used to place the data on the same relative scale; its intensity showed only small fluctuations and was *ca.* 98% of its starting value at the end of the data collection. Of 3 570 independent reflexions measured, 1 924 (53.9%) having intensities $> 2\,\sigma(I)$ above background [where $\sigma^2(I) = S + B + (0.05\,S)^2$, with S = scan count and B = background count] were considered observed. Lorentz and polarization corrections were applied and structure amplitudes derived. No corrections were made for absorption.

Structure Analysis.—The distribution of normalized structure factors suggested that the centrosymmetric space group $C2/c$, in which the molecule is required to have either C_i or C_2 symmetry, was correct. The structure was solved by direct methods. Sixteen sets of signs for 300 reflexions with $|E| > 1.779$ were determined by a computer program [11] which uses Sayre relationships in an iterative procedure. One set of signs converged in 7 cycles and had the highest consistency index (0.97),[11] with 159 positive signs and 141 negative signs. An E map was computed using the 300 signed values of E from this set, and the four phosphorus atoms accounted for the four largest peaks on the map. Seven nitrogen atoms were also located on the map. The remaining non-hydrogen atoms were then located from difference maps. The structure was refined by full-matrix least-squares methods, initially with isotropic and finally with anisotropic temperature factors for all non-hydrogen atoms, to R 0.068. At this point a difference map revealed the positions of all 48 hydrogen atoms. These were included in subsequent structure-factor calculations, but their positional and isotropic thermal parameters (B_{iso} 8.0 Å^2) were held fixed during refinement. Convergence was reached at R 0.048 for 1 920 observed reflexions [four reflexions (402, 111, 200, and 402) were omitted from the refinement because of suspected extinction errors]. On the last cycle of refinement no parameter shift was $>0.1\sigma$.

Least-squares refinement was based on the minimization of $\Sigma\omega(|F_o| - |F_c|)^2$. Scattering factors were obtained from

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[9] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1482.

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ref. 12 for all non-hydrogen atoms and from ref. 13 for the hydrogen atoms. During the final stages of refinement a weighting scheme of the form $w = [A + B|F_o| + C|F_o|^2 + D|F_o|^3]^{-1}$ was employed. The coefficients A, B, C, and D were adjusted before each cycle of refinement, the values used in the final cycle being 23.849, −0.599 4, 0.006 6, and −0.000 005. Unobserved reflexions were given zero weight.

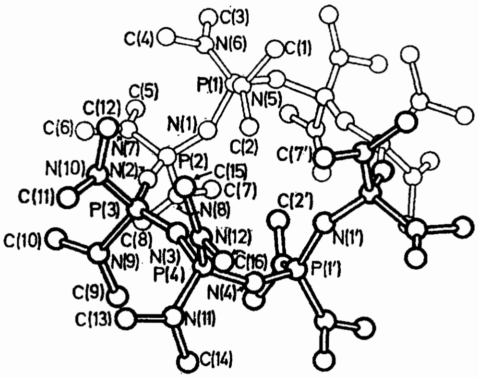

FIGURE 1 Perspective view of $N_8P_8(NMe_2)_{16}$

RESULTS

A perspective view of the molecule is shown in Figure 1, and a stereoscopic view in Figure 2. The arrangement of the molecules in the unit cell is shown in Figure 3. The molecule is centrosymmetric, its centre being at special position 4(d) of $C2/c$. Final anisotropic thermal parameters, the distribution of normalized structure factors, starting set of reflexions, and measured and calculated structure factors are listed in Supplementary Publication No. SUP 21 524 (39 pp., 1 microfiche),* together with ranges of root-mean-square amplitudes of vibration corresponding to the thermal parameters. Final positional parameters, bond lengths and angles with estimated standard deviations are given in Tables 1 and 2.

