

40% of the cell volume and, as noted in our earlier discussion of our electrochemical results, is acidic. The *outer* membrane transport protein for ferric enterobactin has been shown to recognize and transport synthetic analogues.^{8,7} This apparently delivers the iron complex to the periplasmic space. The steps involved in the subsequent transport of iron into the cytoplasm have yet to be characterized.

Conclusion

The electrochemical results presented here show that iron removal via protonation and reduction is a possible mechanism for *in vivo* iron transport of *E. coli*. We suggest that this could occur in the periplasmic space of *E. coli*, a region of the organism known to be relatively acidic. While the interpretive issue of the structure of the protonated ferric enterobactin complex ultimately must await unambiguous assignment from an X-ray diffraction study, we believe the weight of evidence supports what we have described as the "salicylate" mode of bonding.^{4,5} Factual issues which are now completely definitive are the following:

(1) Ferric enterobactin at or above neutral pH is a tris(catechol)iron(III) complex with a Δ chirality.

(2) Protonation of ferric enterobactin, which occurs only below pH 5, is stepwise, in *single*-proton reactions; the first two protonation constants are $10^{4.8}$ and $10^{3.15}$.

(3) Protonation of *ferrous* enterobactin begins at pH 10.4, resulting in the strongly pH-dependent redox potential reported here. The formal electrochemical potentials for iron(III,II) enterobactin are (at pH noted) -0.99 (> 10.4), -0.79 (7.4), -0.57 (6.0) V (vs. NHE).

(4) In (or from) aqueous solution, all of the protonated ferric enterobactin species, including the neutral $[\text{Fe}^{\text{III}}\text{H}_3\text{ent}]^0$, contain exclusively high-spin iron(III).

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Registry No. $[\text{Fe}(\text{ent})]^{3-}$, 61481-53-6; Fe, 7439-89-6.

Preparation and Conformations of the Medium-Ring Dimethylphosphazenes $(\text{NPMe}_2)_{9-12}$: Crystal and Molecular Structures of Octadecamethylcyclononaphosphazene, Eicosamethylcyclodecaphosphazene, Docosamethylcycloundecaphosphazene, and Tetracosamethylcyclododecaphosphazene

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Abstract: With the extension of the series by the preparation of $(\text{NPMe}_2)_{9-12}$, the dimethylphosphazenes form the longest known series of cyclic compounds with full structural characterization. Crystal data for $(\text{NPMe}_2)_n$ are as follows: $n = 9$, triclinic, $P\bar{1}$, $a = 20.6208$ (10) Å, $b = 15.2473$ (7) Å, $c = 13.3132$ (7) Å, $\alpha = 90.492$ (4)°, $\beta = 88.516$ (4)°, $\gamma = 119.740$ (4)°, $Z = 4$, $R = 0.040$ for 7008 reflections; $n = 10$, orthorhombic, $Acam$, $a = 20.5498$ (11) Å, $b = 8.1798$ (5) Å, $c = 23.4152$ (14) Å, $Z = 4$, $R = 0.035$ for 1124 reflections; $n = 11$, triclinic, $P\bar{1}$, $a = 8.2739$ (7) Å, $b = 12.533$ (2) Å, $c = 21.651$ (3) Å, $\alpha = 86.43$ (1)°, $\beta = 83.96$ (1)°, $\gamma = 84.89$ (1)°, $Z = 2$, $R = 0.033$ for 5589 reflections; $n = 12$, triclinic, $P\bar{1}$, $a = 8.397$ (3) Å, $b = 12.007$ (4) Å, $c = 13.390$ (2) Å, $\alpha = 114.24$ (2)°, $\beta = 99.57$ (2)°, $\gamma = 92.97$ (3)°, $Z = 1$, $R = 0.051$ for 3422 reflections. The mean P-N bond length (1.595 Å) is independent of ring size and is greater than it is in chloro- or fluoro-phosphazenes, a result of the low electronegativity of the methyl group. The geometry of the PC_2 group ($\text{P-C} = 1.808$ Å, $\text{CPC} = 103.9^\circ$) is independent of ring size, but electronic changes within the ring cause the NPN angle to decrease steadily from 119.8° in $(\text{NPMe}_2)_4$ to 116.3° in $(\text{NPMe}_2)_{12}$. The stereochemical effectiveness of the nitrogen lone pairs is reduced by their partial delocalization into $d\pi$ -orbitals of phosphorus, so that the PNP angles are both large and variable. The conformations, controlled primarily by steric interactions between methyl groups, are related to those of the cycloalkanes, where known, of the same polymeric number. The comparability depends on the weakness of the steric interactions of the nitrogen atoms; systematic differences arise because the $\text{Me}\cdots\text{Me}$ interactions are net attractive. Although the molecules are flexible in solution, a medium-ring effect, analogous to that in the cycloalkanes, is found in $(\text{NPMe}_2)_9$, in which many of the local interactions are of high energy, and also in the probable steric hindrance to the final step in the methylation of the fluoride to $(\text{NPMe}_2)_{10}$.

Much of our systematic knowledge of cyclic molecules comes from the study of the cycloalkanes and their derivatives. The difficulties encountered in the synthesis of medium-ring compounds and the dependence of their chemical properties and heats of formation on ring size were early traced to the high torsional barrier to rotation about skeletal bonds and, later, to transannular repulsive interactions. The resultant structural effects have been the subject of numerous investigations.²

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Inorganic cyclic compounds³ include the various molecular forms of sulfur, the metaphosphates $(\text{OPO}_2^-)_n$, the siloxanes

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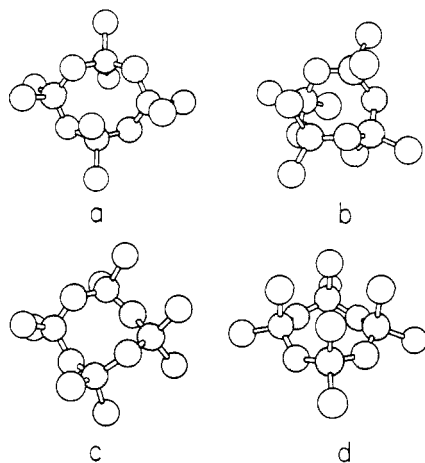


Figure 1. Symmetrical frameworks found in $(ABX_2)_4$ molecules; skeletal atoms shaded. (a) Chair, as in $P_4O_{12}^{3-}$ and in $(OSiMe_2)_4$.^{4,5} (b) Tub, as in $P_4O_{12}^{3-}$ and in $(NPCl_2)_4$.^{6,7} (c) Saddle, as in $(NPM_2)_4$ and in $(OSeO_2)_4$.^{8,9} (d) Crown, as in $(NPCIPh)_4$ and (with substituents on alternate atoms) in $(NMe\cdot PMe)_4$.^{10,11}

$(OSiR_2)_n$ and the phosphazenes $(NPR_2)_n$. The structural evidence relates mainly to the smaller molecules, and it is particularly abundant for those based on an eight-membered ring. Figure 1 shows most of the symmetrical frameworks found in $(ABX_2)_4$ and related molecules. They differ among themselves and from the most stable form of cyclooctane (chair-boat, see below) because the attractive and repulsive forces are balanced differently;^{12,13} polar interactions are often decisive. Although many of these structures are understood semiquantitatively, the energy parameters are not known accurately enough to allow reliable predictions of the conformations of corresponding macrocyclic compounds. Reciprocally, we can expect that a study of compounds based on the larger rings will not only be interesting in itself, but will also tell us more about bonding and nonbonding interactions in inorganic molecules. We can also expect to find out whether the medium-ring effect on structure and chemistry, as found in cycloalkanes, has a parallel in inorganic chemistry.

Only the poly(dimethylsiloxanes) have been compared systematically with cyclic hydrocarbons,¹⁴ mainly on the basis of thermochemical and spectroscopic measurements. The general conclusions are referred to later; since there are few known structures, the direct evidence on conformational preferences is limited. The cyclic phosphazenes $(NPR_2)_n$ are isoelectronic with the siloxanes $(OSiR_2)_n$, and some structural relationship between the two series is to be expected, even though the phosphazenes are formally unsaturated. The simplest are the halides $(NPX_2)_2$, but molecular structures are unknown beyond the pentamers ($n = 3, 4, 5$; $X = F$,^{15a-c} Cl ,^{15d-g} Br ^{15h-j}). The series of fluorophosphazenes is long,¹⁶ but only the trimer and tetramer are solid

at room temperature. For a study of the effect of ring size on conformation, the dimethylphosphazenes are particularly appropriate, since they are all crystalline at room temperature¹⁷ and the methyl group carries no unshared electrons. Conjugative interactions between the substituent and the π -system of the ring, which have a significant effect on the chemistry of, for example, phosphazene carbanions,¹⁸ are thereby avoided, and the direct steric interactions are more easily distinguished.

The structures of $(NPM_2)_{3-8}$ were determined earlier.^{19a,8,19b-e} In this paper we describe the preparation of the further four compounds $(NPM_2)_{9-12}$, some of their properties, and the determination of their crystal and molecular structures. Taken together, the dimethylphosphazenes form the longest series of cyclic molecules, organic or inorganic, with known structures. A close but indirect geometrical relationship has been found between the phosphazenes and the cycloalkanes, and it seems likely that steric interactions may be responsible for some features of the preparative reactions. The π -electronic interactions, which in principle relate the series to the annulenes, do not show in any tendency to molecular planarity but rather in perturbation effects, typically those induced by complex formation and quaternization.

Experimental Section

The fluorophosphazenes $(NPF_2)_{6-12}$ were prepared by the reaction of a mixture of chlorophosphazenes $(NPCl_2)_n$ ($n > 5$) with potassium fluorosulfite.^{16b} The individual compounds were separated by distillation and purified by gas-liquid chromatography. Methylmagnesium bromide was freshly prepared from magnesium turnings and methyl bromide. Diethyl ether was dried by distillation from lithium aluminum hydride. NMR spectra were obtained on a Varian XL100 spectrometer (1H , 100 MHz; ^{31}P , 40.1 MHz) and on a CFT20 (^{13}C , 20.0 MHz). Infrared spectra were obtained from Nujol mulls and solutions in carbon tetrachloride by using a Perkin-Elmer 457 spectrophotometer.

Preparation of $(NPM_2)_{6-12}$. The preparative method used has already been described for $(NPM_2)_7$.^{19d} Melting points, yields, and analyses follow: Anal. Calcd for C_7H_6NP : C, 32.0; H, 8.1; N, 18.7. $(NPM_2)_6$, 163–165 °C, 67%. Anal. Found: C, 32.0; H, 8.1; N, 18.7. $(NPM_2)_7$, 128–130 °C, 40% ref 19d. $(NPM_2)_8$, 171–173 °C, 40%. Anal. Found: C, 32.4; H, 7.9; N, 18.8. $(NPM_2)_9$, 123–125 °C, 28%. Anal. Found: C, 32.3; H, 8.2; N, 18.3. $(NPM_2)_{10}$, 100–102 °C, 4%. Anal. Found: C, 31.7; H, 8.1; N, 18.6. $(NPM_2)_{11}$, 101–102 °C, 46%. Anal. Found: C, 32.1; H, 8.0; N, 18.9. $(NPM_2)_{12}$, 120–122 °C, 24%. Anal. Found: C, 31.9; H, 8.0; N, 18.9. In some of the reactions which gave poor yields, the reaction mixture formed a sticky paste of magnesium salts rather than a fine powder. The small yield of the decamer seems to have a different cause, because although the reaction was apparently clean, it was not quite complete even after several weeks of reaction time; some residual fluorine remained.

X-ray Crystallographic Analyses of $(NPM_2)_n$ ($n = 9-12$). Crystallographic data for the four compounds are given in Table I. Final unit-cell parameters were obtained by least squares on $2 \sin \theta / \lambda$ values for 25 reflections (with $2\theta = 90-100^\circ$ for $n = 9$ and $25-50^\circ$ for $n = 10-12$). The intensities of three check reflections were measured every hour throughout the data collections and in each case showed only small random fluctuations. Absorption corrections were applied using the Gaussian integration method;²⁰⁻²² transmission factor ranges are given in Table I.

