reaction mixture was heated at reflux temperature for 24 h. This solution was then rotoevaporated under reduced pressure until the onset of the blue precipitate of the macrocycle. The product was collected and recrystallized from an isopropyl alcohol-dioxane mixture. Yield: 2.18 g (74.6%).

Acknowledgment. We thank the National Science Foundation (Grant RII 8312292) for financial support of this work.

Registry No. I, 37572-55-7; trien, 112-24-3; [Ni(trien)]$ZnCl_4$, 55279-13-5; [Ni(trien)][ClO_4]$_2$, 15609-09-3; [Cu(trien)][ClO_4]$_2$, 40192-39-0; [Pd(trien)][$PdCl_4$]$_2$, 117251-42-0; [Ni16N6]I_2, 117251-36-2; [Ni16N6]Br_2, 117251-37-3; [Ni16N6]Cl_2, 117251-38-4; [Cu16N6](ClO_4)$_2$, 117251-40-8; [Pd16N6]Cl_2, 117251-41-9.

Contribution from the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India, and Department of Chemistry, Dalhousie University, Halifax, Canada B3H 4J3

Syntheses and Structural Studies of New Bicyclic 1,3-Diphenyl-1,3,2λ^3,4λ^3-diazadiphosphetidines

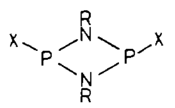
Santhanathan S. Kumaravel,[1a] Setharampattu S. Krishnamurthy,*[,1a] T. Stanley Cameron,[1b] and Anthony Linden[1b]

Received March 17, 1988

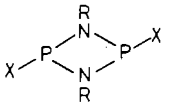
Reactions of *cis*-[(C_6H_5N)PCl]$_2$ (**1**) with the difunctional reagents HO(CH_2)$_2$OH, H(CH_3)N(CH_2)$_2$N(CH_3)H, H(CH_3)N(CH_2)$_2$OH, and HO(CH_2)$_3$OH in the presence of triethylamine yield the new bicyclic 1,3,2λ^3,4λ^3-diazadiphosphetidines [(C_6H_5N)P]$_2$[-O(CH_2)$_2$O-] (**2**), [(C_6H_5N)P]$_2$[-(CH_3)N(CH_2)$_2$N(CH_3)-] (**3**), [(C_6H_5N)P]$_2$[-(CH_3)N(CH_2)$_2$O-] (**4**), and [(C_6H_5N)P]$_2$[-O(CH_2)$_3$O-] (**5**), respectively. The products have been characterized by elemental analyses and IR and NMR spectroscopic data. The structures of **4** and **5** have been determined by single-crystal X-ray analysis. Crystal data for **4**: monoclinic, $P2_1/c$, $a = 9.823$ (2) Å, $b = 8.608$ (1) Å, $c = 18.423$ (3) Å, $\beta = 90.55$ (1)°, $Z = 4$. Crystal data for **5**: monoclinic, $P2_1/c$, $a = 9.727$ (2) Å, $b = 8.064$ (2) Å, $c = 19.702$ (4) Å, $\beta = 91.31$ (1)°, $Z = 4$. The structures have been solved by direct methods and refined to $R = 0.028$ for **4** and $R = 0.050$ for **5**. Compound **4** is the first example of an aminoalkoxy-1,3,2λ^3,4λ^3-diazadiphosphetidine. The P_2N_2 ring is slightly puckered in both **4** and **5** and the puckering occurs in a manner opposite to that observed for *cis*-[(RN)PX]$_2$ structures.

Introduction

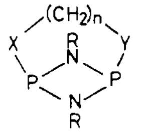
There has been considerable interest in the cis-trans isomerization of 1,3,2λ^3,4λ^3-diazadiphosphetidines,[2-10] and some generalizations have been made concerning the factors that determine the relative proportions of the two isomers Ia and Ib. The ^{31}P NMR chemical shifts of the two geometrical isomers (Ia, cis, and Ib, trans) differ by 50-90 ppm. Our previous work[10] and that of others[3-7] have clearly demonstrated that for both *N*-alkyl- and *N*-aryl-substituted diazadiphosphetidines, the low-field ^{31}P chemical shift corresponds to the trans isomer and the high-field shift corresponds to the cis counterpart.



Ia



Ib

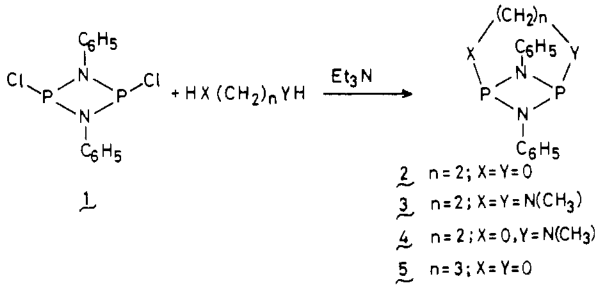


Ic

The ^{31}P chemical shifts of bicyclic derivatives Ic[7,8,11] obtained from the reaction of *N-tert*-butylchlorodiazadiphosphetidine (Ia, R = t-C_4H_9, X = Cl) with difunctional reagents lie inbetween the values for the cis and trans isomers even though in these compounds the atoms of the bridging group attached to the phosphorus must have a mutual cis orientation with respect to the P-N ring. Structural studies, which may provide a clue to the origin of these shifts have not been carried out on these compounds. We now report the synthesis of a series of bicyclic compounds (**2-5**) derived from the *N*(ring)-phenyldiazadiphosphetidine, [(PhN)PCl]$_2$ (**1**), their spectroscopic characterization, and the X-ray crystal structure analysis of two of these derivatives, **4** and **5**.[12] The structural features are compared with those available for geometrical isomers of diazadiphosphetidines and also the related *ansa*-cyclotriphosphazenes and trans-annular bridged cyclotetraphosphazenes.

