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Substituent Effects on Bonding Properties in Diphosphenes, Disilenes, and Diimines

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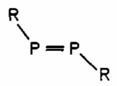
The compounds RP=PR, RSi=SiR, and RN=NR (**1-3**, R = NH_2) represent (linear) six-electron four-center π systems. They possess low rotational barriers for the terminal amino groups. The preference of a bisorthogonal over a coplanar conformation is promoted with increasing electropositive character of the central π-bonding atoms, due to increasing overlap repulsion between the lone pairs at the amino groups and the central π bond. In addition the effects of alkyl (silyl) groups at the amino groups as well as phenyl substitution (at the central π bond) on the rotational barriers in **1-3** are explored.

Double-bond systems constituted from the second row in the periodic table of elements are a matter of current interest.[1] Recent reported representatives are the substituted diphosphenes[2] **1** and disilenes[3] **2**. In general bulky substituents are required for the kinetic stabilization of the π systems. From the synthetic point of view disilylamino or mesityl groups are utilized as substituents for this purpose. It is remarkable that for **1** (R = mesityl, $N(SiR_3)_2$) the π systems (p orbitals) belonging to the substituents are perpendicular to the central π bond. This is in contrast to the isovalent tetrazene **3** (R = NR_2), which adopts a coplanar structure.[4]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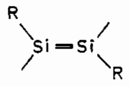
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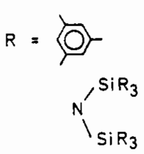

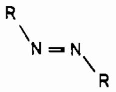
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Here we present theoretical evidence that the conformations of **1-3** depend strongly (a) on the central π bond and (b) on the nature of the substituents attached to it.

Theoretical Procedure

Our analysis of bonding in these systems is based on results of extended Hückel[5] and ab initio SCF calculations. A few selected calculations were also performed with inclusion of electron correlation using the PNO-CI and CEPA-PNO schemes.[6,7] PNO-CI is a configuration interaction method that includes all configurations which are singly or doubly excited with respect to the SCF determinant ("all" means all configurations that can be constructed within a given basis). Pair natural orbitals (PNO's) are used to reduce the size of the final CI matrix. The CEPA-PNO method[7] corrects for the size inconsistency of the CI method.[8]

The following basis sets were used for the ab initio calculations:

(1) Basis I refers to a minimal GTO basis set for first- and second-row elements as developed by Pople et al.[9]

(2) Basis II consists of Gaussian lobe functions.[10] It is of double-ζ (DZ) quality, constructed from the following Huzinaga[11] bases: N, (7/3) in the contraction (4, 3 × 1/2, 1); P, (9/5) in the contraction (5, 4 × 1/3, 1, 1); H, (2, 1).

(3) Basis III consists of Gaussian lobe functions, DZ quality for the substituents, DZ + *P* (DZ + one set of polarization functions) at the central atoms. The s, p functions were again taken from Huzinaga's tables[11] and the d exponents from Ahlrichs et al.[6] The contraction scheme is as follows: N, (8, 4, 1) in the contraction (5, 3 × 1/3, 1/1), $\zeta_d = 0.95$; P, (10, 6, 1) in the contraction (5, 5 × 1/4, 2 × 1/1), $\zeta_d = 0.5$; Si, (10 , 6, 1) in the contraction (5, 5 × 1/4, 2 × 1/1), $\zeta_d = 0.4$; H, (3, 1).

Calculations of electron correlation effects were only performed with basis III.

Results and Discussion

a. Polarization in Linear Six-Electron Four-Center π Systems. Consider first the π orbitals in *trans*-butadiene. The familiar set deduced from EH calculations is presented in Figure 1. In the case of four electrons occupying the π systems, this causes strong peripheral π bonds and a weak central π bond. Further adding of two electrons into π^*_3

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(1) P. Jutzi, *Chem. Unserer Zeit*, **15**, 149 (1981).