In each case there was a choice between noncentrosymmetric and centrosymmetric space groups, the latter being indicated by the E statistics for all four structures. The structures of the $n = 10$ and 12

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Table I. Crystallographic Data^a

compd	(NPM ₂) ₉	(NPM ₂) ₁₀	(NPM ₂) ₁₁	(NPM ₂) ₁₂
formula	C ₁₈ H ₅₄ N ₉ P ₉	C ₂₀ H ₆₀ N ₁₀ P ₁₀	C ₂₂ H ₆₆ N ₁₁ P ₁₁	C ₂₄ H ₇₂ N ₁₂ P ₁₂
fw	675.45	750.50	825.56	900.61
cryst sys	triclinic	orthorhombic	triclinic	triclinic
space group	<i>P</i> 1 ^b	<i>Acam</i> ^c	<i>P</i> 1 ^d	<i>P</i> 1 ^d
<i>a</i> , Å	20.6208 (10)	20.5498 (11)	8.2739 (7)	8.397 (3)
<i>b</i> , Å	15.2473 (7)	8.1798 (5)	12.533 (2)	12.007 (4)
<i>c</i> , Å	13.3132 (7)	23.4152 (14)	21.651 (3)	13.390 (2)
α , deg	90.492 (4)	90	86.43 (1)	114.24 (2)
β , deg	88.516 (4)	90	83.96 (1)	99.57 (2)
γ , deg	119.740 (4)	90	84.89 (1)	92.97 (3)
<i>V</i> , Å ³	3633.2 (4)	3935.9 (4)	2220.6 (5)	1203.0 (8)
<i>Z</i>	4	4	2	1
<i>D_c</i> , g/cm ³	1.235	1.266	1.235	1.243
<i>F</i> (000)	1440	1600	880	480
μ (Mo K α), cm ⁻¹	42.74 ^e	4.56	4.44	4.47
cryst dimens, mm	0.35 × 0.40 × 0.50	0.13 × 0.25 × 0.30	0.22 × 0.23 × 0.45	0.11 × 0.35 × 0.40
transmission factors	0.387–0.631	0.838–0.960	0.891–0.928	0.827–0.953
scan type	ω -2 θ	ω -2 θ	ω -2 θ	ω
scan range, deg in ω	0.60 + 0.14 tan θ	0.70 + 0.35 tan θ	0.60 + 0.35 tan θ	0.90 + 0.35 tan θ
scan speed, deg/min	0.61–10.06	1.12–10.06	1.26–10.06	0.81–6.71
data collectd	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
2 θ_{\max} , deg	150	55	50	54
unique refltns	14461	2310	7754	6407
refltns with <i>I</i> ≥ 3 σ (<i>I</i>)	7008	1124	5589	3422
no. of variables	649	155	661	361
<i>R</i>	0.040	0.035	0.033	0.051
<i>R_w</i>	0.051	0.042	0.043	0.064
<i>S</i>	1.129	1.881	1.547	1.004
mean Δ/σ (final cycle)	0.05	0.001	0.03	0.05
max Δ/σ (final cycle)	0.29	0.007	0.28	0.54
residual density, e/Å ³	0.47	0.34	0.60	0.38

^a Temperature 22 °C, Enraf-Nonius CAD4-F diffractometer, Mo K α radiation ($\lambda_{K\alpha 1} = 0.70930$, $\lambda_{K\alpha 2} = 0.71359$ Å), graphite monochromator, takeoff angle 2.7°, aperture (2.0 + tan θ) × 4.0 mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (*S* = scan count, *B* = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, and $S = (\sum w(|F_o| - |F_c|)^2 / (m - n))^{1/2}$. Values given for *R*, *R_w*, and *S* are based on those reflections with *I* ≥ 3 σ (*I*). For (NPM₂)₉: Cu K α radiation ($\lambda_{K\alpha 1} = 1.540562$, $\lambda_{K\alpha 2} = 1.544390$ Å), $\sigma^2(I) = S + 2B + [0.05(S - B)]^2$. ^b The reduced cell has *a* = 13.3132 (7) Å, *b* = 15.2473 (7) Å, *c* = 18.594 (9) Å, $\alpha = 105.656$ (4)°, $\beta = 91.242$ (4)°, and $\gamma = 90.492$ (4)° and is related to the cell given above by the transformation:

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & -1 & 0 \end{pmatrix}$$

^c Nonstandard setting of *Cmca*, equivalent positions: (0,0,0)±, (0,1/2,1/2)±, (x,y,z), (-x,-y,z), 1/2-x, 1/2+y,z, 1/2+x, 1/2-y,z. ^d Reduced cell. ^e μ (Cu K α).

compounds were solved by conventional heavy-atom techniques, the phosphorus atoms being positioned from the Patterson functions and the remaining atoms (including hydrogen) from subsequent difference maps. The two other structures (*n* = 9 and 11) were solved by direct methods, the phosphorus positions being determined from *E* maps and those of the remaining atoms from subsequent difference maps. The solution of the structure of (NPM₂)₉ (with two molecules in the asymmetric unit) proved to be unusually difficult. In spite of numerous attempts by direct, heavy-atom, and trial and error methods, the problem defied solution for 3 years. The structure was finally solved on the first attempt with the 1980 update of MULTAN using the 120 largest *E*'s.²³

In the final stages of full-matrix least-squares refinement all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic thermal parameters for *n* = 10–12 [except for H(2b) in (NPM₂)₁₀ which was kept fixed in a calculated position]. For *n* = 9 the hydrogen atoms were fixed in idealized, staggered positions (C–H = 0.98 Å). Neutral atom scattering factors from ref 24 were used for the non-hydrogen atoms and those of ref 25 for hydrogen atoms. Anomalous scattering factors from ref 26 were employed for P atoms.

Final positional and isotropic [or equivalent isotropic, $U_{eq} = 1/3$ trace (U_{diag})] thermal parameters are given in Table II. Anisotropic thermal parameters, calculated hydrogen parameters for (NPM₂)₉, and measured and calculated structure factors (Tables III–V) are included as supplementary material.

The thermal motion in all four structures has been analyzed in terms of the rigid-body modes of translation, libration, and screw motion.²⁷ The root mean square errors in the temperature factors, σU_{ij} (derived from the least-squares analyses) are 0.0028, 0.0024, 0.0021, and 0.0026 Å² for *n* = 9–12, respectively. For (NPM₂)_{9–12}, analyses of each of the independent PN₂C₂ groups gave physically reasonable results and rms ΔU_{ij} values in the range 0.0008–0.0029 Å². The bond distances have been corrected for libration^{27,28} by using shape parameters *q*² of 0.08 for all atoms. Corrected and uncorrected bond lengths are given in Table VI and bond angles in Table VII (supplementary material). Intraannular torsion angles appear in Table VIII. Bond lengths and angles involving hydrogen atoms and complete listings of torsion angles (Tables IX–XI) are included as supplementary material. In Tables VII and VIII primed and double-primed atoms for (NPM₂)₁₀ have coordinates related to those in Table II by the symmetry operations *x*, *y*, -*z* and -*x*, -*y*, *z*, respectively, and for [NPM₂]₁₂ primed atoms are related by 1 - *x*, 1 - *y*, 1 - *z*.

Results and Discussion

Preparation of Dimethylphosphazenes. No single preparative method is suitable for the whole range (NPM₂)_{3–12}. Although (NPM₂)_{3,4} can be prepared in good yield by condensation reactions,^{17,29} the higher cyclic oligomers can be obtained only by substitution reactions on the halides (NPX₂)_{*n*} (*X* = F, Cl). Organometallic alkylating agents can react in different ways. For instance, methylation of (NPF₂)₃ with methylolithium³⁰ cannot be carried beyond *gem*-N₃P₃F₄Me₂; the difficulty is common with trimeric phosphazenes, and results both from skeletal cleavage^{31a} and from the elimination of alkyl halide.^{32b,c} Degradation reactions appear to dominate the alkylation of (NPCl₂)₄, but the reaction of (NPF₂)₄ with methylolithium produces (NPM₂)₄ in 70% yield;³² the pentamer can be prepared in the same way.³³ The fluorides give better results than the chlorides, possibly because their phosphazene skeleton is the stronger and because the strength of the P–F bond makes the elimination of alkyl halide less likely.³⁴ Yields are further improved by the use of the milder methylmagnesium bromide instead of methylolithium, but even then the reaction does not proceed uniformly well. There are two points of interest. First, if *n* > 5, the dimethylphosphazenes (NPM₂)_{*n*} form insoluble complexes with magnesium or lithium ions, which must be decomposed with alkali. Second, the (qualitative) rate

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(34) The phenylphosphazenes (NPPH₂)_{4–6} can be prepared similarly from the fluorides in high yield. (Todd, S. M.; Paddock, N. L., unpublished results).

Table II. Final Positional (Fractional $\times 10^4$, $P \times 10^5$, $H \times 10^3$) and Isotropic Thermal Parameters ($U \times 10^3 \text{ \AA}^2$) with Estimated Standard Deviations in Parentheses

(NPM ₂) ₉									
atom	x	y	z	U_{eq}/U_{iso}	atom	x	y	z	U_{eq}/U_{iso}
P(1)	41126 (7)	34002 (9)	12353 (9)	45	C(1)	3258 (3)	2228 (4)	1411 (4)	70
P(2)	54795 (6)	40591 (9)	23635 (8)	44	C(2)	4345 (4)	3385 (5)	-64 (4)	82
P(3)	56363 (6)	25314 (9)	34607 (9)	45	C(3)	6179 (4)	4466 (5)	1400 (5)	91
P(4)	48033 (7)	19326 (10)	53911 (9)	49	C(4)	5546 (3)	5205 (4)	2820 (4)	58
P(5)	32475 (7)	5268 (9)	50006 (9)	48	C(5)	5425 (4)	1762 (4)	2366 (4)	78
P(6)	20939 (6)	8163 (9)	59882 (9)	45	C(6)	6567 (3)	2833 (5)	3754 (5)	84
P(7)	17398 (6)	17840 (9)	43054 (8)	44	C(7)	5173 (3)	1394 (5)	6251 (5)	84
P(8)	30489 (6)	37366 (9)	39768 (8)	42	C(8)	5187 (3)	3211 (4)	5776 (4)	67
P(9)	34434 (6)	46285 (9)	19544 (8)	41	C(9)	3262 (3)	836 (4)	3705 (4)	69
P(10)	649 (6)	-20683 (9)	95088 (8)	43	C(10)	3316 (3)	-596 (5)	4981 (5)	90
P(11)	16056 (6)	-5239 (9)	97792 (9)	45	C(11)	1203 (3)	-151 (4)	6464 (4)	71
P(12)	27925 (7)	-7763 (10)	88334 (9)	52	C(12)	2606 (3)	1510 (4)	7060 (4)	63
P(13)	32374 (7)	-15346 (9)	105916 (9)	48	C(13)	1364 (3)	688 (4)	3521 (4)	67
P(14)	20095 (6)	-35317 (9)	110008 (8)	41	C(14)	950 (3)	1965 (4)	4543 (4)	69
P(15)	16079 (7)	-42450 (11)	130234 (9)	52	C(15)	2831 (3)	4266 (4)	5060 (3)	55
P(16)	6952 (7)	-33388 (9)	138505 (8)	48	C(16)	3784 (3)	3543 (4)	4406 (4)	56
P(17)	-6444 (6)	-42071 (9)	126908 (8)	43	C(17)	2534 (3)	3943 (4)	1417 (4)	61
P(18)	-6691 (6)	-25925 (9)	115125 (8)	41	C(18)	3786 (3)	5927 (4)	1629 (3)	53
N(1)	4680 (2)	3312 (3)	1944 (3)	67	C(19)	-287 (3)	-3364 (4)	9197 (4)	63
N(2)	5687 (3)	3582 (3)	3261 (3)	65	C(20)	-331 (3)	-1610 (5)	8596 (4)	74
N(3)	5077 (2)	1829 (3)	4298 (3)	65	C(21)	1457 (3)	537 (4)	9632 (5)	71
N(4)	3925 (2)	1411 (3)	5571 (3)	50	C(22)	1626 (3)	-652 (4)	11112 (4)	69
N(5)	2448 (2)	201 (3)	5483 (3)	55	C(23)	2278 (3)	-1551 (5)	7803 (4)	76
N(6)	1995 (2)	1613 (3)	5359 (3)	59	C(24)	3661 (3)	183 (5)	8296 (5)	96
N(7)	2349 (2)	2688 (3)	3645 (3)	49	C(25)	4088 (3)	-1583 (5)	10407 (4)	76
N(8)	3364 (2)	4591 (3)	3139 (3)	57	C(26)	3531 (3)	-402 (4)	11306 (5)	84
N(9)	3998 (2)	4343 (3)	1383 (3)	56	C(27)	1219 (3)	-3444 (4)	10602 (4)	56
N(10)	942 (2)	-1522 (3)	9314 (3)	47	C(28)	2229 (3)	-4062 (4)	9921 (3)	54
N(11)	2406 (2)	-180 (3)	9289 (3)	54	C(29)	1232 (3)	-5491 (5)	13526 (4)	89
N(12)	2949 (3)	-1483 (3)	9515 (3)	66	C(30)	2467 (3)	-3511 (5)	13661 (4)	75
N(13)	2681 (2)	-2447 (3)	11283 (3)	55	C(31)	789 (3)	-3431 (5)	15178 (4)	80
N(14)	1773 (2)	-4344 (3)	11877 (3)	48	C(32)	1164 (4)	-2016 (5)	13621 (6)	140
N(15)	1061 (3)	-3832 (6)	13230 (4)	115	C(33)	-564 (3)	-5234 (4)	12165 (4)	61
N(16)	-172 (2)	-3790 (3)	13677 (3)	55	C(34)	-1600 (3)	-4785 (5)	13157 (4)	74
N(17)	-498 (2)	-3468 (3)	11777 (3)	54	C(35)	-1655 (3)	-3116 (4)	11314 (4)	66
N(18)	-223 (2)	-1923 (3)	10579 (3)	52	C(36)	-491 (3)	-1735 (4)	12525 (4)	68
(NPM ₂) ₁₀									
atom	x	y	z	U_{eq}/U_{iso}	atom	x	y	z	U_{eq}/U_{iso}
P(1)	15386 (6)	-11551 (16)	0	35	H(2a)	49 (2)	-171 (5)	28 (2)	81 (17)
P(2)	15999 (4)	7448 (11)	10606 (4)	38	H(2b)	54	11	0	82
P(3)	6230 (4)	-7868 (11)	18491 (4)	35	H(3a)	219 (2)	157 (5)	182 (2)	75 (15)
N(1)	1830 (2)	-457 (5)	570 (2)	70	H(3b)	272 (2)	131 (5)	129 (2)	80 (14)
N(2)	951 (2)	361 (4)	1392 (2)	55	H(3c)	250 (2)	-7 (7)	161 (2)	82 (17)
N(3)	0	0	2146 (2)	39	H(4a)	118 (3)	351 (8)	115 (3)	169 (28)
C(1)	1720 (4)	-3284 (8)	0	64	H(4b)	185 (3)	328 (6)	58 (2)	117 (21)
C(2)	674 (3)	-1055 (11)	0	66	H(4c)	114 (2)	272 (6)	59 (2)	68 (16)
C(3)	2291 (2)	908 (7)	1524 (2)	58	H(5a)	89 (2)	-199 (5)	272 (2)	73 (14)
C(4)	1500 (3)	2797 (6)	815 (2)	63	H(5b)	150 (2)	-177 (5)	231 (2)	60 (14)
C(5)	1165 (2)	-1269 (6)	2425 (2)	52	H(5c)	127 (2)	-23 (6)	267 (2)	76 (15)
C(6)	426 (3)	-2742 (6)	1553 (2)	55	H(6a)	23 (2)	-347 (5)	186 (2)	61 (12)
H(1a)	152 (2)	-384 (6)	42 (3)	113 (19)	H(6b)	75 (2)	-328 (5)	137 (2)	69 (14)
H(1b)	213 (4)	-289 (10)	0	103 (30)	H(6c)	13 (2)	-258 (6)	130 (2)	66 (16)
(NPM ₂) ₁₁									
atom	x	y	z	U_{eq}/U_{iso}	atom	x	y	z	U_{eq}/U_{iso}
P(1)	24327 (10)	8275 (6)	5344 (3)	42	H(4c)	-150 (7)	195 (5)	188 (3)	133 (21)
P(2)	-683 (9)	24388 (6)	10227 (4)	44	H(5a)	-112 (5)	546 (3)	119 (2)	68 (12)
P(3)	13494 (10)	45319 (6)	10099 (3)	42	H(5b)	25 (6)	625 (4)	107 (2)	103 (17)
P(4)	30205 (10)	41284 (7)	21718 (4)	48	H(5c)	-38 (5)	573 (4)	50 (2)	97 (15)
P(5)	11348 (9)	51500 (7)	32162 (3)	44	H(6a)	391 (5)	432 (4)	50 (2)	92 (16)
P(6)	28706 (9)	50381 (6)	43039 (3)	39	H(6b)	273 (4)	495 (3)	6 (2)	77 (12)
P(7)	28872 (9)	27259 (6)	46743 (3)	41	H(6c)	343 (6)	540 (4)	56 (2)	95 (16)
P(8)	51859 (9)	13269 (6)	39598 (3)	38	H(7a)	486 (8)	553 (6)	198 (3)	200 (31)
P(9)	32744 (10)	-1767 (7)	33957 (4)	48	H(7b)	575 (6)	431 (4)	227 (2)	105 (16)
P(10)	51867 (10)	-9736 (6)	22959 (4)	44	H(7c)	533 (6)	466 (4)	156 (3)	119 (22)
P(11)	29906 (10)	-10851 (6)	12935 (4)	43	H(8a)	243 (6)	252 (3)	234 (2)	44 (14)
N(1)	1013 (3)	1338 (2)	1011 (1)	52	H(8b)	397 (8)	254 (5)	165 (3)	239 (27)
N(2)	799 (4)	3474 (2)	770 (1)	67	H(8c)	423 (7)	232 (5)	246 (3)	140 (22)
N(3)	1744 (3)	4578 (2)	1706 (1)	56	H(9a)	212 (7)	692 (4)	293 (2)	143 (21)
N(4)	2499 (4)	4361 (3)	2873 (1)	69	H(9b)	98 (5)	647 (3)	243 (2)	99 (15)
N(5)	1272 (3)	5187 (2)	3940 (1)	43	H(9c)	36 (5)	698 (3)	310 (2)	69 (12)
N(6)	3567 (3)	3860 (2)	4499 (1)	48	H(10a)	-89 (5)	408 (3)	332 (2)	79 (14)
N(7)	4232 (3)	1731 (2)	4590 (1)	43	H(10b)	-159 (6)	517 (4)	332 (2)	97 (21)
N(8)	4173 (3)	874 (2)	3464 (1)	47	H(10c)	-98 (5)	479 (3)	270 (2)	88 (14)