Results and Discussion

Syntheses and NMR Spectra. The reactions of *cis*-[(C_6H_5N)PCl]$_2$ (**1**)[3,13] with the diols HO(CH_2)$_n$OH (n = 2 or 3), the diamine H(CH_3)N(CH_2)$_2$N(CH_3)H and the amino alcohol H(CH_3)N(CH_2)$_2$OH afford bicyclic 1,3-diphenyl-1,3,2λ^3,4λ^3-diazadiphosphetidines **2-5**. Triethylamine is used as a hydrogen chloride acceptor in all of the reactions except in the reaction with the diamine, where the reactant diamine itself functions as a scavenger of hydrogen chloride.



The reaction conditions vary depending on the nature of di-

---

* To whom correspondence should be addressed.

(1) (a) Indian Institute of Science. (b) Dalhousie University.

(2) Keat, R. *Top. Curr. Chem.* **1982**, *102*, 89.

(3) Chen, H. J.; Haltiwanger, R. C.; Hill, T. G.; Thompson, M. L.; Coons, D. E.; Norman, A. D. *Inorg. Chem.* **1985**, *24*, 4725.

(4) Kamil, W. A.; Bond, M. R.; Willett, R. D.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 2829.

(5) Kamil, W. A.; Bond, M. R.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 2015.

(6) Bulloch, G.; Keat, R.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1977**, 99.

(7) Keat, R.; Rycroft, D. S.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1979**, 1224.

(8) Keat, R.; Rycroft, D. S.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1980**, 321.

(9) Zeiss, W.; Weis, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *B32*, 485.

(10) Kumaravel, S. S.; Krishnamurthy, S. S.; Vincent, B. R.; Cameron, T. S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *B41*, 1067.

(11) Keat, R.; Thompson, D. G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 797.

(12) While this work was in progress, a report appeared on the synthesis of bicyclic derivatives by the reaction of Ia (R = t-C_4H_9, X = Cl) with fluorinated diols, but owing to the oily nature of the products, X-ray structural studies could not be undertaken on the bicyclic derivatives.[4]

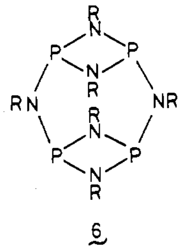
(13) (a) Michaelis, A.; Schroeter, G. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 490. (b) Davies, A. R.; Dronsfield, A. T.; Haszeldine, R. N. *J. Chem. Soc., Perkin Trans. 1* 1973, 379.

0020-1669/88/1327-4546$01.50/0

functional reagents (see Experimental Section). The yields of the bicyclic compounds **3**–**5** are considerably reduced owing to the formation of other (presumably polymeric) products, from which the bicyclic diazadiphosphetidines could be separated by filtration through a silica gel column or by extraction with a less polar solvent such as petroleum ether (bp 60–80 °C).

The products have been characterized by spectroscopic and analytical data. Compound **4** represents the first example of an aminoalkoxy-1,3,2λ^3,4λ^3-diazadiphosphetidine; 2-alkoxy-4-amino-1,3,2λ^3,4λ^3-diazadiphosphetidines are unknown.[14] In the IR spectra of the bicyclic compounds (**2**–**5**), the asymmetric stretching vibration, ν_{asym}(P-N-P) associated with the P_2N_2 ring, appears in the range 870–900 cm^{-1}. In the ^{1}H NMR spectrum of **3**, the $^3J_{PH}$ value for "–NCH$_3$" protons is higher than that for the "–NCH$_2$–" protons (13 and 4.5 Hz respectively). In the ^{1}H NMR spectrum of **4**, the ring "–NCH$_2$–" proton resonances appear as broad featureless hump that overlaps with the "–NCH$_3$" doublet. The "–OCH$_2$–" protons give rise to a doublet of triplets. The broad peak observed for "–NCH$_2$–" protons at δ 3.07 splits into two sets of complex patterns at δ 3.41 and 2.81 when the spectrum is recorded at −40 °C. The "–OCH$_2$–" multiplet also undergoes further splitting. This result indicates some kind of a flipping process for the NC$_2$O segment of the bicyclic molecule. More detailed variable-temperature NMR measurements are required to comment further on the nature of the exchange process.

The ^{31}P NMR chemical shifts for *N*(ring)-aryl bicyclic diazadiphosphetidines and *N*(ring)-alkyl bicyclic diazadiphosphetidines[4,11] are summarized in Table I, and where direct comparisons are possible, the values are remarkably close. The ^{31}P{^{1}H} NMR spectrum of **4** consists of an AB quartet. From a comparison of the ^{31}P chemical shifts for **2** and **3**, the peaks centered at δ 158.9 can be assigned to the phosphorus that is connected to the nitrogen atom of the NC$_2$O bridge in **4** and the peaks centered at δ 164.4 to the phosphorus that is connected to oxygen. There is a sharp decrease in the ^{31}P chemical shift when the size of the bridging loop changes from a four to a five-atom segment (cf. compounds **2** and **5**). When the size of the bridging loop is six or seven, the ^{31}P shift increases (downfield); these compounds contain fluorinated dioxy bridging loops where contribution to deshielding by fluorine atoms may be considerable. For example, the ^{31}P chemical shift value is 131.4 ppm for *cis*-[(*t*-C$_4$H$_9$N)P(OCH$_2$CH$_3$)]$_2$ and 143.3 ppm for *cis*-[(*t*-C$_4$H$_9$N)P(OCH$_2$CF$_3$)]$_2$.[7] The values in Table I may be compared with the ^{31}P shift (145.8 ppm) for compound **6**,[15] where the size of the bridging loop can be taken as five.