(2) (a) M. Yoshifuji, J. Shima, and N. Inamoto, *J. Am. Chem. Soc.*, **103**, 4587 (1981); **104**, 6167 (1982); (b) B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 691 (1982); (c) G. Bertrand, C. Couret, J. Escudié, S. Majid, and J.-P. Majoral, *Tetrahedron Lett.*, 3567 (1982); (d) A. H. Cowley, J. E. Kilduff, T. H. Newman, and M. Pakulski, *J. Am. Chem. Soc.*, **104**, 5820 (1982); (e) C. Couret, J. Escudié, and J. Satgé, *Tetrahedron Lett.*, 4941 (1982); (f) E. Niecke, R. Rüger, M. Lysek, S. Pohl, and W. W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, **22**, 486 (1983); (g) E. Niecke and R. Rüger, *Angew. Chem., Int. Ed. Engl.*, **22**, 155 (1983).

(3) (a) R. West, M. J. Fink, and J. Michl, *Science (Washington, D.C.)*, **214**, 1343 (1981); M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West, and J. Michl, *J. Chem. Soc., Chem. Commun.*, 1010 (1983); K. W. Zilm, D. M. Grant, J. Michl, M. J. Fink, and R. West, *Organometallics*, **2**, 193 (1983). (b) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. F. Blount, *J. Am. Chem. Soc.*, **104**, 1150 (1982). (c) P. Boudjouk, B.-H. Hand, and K. R. Anderson, *J. Am. Chem. Soc.*, **104**, 4992 (1982). (d) Quantum-mechanical investigations on the parent disilene have been reported L. C. Snyder and Z. R. Wassermann, *J. Am. Chem. Soc.*, **101**, 5222 (1979); R. Daudel, R. E. Kari, R. A. Poirier, J. D. Goddard, and I. G. Csizmadia, *J. Mol. Struct.*, **50**, 115 (1978); R. A. Poirier and J. D. Goddard, *Chem. Phys. Lett.*, **80**, 37 (1981); J. Lischka and H.-J. Koehler, *Chem. Phys. Lett.*, **85**, 467 (1982); T. Fjeldberg, A. Haaland, M. F. Lappert, B. E. R. Schilling, R. Seip, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1408 (1982).

(4) M. Veith, *Acta Crystalogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, **B31**, 678 (1975).

(5) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); The parameters for the extended Hückel calculations were chosen according to H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953); *Chem. Rev.*, **55**, 745 (1955). The Slater exponents were taken from J. C. Slater, *Phys. Rev.*, **36**, 57 (1930). (b) Bonding parameters for **1-3** were obtained from the structural data: for **1**, see ref 2f; for **2**, see Snyder and Wassermann[3d], assuming a planar π system; for **3**, see ref 4. The additional bonding parameters (bond lengths in angstrom units, bond angles in degrees) are estimated to $r_{SiSi} = 2.083$, $r_{SiH} = 1.477$, $r_{SiN} = 1.76$, $r_{NH} = 0.90$, $\angle NSiSi = 122.8$, and $\angle HSiSi = 122.8$.

(6) R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1225 (1975).

(7) W. Meyer, *Int. J. Quantum Chem., Symp.*, **5**, 341 (1971); *J. Chem. Phys.* **58**, 1017 (1973).

(8) For a lucid review on these methods see W. Kutzelnigg in "Modern Theoretical Chemistry", H. F. Schaefer III, Ed., Plenum Press, New York, 1977.

(9) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

(10) The computer program used is described by R. Ahlrichs, *Theor. Chim. Acta*, **33**, 157 (1974); see also ref 6.

(11) S. Huzinaga, "Approximate Atomic Functions. II", Technical Report, The University of Alberta, Edmonton, Alberta, Canada, 1971.

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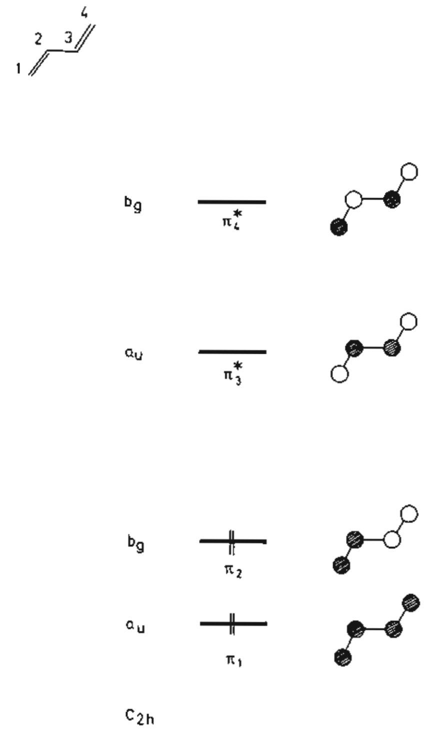


Figure 1. π-orbital system of *trans*-butadiene, deduced from EH calculations. Symmetry designations refer to C_{2h}.