Table II (Continued)

atom	x	y	z	U_{eq}/U_{iso}	atom	x	y	z	U_{eq}/U_{iso}
N(9)	4207 (3)	-1063 (2)	2959 (1)	54	H(11a)	156 (5)	550 (3)	526 (2)	81 (13)
N(10)	4242 (3)	-652 (2)	1705 (1)	56	H(11b)	331 (6)	576 (3)	519 (2)	88 (14)
N(11)	2805 (3)	-434 (2)	650 (1)	48	H(11c)	201 (4)	651 (3)	487 (2)	72 (11)
C(1)	1980 (7)	1023 (4)	-262 (2)	66	H(12a)	489 (4)	535 (3)	354 (2)	69 (12)
C(2)	4258 (5)	1482 (3)	561 (2)	57	H(12b)	425 (4)	638 (3)	376 (2)	71 (11)
C(3)	-1749 (6)	2361 (5)	572 (3)	91	H(12c)	540 (5)	556 (3)	414 (2)	74 (12)
C(4)	-974 (7)	2539 (4)	1813 (3)	74	H(13a)	294 (5)	262 (3)	572 (2)	67 (12)
C(5)	-197 (6)	5618 (4)	918 (2)	69	H(13b)	133 (5)	316 (4)	557 (2)	91 (15)
C(6)	3040 (6)	4863 (4)	461 (2)	63	H(13c)	158 (4)	199 (3)	556 (2)	71 (11)
C(7)	4974 (6)	4665 (6)	1957 (3)	97	H(14a)	154 (6)	245 (4)	389 (2)	86 (17)
C(8)	3562 (8)	2716 (4)	2124 (3)	89	H(14b)	76 (4)	190 (3)	439 (1)	64 (10)
C(9)	1111 (8)	6485 (3)	2861 (2)	79	H(14c)	28 (4)	307 (3)	433 (2)	70 (10)
C(10)	-867 (6)	4778 (5)	3126 (3)	77	H(15a)	639 (5)	-14 (3)	446 (2)	74 (14)
C(11)	2374 (6)	5806 (3)	4982 (2)	56	H(15b)	736 (5)	8 (3)	385 (2)	82 (12)
C(12)	4548 (5)	5666 (3)	3886 (2)	57	H(15c)	755 (5)	64 (3)	442 (2)	77 (13)
C(13)	2088 (6)	2636 (4)	5479 (2)	62	H(16a)	542 (6)	299 (4)	336 (2)	117 (17)
C(14)	1177 (5)	2538 (3)	4251 (2)	56	H(16b)	697 (5)	261 (3)	379 (2)	88 (13)
C(15)	6766 (5)	355 (4)	4194 (2)	62	H(16c)	689 (4)	212 (3)	321 (2)	65 (10)
C(16)	6247 (6)	2386 (3)	3545 (2)	61	H(17a)	367 (6)	-116 (4)	431 (2)	105 (20)
C(17)	2732 (9)	-871 (5)	4130 (2)	84	H(17b)	214 (6)	-33 (4)	438 (2)	112 (19)
C(18)	1353 (6)	251 (5)	3111 (3)	81	H(17c)	223 (6)	-141 (4)	407 (2)	107 (18)
C(19)	6363 (7)	-2250 (4)	2215 (3)	80	H(18a)	150 (7)	58 (4)	277 (3)	108 (24)
C(20)	6691 (5)	-10 (4)	2260 (2)	66	H(18b)	63 (5)	-39 (4)	311 (2)	97 (14)
C(21)	3615 (7)	-2438 (3)	1085 (2)	68	H(18c)	76 (5)	74 (4)	333 (2)	88 (15)
C(22)	1022 (5)	-1148 (4)	1720 (2)	69	H(19a)	564 (6)	-283 (4)	230 (2)	111 (19)
H(1a)	108 (6)	60 (4)	-33 (2)	110 (17)	H(19b)	690 (5)	-226 (3)	177 (2)	94 (16)
H(1b)	189 (4)	174 (3)	-36 (2)	70 (12)	H(19c)	707 (6)	-237 (4)	253 (2)	107 (16)
H(1c)	277 (5)	74 (3)	-52 (2)	70 (12)	H(20a)	626 (5)	74 (4)	227 (2)	103 (15)
H(2a)	470 (5)	139 (3)	96 (2)	78 (13)	H(20b)	735 (6)	-27 (3)	257 (2)	94 (15)
H(2b)	498 (5)	121 (3)	27 (2)	76 (13)	H(20c)	730 (4)	-2 (3)	187 (2)	71 (11)
H(2c)	402 (4)	226 (3)	48 (2)	79 (11)	H(21a)	469 (5)	-249 (3)	87 (2)	77 (13)
H(3a)	-126 (4)	231 (3)	13 (2)	64 (10)	H(21b)	353 (5)	-284 (3)	142 (2)	75 (15)
H(3b)	-235 (6)	170 (4)	72 (2)	116 (18)	H(21c)	293 (6)	-267 (4)	88 (2)	105 (18)
H(3c)	-242 (6)	297 (4)	57 (2)	112 (17)	H(22a)	64 (5)	-38 (4)	178 (2)	87 (14)
H(4a)	-21 (8)	244 (5)	207 (3)	158 (27)	H(22b)	49 (6)	-149 (4)	151 (2)	95 (19)
H(4b)	-167 (6)	308 (4)	180 (2)	103 (18)	H(22c)	108 (4)	-150 (3)	210 (2)	62 (10)
(NPM ₂) ₁₂									
atom	x	y	z	U_{eq}/U_{iso}	atom	x	y	z	U_{eq}/U_{iso}
P(1)	22973 (6)	10867 (4)	32304 (4)	44	H(3a)	-185 (3)	154 (3)	95 (3)	69 (8)
P(2)	2657 (6)	25589 (4)	24141 (4)	39	H(3b)	-218 (4)	162 (3)	209 (3)	90 (10)
P(3)	19787 (6)	30331 (4)	9029 (4)	39	H(3c)	-256 (5)	281 (4)	177 (3)	119 (13)
P(4)	28008 (5)	54708 (4)	11305 (3)	34	H(4a)	130 (4)	388 (3)	428 (3)	91 (10)
P(5)	58159 (5)	67972 (4)	28371 (4)	37	H(4b)	-25 (5)	427 (4)	374 (3)	109 (12)
P(6)	48424 (5)	76332 (4)	49683 (4)	37	H(4c)	-50 (3)	319 (3)	420 (2)	77 (8)
N(1)	1082 (2)	1380 (2)	2366 (1)	49	H(5a)	-37 (7)	195 (5)	-46 (4)	135 (19)
N(2)	1010 (2)	3380 (2)	1889 (2)	48	H(5b)	147 (5)	148 (4)	-64 (3)	117 (16)
N(3)	2107 (2)	4047 (1)	432 (1)	41	H(5c)	102 (4)	98 (3)	-7 (3)	88 (9)
N(4)	4537 (2)	5701 (2)	1923 (1)	43	H(6a)	461 (4)	357 (3)	207 (3)	104 (11)
N(5)	5224 (2)	7768 (2)	3896 (1)	42	H(6b)	391 (4)	204 (3)	153 (3)	89 (10)
N(6)	6323 (2)	7812 (2)	5948 (1)	45	H(6c)	452 (5)	251 (3)	79 (3)	105 (12)
C(1)	1144 (4)	579 (4)	4029 (4)	91	H(7a)	374 (3)	567 (2)	-32 (2)	58 (6)
C(2)	3157 (5)	-238 (3)	2435 (3)	86	H(7b)	183 (3)	590 (2)	-37 (2)	56 (6)
C(3)	-1833 (3)	2003 (4)	1724 (3)	73	H(7c)	323 (3)	695 (3)	49 (2)	63 (7)
C(4)	193 (4)	3616 (2)	3824 (2)	61	H(8a)	104 (3)	591 (2)	237 (2)	65 (7)
C(5)	998 (6)	1649 (3)	-271 (3)	80	H(8b)	175 (4)	703 (3)	228 (2)	73 (9)
C(6)	3968 (3)	2705 (3)	1346 (4)	75	H(8c)	50 (3)	619 (2)	140 (2)	55 (6)
C(7)	2890 (3)	6071 (2)	110 (2)	48	H(9a)	595 (4)	809 (3)	196 (2)	71 (9)
C(8)	1346 (3)	6278 (2)	1907 (2)	48	H(9b)	760 (5)	834 (4)	278 (3)	108 (12)
C(9)	6730 (4)	7694 (3)	2239 (2)	60	H(9c)	714 (4)	721 (3)	154 (3)	95 (10)
C(10)	7460 (3)	6055 (3)	3250 (2)	64	H(10a)	703 (4)	550 (3)	356 (3)	95 (11)
C(11)	3422 (3)	8709 (3)	5454 (2)	59	H(10b)	792 (5)	564 (4)	253 (3)	117 (12)
C(12)	3737 (4)	6155 (3)	4623 (3)	61	H(10c)	813 (6)	657 (4)	365 (4)	137 (16)
H(1a)	42 (5)	-17 (4)	352 (3)	104 (12)	H(11a)	394 (3)	952 (2)	556 (2)	54 (6)
H(1b)	202 (6)	30 (4)	431 (4)	128 (15)	H(11b)	245 (4)	844 (3)	487 (2)	71 (8)
H(1c)	39 (6)	143 (5)	455 (4)	138 (19)	H(11c)	310 (4)	874 (3)	602 (3)	84 (9)
H(2a)	242 (5)	-80 (4)	176 (4)	118 (14)	H(12a)	435 (4)	561 (3)	439 (3)	74 (9)
H(2b)	379 (5)	7 (4)	205 (3)	109 (16)	H(12b)	339 (3)	619 (3)	527 (2)	69 (8)
H(2c)	397 (7)	-58 (5)	278 (4)	179 (19)	H(12c)	282 (4)	594 (3)	407 (3)	81 (9)

of alkylation of (NPF₂)_{10,12} appears to be very slow, the reaction of the decamer being particularly difficult to bring to completion. The possibility that both these features have a steric origin lends further point to the structure determinations.