R = i - C$_3$H$_7$

6

Table I. ^{31}P NMR Chemical Shifts for Bicyclic 1,3,2λ^3,4λ^3-Diazadiphosphetidines, $\overline{\mathrm{P(NR)_2P}}$–XY

no. of atoms in the bridging loop	XY	^{31}P chem shift, ppm	
		R = *t*-C$_4$H$_9$[a]	R = C$_6$H$_5$[b]
4	–O(CH$_2$)$_2$O–	177.5	172.3
4	–(CH$_3$)N(CH$_2$)$_2$N(CH$_3$)–	155.0	151.9
4	–(CH$_3$)N(CH$_2$)$_2$O–		158.9, 164.4 (AB; *J* = 25.5 Hz)
5	–O(CH$_2$)$_3$O–	135.4	137.3
6	–OCH$_2$(CF$_2$)$_2$CH$_2$O–	221.5	
7	–OCH$_2$(CF$_2$)$_3$CH$_2$O–	222.3	

[a] From ref 4 and 11. [b] This work.

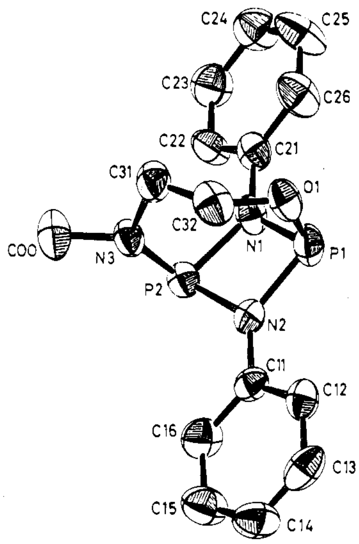
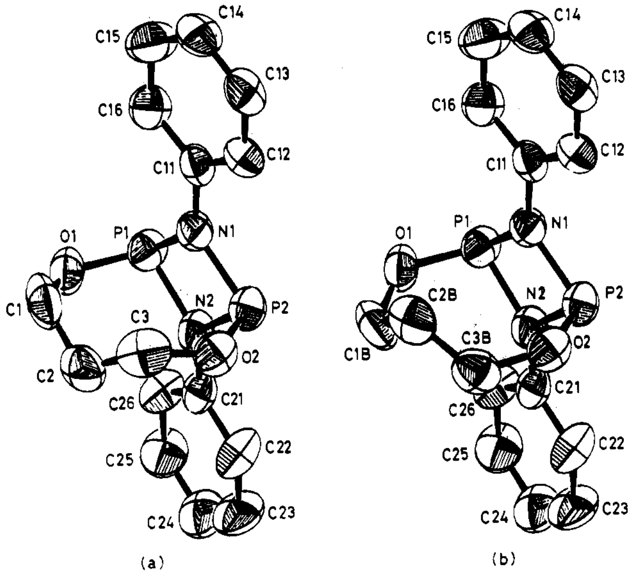


Figure 1. ORTEP diagram of **4** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.



(a) (b)

Figure 2. ORTEP diagram of **5** showing 50% probability ellipsoids (a) with site occupation of disordered atoms (C(1)–C(3)) of 0.655 and (b) with site occupation of disordered atoms (C(1B)–C(3B)) of 0.345. Hydrogen atoms have been omitted for clarity.

Reactions with Sulfur and Diketones. The bicyclic derivatives **2**–**5** are resistant to oxidation when they are treated with S$_8$ under the conditions[7] where the other 2,4-dialkoxy- or diaminodiazadiphosphetidines readily undergo such oxidation reactions. Under more forcing conditions (see Experimental Section), only decomposed products that could not be characterized are obtained. The relative inertness of **2**–**5** to oxidation by sulfur appears to be steric in origin. The P$_2$N$_2$ ring in **4** and **5** exhibits a novel type of puckering (see below), and to what extent this puckering affects the reactivity of phosphorus is not clear. Goetze et al. report that the bicyclic derivative P(NCH$_3$NCH$_3$)$_3$P is less reactive toward sulfur than P(N(CH$_3$)$_2$)$_3$, and the reduced reactivity is attributed to the cage structure of the former.[16]

---

(14) An attempt to prepare 2-methoxy-4-(dimethylamino)-1,3-diphenyl-1,3,2λ^3,4λ^3-diazadiphosphetidine, (CH$_3$O)[P(C$_6$H$_5$N)$_2$P](N(CH$_3$)$_2$), by the reaction of *cis*-[(C$_6$H$_5$N)PCl]$_2$ (**1**) with 1 equiv of methanol in the presence of triethylamine followed by treatment with an excess of dimethylamine at low temperatures was not successful. Only an equimolar mixture of [(C$_6$H$_5$N)P(OCH$_3$)]$_2$ and [(C$_6$H$_5$N)P(N(CH$_3$)$_2$)]$_2$ was obtained; the ^{31}P NMR spectrum of the reaction mixture showed only two peaks at δ 166.5 (s) and at δ 193.0 (s), corresponding to the diamino and dialkoxy compounds respectively.

(15) Scherer, O. J.; Andres, K.; Krüger, C.; Tsay, Y.-H.; Wolmerhauser, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 751.

(16) Goetze, R.; Nöth, H.; Payne, D. S. *Chem. Ber.* **1972**, *105*, 2637.