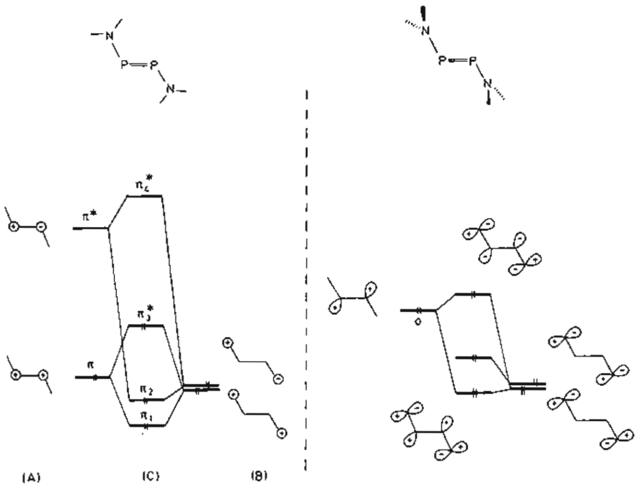
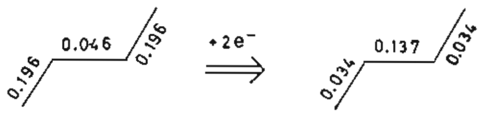


Figure 2. Interaction diagram for the composition of the molecular orbital system of **1** (R = NH_2) from the fragment orbitals of an inner set (A) and outer set (B), leading to a coplanar (left) or bisorthogonal (right) conformation.

introduces antibonding interaction between C(1) and C(2) (C(3) and C(4)) and bonding interaction between C(2) and C(3), as revealed by the Mulliken populations for the corresponding π bonds (obtained from EH calculations):



The π system of **1** (R = NH_2) can be analyzed in more detail in a fragment orbital picture (Figure 2, left). Part A (inner set of fragment orbitals) corresponds to the bonding (π) or antibonding (π*) combination of orbitals at the central bond. Part B (outer set of fragment orbitals) is viewed as two nonbonding p orbitals representing the peripheral amino groups. The interactions between the fragments are as follows: (1) The interaction of the orbital π with the combination $P_{N(1)} + P_{N(4)}$ is a closed-shell, four-electron destabilizing[12] one while (2) the interaction between π* and $P_{N(1)} - P_{N(4)}$ is stabilizing. Concomitant is the polarization[13] of the orbital system. A balance must be struck between repulsion and attraction. Without numerical calculations it is difficult to decide which interaction will dominate.

Table I. Energies for the Various Conformations of 1-3 (R = NH_2) Obtained from EH Calculations[a]

structure	R_1	R_2	E, eV	ΔE, kJ/mol
1	H (p)	H (p)	−439.7163 (−441.2002)	0 (0)
	(p)	(o)	−439.5294 (−441.0585)	18 (14)
	(o)	(o)	−439.3178 (−440.8924)	39 (30)
2	H (p)	H (p)	−428.0364	0
	(p)	(o)	−427.9707	6
	(o)	(o)	−427.9022	13
3	H (p)	H (p)	−475.5645	0
	(p)	(o)	−475.1243	43
	(o)	(o)	−474.4994	103

[a] In parentheses are the values with inclusion of d orbitals (at phosphorus) in the basis set. R_1, R_2 refer to disubstitution at N(1), N(4), and (o) refers to an orthogonal and (p) to a planar conformation of the amino groups (s) with respect to the central π system.

In the next step consider the replacement of the inner set of atoms (part A in Figure 2) by more electronegative (N as in **3**) or more electropositive (Si as in **2**) atoms. This has the consequence that the π (π*) orbitals of A are lowered (raised) in energy. Hence, in the latter case the four-electron destabilization comes to the fore. As will be shown by the numerical calculations this holds for **2** (R = NH_2).