Structures of (NPM₂)₉₋₁₂. Stereoscopic views of the molecules (NPM₂)₉₋₁₂ are shown in Figures 2 and 3. The molecules are separated by normal van der Waals distances (Table XII), there being no evident systematic relation between the intermolecular

interactions and ring conformation. On the other hand, the dimethylphosphazenes (NPM₂)₉₋₁₂ are distinguished from the lower members of the series by their transannular Me...Me interactions, which often have a decisive effect on conformation. The qualitative similarity between the series of melting points of the dimethylsiloxanes and the halogenophosphazenes noted by Dale³⁵ is found

Table VIII. Intraannular Torsion Angles (deg) Standard Deviations in Parentheses

atoms	value, deg	atoms	value, deg
(NPMe ₂) ₉			
N(9)-P(1)-N(1)-P(2)	-42.1 (5)	N(11)-P(1)-N(1)-P(2)	-164.3 (2)
N(1)-P(1)-N(9)-P(9)	-95.7 (5)	N(1)-P(1)-N(11)-P(11)	-45.0 (3)
N(2)-P(2)-N(1)-P(1)	165.8 (4)	N(2)-P(2)-N(1)-P(1)	-38.5 (3)
N(1)-P(2)-N(2)-P(3)	46.1 (5)	N(1)-P(2)-N(2)-P(3)	-111.5 (4)
N(3)-P(3)-N(2)-P(2)	-112.9 (4)	N(3)-P(3)-N(2)-P(2)	26.1 (4)
N(2)-P(3)-N(3)-P(4)	-40.3 (6)	N(2)-P(3)-N(3)-P(4)	69.1 (4)
N(4)-P(4)-N(3)-P(3)	128.6 (4)	N(4)-P(4)-N(3)-P(3)	-169.7 (3)
N(3)-P(4)-N(4)-P(5)	21.8 (4)	N(3)-P(4)-N(4)-P(5)	-14.9 (4)
N(5)-P(5)-N(4)-P(4)	176.7 (3)	N(5)-P(5)-N(4)-P(4)	-172.1 (3)
N(4)-P(5)-N(5)-P(6)	38.5 (4)	N(4)-P(5)-N(5)-P(6)	31.6 (3)
N(6)-P(6)-N(5)-P(5)	63.3 (4)	N(6)-P(6)-N(5)-P(5)	-84.9 (2)
N(5)-P(6)-N(6)-P(7)	42.9 (6)	N(5)-P(6)-N(6)-P(7)	-29.1 (3)
N(7)-P(7)-N(6)-P(6)	-118.6 (5)	N(7)-P(7)-N(6)-P(6)	158.5 (2)
N(6)-P(7)-N(7)-P(8)	-29.8 (4)	N(6)-P(7)-N(7)-P(8)	-66.4 (2)
N(8)-P(8)-N(7)-P(7)	-160.2 (3)	N(8)-P(8)-N(7)-P(7)	-65.0 (2)
N(7)-P(8)-N(8)-P(9)	-33.4 (5)	N(7)-P(8)-N(8)-P(9)	-72.7 (3)
N(9)-P(9)-N(8)-P(8)	-67.8 (5)	N(9)-P(9)-N(8)-P(8)	-101.0 (3)
N(8)-P(9)-N(9)-P(1)	62.8 (5)	N(8)-P(9)-N(9)-P(10)	-44.1 (3)
N(18)-P(10)-N(10)-P(11)	-27.8 (4)	N(10)-P(10)-N(9)-P(9)	-70.9 (3)
N(10)-P(10)-N(18)-P(18)	-115.6 (4)	N(9)-P(10)-N(10)-P(11)	-67.5 (3)
N(11)-P(11)-N(10)-P(10)	-174.0 (3)	N(11)-P(11)-N(10)-P(10)	-167.3 (3)
N(10)-P(11)-N(11)-P(12)	-34.2 (4)	N(10)-P(11)-N(11)-P(1)	-51.9 (3)
N(12)-P(12)-N(11)-P(11)	-64.0 (4)	(NPMe ₂) ₁₂	
N(11)-P(12)-N(12)-P(13)	-41.8 (6)	N(6')-P(1)-N(1)-P(2)	-37.1 (2)
N(13)-P(13)-N(12)-P(12)	121.3 (5)	N(1)-P(1)-N(6')-P(6')	-179.4 (1)
N(12)-P(13)-N(13)-P(14)	24.7 (5)	N(2)-P(2)-N(1)-P(1)	100.9 (2)
N(14)-P(14)-N(13)-P(13)	160.3 (3)	N(1)-P(2)-N(2)-P(3)	27.8 (2)
N(13)-P(14)-N(14)-P(15)	48.7 (4)	N(3)-P(3)-N(2)-P(2)	164.89 (13)
N(15)-P(15)-N(14)-P(14)	49.3 (4)	N(2)-P(3)-N(3)-P(4)	54.8 (2)
N(14)-P(15)-N(15)-P(16)	-159.4 (11)	N(4)-P(4)-N(3)-P(3)	50.0 (2)
N(16)-P(16)-N(15)-P(15)	-143.3 (12)	N(3)-P(4)-N(4)-P(5)	-175.6 (2)
N(15)-P(16)-N(16)-P(17)	-35.8 (5)	N(5)-P(5)-N(4)-P(4)	54.6 (2)
N(17)-P(17)-N(16)-P(16)	-64.8 (4)	N(4)-P(5)-N(5)-P(6)	75.7 (2)
N(16)-P(17)-N(17)-P(18)	-74.3 (5)	N(6)-P(6)-N(5)-P(5)	80.5 (2)
N(18)-P(18)-N(17)-P(17)	165.8 (4)	N(5)-P(6)-N(6)-P(1)	61.6 (2)
N(17)-P(18)-N(18)-P(10)	37.2 (5)	(NPMe ₂) ₁₀	
N(1')-P(1)-N(1)-P(2)	107.0 (4)	N(1')-P(1)-N(1)-P(2)	107.0 (4)
N(2)-P(2)-N(1)-P(1)	56.6 (5)	N(2)-P(2)-N(1)-P(1)	56.6 (5)
N(1)-P(2)-N(2)-P(3)	73.1 (5)	N(1)-P(2)-N(2)-P(3)	73.1 (5)
N(3)-P(3)-N(2)-P(2)	157.5 (4)	N(3)-P(3)-N(2)-P(2)	157.5 (4)
N(2)-P(3)-N(3)-P(3)''	52.25 (15)	N(2)-P(3)-N(3)-P(3)''	52.25 (15)

also for the dimethylphosphazenes (Figure 4) and probably depends on common features of the bonding in and between molecules and on the steric simplicity of the exocyclic groups. The inference that the detailed molecular structures might also correspond is supported by the redetermination³⁶ of the structure of (OSiMe₂)₈ and its comparison^{19c} with (NPMe₂)₈; the present study of the conformations of the dimethylphosphazenes provides a basis for understanding the structures of both series.

The methods of molecular mechanics have been useful in interpreting and predicting the structures of cycloalkanes and other organic compounds, but their application to phosphazenes has not been notably successful; in the structure calculated to be of lowest energy,³⁷ the four nitrogen atoms of (NPCl₂)₄ are coplanar, a conformation that has never been found for tetrameric phosphazenes and that, with experimental bond angles, would bring the centers of two chlorine atoms on each side of the molecule within 2.6 Å of each other. Our own calculations³⁸ show that such a conformation is stable only if the bond angles are much larger. Calculations that include only Coulomb and nonbonded interactions (Lennard-Jones and Devonshire 6-12 potential) within a phosphazene fragment have been used to discuss the local conformations of the four angular groups meeting at phosphorus in the cyclic methoxyphosphazenes,³⁹ with results that agree with

Table XII. Intermolecular Me...Me Contacts <4 Å for (NPMe₂)₉₋₁₂

(NPMe ₂) ₉			
C(5)...C(26) ^a	3.943 (9)	C(13)...C(32) ^a	3.937 (10)
C(6)...C(34) ^b	3.792 (8)	C(14)...C(29) ^d	3.876 (8)
C(7)...C(24) ^c	3.805 (8)	C(18)...C(25) ^d	3.893 (7)
C(9)...C(26) ^a	3.863 (8)		
(NPMe ₂) ₁₀			
C(1)...C(4) ^e	3.755 (7)	C(3)...C(4) ^f	3.924 (8)
(NPMe ₂) ₁₁			
C(2)...C(3) ^g	3.577 (6)	C(10)...C(16) ⁱ	3.999 (7)
C(2)...C(21) ^h	3.970 (7)	C(11)...C(14) ⁱ	3.744 (6)
C(4)...C(20) ⁱ	3.898 (7)	C(11)...C(12) ^m	3.977 (6)
C(6)...C(6) ^j	3.658 (8)	C(13)...C(15) ⁿ	3.824 (6)
C(6)...C(21) ^k	3.806 (6)	C(15)...C(17) ⁿ	3.797 (7)
C(9)...C(22) ^k	3.741 (6)	C(20)...C(22) ^g	3.828 (6)
(NPMe ₂) ₁₂			
C(1)...C(11) ^o	3.885 (4)	C(3)...C(6) ⁱ	3.669 (4)
C(2)...C(5) ^p	3.930 (5)	C(4)...C(4) ⁱ	3.597 (5)
C(2)...C(9) ^o	3.966 (4)	C(5)...C(9) ^j	3.801 (4)

^{a-p}Symmetry operations: ^a*x*,*y*,*z* - 1, ^b1-*x*,1+*y*,*z*-1, ^c*x*,*y*,*z*. ^d1+*x*,1+*y*,*z*-1, ^e*x*,*y*-1,*z*, ^f1/2-*x*,*y*-1/2,*z*, ^g1+*x*,*y*,*z*, ^h1-*x*,*y*,*z*, ⁱ1-*x*,1-*y*,*z*, ^j1-*x*,1-*y*,*z*, ^k*x*,1+*y*,*z*, ^l-*x*,1-*y*,1-*z*, ^m1-*x*,1-*y*,1-*z*, ⁿ1-*x*,*y*,1-*z*, ^o*x*,*y*-1,*z*, ^p-*x*,*y*,*z*.