Table II. Selected Structural Parameters for **4** and **5**

4		**5**	
	(a) Bond Distances (Å)		
P(1)-N(1)	1.709 (5)	P(1)-N(1)	1.710 (7)
P(1)-N(2)	1.714 (4)	P(1)-N(2)	1.719 (7)
P(2)-N(1)	1.733 (4)	P(2)-N(1)	1.724 (7)
P(2)-N2	1.734 (5)	P(2)-N(2)	1.704 (7)
P(2)-N(3)	1.661 (4)	P(1)-O(1)	1.591 (6)
P(1)-O(1)	1.621 (3)	P(2)-O(2)	1.600 (6)
N(3)-C(00)	1.449 (8)	O(1)-C(1)	1.42 (1)
N(3)-C(31)	1.459 (6)	O(2)-C(3)	1.42 (2)
C(31)-C(32)	1.497 (8)	C(1)-C(2)	1.52 (2)
O(1)-C(32)	1.448 (8)	C(2)-C(3)	1.53 (2)
	(b) Bond Angles (deg)		
N(1)-P(1)-N(2)	79.94 (2)	N(1)-P(1)-N(2)	79.5 (3)
N(1)-P(2)-N(2)	78.74 (2)	N(1)-P(1)-O(1)	106.2 (3)
N(1)-P(1)-O(1)	102.88 (2)	N(2)-P(1)-O(1)	105.4 (3)
O(1)-P(1)-N(2)	104.60 (2)	N(1)-P(2)-N(2)	79.6 (3)
N(1)-P(2)-N(3)	103.56 (2)	N(1)-P(2)-O(2)	104.0 (3)
N(2)-P(2)-N(3)	101.48 (2)	N(2)-P(2)-O(2)	105.5 (3)
P(1)-O(1)-C(32)	122.34 (3)	P(1)-N(1)-P(2)	100.1 (3)
O(1)-C(32)-C(31)	116.82 (4)	P(1)-N(1)-C(11)	130.4 (6)
C(32)-C(31)-N(3)	116.15 (4)	P(2)-N(1)-C(11)	128.7 (6)
C(31)-N(3)-C(00)	115.21 (4)	P(1)-N(2)-P(2)	100.5 (3)
C(00)-N(3)-P(2)	117.79 (3)	P(1)-N(2)-C(21)	129.6 (6)
C(31)-N(3)-P(2)	122.65 (3)	P(2)-N(2)-C(21)	129.3 (5)
P(1)-N(1)-C(21)	130.44 (3)	P(1)-O(1)-C(1)	129.3 (7)
P(2)-N(1)-C(21)	129.49 (3)	P(1)-O(1)-C(1B)	126.3 (12)
P(1)-N(1)-P(2)	100.03 (2)	P(2)-O(2)-C(3)	129.3 (7)
P(1)-N(2)-C(11)	130.10 (3)	P(2)-O(2)-C(3B)	131.1 (9)
P(2)-N(2)-C(11)	129.80 (3)	O(1)-C(1)-C(2)	116.2 (10)
P(1)-N(2)-P(2)	99.77 (2)	O(1)-C(1B)-C(2B)	123 (2)
		C(1)-C(2)-C(3)	117.1 (11)
		C(1B)-C(2B)-C(3B)	116 (2)
		O(2)-C(3)-C(2)	120.4 (10)
		O(2)-C(3B)-C(2B)	111.0 (14)
	(c) Deviations of Atoms from the Least-Squares Plane through P(1), N(1), P(2), and N(2) (Å)		
P(1)	0.071	P(1)	0.030
P(2)	0.069	P(2)	0.030
N(1)	−0.070	N(1)	−0.030
N(2)	−0.070	N(2)	−0.030

Attempted oxidative-addition reactions of **2–5** with 1,2-diketones also lead to ring cleavage (IR and ^1H NMR evidence), and no identifiable product can be isolated.

X-ray Structural Studies. Single-crystal X-ray analyses have been carried out for compounds **4** and **5**, which contain the bridging moiety as part of seven- and eight-membered rings respectively. ORTEP views of molecules **4** and **5** with the numbering scheme are shown in Figures 1 and 2, respectively, and selected structural parameters are listed in Table II.

Compound **4** is the first example of an unsymmetrically substituted 1,3,2λ^3,4λ^3-diazadiphosphetidine for which the X-ray structure has been determined. The P–N bonds of the P_2N_2 ring at the P–O end are shorter than those at the P–N end. The four cyclic P–N bond distances for compound **5** appear to be slightly nonequivalent. The N atoms of the P_2N_2 rings in both molecules are trigonal planar, with the angles around N atoms summing up to ca. 360°. The four-membered ring is slightly puckered, successive atoms being displaced by 0.070 Å in **4** and by 0.030 Å in **5** alternatively above and below the mean P_2N_2 plane. The two atoms of the *ansa*-arch connected to the phosphorus centers are displaced from the mean P_2N_2 plane in the same direction as the phosphorus atoms. This situation is in contrast to that observed for cis isomers of 2,4-disubstituted 1,3,2λ^3,4λ^3-diazadiphosphetidines (Ia) wherein the substituents at the phosphorus centers are displaced from the mean P_2N_2 plane in the same direction as the nitrogen atoms.[5,17] The two types of puckering are illustrated in Figure 3. The dihedral angle between the planes P(1)-P(2)-N(1) and P(1)-P(2)-N(2) is 165.5° in **4** and 173.7° in **5**. Thus the extent of puckering of the P_2N_2 ring in **4** and **5** is not as much as one would expect for such a strained system. Two opposing factors determine the extent of puckering. First, *cis*-diazadiphosphetidines undergo puckering of the P_2N_2 ring in order to relieve steric interactions of the substituents at the phosphorus centers. Second, in order to reduce the strain in the bridging chain, the P_2N_2 ring departs from planarity in such a way as to bring the atoms of the bridge connected to the phosphorus centers close. A compromise between these two factors is reached here. The angles at O(1), N(3), C(31), and C(32) in **4** and at O(1), O(2), C(1), C(2), and C(3) in **5** are in the range 111–132°, which are relatively large compared with the expected tetrahedral angle. The P···P nonbonded distances (2.64 Å in **4** and 2.63 Å in **5**) are close to those observed for *trans*-$[(C_6H_5N)P(OCH_2CF_3)]_2$ (2.63 Å)[10] and *trans*-$[(C_6H_5N)P(N(C_6H_5)_2)]_2$ (2.64 Å)[3] but are slightly more than those observed in *cis*-$[(t\text{-}C_4H_9N)PCl]_2$ (2.53 Å)[17], *cis*-$[(C_6H_5N)PCl]_2$ (2.59 Å)[3] and *cis*-$[(t\text{-}C_4H_9N)P(OC_6F_5)]_2$ (2.42 Å).[5]

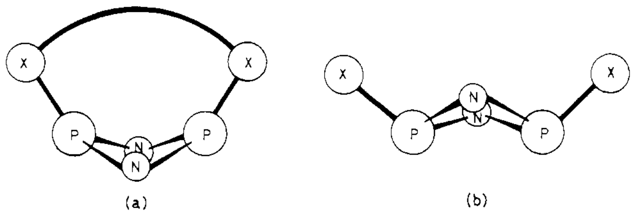


Figure 3. Schematic representation of puckering of the P_2N_2 ring in (a) bicyclic derivatives **4** and **5** and (b) *cis*-$[(RN)PX]_2$ structures.