In the bisorthogonal conformation (Figure 2, right) the p orbitals at the amino groups (part B) are locked off the π system. Now they interact ($p_{N(1)} - p_{N(4)}$) via four-electron destabilization with the lone pairs (Si–H bonds in **2**). The repulsion is probably smaller in **2** (Si–H bond orbital) than in **1** or **3** (lone pair).

b. Quantitative Assessment of Rotational Barriers. Our discussion will now be substantiated by numerical calculations. First we present the results of the calculations on the EH (Table I) and on the ab initio level (Table II). Our studies of the various conformations of **1**–**3** (at times R = NH_2) were restricted to orthogonal (o) and/or planar (p) orientation of the p orbitals at the amino groups with respect to the central π system. In our notation (o/o) refers to a bisorthogonal and (p/p) to a coplanar orientation of the amino groups. The CEPA calculations were carried out with the largest basis (basis III) and with inclusion of all doubly excited configurations from localized orbitals, except for the terminal N–H orbitals, which were not correlated.

The various quantum-chemical methods agree in the following aspects: (1) The rotational barriers in parent **1**–**3** (R = NH_2) decrease with increasing difference in electronegativity between the central (N, P, Si) and peripheral (N) atoms. (2) The inclusion of d orbitals in the basis set does not essentially alter this picture. However, as an overall trend the bisorthogonal (o/o) conformation is stabilized slightly more than the coplanar (p/p) one. (3) The inclusion of electron correlation (CEPA and PNO–CI) does not change the SCF results, markedly.

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(12) L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970); R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972).

(13) R. Hoffmann and C. Libit, *J. Am. Chem. Soc.*, **96**, 1370 (1974); W. Kutzelnigg, "Einführung in die Theoretische Chemie", Verlag Chemie, Weinheim, West Germany, 1978.

Table II. Energies for the Planar and Bisorthogonal Conformations of **1**-**3** on the SCF Level with Various Basis Sets and with Inclusion of Configuration Interaction on the CEPA and PNO-CI Levels

			absolute energies, au				
			SCF			CEPA	CI
structure	R_1	R_2	basis I	basis II	basis III	basis III	basis III
1	H (p)	H (p)	−783.4901	−791.8571 (−791.9511)[a]	−792.3167	−792.6083	−792.5711
	(p)	(o)	−783.4836				
	(o)	(o)	−783.4699	−791.8371 (−791.9323)[a]	−792.3007	−792.5917	−792.5541
2	H (p)	H (p)	−681.9882		−689.8593	−690.0880	−690.0638
	(p)	(o)	−681.9922				
	(o)	(o)	−681.9921		−689.8635	−690.0938	−690.0690
3	H (p)	H (p)	−217.0946	−219.6088	−219.8441	−220.2344	−220.2294
	(p)	(o)	−217.0729				
	(o)	(o)	−217.0403	−219.5573	−219.8917	−220.2915	−220.2409

			relative energies, kJ/mol				
			SCF			CEPA	CI
structure	R_1	R_2	basis I	basis II	basis III	basis III	basis III
1	H (p)	H (p)	0	0 (0)	0 (0)	0	0
	(p)	(o)	17 [21][b]				
	(o)	(o)	53 [66]	53 (49)[a]	42	44	45
2	H (p)	H (p)	0		0	0	0
	(p)	(o)	−11				
	(o)	(o)	−10 [−10]		−11	−15	−14
3	H (p)	H (p)	0	0	0	0	0
	(p)	(o)	57				
	(o)	(o)	143 [126]	135	125	150	143

[a] Plus one set of d functions at P ($\zeta = 0.50$). [b] Values in brackets are energy optimized (basis I); see also Table III.

Table III. Bonding Properties of the Various Structures for **1**-**3** ($R = NH_2$)[a]

			atoms				
structure	R_1	R_2	(2)-(3)	(1)-(2)	(3)-(4)	∠(1)(2)(3)	∠(2)(3)(4)
1	H (p)	H (p)	1.977	1.709		99.2	
	(p)	(o)	1.988	1.693	1.729	99.9	99.0
	(o)	(o)	1.982	1.732		99.6	
2	H (p)	H (p)	1.996	1.726		123.1	
	(o)	(o)	1.999	1.718		121.8	
3	H (p)	H (p)	1.279	1.403		108.9	
	(o)	(o)	1.279	1.448		107.8	

[a] Bond lengths are in angstrom units and bond angles in degrees. All structures are optimized with respect to C_s (C_{2h}) symmetry, at the basis I level. The nitrogens at the amino groups are adopted to an sp^2 conformation. For the numbering of atoms see Figure 1.