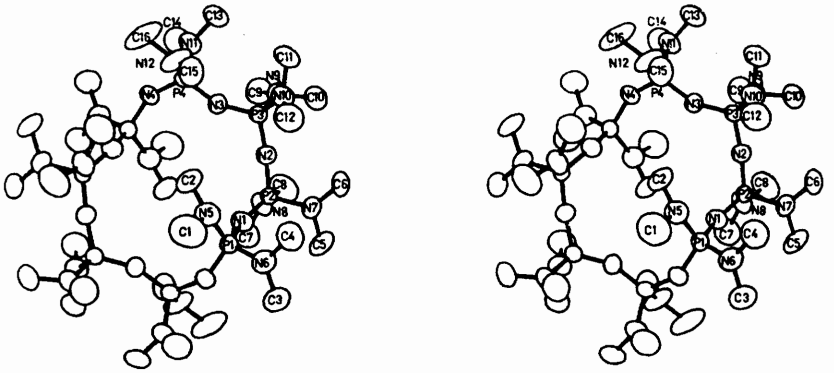

FIGURE 2 Stereoview of the molecule

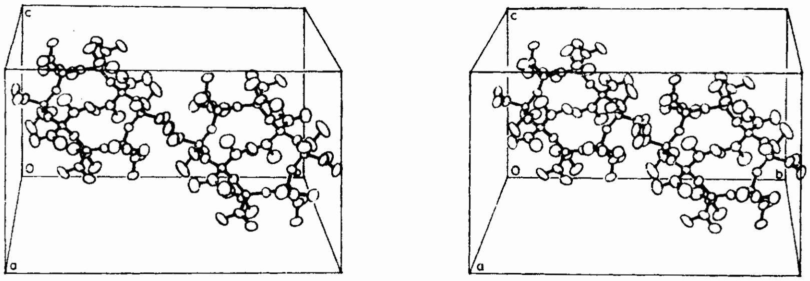

FIGURE 3 Stereoview of the arrangement of the molecules in the unit cell. Only molecules with centres at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$) and ($\frac{3}{4}$,$\frac{3}{4}$,$\frac{1}{2}$) are shown, for clarity

DISCUSSION

Intermolecular distances are of the magnitude expected for van der Waals interactions, the only contacts <4.0 Å being between methyl groups. Of these, only three are <3.8 Å:† $\mathrm{C(1)\cdots C(1)^{I}}$ 3.46, $\mathrm{C(7)\cdots C(15)^{II}}$ 3.67, $\mathrm{C(6)\cdots C(12)^{III}}$ 3.70 Å. We need therefore consider interactions only within a single molecule.

The conformation of the N_8P_8 ring in $[NP(NMe_2)_2]_8$ is strikingly similar to that in $N_8P_8(OMe)_{16}$.[14] In both molecules the centrosymmetric phosphazene ring consists of two nearly planar seven-atom segments [P(2), N(2), P(3), N(3), P(4), N(4), P(1')], joined by a step at N(1), N(1'). Partly as a result of large bond angles at nitrogen, the segments are more nearly planar in the dimethylamide, the mean deviation from the mean plane being

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

† Roman numeral superscripts denote the following translations of atoms, relative to the reference molecule at x, y, z: I $1 - x, y, 1\frac{1}{2} - z$; II $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; III $1 - x, y, \frac{1}{2} - z$.