Table III. P···P Nonbonded Distances in Cyclic P–N Compounds with and without Trans-Annular Bridging

type of ring	mean P···P dist, Å	
	with trans-annular bridge	without trans-annular bridge
P_2N_2	2.64 ± 0.01[a]	cis: 2.50 ± 0.08[b] trans: 2.63 ± 0.01[c]
P_3N_3[d]	2.68 ± 0.04[e]	2.77 ± 0.03[e]
P_4N_4[d]	2.78 ± 0.01[f]	4.00 ± 0.08[e]

[a] This work. [b] References 3, 5, and 17. [c] References 3 and 10. [d] For illustrations of the types of compounds considered, see ref 18. [e] References 18 and 19. [f] Reference 20.

When we consider the P···P nonbonded distances in larger ring systems such as *ansa*-cyclotriphosphazene derivatives[18,19] and trans-annular bridged cyclotetraphosphazenes[20] (Table III), it is noted that in the former case, the nonbonded distances between the P atoms connected by the *ansa*-arch decrease compared to their mean value in homogeneously substituted $N_3P_3X_6$ derivatives whereas for the latter (bicyclic P_4N_5 system), the decrease of P···P nonbonded distance is more pronounced due to bridging, which reflects the conformational flexibility of the eight membered P–N ring.[21]

In both compounds **4** and **5**, the two phosphorus atoms and the two atoms of the bridge connected to the phosphorus centers [O(1) and N(3) in **4**; O(1) and O(2) in **5**] lie approximately in a plane (the deviations of each of the atoms from the mean plane are less than 0.02 Å in **4** and 0.01 Å in **5**). This plane is almost perpendicular to the mean plane of the P_2N_2 ring (the dihedral angle being 89.8° for **4** and 89.7° for **5**). The carbon atoms of the bridge deviate appreciably from the above plane to make the bridging arch highly puckered. Thus in **4**, the distances of C(31) and C(32) from the plane P(1)-P(2)-N(3)-O(1) are −0.39 and +0.40 Å, respectively. In **5**, there is, in addition, a disorder of the carbon atom positions of the $(CH_2)_3$ chain in the loop connecting the two phosphorus atoms (see Figure 2 and Experimental Section). Each

---

(17) Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 259.

(18) Contractor, S. R.; Hursthouse, M. B.; Parkes, H. G.; Shaw, L. A.; Shaw, R. A.; Yilmaz, H. *Phosphorus Sulfur* **1986**, *28*, 267.

(19) Labarre, J.-F. *Top. Curr. Chem.* **1985**, *129*, 173.

(20) (a) Cameron, T. S.; Mannan, Kh. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 443. (b) Cameron, T. S.; Cordes, R. E.; Jackman, F. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 980. (c) Cameron, T. S.; Cordes, R. E.; Vincent, B. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1242.

(21) Krishnamurthy, S. S.; Sau, A. C.; Woods, M. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41.

of the disordered arrangements is puckered across the P(1)–P(2)–O(1)–O(2) plane, but in an opposite direction from the other. The distances of C(1), C(2), and C(3) from the P(1)–P(2)–O(1)–O(2) plane are +0.34, –0.43, and +0.24 Å, respectively, while C(1B), C(2B) and C(3B) deviate by –0.21, +0.46, and –0.37 Å, respectively. The phenyl rings in both **4** and **5** are slightly inclined with respect to the four-membered ring. The dihedral angles between the mean P(1)–P(2)–N(1)–N(2) plane and the phenyl rings are 17.9 and 11.7° for **4** and 8.9 and 3.2° for **5**.

It is well documented that the lengths of the P–N bonds within the P–N ring in cyclophosphazenes vary with the electronegativity of the substituents bound to the phosphorus atoms at the end of the P–N–P island.[19] The P–N distance will be shorter when the P atom is connected to a more electronegative substituent on account of enhanced skeletal π-bonding.[21] Such differential P–N distances within the P–N ring are also observed for the unsymmetrically substituted diazadiphosphetidine **4**.

Experimental Section

Apparatus and Materials. All manipulations were carried out in an atmosphere of dry N_2, and standard Schlenk-type glasswares were used.[22] Infrared spectra (4000–400 cm^{-1}) were recorded with a Carl-Zeiss UR-10 spectrometer; ^{1}H NMR spectra were obtained from Bruker WH-270 (270 MHz) and Varian T-60 (60 MHz) spectrometers, with Me_4Si (TMS) as the internal standard. The ^{31}P NMR spectra were recorded at 32.2 MHz on a Varian FT-80A spectrometer. Chemical shifts downfield from the external standard 85% H_3PO_4 are assigned positive values. Elemental analyses were performed at City University, London, U.K., by Dr. S. A. Matlin. X-ray diffraction data were collected by using a CAD-4 diffractometer (Mo Kα_1 radiation, λ = 0.709 26 Å) equipped with a graphite monochromator. The mass spectrum of **2** was obtained from a JEOL-DX300 mass spectrometer (EI conditions, 70 eV, 300 μA). The sample was introduced via the direct inlet system without any heating.