For **2** ($R = NH_2$) the SCF and CEPA calculations already predict a preference of the (o/o) over the (p/p) conformation, in agreement with the qualitative considerations (section a).

For the calculations with the large basis sets and the EH calculations standard geometries were taken.[5b] In order to prove the validity of this assumption, we have optimized the various geometries of parent **1**-**3** ($R = NH_2$) on the minimal basis level (basis I). The results are summarized in Table III. For all structures the investigations reveal only small changes in the bond lengths and bond angles during the rotation of the amino groups. In **1** and **3** the (peripheral) PN (NN) bonds are elongated and in **2** shortened in the (o/o) conformation, as compared with the lengths in the (p/p) conformation. This confirms the qualitative model of section a. In general the bond lengths obtained on the basis I level are too short compared with those in high-quality ab initio calculations on model systems, e.g. P_2H_2 (trans).[14] Nevertheless, the small changes in the bonding parameters give credit to the calculations with fixed geometries (EH level and basis II and basis III) taken from experiment.[5b]

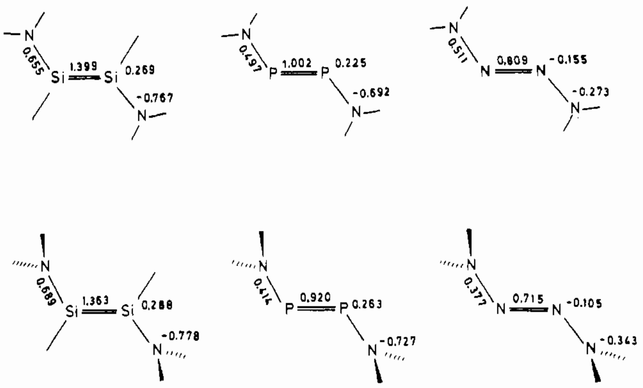

Figure 3. Total Mulliken populations between bonds and at atoms (effective charges) for the structures **1**–**3**, obtained at the ab initio basis III level.

Finally our picture will be completed by an analysis of bonding in the various structures **1**-**3**. The values recorded in Figure 3 correspond to total Mulliken overlap populations

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[14] Previous ab initio calculations of double-ζ quality yield the following values for the PP (double) bond length; (a) 2.004 Å (ref 16a, Table II), (b) 1.996 Å (M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, *J. Am. Chem. Soc.*, **105**, 2495 (1963); J.-G. Lee, A. H. Cowley, and J. E. Boggs, *Inorg. Chim. Acta*, **77**, L61 (1983)). The experimental value is 2.034 Å.[2a,f]

Table IV. EH Calculations for Various Conformations for the Derivatives of **1**

R_1	R_2	ΔE, kJ/mol	ΔE,[a] kJ/mol
H_3C (p)	H (p)	0	0[a]
(o)	(p)	−13	−13
(p)	(o)	18	13
(o)	(o)	9	4
H_3Si (p)	H (p)	0	0
(o)	(p)	−80	−44
(p)	(o)	18	16
(o)	(o)	63	−30
H_3Si (p)	H_3Si (p)	0	0
(o)	(p)	−81	−44
(o)	(o)	−161	−88

[a] Values with inclusions of d orbitals at phosphorus and silicon.

between bonds or effective charges (i.e. total Mulliken overlap populations) at atoms, at times obtained at basis III level. Consider the two extreme cases **2** and **3** (R = NH_2). In **2** the rotation of the two amino groups from the bisorthogonal (o/o) to the coplanar (p/p) conformation causes a decrease in the overlap population (−0.034) between N and Si but an increase (0.036) of bonding between the Si atoms. In contrast, in **3** the in-plane rotation of the amino groups causes an increase of bonding of both types of bonds; **1** reveals an intermediate bonding situation. Further analysis (not recorded here) indicates that the changes in the populations are due to changes in the π system.

c. Competing π-Donor/π-Acceptor Interaction. The good agreement between the one-electron treatment (EH theory) and the SCF (+CI) calculations gives support for further investigations at the EH level. Since detailed quantum-chemical studies of the substituent effects by more elaborate methods (at the double-ζ level) are beyond our computing facilities, the following discussions of the substituent effects will remain qualitative.