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more detailed calculations⁴⁰ and with the determined structures^{40,41} of related molecules, and to relate conformation and configuration in oxophosphazenes;⁴² they also reproduce the skeletal confor-

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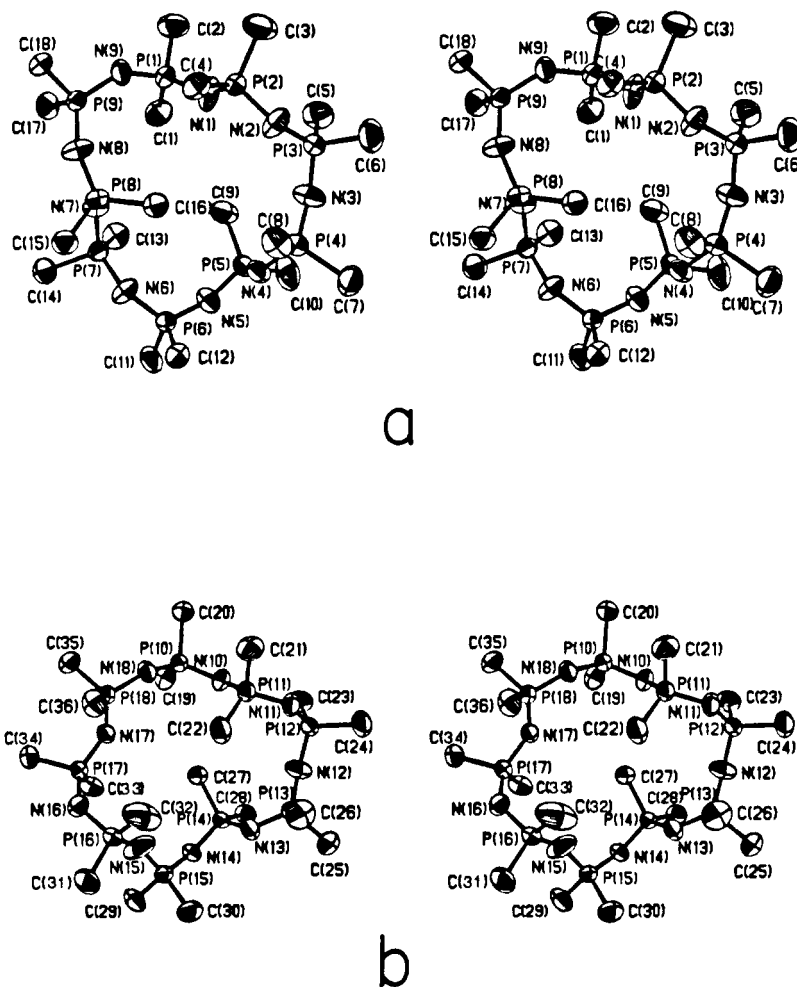


Figure 2. Stereoscopic views of $(\text{NPMe}_2)_9$: (a) molecule 1, (b) molecule 2.

mations found in the phosphazene high polymers and their flexibility.⁴³

The local conformations of the dimethylphosphazenes can be understood qualitatively in terms of interactions within an $\text{Me}_2\text{P}(\text{NP})_2$ unit (Figure 5). The interactions of an outer P atom with the central PMe_2N group have approximate 3-fold symmetry, staggered conformations (G and T) being preferred, as in cycloalkanes. The torsion angles about a pair of P–N bonds meeting at phosphorus are then correlated through interactions of the outer P atoms. Conformations **5d–f** are of high energy, **5d,e** because the P–N bonds are eclipsed and **5f** because of repulsive P···P interactions. Calculations using a range of potential constants show that the energy of the GG conformation (**5a**), usually lower than that of GT (**5b**), is raised by polar interactions, which also brings the region of stability closer to CT (**5c**). Further detail on the conformation of two angular groups attached to phosphorus is given elsewhere.³⁹

The experimental results on $(\text{NPMe}_2)_{5-8}$ are fairly well reproduced by the potential diagram of Figure 5. In these molecules, the GG and GT conformations are almost equally numerous. The plot is conceptually useful but numerically limited, because of the drastic averaging of the effects of torsion about the outer P–N bond and because the bond angle at nitrogen is large and variable (122 – 156° , mean 135°). As the torsion angle approaches 180° , it loses its meaning and its conformational control. Consequently, although the two groups of conformations are distinct, the angular

correlation between τ_1, τ_2 is weak, the mean values for $(\text{NPMe}_2)_{5-8}$ (plotted in Figure 5) being $46 \pm 21^\circ$, $74 \pm 5^\circ$ (GG) and $30 \pm 20^\circ$, $191 \pm 29^\circ$ (GT). The distinction is weakest in the octamer, in which the angle at nitrogen is greatest and, as discussed below, disappears in the nonamer, which is large enough for transannular $\text{Me} \cdots \text{Me}$ interactions to be decisive.

One general feature of the conformations of the whole molecules can be better seen from a different point of view. Figures 2 and 3 show that the molecules are compact, the ring atoms being folded in toward the center, so that the covering methyl groups are separated by normal van der Waals distances. The extent of the folding can be characterized as shown in Figure 6 for a phosphorus atom. The angle of fold is taken to be the angle between the normals to the planes CNN' , $\text{NN}'\text{P}$, C being the molecular centroid, and analogously for the nitrogen atoms. The mean absolute values for each ring size are shown in Figure 7. The mean angles of fold of both nitrogen and phosphorus increase (irregularly) with ring size. The general variation is a result of the increasing number of transannular interactions in the larger molecules, which are thereby made more compact.

In the limit of P–N–P linearity, the nitrogen atoms would have no effect on conformation. If they are ignored, as a simplifying assumption, the conformation depends on two parameters, the P–P distance and the distance from a phosphorus center to the periphery of the methyl group. If a conventional van der Waals radius is used for the methyl group, $(\text{P}-\text{CH}_3)/(\text{P}-\text{P})$ is 1.31, compared with $(\text{C}-\text{H})/(\text{C}-\text{C}) = 1.49$ in hydrocarbons. If these numbers were the same, similar conformations would be expected in the two series, and, as will be seen below, they are close enough to support a direct relationship between the cycloalkane and the dimethylphosphazene structures. Differences arise because the ratio of distances is somewhat smaller in the phosphazenes, so that those interactions that are repulsive in hydrocarbons are normally

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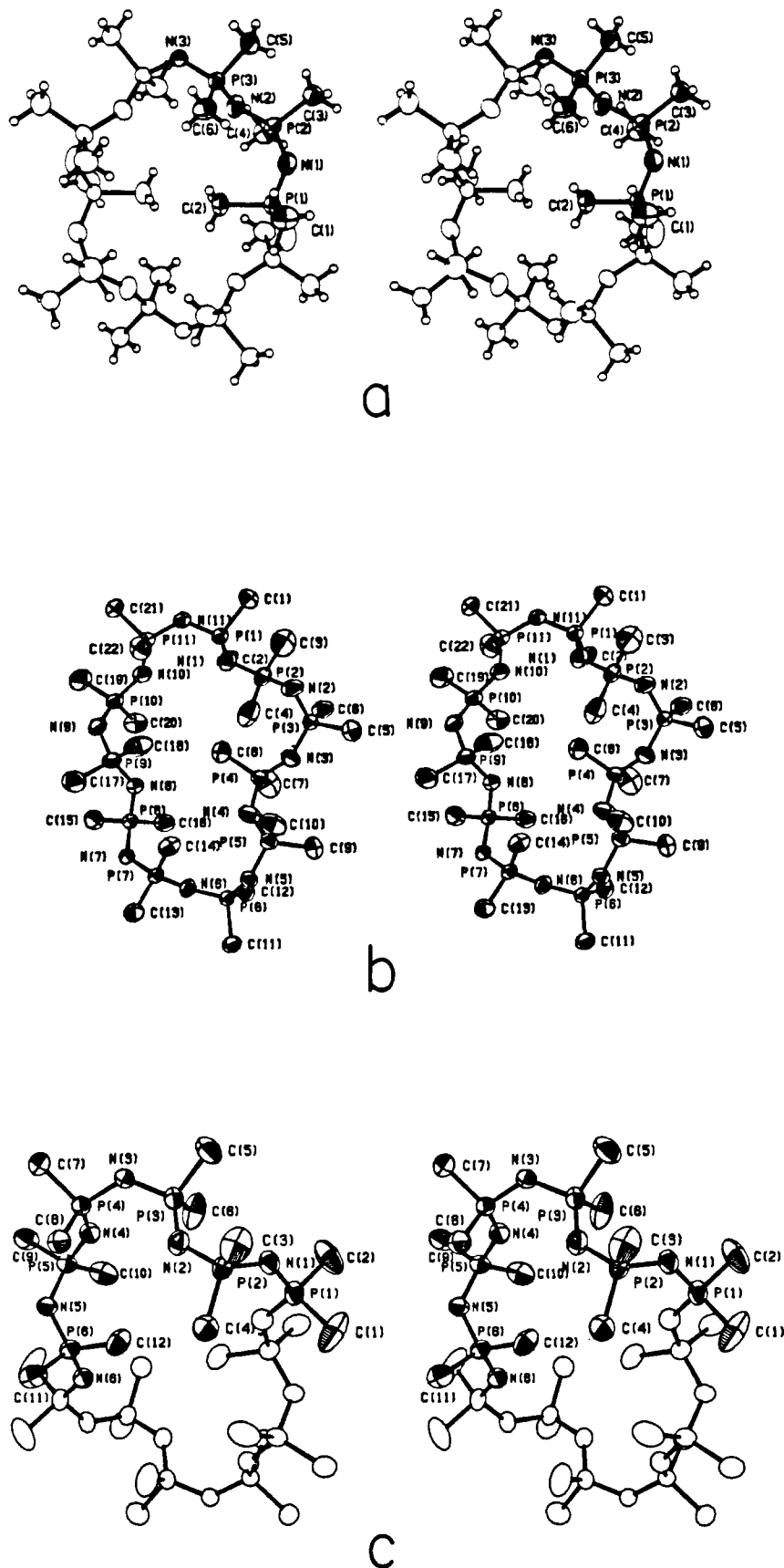


Figure 3. Stereoscopic views of (a) $(\text{NPMe}_2)_{10}$, (b) $(\text{NPMe}_2)_{11}$, and (c) $(\text{NPMe}_2)_{12}$.

attractive in dimethylphosphazenes of the same conformation; as ring size increases, the possible conformations become more diverse, and systematic structural differences between the two series appear. We can, then, recognize two interconnected factors which control conformation: (1) The attainment of low-energy

local conformations at P (Figure 5a-c) and (2) attractive intramolecular interactions between methyl groups on different phosphorus atoms. As discussed below for the individual molecules, the second factor increases in importance with increase in ring size.

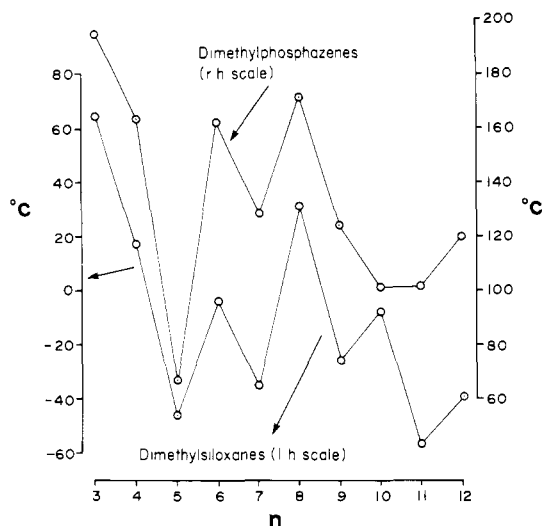


Figure 4. Melting points of cyclic dimethylphosphazenes and dimethylsiloxanes. The melting point of $(\text{NPMe}_2)_{10}$ is lowered by a fluorine-containing impurity.

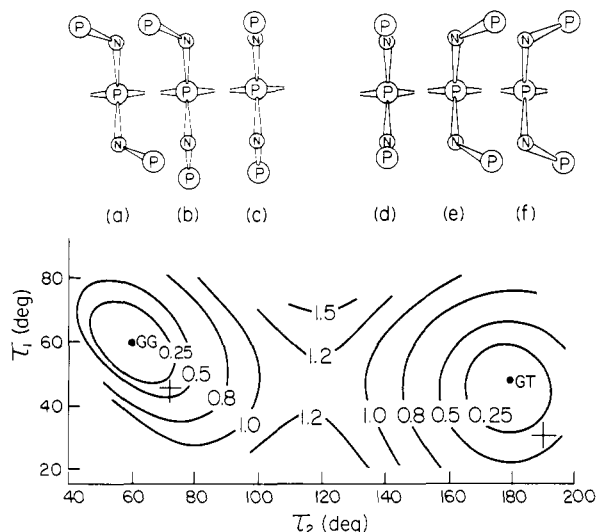


Figure 5. Local conformations (a-f) and potential energy (kcal/mol) of $\text{Me}_2\text{P}(\text{NP})_2$ fragment, using the parameters of ref 39 and average bond lengths and angles. τ_1 and τ_2 are measured from the cis-coplanar conformation d. The crosses are experimental points; see text.

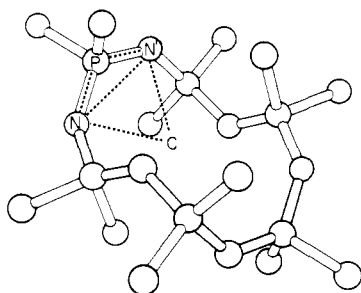


Figure 6. Definition of fold angle [in $(\text{NPMe}_2)_6$] (see text).

In terms of the P-P framework, the structure of $(\text{NPMe}_2)_{10}$ is chair-shaped (Figure 6), like cyclohexane, but only the center of symmetry of D_{3d} is retained. The structure is skewed to accommodate the angles at nitrogen, so that the axial P-C bonds are not parallel, but the qualitative similarity of the structures seems significant. Although the detailed structure of cycloheptane is unknown, calculations,⁴⁴ vibrational spectra,⁴⁵ and the NMR

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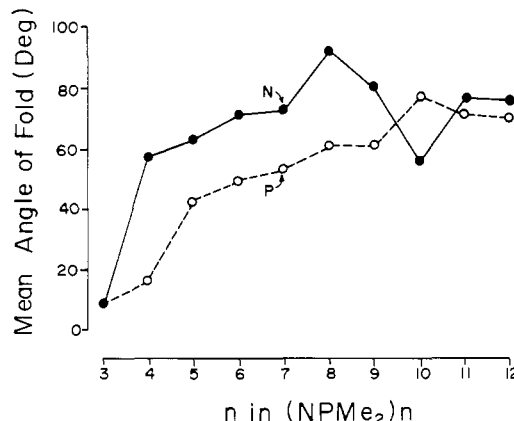


Figure 7. Mean fold angles of phosphorus and nitrogen atoms.

spectra of fluorocycloheptanes⁴⁶ show that the twist-chair (symmetry C_2) is the most stable, the energy of the chair form (C_s) being about 1.4 kcal/mol higher. The C_2 conformation is also found in a cycloheptanone peroxide⁴⁷ and the chair form in the hexamethyleneammonium ion.⁴⁸ $(\text{NPMe}_2)_7$ has C_2 symmetry and the twist-chair conformation,^{19d} the torsion angles about successive P-P vectors, starting at the unique phosphorus atom, being -42.5° , 62.7° , -97.3° , and 49.8° ; the corresponding angles calculated for cycloheptane^{44a} are -54.3° , 72.3° , -88.1° , and 39.1° .