The chloro compound *cis*-$[(C_6H_5N)PCl]_2$ (**1**) was prepared by the method originally reported by Michaelis and modified by Davis et al.[13] $HO(CH_2)_2OH$ (Fluka), $HO(CH_2)_3OH$ (Koch-light), $H(CH_3)N(CH_2)_2OH$ (Fluka), and $H(CH_3)N(CH_2)_2N(CH_3)H$ (Fluka) were purified by distillation under reduced pressure (0.5 Torr). Solvents and triethylamine were purified by standard methods.

$[(C_6H_5N)P]_2[-OCH_2CH_2O-]$ (2). A solution of *cis*-$[(C_6H_5N)PCl]_2$ (**1**) (4.7 g, 15 mmol) in 50 mL of benzene was added dropwise to a mixture of $HO(CH_2)_2OH$ (1.0 g, 16 mmol) and triethylamine (3.63 g, 36 mmol) in 50 mL of $CHCl_3$ at 25 °C with stirring. After 12 h, the solution was filtered, and the filtrate was passed through a small glass column containing silica gel. Solvent was evaporated in vacuo, and the residue was washed with methanol to obtain **2** (3.2 g, 70%). The product was recrystallized from CH_2Cl_2; mp 122–125 °C dec. IR (Nujol): 1600 (s), 1570 (m), 1550 (w), 1515 (m), 1490 (s), 1285 (s), 1260 (s), 1240 (m), 1180 (m), 1165 (w), 1105 (w), 1085 (m), 1060 (s), 1035 (m), 1000 (w), 930 (s), 920 (s), 875 (s), 745 (m), 560 (w), 520 (w), 480 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O_2P_2$: C, 55.3; H, 4.6; N, 9.2. Found: C, 55.2; H, 4.6; N, 9.2. MS: *m/e* 304 (M^+), 35%; *m/e* 276 [$(M - C_2H_4)^+$], 16%; *m/e* 213 [$(M - C_6H_5N)^+$], 5%; *m/e* 122 [$(C_6H_5NP)^+$], 100%. ^{1}H NMR ($CDCl_3$): δ 4.00 (d with virtual coupling,[6] CH_2, J_{PH} = 9 Hz), 6.8–7.3 (m, C_6H_5). ^{31}P NMR ($CHCl_3$): δ 172.3 (s).

$[(C_6H_5N)P]_2[-(CH_3)NCH_2CH_2N(CH_3)-]$ (3). A solution of $H(CH_3)N(CH_2)_2N(CH_3)H$ (2.65 g, 30 mmol) in 50 mL of diethyl ether was added dropwise to *cis*-$[(C_6H_5N)PCl]_2$ (4.7 g, 15 mmol) in 100 mL of diethyl ether with stirring at 0 °C. Stirring was continued for further 12 h and filtered. Diethyl ether was evaporated in vacuo and the residue was washed with methanol to obtain **3** (0.5 g, 10%). The product was recrystallized from petroleum ether (bp 60–80 °C); mp 118–120 °C dec. IR (Nujol): 1600 (s), 1580 (s), 1500 (s), 1490 (s), 1430 (w), 1370 (m), 1325 (s), 1295 (s), 1250 (w), 1210 (s), 1185 (m), 1160 (m), 1140 (s), 1110 (m), 1085 (s), 1070 (m), 1025 (s), 1005 (m), 980 (w), 910 (s), 900 (s), 885 (m), 870 (s), 825 (w), 755 (s), 695 (s), 635 (s), 520 (m), 450 (m), 430 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.93 (d with virtual coupling, CH_2, J_{PH} = 4.5 Hz), 2.96 (d, CH_3, J_{PH} = 13 Hz), 6.66–7.37 (m, C_6H_5). ^{31}P NMR ($CHCl_3$): δ 151.9 (s).

$[(C_6H_5N)P]_2[-(CH_3)NCH_2CH_2O-]$ (4). This compound was prepared in a manner similar to that described for **2** (15% yield) and the product was recrystallized from diethyl ether; mp 112–115 °C dec. IR (Nujol): 1600 (s), 1580 (m), 1570 (w), 1505 (s), 1495 (s), 1315 (m), 1290 (s), 1220 (m), 1185 (w), 1170 (w), 1150 (w), 1080 (m), 1045 (m), 1020 (s), 1005 (m), 980 (w), 920 (s), 900 (s), 890 (s), 870 (s), 760 (s), 700 (m), 680 (m), 650 (w), 560 (w), 520 (w), 470 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{17}N_3OP_2$: C, 56.8; H, 5.4; N, 13.3. Found: C, 55.9; H, 5.4; N, 13.2. ^{1}H NMR ($CDCl_3$): δ 3.05 (d, CH_3, J_{PH} = 13 Hz), 3.07 (m, NCH_2), 3.97 (m, OCH_2), 6.90–7.29 (m, C_6H_5). ^{31}P NMR ($CHCl_3$): AB pattern, δ 158.9 and 164.4 (J_{PP} = 25.5 Hz).

Table IV. Crystal Data and Details of the Structure Determination for **4** and **5**

	4	5
molecular formula	$C_{15}H_{17}N_3OP_2$	$C_{15}H_{16}N_2O_2P_2$
M_r	317.3	318.2
space group	$P2_1/c$	$P2_1/c$
a, Å	9.823 (2)	9.727 (2)
b, Å	8.608 (1)	8.064 (2)
c, Å	18.423 (3)	19.702 (4)
β, deg	90.55 (1)	91.31 (1)
V, Å^3	1557.7	1545.0
Z	4	4
d_c, g cm^{-3}	1.35	1.37
μ, cm^{-1}	2.33	2.90
cryst size, [mm]	0.4 × 0.3 × 0.1	0.6 × 0.3 × 0.25
F(000)	664	664
no. of reflcns collcd	2597	3653
no. of unique reflcns	2169	2710
no. of obsd reflcns	765 [$I > 3\sigma(I)$]	1151 [$I > \sigma(I)$]
max 2θ, deg	46	50
R	0.028	0.066^a
R_w		0.065
weight (*w*)	$1/[\sigma^2\lvert F_o\rvert + 0.004\lvert F_o\rvert^2]$	

^{a} R = 0.050 for 835 reflections with $I > 2\sigma(I)$.