Suppose **1** (R = NH_2) adopts a bisorthogonal (o/o) conformation. The lone pairs at the PP double bond suffer then from repulsion of the p orbitals at N. Consider next substituents attached to the nitrogens of the amino gropus, such as methyl or silyl groups. The lone pair at nitrogen will interact via hyperconjugation[12,13] with the π-type orbitals of a methyl (silyl) group. Hence they delocalize the lone pair at nitrogen in the planar as well as the bisorthogonal conformation. The stabilization via π acceptors is larger than the corresponding one in the coplanar conformation, due to the minor repulsion between the PP double-bond π orbital and the p orbitals at the amino groups.

The qualitative considerations are confirmed by EH calculations, presented for substituted **1** in Table IV. Accordingly, silyl groups cause a preference of an orthogonal over a planar conformation of the corresponding amino groups. Again, the results are not substantially altered if d orbitals are included in the basis set at phosphorus and silicon. It must be emphasized that the absolute values for the rotational barriers are not reliably predicted by EH theory, but the qualitative trends are certainly correct.[15]

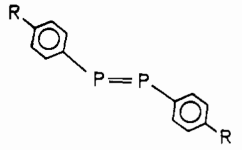
Comparable substituent effects are also obtained for **2**; i.e., methyl or silyl groups change the shape of the rotational barriers in favor of the bisorthogonal conformation. Since the effects are similar to those in **1**, we will not discuss them. In tetrazene **3**, on the other hand, the introduction of methyl (silyl) groups is not sufficient to stabilize the bisorthogonal form (Table V).

Table V. EH Calculations for Various Conformations for the Derivatives of **3**

R_1	R_2	ΔE, kJ/mol	ΔE,[a] kJ/mol
H_3C (p)	H (p)	0	
(p)	(o)	31	
(o)	(p)	65	
(o)	(o)	127	
H_3Si (p)	H (p)	0	0
(o)	(p)	12	19
(p)	(o)	40	45
(o)	(o)	62	70

[a] Values with inclusion of d orbitals at silicon.

The concept we have presented for the substituent effects on diphosphene, disilene, and diimine[16] does hold equally for other systems as well. Consider *trans*-diphenyldiphosphene (**4**, R = H).[2a] A phenyl group possesses an energetically high-lying HOMO and a low-lying LUMO.[13] On the basis of the fragment orbital approach (see section a) π-electron-attracting substituents R (NO_2, etc.) bring the acceptor properties of the phenyl group to the fore and promote a bisorthogonal conformation. The opposite holds true for π-electron donors (NR_2, etc.). These considerations are in agreement with the results of EH calculations (no documented here).



4

Conclusions

The results of our study can be summarized as follows: (1) The systems **1**–**3** represent linear four-center π systems with six electrons. Their orbital system is analogous to butadiene with double occupation of the first antibonding π^*_3 orbital. (2) As a consequence the π-bond orders toward the peripheral atoms are weak, resulting in low energy barriers for rotation. (3) The magnitude of the rotational barriers (planar vs. orthogonal conformations) depends on the electronegativity of the central π-bonding atoms (relative to those of the peripheral atoms). With increasing electropositive character a bisorthogonal over a coplanar conformation is favored, i.e. in the order **3** < **1** < **2**. (4) In case the central atoms are fifth-column elements (P, N), they bear lone pairs that can interact with electron-accepting substituents, promoting a bisorthogonal conformation; this is the case for **1**, R = $N(SiMe_3)_2$.