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TABLE 1

Final positional parameters (fractional × 10^4; × 10^3 for the hydrogen atoms), with standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	3 407(1)	1 508(1)	4 443(1)
P(2)	2 745(1)	2 310(1)	2 771(1)
P(3)	3 152(1)	3 536(1)	3 279(1)
P(4)	2 733(1)	4 134(1)	4 873(1)
N(1)	2 865(4)	1 898(2)	3 623(4)
N(2)	3 018(4)	2 914(2)	3 008(4)
N(3)	2 886(4)	3 727(2)	4 129(4)
N(4)	2 070(4)	3 976(2)	5 291(5)
N(5)	3 937(4)	1 898(3)	5 379(4)
N(6)	4 143(4)	1 183(3)	4 195(5)
N(7)	3 213(4)	2 082(3)	2 038(5)
N(8)	1 751(4)	2 289(3)	2 124(4)
N(9)	2 695(4)	3 946(2)	2 327(4)
N(10)	4 136(4)	3 657(2)	3 466(5)
N(11)	2 459(4)	4 768(2)	4 451(5)
N(12)	3 622(4)	4 249(3)	5 758(5)
C(1)	4 418(7)	1 608(5)	6 259(6)
C(2)	3 649(6)	2 423(4)	5 568(6)
C(3)	4 125(7)	624(4)	3 909(9)
C(4)	4 814(6)	1 494(4)	4 073(8)
C(5)	3 003(8)	1 539(4)	1 638(8)
C(6)	3 646(7)	2 403(4)	1 604(7)
C(7)	1 230(6)	1 851(4)	2 180(7)
C(8)	1 454(6)	2 588(4)	1 216(6)
C(9)	1 861(6)	4 135(4)	2 118(6)
C(10)	2 902(6)	3 868(4)	1 446(6)
C(11)	4 460(5)	4 211(3)	3 568(7)
C(12)	4 752(5)	3 231(4)	3 874(7)
C(13)	3 016(7)	5 113(3)	4 168(8)
C(14)	1 631(6)	4 976(4)	4 146(7)
C(15)	4 345(5)	3 947(4)	5 942(6)
C(16)	3 633(6)	4 607(4)	6 561(8)
H(1,1) *	483	170	674
H(1,2)	471	119	616
H(1,3)	413	152	678
H(2,1)	318	255	484
H(2,2)	348	235	616
H(2,3)	406	270	596
H(3,1)	358	39	387
H(3,2)	446	37	397
H(3,3)	400	77	311
H(4,1)	490	147	335
H(4,2)	490	187	413
H(4,3)	537	126	457
H(5,1)	339	129	157
H(5,2)	257	150	93
H(5,3)	258	127	177
H(6,1)	390	282	199
H(6,2)	338	241	84
H(6,3)	420	223	152
H(7,1)	149	156	284
H(7,2)	126	148	169
H(7,3)	63	199	205
H(8,1)	141	237	48
H(8,2)	166	298	101
H(8,3)	83	266	92
H(9,1)	183	455	182
H(9,2)	142	399	151
H(9,3)	188	413	286
H(10,1)	247	362	97
H(10,2)	261	421	104
H(10,3)	360	384	171
H(11,1)	396	452	318
H(11,2)	480	436	428
H(11,3)	482	437	327
H(12,1)	448	288	391
H(12,2)	516	328	449
H(12,3)	513	338	338
H(13,1)	279	508	342
H(13,2)	308	548	433
H(13,3)	350	491	423
H(14,1)	140	508	343
H(14,2)	128	461	441
H(14,3)	144	533	418
H(15,1)	457	378	665
H(15,2)	489	413	613
H(15,3)	457	370	533
H(16,1)	403	490	678
H(16,2)	305	477	660
H(16,3)	393	445	733

* Atom H(*i*,*j*) is bonded to atom C(*i*).

0.07 Å (0.14 Å in the methoxide). Details of the planes, the atomic displacements, and comparative dihedral angles are given in Table 3. There is a similar correspondence between the conformations of $N_6P_6(NMe_2)_{12}$ (ref. 5) and $N_6P_6(OMe)_{12}$,[15] and other structural details in the two series can be usefully compared (Table 4). We discuss the steric effects first.

The NC_2 planes of the pair of dimethylamino-groups belonging to the same phosphorus atom are twisted in opposite directions away from the exocyclic NPN planes by approximately equal angles (see Figures 1 and 2), each NC bond being approximately *trans* to a ring bond, and, to the extent that the PNC_2 group approaches planarity, the other NC bond is *cis* to the same ring bond. Although the directional preference of an NMe_2 group may therefore be less strong than that of an OMe group, the shortest Me ··· Me distance within the $P(NMe_2)_2$ fragment is remarkably constant, at 3.5 ± 0.1 Å for all. There is a less direct effect on the relative magnitude of the exo- and endo-cyclic NPN angles. In the methoxide series, the tendency of these angles to vary in the same sense was traced [15] to a balance of attractive and repulsive interactions which was dependent on the local conformation. In $N_8P_8(NMe_2)_{16}$ also, the angles at P(2), both large, are associated with a *GG* configuration of the $P(NP)_2$ group, and the smaller pairs of angles at P(1), P(3), and P(4) with a *GT* configuration (*G* = *gauche*, *T* = *trans*). The magnitude of the difference is surprising, since the large angles at the ring nitrogen atoms reduce the sharpness of the *GG*/*GT* distinction, but the effect seems to be real.