$[(C_6H_5N)P]_2[-OCH_2CH_2CH_2O-]$ (5). This compound was prepared in a manner similar to that described for **2** (20% yield), and the product was recrystallized from light petroleum ether (bp 60–80 °C); mp 126–128 °C dec. IR (Nujol): 1600 (s), 1580 (s), 1570 (s), 1500 (s), 1420 (m), 1350 (m), 1285 (s), 1265 (s), 1180 (m), 1160 (m), 1110 (m), 1085 (m), 1060 (s), 1035 (m), 1000 (w), 970 (m), 960 (m), 900 (s, br), 820 (s), 750 (m), 690 (w), 545 (w), 520 (w) cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_2O_2P_2$: C, 56.6; H, 5.1; N, 8.8. Found: C, 56.5; H, 5.1; N, 8.7. ^{1}H NMR ($CDCl_3$): δ 2.22 (quintet, (C)CH_2(C), J_{HH} = 5 Hz), 4.20 (m, OCH_2), 6.98–7.35 (m, C_6H_5). ^{31}P NMR ($CHCl_3$): δ 137.3 (s).

Attempted Oxidation Reactions of 2–5 with Sulfur and Oxidative-Addition Reactions with 1,2-Diketones. Compounds **2**–**5** were treated with sulfur or the 1,2-diketones biacetyl, benzil, or *o*-chloranil. In no case, could a definitive product be isolated. Typically, **2** and S_8 (in a 1:2 molar ratio) were heated under reflux in benzene for 12 h. The ^{31}P NMR spectrum of the reaction mixture showed only a single peak corresponding to **2**. When the same reaction was repeated in boiling *p*-xylene, an oil was obtained that could not be characterized. Similarly **3** and benzil ($C_6H_5COCOC_6H_5$) (1:2 molar ratio) were heated under reflux in benzene for 1 h. Solvent was then removed to obtain a viscous oil. The ^{1}H NMR spectrum of the product revealed extensive decomposition.

Data Collection and Structural Analysis for $[(C_6H_5N)P]_2[-(CH_3)NCH_2CH_2O-]$ (4) and $[(C_6H_5N)P]_2[-OCH_2CH_2CH_2O-]$ (5). Crystals for X-ray diffraction were obtained by crystallizing **4** from diethyl ether, and **5** from petroleum ether (bp 60–80 °C). The crystal data for **4** and **5** and the details of the structure determination are summarized in Table IV.

The unit cell parameters for **4** and **5** were determined from a CAD-4 diffractometer and were refined from the circle angles of 25 general reflections with the Bragg angle in the range 10–14°.

The intensities of the reflections were reduced to a standard scale by using routine procedures.[23] Lorentz and polarization corrections were made, but no absorption or extinction corrections were applied. Scattering factors for neutral atoms were taken from ref 24 and were corrected for the real part of the anomalous effect. The structures were solved by using direct methods (MULTAN)[25] and refined by full-matrix least-squares procedures (SHELX-76).[26] The *E* maps from the solution with the lowest Karle *R* factor clearly showed the positions of all P, O, N, and C atoms. The structures were refined initially by a large-block

---

(22) Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; McGraw-Hill: New York, 1969.

(23) Cameron, T. S.; Cordes, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 748.

(24) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV.

(25) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

(26) Sheldrick, G. M. "SHELX-76: Program for Crystal Structure Determination"; University of Cambridge, Cambridge, U.K., 1976.

Table V. Atomic Positional Parameters of Non-Hydrogen Atoms for **4** with Estimated Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*
P(1)	0.07873 (16)	0.36838 (14)	0.12912 (8)
P(2)	0.01448 (14)	0.09747 (17)	0.18619 (8)
O(1)	0.1606 (3)	0.3168 (3)	0.0570 (1)
N(1)	−0.0543 (4)	0.2405 (5)	0.1307 (2)
N(2)	0.1351 (4)	0.2434 (4)	0.1954 (2)
N(3)	0.0904 (4)	−0.0216 (4)	0.1283 (2)
C(11)	0.2530 (5)	0.2490 (6)	0.2388 (2)
C(12)	0.3589 (6)	0.3447 (7)	0.2241 (3)
C(13)	0.4734 (6)	0.3499 (8)	0.2676 (3)
C(14)	0.4826 (7)	0.2538 (8)	0.3274 (3)
C(15)	0.3771 (6)	0.1571 (7)	0.3418 (3)
C(16)	0.2615 (5)	0.1543 (7)	0.2984 (3)
C(21)	−0.1805 (5)	0.2452 (6)	0.0953 (2)
C(22)	−0.2803 (5)	0.1386 (6)	0.1120 (3)
C(23)	−0.4050 (5)	0.1445 (8)	0.0771 (3)
C(24)	−0.4325 (6)	0.2559 (8)	0.0269 (3)
C(25)	−0.3360 (6)	0.3603 (7)	0.0090 (2)
C(26)	−0.2091 (5)	0.3558 (6)	0.0429 (2)
C(00)	0.0960 (6)	−0.1851 (6)	0.1466 (3)
C(31)	0.1938 (5)	0.0311 (6)	0.0775 (3)
C(32)	0.1530 (5)	0.1608 (7)	0.0278 (2)