The structure of $(\text{NPMe}_2)_8$ ^{19c} is also related to those of eight-membered rings. For cyclooctane itself, the form of lowest energy is calculated^{44a,49} to be the chair-boat, though the energies of the crown and double-tub forms are not much higher. Experimentally, several conformations occur in the vapor⁵⁰ and, in solution, the chair-boat is accompanied by some of the crown form.⁵¹ Among heterocyclic compounds, 1,3,5,7-tetrathiocane $(\text{CH}_2\text{S})_4$ adopts the chair-boat conformation⁵² although the analogous 1,3,5,7-tetraoxocane has the crown conformation.⁵³ Clearly these two conformations are energetically close together, and calculations show that the crown is favored as repulsive interactions diminish. In $(\text{NPMe}_2)_8$, the crown conformation found for the phosphorus atoms appears to be stabilized by the attractive $\text{CH}_3 \cdots \text{CH}_3$ interactions (3.8, 4.0 Å) and by the occurrence of the stable GG and GT local conformations of successive PN_2P_2 segments.

The correspondence between the structures of phosphazenes and hydrocarbons is weaker in $(\text{NPMe}_2)_9$, but the principle on which it is based, that of the secondary importance of the steric interactions of the nitrogen atoms, is not lost. The crystallographic asymmetric unit of $(\text{NPMe}_2)_9$ consists of two independent molecules with different conformations, shown in Figure 8. The two conformations are similar over the 10-atom ranges $\text{P}(2)\text{N}(2)\text{P}(3) \cdots \text{P}(6)\text{N}(6)$ and $\text{P}(11)\text{N}(11)\text{P}(12) \cdots \text{P}(15)\text{N}(15)$. The conformation of molecule 2 (Figure 8b) is obtained from that of molecule 1 by making the three displacements shown in Figure 8a: outward and inward rotations, respectively, of the PMe_2 groups at P(7) and P(8) and a smaller inward rotation at P(2). The movement is made possible by the easy deformability of the angles at nitrogen [PNP increases from 142.5° at N(6) to 155.7° at N(15)], and a different network of $\text{Me} \cdots \text{Me}$ interactions results. In molecule 1, the shortest such distance is 3.62 Å [C(1)C(17)],

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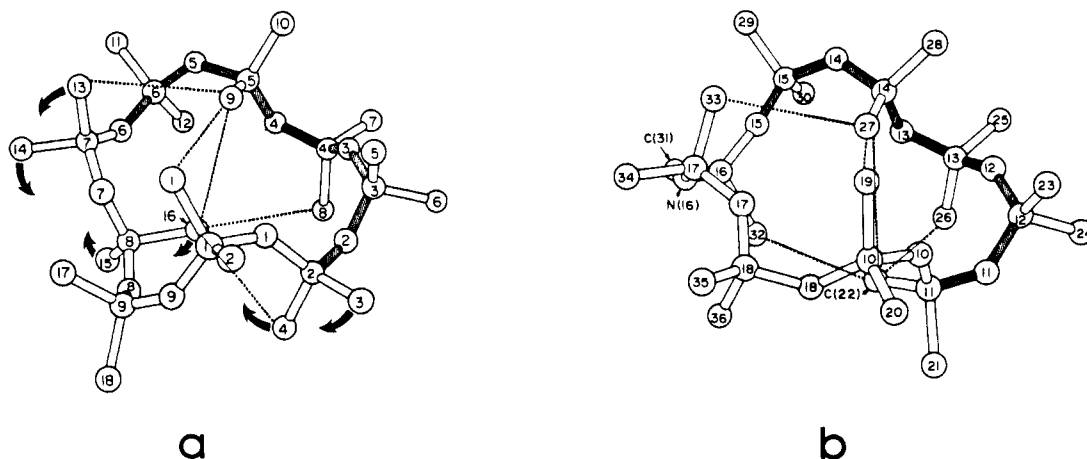


Figure 8. (NPM₂)₉: (a) molecule 1, (b) molecule 2. The common conformational fragment is shaded. Dotted lines join methyl groups separated by intraannular distances of 4.0 Å or less. The arrows show the movements required to convert molecule 1 to molecule 2.

Table XIII. Torsion Angles (deg) about P–P Vectors in (NPM₂)₉^{a,b}

vector	P(1)P(2)	P(2)P(3)	P(3)P(4)	P(4)P(5)	P(5)P(6)	P(6)P(7)	P(7)P(8)	P(8)P(9)	P(9)P(1)
molecule 1	125	-79	79	-133	101	-67	148	-79	-68
vector	P(10)P(11)	P(11)P(12)	P(12)P(13)	P(13)P(14)	P(14)P(15)	P(15)P(16)	P(16)P(17)	P(17)P(18)	P(18)P(10)
molecule 2	115	-88	89	-130	100	-69	143	-80	-65

^a Mean difference between corresponding torsion angles 5°. ^b The torsion angles about the N–N vectors are less regular; the mean difference between corresponding angles is 24°.

with 10 contacts at 4.00 Å or less, and there are eight more in the range 4.01–4.50 Å. In molecule 2, the shortest Me...Me distance is 3.56 Å [C(34)C(35)], and there are again 18 contacts less than 4.50 Å, eight at 4.00 Å or less. The transannular contacts (five for each conformer) are shown in Figure 8. Remarkably, the different dispositions of the nitrogen atoms and methyl groups leave the basic conformation of the phosphorus atoms qualitatively unchanged; Table XIII shows that the sequence of signs of the torsion angles about successive P–P vectors is the same for each.

The comparison with hydrocarbon structures is less simple than for the earlier members of the series. Some stereochemical complication is to be expected at cyclononane, because its thermochemical strain energy, which reflects both the deviations from ideal local conformations and the transannular repulsions between hydrogen atoms, is (with that of cyclodecane) the largest of the cycloalkane series.⁵⁴ Calculations have shown that there are at least four low-energy forms within an energy range of at most 3.9 kcal/mol, here denoted by A (twist-boat-chair, *D*₃),^{44a,49b,55} B (unsymmetrical twist-chair-boat, ideally *C*₂),^{44a,49b,c,55} C (unsymmetrical, labeled [234]⁵⁵), D (unsymmetrical, labeled cyclononane II^{49b}). The four conformations differ in the relative signs of their torsion angles, and the relative energies of A and B are critically dependent on the assumed van der Waals radius of the hydrogen atom.^{49c} Although the structure of cyclononane itself has not been determined by diffraction methods, conformation A is found crystallographically⁵⁶ for trimeric acetone peroxide and by NMR for cyclononane and its methyl derivatives⁵⁷ and B crystallographically in cyclononylamine hydrobromide⁵⁸ and in octamethyleneammonium tosylate⁴⁸ (greater departure from *C*₂ symmetry). Forms C and D have energies intermediate between those of A and B, and C has been found spectroscopically in 1,4,7-trioxacyclononane.⁵⁹ Form D is found, uniquely so far, in the phosphorus skeleton of (NPM₂)₉, which therefore corresponds to one of the lower energy forms available to cyclononane. Conformations B and D are in fact closely related, being inter-

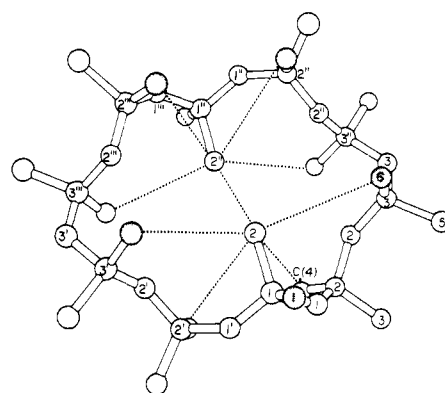


Figure 9. (NPM₂)₁₀: Short intraannular Me...Me distances dotted. The axial methyl groups exhibit approximate pentagonal symmetry; one of two sets is shaded.

converted by changing the signs of two adjacent torsion angles, about P(2)–P(3), P(3)–P(4) and P(11)–P(12), P(12)–P(13), respectively. Form D allows the attractive transannular interactions C(9)–C(16) and C(22)–C(27).

In contrast to the nonamer, (NPM₂)₁₀ has a remarkably regular structure (Figure 9), which is different from, but directly related to, that of cyclodecane. The conformation of the hydrocarbon⁶⁰ is of the "diamondoid" type⁶¹ and persists in a sufficient number of its derivatives to show that the skeletal conformation is intrinsically stable; it is shown in Figure 10a. It is slightly distorted to accommodate the close approach (1.93 Å) of three hydrogen atoms on each side of the molecule. In the crystal, (NPM₂)₁₀ has the same symmetry as cyclodecane (*C*_{2h}), but, because the dominant interactions are now attractive, the conformation is different. It is related to that of (NPM₂)₈^{19c} in that the methyl groups are sharply divided into equal axial and equatorial sets. In the octamer, all the equatorial methyl groups are directed outward; in the decamer, two [C(2), C(2'')] are directed inward, thereby increasing the number of Me...Me contacts. The relationship to the cyclodecane structure is shown in Figure 10; as the PMe₂ groups are turned inward (*C*_{2h} symmetry

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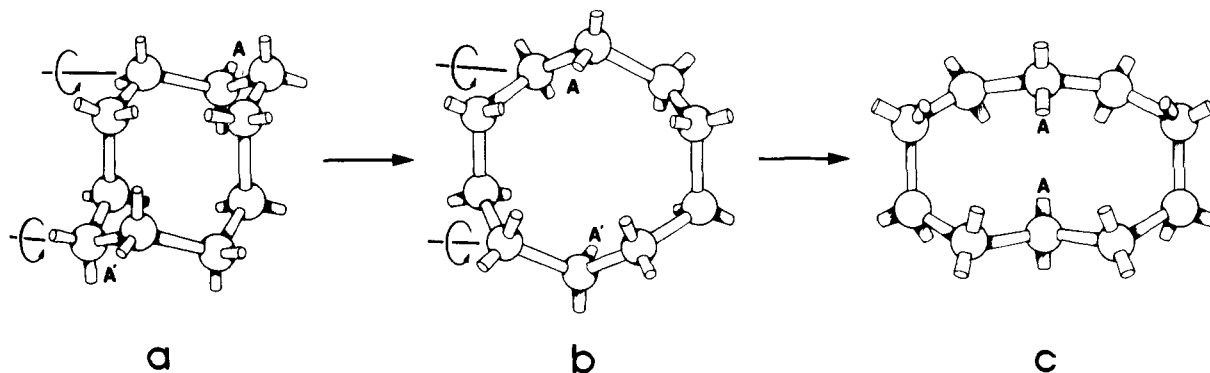


Figure 10. The deformation of the skeletal structure of cyclodecane into that of $(\text{NPMe}_2)_{10}$ with a short central transannular distance, through an intermediate of symmetry D_{5d} .

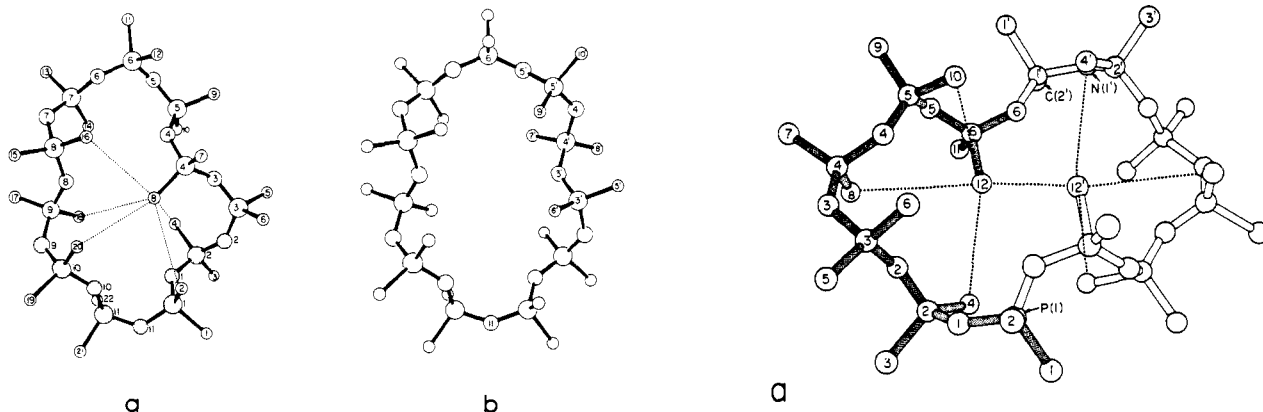


Figure 11. (a) $(\text{NPMe}_2)_{11}$, showing transannular $\text{Me}\cdots\text{Me}$ contacts and (shaded) the nine-atom skeletal fragment referred to in the text. (b) The hypothetical structure with 2-fold symmetry (see text).

being preserved), the structure goes through a stage exhibiting full 5-fold symmetry (Figure 10b), and then, as the deformation is continued (Figure 10c), the exocyclic groups are folded in toward the center, creating a particularly short transannular contact [3.26 Å in $(\text{NPMe}_2)_{10}$]. There are nine internal short contacts (mean 3.84 Å), as shown in Figure 9. To these can be added the contacts within the two sets of five axial methyl groups, mean 4.30 Å (Figure 9). Each set exhibits close to pentagonal symmetry; the whole molecule is the most compact of the series.