The methyl groups of different $P(NMe_2)_2$ groups are linked by a network of Me ··· Me distances which are little greater than the intra-group value of 3.5 Å. The shortest is C(2) ··· C(7′) 3.67, and C(6) ··· C(12) 3.75, and C(4) ··· C(5) 3.81 Å are typical. The multiplicity of such contacts is the greater because the N(5)C(1)C(2) group is inclined towards the centre of the molecule, the C(2) ··· C(2′) distance (through the ring) being 3.74 Å. Like $N_8P_8(OMe)_{16}$,[14] the molecule is well covered, almost triangulated, by methyl groups, and it is clear that non-bonded interactions have an important influence on ring conformation.

Perhaps the most striking feature of the structure of $N_8P_8(NMe_2)_{16}$ is that it exhibits both the largest angle at nitrogen so far found in a phosphazene (170.2°) and the largest mean value (156.5°). Wagner and Vos [5] found a very large value (147.5°) in $N_6P_6(NMe_2)_{12}$, and showed that similar model structures of the same symmetry,

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[15] M. W. Dougill and N. L. Paddock, *J.C.S. Dalton*, 1974, 1022.

but with a reduced angle at nitrogen, had some unacceptably short C–C distances. Their conclusion that the conformation is controlled by the bulky NMe_2 groups may well be correct, but attractive, as well as repulsive, forces are also important, as shown [15] for $N_6P_6(OMe)_{12}$. The structure of $N_6P_6(NMe_2)_{12}$ in complexes with metal ions is interesting in this connection, since there is necessarily a large conformational change, which is accompanied in $N_6P_6(NMe_2)_{12}CuCl^+$ by a reduction in mean P–N–P to 134°; there are nevertheless no $CH_3 \cdots CH_3$ contacts <3.5 Å.[9] The formation of the complex forces apart some methyl groups which were otherwise close, suggesting that attractive forces also are important in stabilising the structures of uncomplexed $N_6P_6(NMe_2)_{12}$ and $N_8P_8(NMe_2)_{16}$. Large angles at nitrogen are evidently compatible with this requirement, though we have not been able to show that they are uniquely so.

TABLE 2

Bond lengths (Å) (corrected length * in square brackets) and angles (°), with standard deviations in parentheses (σ for the mean values, when given, is the root-mean-square deviation from the mean).

(*a*) Distances

Bond	Length	Bond	Length
P(1)–N(1)	1.549(6)	N(5)–C(1)	1.44(1) [1.50(1)]
P(1)–N(4′)	1.562(6)	N(5)–C(2)	1.43(1) [1.45(1)]
P(2)–N(2)	1.536(6)	N(6)–C(3)	1.41(1) [1.45(1)]
P(2)–N(1)	1.549(6)	N(6)–C(4)	1.45(1) [1.49(1)]
P(3)–N(2)	1.549(6)	N(7)–C(5)	1.43(1) [1.48(1)]
P(3)–N(3)	1.548(6)	N(7)–C(6)	1.38(1) [1.42(1)]
P(4)–N(3)	1.558(6)	N(8)–C(7)	1.42(1) [1.44(1)]
P(4)–N(4)	1.536(6)	N(8)–C(8)	1.43(1) [1.48(1)]
Mean P–N (endo)	1.548(9)	N(9)–C(9)	1.44(1) [1.47(1)]
P(1)–N(5)	1.644(6)	N(9)–C(10)	1.47(1) [1.49(1)]
P(1)–N(6)	1.649(6)	N(10)–C(11)	1.44(1) [1.46(1)]
P(2)–N(7)	1.658(6)	N(10)–C(12)	1.45(1) [1.48(1)]
P(2)–N(8)	1.644(6)	N(11)–C(13)	1.45(1) [1.48(1)]
P(3)–N(9)	1.661(6)	N(11)–C(14)	1.44(1) [1.46(1)]
P(3)–N(10)	1.658(6)	N(12)–C(15)	1.39(1) [1.39(1)]
P(4)–N(11)	1.655(6)	N(12)–C(16)	1.45(1) [1.49(1)]
P(4)–N(12)	1.641(6)	Mean N–C	1.43(2) [1.46(3)]
Mean P–N (exo)	1.651(7)		