Our findings rely on EH and ab initio calculations, at a double-ζ level and with inclusion of electron correlation. In principle the structures **1**–**3** have an "electron surplus" in their coplanar conformations; i.e., electrons are filled into antibonding molecular orbitals. In this respect they resemble the cyclic SN compounds, such as S_2N_2.[17] Our considerations hold equally well for substituent effects in other π-bonded systems, such as the recently reported AsAs double bond.[18]

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(15) Our theoretical findings also explain some structural features in aminoiminophosphanes. In the case of silylamino groups the π system is considerably twisted while it is not in the case of alkylamino groups (S. Pohl, *Chem. Ber.*, **112**, 3159 (1979)).

(16) For high-quality ab initio calculations on respectively diphosphene and diimine see (a) W. W. Schoeller and C. Lerch, *Inorg. Chem.*, **22**, 2992 (1983) and (b) R. Ahlrichs and V. Staemmler, *Chem. Phys. Lett.*, **37**, 77 (2976).

(17) Reviews: H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, **18**, 91 (1979); A. J. Banister, *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **3**, 41 (1975); T. Chivers and R. T. Oakley, *Top. Curr. Chem.*, **102**, 117 (1982).

(18) C. Couret, J. Escudié, Y. Madaule, H. Ranaivonjatovo, and J.-G. Wolf, *Tetrahedron Lett.*, 2769 (1983).

Registry No. 1 ($R_1 = R_2 = NH_2$), 91759-18-1; 1 ($R_1 = R_2 = NHMe$), 91759-21-6; 1 ($R_1 = R_2 = NHSiH_3$), 91759-22-7; 1 ($R_1 = R_2 = N(SiH_3)_2$), 91759-23-8; 2 ($R_1 = R_2 = NH_2$), 91759-19-2; 2 ($R_1 = R_2 = NHMe$), 91759-26-1; 2 ($R_1 = R_2 = NHSiH_3$), 91759-27-2; 3 ($R_1 = R_2 = NH_2$), 91759-20-5; 3 ($R_1 = R_2 = NHMe$), 91759-24-9; 3 ($R_1 = R_2 = NHSiH_3$), 91759-25-0; 4 (R = H), 91759-28-3; 4 ($R = NO_2$), 91759-29-4; *trans*-1,3-butadiene, 106-99-0; *trans*-1,3-butadiene dianion, 63365-91-3.

Contribution from the Department of Chemistry and Ames Laboratory—DOE, Iowa State University, Ames, Iowa 50011,
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Stereoelectronic Effects of Cyclization in Aminophosphine Systems: Structural, PES, and NMR Study of $Me_2NP(OCH_2)_2CMe_2$ and $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$

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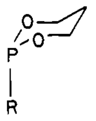
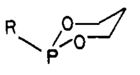
X-ray diffraction and NMR and PE spectral evidence is presented for equatorial R_2N groups in the solid, solution, and gas phases of the title 1,3,2-dioxaphosphorinanes (**1** and **2**, respectively). This contrasts with the behavior of MeO-substituted analogues wherein the MeO substituent strongly prefers the axial position:[5b] In the solid state, **1** (a = 6.542 (1) Å, b = 11.731 (3) Å, c = 6.440 (2) Å, α = 101.53 (4)°, β = 83.52 (3)°, γ = 90.96 (3)°, triclinic, Z = 2) and **2** (a = 8.464 (1) Å, b = 9.868 (2) Å, c = 27.832 (2) Å, $\alpha = \beta = \gamma$ = 90°, orthorhombic, *Pbna*, Z = 8) display a planar stereochemistry about the nitrogen with the plane nearly containing the P-lone pair axis. The structural parameters are also consistent with substantial $N \rightarrow P$ π bonding. Perhaps because of overlap of the IE_N and IE_p lone-pair bands in **1**, **2**, and $Me_2NP(OCH_2)_2CH_2$ (**7**),[23] the conclusion based on a rough comparison of the IE_p data that these compounds are more basic than $Me_2NP(OMe)_2$[21a] is rendered tentative. Support for this conclusion can, however, be found in a comparison of $^1J_{PSe}$ values for $Me_2NP(OMe)_2$ and a conformationally rigid selenide analogue of **1**. The validity of comparing trends in IE_p data on classes of trivalent phosphorus compounds with those in $^1J_{PSe}$ values of their selenide derivatives is verified by showing that these parameters yield a linear correlation in the case of phosphite esters and their selenophosphate derivatives.