The structure of $(\text{CH}_2)_{11}$ is unknown. The undecamer $(\text{NPMe}_2)_{11}$ has an unsymmetrical structure, which is nevertheless related to the other phosphazene structures. The nine skeletal atoms $\text{N}(9)\text{P}(10)\text{N}(10)\text{P}(11)\text{N}(11)\text{P}(1)\text{N}(1)\text{P}(2)\text{N}(2)$ (Figure 11a) are related by an approximate 2-fold axis, and this arrangement of atoms is found also in $(\text{NPMe}_2)_{17}^{19d}$ and $(\text{NPMe}_2)_{10}$, in both of which the 2-fold axis is exact, and also, as discussed below, in $(\text{NPMe}_2)_{12}$, in which it is approximate. This structural motif owes its stability to the pair of consecutive GT local conformations at $\text{P}(1), \text{P}(11)$ [in $(\text{NPMe}_2)_{11}$]. If the whole molecule had a 2-fold axis through $\text{N}(11)\text{P}(6)$, it would have the plausible structure of Figure 11b, in which all the local conformations are of low energy. The real structure can be regarded as formed from it by folding in the segment $\text{P}(3')$ to $\text{P}(5')$, so that $\text{C}(8)$ forms close contacts with $\text{C}(2)$, $\text{C}(4)$, $\text{C}(16)$, $\text{C}(18)$, and $\text{C}(20)$ (mean 3.98 Å). Of a total of 25 intramolecular contacts less than 4.5 Å, 10 are less than 4.0 Å.

The structure of the dodecamer $(\text{NPMe}_2)_{12}$ has some connections with that of cyclododecane,⁶² in that the local conformations of five of the phosphorus atoms and of all of the carbon atoms are of low energy, being either of the GG or GT types [$\text{P}(2)$ has a conformation of higher energy]. The global conformations are also related. In the nomenclature of Dale,⁵⁵ both cyclo-

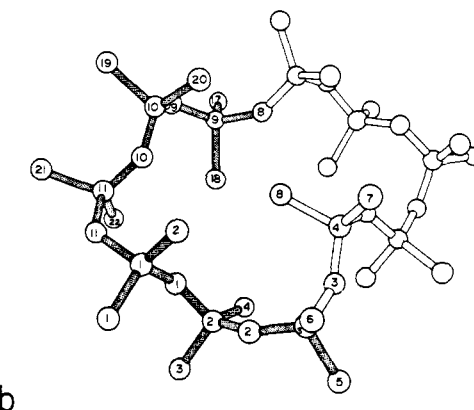


Figure 12. (a) $(\text{NPMe}_2)_{12}$, showing transannular $\text{Me}\cdots\text{Me}$ contacts and (shaded) the structural fragment found also (b) in $(\text{NPMe}_2)_{11}$. The fragment $\text{P}(4)\cdots\text{P}(5)\cdots\text{N}(6)$ in (a) is a candidate repeating unit for a high polymer structure.

dodecane and $(\text{NPMe}_2)_{12}$ (phosphorus atoms only) have [4444] conformations, square and rhomboidal, respectively, and for half of each molecule the patterns of signs of displacements are the same. The two halves are related by a 2-fold axis in the hydrocarbon and a center of symmetry in the phosphazene. The structure found for $(\text{NPMe}_2)_{12}$ allows a close approach of $\text{C}(12), \text{C}(12')$ (3.86 Å), and the set of seven close $\text{Me}\cdots\text{Me}$ contacts is shown in Figure 12a (mean 3.86 Å); altogether, there are 27 intramolecular contacts less than 4.5 Å, 15 less than 4.0 Å. The short transannular distance $\text{C}(12)\cdots\text{C}(12')$ brings out the close similarity to the structure of the decamer; the structure of the dodecamer is obtained from that of the decamer by inserting the $\text{C}(1')\text{C}(2')\text{P}(1')\text{N}(1')$ and $\text{C}(1)\text{C}(2)\text{P}(1)\text{N}(1)$ units of $(\text{NPMe}_2)_{12}$, with GT local conformations, between $\text{N}(1'')\text{P}(2'')$ and $\text{N}(1')\text{P}(2')$ of $(\text{NPMe}_2)_{10}$. The conformations are otherwise identical. There is an equally close relationship with the structure of $(\text{NPMe}_2)_{11}$ (as can be seen from a comparison of Figures 12a,b); the structure

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Table XIV. Mean Geometries of the Cyclic Dimethylphosphazenes (NPMe₂)_n^a

	<i>n</i>										
	3	4	5 ^c	6 ^d	7	8	9 ^d	10	11	12	mean
P-N, Å	1.606 (4)	1.596 (5)	1.596 (4)	1.593 (5)	1.592 (4)	1.590 (10)	1.593 (6)	1.592 (6)	1.596 (5)	1.596 (5)	1.595 (3)
P-C, Å	1.810 (9)	1.805 (3)	1.816 (7)	1.808 (3)	1.804 (7)	1.811 (2)	1.808 (7)	1.802 (2)	1.811 (2)	1.809 (6)	1.808 (3)
NPN, deg	116.8 (7)	119.8 ^e	118.7 (13)	118.3 (15)	117.1 (14)	117.2 (21)	116.7 (22)	116.4 (22)	116.6 (21)	116.3 (22)	117.4 (9)
PNP, deg	122.6 (3)	132.0 ^e	132.9 (14)	133.1 (29)	132.9 (15)	139.9 (84)	136.1 (43)	138.2 (52)	134.8 (45)	132.8 (40)	133.5 (30)
CPC, deg	102.6 (4)	104.1 ^e	104.3 (6)	104.2 (5)	103.9 (4)	103.5 (9)	104.2 (8)	103.3 (8)	104.2 (9)	104.7 (3)	103.9 (5)
ref	19a	8	19b	19c	19d	19e	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	

^aNumbers in parentheses are mean deviations from the mean, in units of the last place, and are intended to show variability (rather than accuracy), within a particular molecule. ^bThis work. ^cBond lengths corrected by using parameters of ref 19b. ^dTwo molecules/asymmetric unit. The mean parameters of the two sets differ by less than 1σ. ^eAngles equal by symmetry.

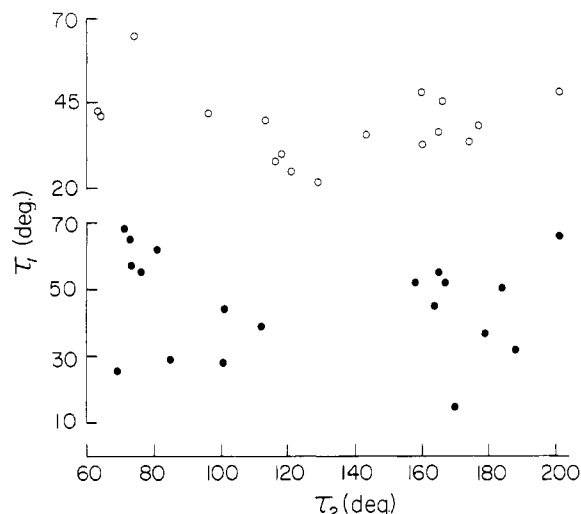


Figure 13. Correlation between torsion angles in (NPMe₂)₉ (upper) and (NPMe₂)₁₀₋₁₂ (lower). There are two additional points at 63°, 292° (nonamer) and 107°, 253° (decamer). For the lower diagram, the centroids of the two distributions are at 50 ± 15°, 82 ± 14° and 47 ± 2°, 172 ± 13°.

of (NPMe₂)₁₂ is formed by the centrosymmetric duplication of the 12-atom segment N(8)P(9)···N(11)···N(2)P(3) of (NPMe₂)₁₁.

Finally, we consider intermolecular interactions, which, in view of the flexibility of the molecules, might have a controlling effect on conformation. Since they would make the molecule more compact, they would reinforce, and hence be difficult to distinguish from, the attractive intermolecular interactions already demonstrated. The occurrence in the crystal of two independent molecules (NPMe₂)₆ with identical conformations, and of two closely related conformers of (NPMe₂)₉, suggests that the intermolecular forces may be of secondary importance, perhaps altering the relative energies of the most stable conformations and stabilizing those with the larger number of transannular interactions.

These first become significant at (NPMe₂)₉, and the upper part of Figure 13 shows that they are strong enough to destroy the division of the local conformations into GG and GT sets. However, as the ring size increases, the distinction reappears (Figure 13, lower), (NPMe₂)₁₀₋₁₂ being evidently large enough to meet the requirements of both local and transannular stability.

Mean bond lengths and bond angles are given in Table XIV. The P-N and P-C bond lengths and the CPC bond angles are remarkably constant. The NPN angles are more variable and the PNP angles especially so, increasing sharply at (NPMe₂)₈ and decreasing irregularly thereafter. The variability can be traced to the nature of the P-N bond. The nitrogen atom contributes to the π-bonding both directly, as in pyridine, and indirectly, through partial delocalization of its formally unshared pair, which thereby loses much of its stereochemical control; it contributes less to the torsional barrier about the P-N bonds and allows the PNP angle to increase. As it does so, improved overlap strengthens the partial triple bond formed by the two mutually perpendicular π-components. Lone-pair delocalization and π-bonding therefore cooperate in increasing the angle at nitrogen, its magnitude being limited by the energy requirements of the changes in σ-hybrid-

ization. The expectation that not only will the angles be large but also that the largest angles will be the most easily deformed is confirmed by the numerical information of Table XIV. Since the angles are "soft", their magnitudes are affected also by the nonbonded interactions, which are specific to a particular molecule, and the mean PNP angle consequently varies irregularly with ring size.

The angles at phosphorus vary less, but more systematically. The mean CPC angle is nearly constant; except in (NPMe₂)₃, all the mean values are within 0.7° of 104.0°. The NPN angles vary less than the angles at nitrogen; after the trimer, they decrease steadily from 119.8° in (NPMe₂)₄ to 116.3° in (NPMe₂)₁₂. The cycloalkanes behave differently. Their calculated steric energies are minimized at CCC angles which, like the thermochemical strain energies,^{2,54} go through a maximum at C₆H₁₈ or C₁₀H₂₀. Where comparison is possible, there is good agreement with the (parenthesized) measured mean angles (in deg): C₆H₁₂, 111.6^{44a} (111.6);⁶³ C₁₀H₂₀; 117.2^{44a} (116.7);⁶⁰ C₁₂H₂₄, 112.6^{49a} (112.0).^{62a} This variation is part of the medium-ring effect. For medium-ring dimethylphosphazenes, typically (NPMe₂)₁₀, the deviations from ideal NPN angles arising from steric interactions alone are expected to be negative rather than positive, but they are affected also by d-orbital interactions, whose angular effect is difficult to assess. Hartsuiker and Wagner^{15c} have recognized that the symmetric interactions of dπ-orbitals at phosphorus, which are indicated by the ionization energies,⁶⁴ would tend to reduce the NPN angle toward 90°, and they have discussed the structures of (NPX₂)₃₋₅ (X = F, Cl, Br) in these terms. The absence of exocyclic π-bonding in the longer dimethylphosphazene series makes it easier to estimate the effects of the d-orbital interactions.

If the σ-orbitals at phosphorus are formed from two equivalent pairs of s/p hybrids (molecular site symmetry C_{2v}) the NPN σ-angle can be calculated from the exo angle. For all except the cyclically constrained trimer and the especially compact decamer, the actual mean value slightly exceeds this ideal angle, the excess being [from (NPMe₂)₃ onward, deg] -1.4, 3.9, 3.1, 2.5, 0.9, 0.4, 0.9, -0.7, 0.8, and 0.8. We draw attention to three features: (1) π-Electron effects cause rather small deviations from expected σ-angles. (2) The limiting value of the excess is small but positive and presumably corresponds to the mutual repulsion of bonding π-electrons. (3) The excess is larger for the smaller, less folded, molecules (n = 4-6), in which it is likely to reflect inequalities in pπ-dπ overlap, but is even then smaller than the (maximum) steric deviation in hydrocarbons. In the larger molecules, these inequalities would be reduced or eliminated by the more even distribution of torsion angles.