(*b*) Angles

P(1)–N(1)–P(2)	151.8(4)	N(11)–P(4)–N(3)	115.0(3)
P(2)–N(2)–P(3)	170.2(5)	N(11)–P(4)–N(4)	102.9(3)
P(3)–N(3)–P(4)	157.9(4)	N(12)–P(4)–N(3)	108.0(3)
P(4)–N(4)–P(1′)	145.9(4)	N(12)–P(4)–N(4)	110.8(4)
Mean P–N–P	156.5	C(1)–N(5)–C(2)	113.0(7)
		C(3)–N(6)–C(4)	113.0(7)
N(4′)–P(1)–N(1)	114.8(3)	C(5)–N(7)–C(6)	115.3(7)
N(1)–P(2)–N(2)	119.2(3)	C(7)–N(8)–C(8)	114.0(7)
N(2)–P(3)–N(3)	115.8(3)	C(9)–N(9)–C(10)	113.5(6)
N(3)–P(4)–N(4)	117.5(3)	C(11)–N(10)–C(12)	114.5(7)
Mean N–P–N (endo)	116.8	C(13)–N(11)–C(14)	114.0(7)
		C(15)–N(12)–C(16)	114.0(7)
N(5)–P(1)–N(6)	102.1(3)	Mean C–N–C	113.9(8)
N(7)–P(2)–N(8)	106.1(3)		
N(9)–P(3)–N(10)	100.7(3)	C(1)–N(5)–P(1)	115.9(6)
N(11)–P(4)–N(12)	101.6(4)	C(2)–N(5)–P(1)	122.7(5)
Mean N–P–N (exo)	102.6	C(3)–N(6)–P(1)	125.8(6)
		C(4)–N(6)–P(1)	120.2(6)
N(5)–P(1)–N(4′)	114.2(3)	C(5)–N(7)–P(2)	117.2(6)
N(5)–P(1)–N(1)	107.3(3)	C(6)–N(7)–P(2)	125.9(6)
N(6)–P(1)–N(4′)	102.9(3)	C(7)–N(8)–P(2)	123.4(6)
N(6)–P(1)–N(1)	115.0(3)	C(8)–N(8)–P(2)	118.1(6)
N(7)–P(2)–N(1)	110.7(3)	C(9)–N(9)–P(3)	120.4(5)
N(7)–P(2)–N(2)	106.2(3)	C(10)–N(9)–P(3)	117.7(6)
N(8)–P(2)–N(1)	104.6(3)	C(11)–N(10)–P(3)	121.6(5)
N(8)–P(2)–N(2)	109.5(3)	C(12)–N(10)–P(3)	120.4(5)
N(9)–P(3)–N(2)	112.5(3)	C(13)–N(11)–P(4)	120.5(6)
N(9)–P(3)–N(3)	107.7(3)	C(14)–N(11)–P(4)	124.2(6)
N(10)–P(3)–N(2)	105.4(3)	C(15)–N(12)–P(4)	126.2(5)
N(10)–P(3)–N(3)	113.9(3)	C(16)–N(12)–P(4)	118.3(6)

* N–C bond lengths were corrected for thermal motion using a riding model, which assumed C to ride on N.

TABLE 3

Comparative conformations of cyclo-octaphosphazenes

Dihedral angles about bond	$N_8P_8(OMe)_{16}$ [a]	$N_8P_8(NMe_2)_{16}$
N(4′)P(1)–N(1)–P(2)	164.4	153.1(3)
P(1)N(1)–P(2)N(2)	−54.2	−79.1(4)
N(1)P(2)–N(2)P(3)	78.6	79.3(4)
P(2)N(2)–P(3)N(3)	27.9	39.3(4)
N(2)P(3)–N(3)P(4)	−169.6	178.4(3)
P(3)N(3)–P(4)N(4)	153.0	155.2(3)
N(3)P(4)–N(4)P(1′)	−61.3	−27.3(4)
P(4)N(4)–P(1′)N(1′)	33.3	64.2(4)
Distance (Å) from mean plane [b] of atom [c]		
P(2)	−0.070	−0.039
N(2)	0.100	−0.012
P(3)	−0.111	0.141
N(3)	0.071	−0.062
P(4)	0.173	−0.133
N(4)	−0.301	0.100
P(1′)	0.140	0.005