Table VI. Atomic Positional Parameters of Non-Hydrogen Atoms for **5** with Estimated Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*
P(1)	0.4050 (2)	0.1267 (3)	0.8679 (1)
P(2)	0.5122 (2)	0.3542 (3)	0.7893 (1)
N(1)	0.3610 (6)	0.2461 (8)	0.7991 (3)
N(2)	0.5508 (6)	0.2455 (8)	0.8614 (3)
O(1)	0.3245 (5)	0.2021 (7)	0.9302 (2)
O(2)	0.4765 (5)	0.5379 (7)	0.8139 (3)
C(1)[a]	0.3292 (15)	0.3641 (12)	0.9574 (6)
C(2)[a]	0.2997 (12)	0.5049 (15)	0.9076 (7)
C(3)[a]	0.4235 (12)	0.5919 (15)	0.8771 (5)
C(1B)[b]	0.286 (2)	0.3701 (13)	0.9387 (14)
C(2B)[b]	0.384 (2)	0.514 (2)	0.9268 (10)
C(3B)[b]	0.373 (2)	0.597 (2)	0.8574 (8)
C(11)	0.2444 (8)	0.2397 (9)	0.7551 (4)
C(12)	0.2444 (8)	0.3249 (12)	0.6942 (4)
C(13)	0.1277 (9)	0.3216 (13)	0.6539 (5)
C(14)	0.0123 (9)	0.2371 (12)	0.6716 (5)
C(15)	0.0153 (9)	0.1537 (14)	0.7309 (5)
C(16)	0.1297 (8)	0.1520 (12)	0.7735 (4)
C(21)	0.6752 (7)	0.2382 (10)	0.8992 (3)
C(22)	0.7824 (7)	0.3431 (11)	0.8838 (4)
C(23)	0.9042 (8)	0.3372 (13)	0.9222 (5)
C(24)	0.9189 (8)	0.2293 (12)	0.9737 (4)
C(25)	0.8134 (8)	0.1262 (11)	0.9902 (4)
C(26)	0.6909 (7)	0.1303 (11)	0.9528 (4)

[a] Atom with site occupation of 0.655. [b] Atom with site occupation of 0.345.

least-squares procedure with isotropic temperature factors on the heavy atoms.

The hydrogen atom positions in compound **4** were determined from a difference Fourier map, and the distances were appropriately constrained (where these parameters were introduced with the refinement) to ensure convergence (C–H bonds to 1.08 Å). The methyl group was refined as a rigid group rotationally adjustable about the N–C axis. The final refinements were made with anisotropic temperature factors for the non-hydrogen atoms and an individual isotropic temperature factor for each hydrogen atom. All constraints were removed at this stage. Unit weights were applied to all reflections during these final cycles of refinement. The final refinement on all the atoms converged to $R = 0.0277$.

In the case of **5**, all phenyl hydrogen atom positions were cleary visible in a difference Fourier synthesis. Unfortunately crystals of **5** were weakly diffracting so that even with a large crystal, only 42% of the reflections had intensities with $I > \sigma(I)$. Therefore, in order to keep the number of refined parameters to a minimum, all hydrogen atoms were placed in their geometrically calculated positions with a C–H distance of 1.08 Å and restrained to ride on their associated carbon atoms. After anisotropic refinement of the non-hydrogen atoms, it was noticed that the methylene carbon atoms had highly elongated thermal ellipsoids perpendicular to the C–C bonds and parallel to the P_2N_2 plane and that these C–C bonds were unreasonably short. In addition, one significant peak remained in the difference map that was close to the middle CH_2 group. This suggested the presence of disorder of the CH_2 groups. This disorder was satisfactorily resolved and resulted in a significant improvement to the R value. As shown in Figure 2, the $O(CH_2)_3O$ group exists in a zigzag conformation. The disordered arrangement reverses the direction of the zigzag. The site occupation of the disordered atoms was refined to 0.655 for C(1)–C(3) and 0.345 for C(1B)–C(3B). It was also necessary to constrain the C–C and C–O bond lengths to 1.53 and 1.42 Å, respectively.

The final refinements were with anisotropic temperature factors on the non-hydrogen atoms and individual isotropic temperature factors on the hydrogen atoms. A three-block-matrix least-squares method was employed, minimizing $\sum w\Delta F^2$ where $w^{-1} = \sigma^2|F_o| + 0.004|F_o|^2$. The refinement converged at $R = 0.066$ and $R_w = 0.065$ for 1151 unique observed reflections ($I > \sigma(I)$) and 244 least-squares parameters (the same atom positions gave $R = 0.050$ for 835 reflections with $I > 2\sigma(I)$). The final difference maps were flat, without recognizable residual features.

The final atomic positional parameters of non-hydrogen atoms for **4** and **5** are given in Tables V and VI respectively.

Acknowledgment. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, India, for a fellowship to S. S. Kumaravel, the International Organization of Chemical Sciences in Development (IOCD) for elemental analyses, and Dr. G. Om Reddy, IDL-Nitro Nobel Basic Research Institute, Bangalore, India, for the mass spectrum.

Registry No. **1**, 67348-02-1; **2**, 117439-35-7; 3, 117439-36-8; **4**, 117439-37-9; **5**, 117439-38-0; $HOCH_2CH_2OH$, 107-21-1; $H(CH_3)NCH_2CH_2N(CH_3)H$, 110-70-3; $HOCH_2CH_2N(CH_3)H$, 109-83-1; $HOCH_2CH_2CH_2OH$, 504-63-2; $[(C_6H_5N)P(OCH_3)]_2$, 60637-23-2; $[(C_6H_5N)P(N(CH_3)_2)]_2$, 62757-66-8; biacetyl, 431-03-8; benzil, 134-81-6; *o*-chloranil, 2435-53-2.

Supplementary Material Available: Tables of atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, and bond angles for **4** and **5** (11 pages); tables of observed and calculated structure factors for **4** and **5** (33 pages). Ordering information is given on any current masthead page.