The lengths of the P-C bonds are all within 0.008 Å of 1.808 Å; little variation is to be expected. In view of the greater complexity of the P-N bonds, the similar constancy of their lengths requires some comment. To some extent, the effects of NPN and PNP angles on the σ-bonds compensate one another, the resultant length being dependent principally on the electronegativity of the substituents. Correction for σ-hybridization⁶⁵ shows that the bond

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Table XV. Infrared Spectra and NMR Parameters of (NPM₂)_n

	n									
	3	4	5	6	7	8	9	10	11	12
$\nu_{\text{as}}(\text{PNP})^a$, cm^{-1}	1185 ^b (1185) ^b	1222, 1240 ^b (1222)	1255 ^b (1255)	1215, 1257 (1252)	1207, 1255 (1238)	1214, 1269 (1225, 1245)	1214, 1240 (1220, 1245)	1209, 1239 (1216, 1247)	1197, 1227, 1250 (1209, 1250)	1185, 1228, 1250 (1209, 1249)
$\delta_{\text{as}}(\text{CH}_3)^c$, cm^{-1}	1424, 1413 ^b	1426, 1415 ^b	1428, 1415 ^b	1428	1424	1418	1423	1421	1421	1421
$\delta_s(\text{CH}_3)^c$, cm^{-1}	1290 ^b	1290 ^b	1290 ^b	1287	1288	1288	1290	1287	1288	1286
δ_{H} , ppm ^d	1.46	1.51	1.50	1.50	1.52	1.53	1.54	1.54	1.52	1.52
J_{PH} , Hz	13.0	11.5	12.0	12.3	12.5	13.0	13.0	13.2	13.5	13.5
δ_{P} , ppm ^{e,f}	21.8	12.2	5.8	3.2	2.8	2.1	2.6	2.9	2.6 ^g	2.5 ^g
δ_{C} , ppm ^h	23.5	22.3	22.1	22.6	22.6	22.6	22.6	22.7	22.6 ⁱ	22.6 ⁱ
J_{PC} , Hz	94.2	98.4	98.0	94.3	96.0	90.3	90.0	90.1	89.3	89.7

^a In Nujol; parenthesized values from dilute solutions in CCl₄. ^b References 30a, 33. ^c Dilute solutions in CCl₄. ^d In CDCl₃, internal reference Me₄Si. ^e In C₆D₆, external reference H₃PO₄. ^f Cf. (NPF₂)_n, n = 3, -9.2; 4, -17.2; 5, -22.1; 6, -22.0; 7, -22.7; 8, -23.1; 9, -23.2. ^g In CDCl₃. ^h In CDCl₃, internal reference Me₄Si. ⁱ Simple doublet structure retained at -90 °C.

contraction attributable to π -bonding is approximately 0.09 Å for the dimethylphosphazene series, compared with 0.16 Å in (NPF₂)₄, reinforcing the previous conclusion that π -bonding is determined to a major extent by the contraction of d-orbitals by electronegative ligands and to a minor extent by ring size.⁶⁵

Infrared and NMR Spectra. The infrared spectra (Table XV) of all the dimethylphosphazenes show $\nu_{\text{s}}(\text{C-H})$ and $\nu_{\text{as}}(\text{C-H})$ near 2923 and 2995 cm⁻¹, respectively. The splitting of the symmetric deformation frequency of the methyl group near 1300 cm⁻¹ into in-phase and out-of-phase components is small but increases slightly with ring size; coupling effects can also be seen in $\delta_{\text{as}}(\text{CH}_3)$ in (NPM₂)₃₋₅, the band becoming broad without change in mean frequency as the ring size increases further. The methyl groups in a particular molecule are equivalent on the ¹H and ¹³C NMR time scales, and the variations of the ¹³C shift between molecules are very small, 0.4 ppm over the range (NPM₂)₄₋₁₂, the mean deviation from 22.6 being 0.05 ppm. By contrast, the range of the ¹⁹F shifts of (NPF₂)₄₋₉ is significantly greater (3.9 ppm), the detailed oscillatory variations being attributed to π -conjugative interactions between the substituents and the ring,⁶⁶ which are evidently absent from the dimethylphosphazenes. The ¹³C shift in substituted methanes is dependent on the electronegativity of the substituent; the effect of the (NP)_n ring on attached methyl groups is similar to that of a chlorine atom (MeCl, δ_{C} = 25.1 ppm).⁶⁷

While the methyl groups are effectively electronically isolated, the ring atoms are strongly coupled. In general, the geometry and the electronic characteristics of the substituents attached to 4-coordinated phosphorus are interrelated, and the ³¹P chemical shift depends on both. Electronegative substituents contract the orbitals, increase shielding,⁶⁸ and provide the conditions for effective π -bonding.⁶⁵ Substituents that release electrons to phosphorus either inductively or (like NMe₂) by conjugation expand its orbitals and reduce both its shielding and the strengths of its bonds. In the dimethylphosphazenes, all the phosphorus atoms in a particular molecule are magnetically equivalent on the NMR time scale. For all phosphazene series (NPX₂)_n the increased shielding with increase of ring size up to an approximate limit (X = F, -23.2 (Table XV); Cl, -18.0;⁶⁹ NMe₂, -10.0;⁷⁰ Me, +2.5) is probably a geometrical effect of the changing bond angles. The limit itself illustrates the electronic effects referred to above

and suggests that π -effects will be weaker in the dimethylphosphazenes than in the other series. The progression to the limit is not quite regular, however, there being a small but significant downfield shift (0.4 ppm) at (NPM₂)₁₀, which presumably corresponds to its unique conformational properties. There is also a conformational effect in the cycloalkanes.⁷¹ Over the range C₇H₁₄ to C₁₁H₂₂, the ¹H shieldings seem low. All the ¹³C shifts (up to C₁₇H₃₄) are to high field of those of the central atoms in linear alkanes, the deviation going through a maximum at C₁₂H₂₄ (6 ppm). There may be a conformational effect on skeletal shielding in the dimethylphosphazenes, but it is much smaller than in the cycloalkanes.

The skeletal stretching frequency $\nu_{\text{as}}(\text{PNP})$ has been discussed elsewhere,⁶⁵ the slow decrease in frequency from (NPX₂)₅ resulting from a mass coupling rather than a decrease in bond strength.⁷² For a fixed ring size, $\nu_{\text{as}}(\text{PNP})$ and ³¹P shielding vary in the same way with the electronegativity of the substituent, the low value for (NPM₂)₈ relative to those of (NPCl₂)₈ (1305 cm⁻¹)⁶⁹ and (NPF₂)₈ (1386 cm⁻¹)^{16b} being consistent with the decreased bond strength in (NPM₂)₃⁷³ compared to (NPCl₂)₃.⁷⁴ The infrared spectra also give some evidence on molecular flexibility, in that the bands are sharp in Nujol [especially those of (NPM₂)₈] but are broadened, with loss of detail, in carbon tetrachloride, in which solvent conformational changes can take place more readily.

Conclusions

The simple formulation of the repeating unit of the dimethylphosphazenes as $-\text{N}=\text{PMe}_2-$ implies the localization of a pair of electrons on nitrogen. In heterocyclic compounds generally, the smaller size of an NH group, as compared with CH₂, usually leads to no qualitative change in structure.⁷⁵ Although the concept is imprecise, the "size" (in a carefully limited sense⁷⁶) of the lone pair in NH₃ is greater than that of the bonding pairs, and we might expect its effect on structure to be comparable to those of an NH group. If this were true of the phosphazenes, we might expect a crown conformation (Figure 1d) [as in S₄(NH)₄⁷⁷ and other sulfur imides] for the cyclotetraphosphazenes, but it is found only for compounds (NPX₁X₂)₄, when X₁ and X₂ have such disparate steric requirements that possible lone pair effects become sterically irrelevant.

The steric effect of the lone pairs is reduced, virtually to extinction, by their partial delocalization into the d π -orbitals of phosphorus, widening the angle at both phosphorus and nitrogen

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and shortening the P-N bond.⁷⁸ Although the mutually perpendicular π -components are not required to be equal by (local) symmetry, any barrier arising from their inequality is too small to have a conformational effect. Also, since the interactions of the methyl groups are attractive,⁷⁹ their deformation energies are small, so that from both causes the dimethylphosphazenes are expected to be more flexible than the hydrocarbons, as found. On the chemical time scale, differences in flexibility may become apparent. The (qualitative) rates of alkylation of $(\text{NPF}_2)_{10,12}$ appear to be very slow, the reaction of the decamer being particularly difficult to bring to completion. It is at least possible that this is a conformational effect, the phosphorus atoms in $(\text{NPF}_2)_{10}$ being folded inward (Figure 7) more than in any other member of the series. The formation of a short transannular $\text{CH}_3 \cdots \text{F}$ bond seems likely, and would need to increase the activation energy by no more than 4 kcal mol⁻¹ to account for a 1000-fold decrease in rate. The structure of the dodecamer is similar but more open, and if it is unaffected by some fluorine substitution, significant retardation arising from intramolecular bonding is to be expected here also and less in the preparation of $(\text{NPF}_2)_{11}$, as found. This may be analogous to the

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"medium-ring" effect described for cycloalkane derivatives many years ago;⁸⁰ structurally, Figure 13 shows the compromises necessary to optimize the steric interactions in the nonamer; in the hydrocarbon series, strain energy is maximized at the same point.

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Registry No. $(\text{NPF}_2)_6$, 64651-81-6; $(\text{NPF}_2)_7$, 64013-20-3; $(\text{NPF}_2)_8$, 64495-80-3; $(\text{NPF}_2)_9$, 98586-82-4; $(\text{NPF}_2)_{10}$, 98586-83-5; $(\text{NPF}_2)_{11}$, 98586-84-6; $(\text{NPF}_2)_{12}$, 98586-85-7; $(\text{NPF}_2)_6$, 19258-93-6; $(\text{NPF}_2)_7$, 14616-93-4; $(\text{NPF}_2)_8$, 14097-20-2; $(\text{NPF}_2)_9$, 19258-96-9; $(\text{NPF}_2)_{10}$, 14500-76-6; $(\text{NPF}_2)_{11}$, 14097-05-3; $(\text{NPF}_2)_{12}$, 19258-99-2; MeBr, 74-83-9.

Supplementary Material Available: Table III, anisotropic thermal parameters; Table IV, calculated hydrogen coordinates and isotropic thermal parameters; Table V, measured and calculated structure factors; Table VI, bond lengths; Table VII, bond angles; Table IX, bond lengths involving hydrogen atoms; Table X, bond angles involving hydrogen atoms; Table XI, torsion angles (166 pages). Ordering information is given on any current masthead page.

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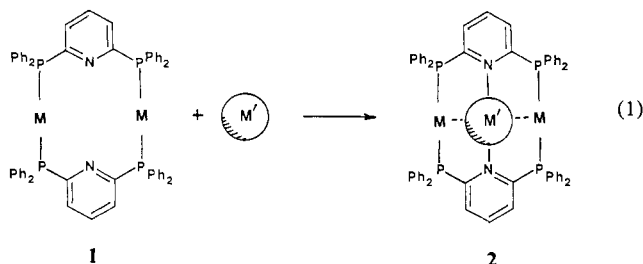
Complexation of Tin(II) Chloride by a Novel Macrocyclic Containing Rhodium and Nitrogen Binding Sites. The Preparation and X-ray Crystal Structure of $\text{Rh}_2\text{Sn}_2(\text{CO})_2\text{Cl}_6[\mu\text{-}2,6\text{-bis}(\text{diphenylphosphino})\text{pyridine}]_2$

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Abstract: Treatment of $\text{Rh}_2(\text{CO})_4(\mu\text{-Cl})_2$ with 2,6-bis(diphenylphosphino)pyridine, $(\text{Ph}_2\text{P})_2\text{py}$, in benzene forms the yellow macrocycle $\text{Rh}_2(\text{CO})_2\text{Cl}_2[\mu\text{-(Ph}_2\text{P)}_2\text{py}]_2$ which in turn reacts with tin(II) chloride to form $\text{Rh}_2\text{Sn}_2(\text{CO})_2\text{Cl}_6[\mu\text{-(Ph}_2\text{P)}_2\text{py}]_2$. Red crystals of $\text{Rh}_2\text{Sn}_2(\text{CO})_2\text{Cl}_6[\mu\text{-(Ph}_2\text{P)}_2\text{py}]_2 \cdot 2\text{CH}_2\text{Cl}_2$ belong to the orthorhombic space group $Pb2_1a$ (No. 29) with $a = 13.959$ (8) Å, $b = 18.441$ (10) Å, $c = 25.585$ (30) Å, $Z = 4$, $R = 0.053$ for 3476 reflections with $I > 4\sigma(I)$ and 450 parameters. The molecular core consists of the bent chain, Rh-Sn-Rh-SnCl_3 . The central Sn resides within the cavity of the macrocycle and is coordinated to two nitrogen atoms, two rhodium atoms, and one chloride. In a highly uncharacteristic fashion one $\text{Sn}^{\text{II}}\text{-Cl}$ bond has undergone oxidative addition to one of the rhodium ions.

The rigid ligand, 2,6-bis(diphenylphosphino)pyridine, $(\text{Ph}_2\text{P})_2\text{py}$, forms a number of 12-membered macrocycles, **1**,^{1,2} which have a relatively open cavity and should be capable of binding a second,



different metal ion in this cavity (eq 1). Complexation of this

sort differs from more traditional macrocyclic chemistry³ in that two of the potential binding sites are metal ions rather than the usual nitrogen or oxygen nucleophiles. As a consequence, metal-metal interactions will provide one of the characteristic features of the products.

Here we describe the synthesis of a macrocycle of type **1** in which M is the *trans*-Cl-Rh-CO unit. This unit prefers to bind phosphorus atoms in mutually *trans* orientations,⁴ and coupled with the rigid nature of $(\text{Ph}_2\text{P})_2\text{py}$, this facilitates the formation of the desired macrocycle while limiting the formation of unwanted, chelated complexes. We further demonstrate the complexation of tin(II) chloride by this macrocycle.

There is an extensive background to tin(II) chloride/groups 8-10 metal interactions, where tin(II) chloride has been used as a reductant,⁵ a cocatalyst,⁶ and an analytical reagent.⁷ In the

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