[a] Ref. 14. [b] Unweighted mean planes through P(2), N(2), P(3), N(3), P(4), N(4), P(1′); equations: $-0.9615X + 0.2040Y - 0.1839Z = -1.3367$ (methoxide, orthogonal co-ords. X, Y, Z with respect to a, b', c^*) and $-0.5729X + 0.3221Y - 0.7537Z = -2.9091$ (dimethylamide, orthogonal co-ords. X, Y, Z with respect to a, b, c^*). [c] Mean |distance| from mean planes 0.138 (methoxide), 0.070 Å (dimethylamide).

The structure of $N_8P_8(NMe_2)_{16}$ otherwise reflects a balance between endo- and exo-cyclic π-bonding which is slightly, but systematically, different from that in the other three dimethylamides. The mean sum of angles at the exocyclic atoms is closer to 360° than it is in the

TABLE 4

Comparison of geometrical parameters of $N_nP_n(OMe)_{2n}$ and $N_nP_n(NMe_2)_{2n}$

n	Ring P–N/Å	Ring N–P–N/°	Ring P–N–P/°
Methoxy-compounds			
4 [a]	1.570(10)	121.0(6)	132.2(7)
6 [b]	1.567(7)	118.5(4)	134.3(5)
8 [c]	1.561(14)	116.7(7)	136.7(10)
Dimethylamide-compounds			
3 [d]	1.588(3)	116.7(4)	123.0(4)
4 [e]	1.578(10)	120.0(5)	133.0(6)
6 [f]	1.563(10)	120.1(5)	147.5(7)
8	1.548(9)	116.8	156.4
	Exocyclic P–N/Å	Exocyclic N–P–N/°	N–C/Å
3	1.652(4)	101.5(8)	1.45(2), [1.48(1)] [g]
4	1.678(10)	103.8(5)	1.45(2)
6	1.669(10)	102.9(5)	1.46(2)
8	1.651(7)	102.6	1.43(2), [1.46(3)]
	C–N–C/°	Mean sum angles (°) at exo. N	
3	113.9(12)	353.3	
4	115.8(10)	354.0	
6	112.9	353.1	
8	113.9(8)	356.3	

[a] G. B. Ansell and G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 2498. [b] Ref. 15. [c] Ref. 14. [d] Ref. 3. [e] Ref. 4. [f] Ref. 5. [g] Corrected for thermal libration using a riding model; carbon atoms assumed to ride on the nitrogen atoms to which they are bonded.

other compounds, and the exocyclic P–N bond is apparently shorter (Table 4). Taken together, the two effects may be a just significant indication of stronger exocyclic π-bonding in the largest molecule. The mean internal angle at phosphorus in $N_8P_8(NMe_2)_{16}$ is certainly significantly less than that in the tetramer or hexamer, and together with the exocyclic geometry and the large mean angle at the ring nitrogen atom, is consistent with an increasing drift of π-electrons towards the ring nitrogen atom as the ring size is enlarged. It does not seem possible to decide, on the structural evidence alone, whether the drift is a contributory cause of the large angles at the ring nitrogen atoms, or whether the angles are a direct result of steric interactions. The nature of the σ-hybridisation cannot therefore be determined exactly, and the bond-length variations cannot properly be divided into σ- and π-components by the approximate method devised previously.[16] Nevertheless, the large mean angle at nitrogen implies a large, even if inaccurately known, *s* component in the σ-bonds, and it is likely that, as argued for other series,[16] the decrease in mean P–N bond length with increasing ring size is principally a σ-effect, the π-bond strength varying much less with ring size than the values of the unadjusted bond lengths would suggest. Whatever the primary cause of the bond-angle variations, mean values of the ring bond lengths and angles at nitrogen (Table 4) show that, for the same angle, the ring bonds are longer in the dimethylamide than in the methoxide series, confirming the importance of ligand electronegativity in determining bond lengths, independently of variation in σ-hybridisation.

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[16] D. P. Craig and N. L. Paddock, in 'Nonbenzenoid Aromatics,' Academic Press, New York, 1971, vol. 2, p. 273.