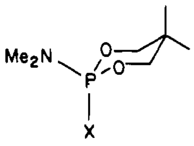
Introduction

The molecular structures of aminophosphorus compounds continue to be interesting because of the variety of bond angles around nitrogen that they display,[2] the controversies regarding the preferred conformation of the NR_2 groups in molecules such as $P(NMe_2)_3$[2] and $R_2N\overline{PNMeCH_2CH_2N}Me$,[3] and the influences of these stereochemical effects on electronic properties such as the basicity of phosphorus.[2,4] Owing to a lack of crystallinity, solid-state structural information on aminophosphorus compounds in which phosphorus is trivalent is currently small compared to that for cognates which incorporate four-coordinate phosphorus. Constraints imposed on P(III) substituents that are linked to form five-or six-membered rings generally lead to substantial changes in phosphorus basicity.[5] Moreover, the exocyclic group in six-membered ring systems of the type

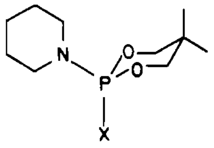




may adopt the axial position for electronic reasons or the equatorial location for primarily steric causes[6,7] The above considerations and the observation that **1** and **2** are crystalline

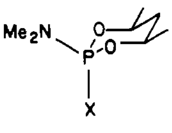


1: X = lone pair
1a: X = Se

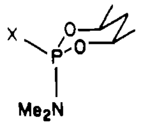


2: X = lone pair
2a: X = Se

led us to investigate the molecular structures of these compounds by X-ray diffraction, their photoelectron spectral properties, and the $^1J_{PSe}$ spin-spin couplings of their corresponding selenides **1a** and **2a**. We present evidence that both **1** and **2** prefer the conformations shown in the solid, solution, and gaseous states, that the nitrogens are nearly planar in the solid state, and that the phosphorus atoms in the solution and gas phases are more basic than that of the acyclic analogue $Me_2NP(OMe)_2$. Of aid in these studies were the ^{31}P NMR spectra of the conformationally rigid **3** and **4**[8] and their selenide derivatives **3a** and **4a**, which served as model compounds for comparison.



3: X = lone pair
3a: X = Se



4: X = lone pair
4a: X = Se

Experimental Section

Preparations. Compound **1** and **2** were prepared by following a previous report[9] and were purified by repeated sublimation under

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[1] (a) Department of Chemistry, Iowa State University. (b) Ames Laboratory—DOE, Iowa State University. (c) Department of Chemistry, University of Texas at Austin.

[2] (a) Cowley, A. H.; Lattman, M.; Stricklen, P. M.; Verkade, J. G. *Inorg. Chem.* **1982**, *21*, 543. See also: (b) Gonbeau, D.; Sanchez, M.; Pfister-Guillouzo, G. *Ibid.* **1981**, *20*, 1966.

[3] Worley, S. D.; Hargis, J. H.; Chang, L.; Mattson, G. A.; Jennings, W. B. *Inorg. Chem.* **1979**, *18*, 3581.

[4] (a) Kroshefsky, R. D.; Weiss, R.; Verkade, J. G. *Inorg. Chem.* **1979**, *18*, 469. (b) Kroshefsky, R. D.; Verkade, J. G.; Pipal, J. R. *Phosphorus Sulfur* **1979**, *6*, 377. (c) Kroshefsky, R. D.; Verkade, J. G. *Phosphorus Sulfur* **1979**, *6*, 391.

[5] (a) Vande Griend, L. J.; Verkade, J. G.; Pennings, J. F. M.; Buck, H. M. *J. Am. Chem. Soc.* **1977**, *99*, 2459. (b) Hodges, R. V.; Houle, F. A.; Beauchamp, J. L.; Montag, R. A.; Verkade, J. G. *J. Am. Soc.* **1980**, *102*, 932. (c) Lee, T. H.; Jolly, W. L.; Bakke, A. A.; Weiss, R.; Verkade, J. G. *J. Am. Chem. Soc.* **1980**, *102*, 2631.

[6] Verkade, J. G. *Phosphorus Sulfur* **1976**, *2*, 251.

[7] Maryanoff, B. E.; Hutchins, R. O.; Maryanoff, C. A. *Top. Stereochem.* **1979**, *11*, 187.

[8] Mosbo, J. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 4659.

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