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σ-Electrons in Silanes and Phosphanes: Geminal Bond Interaction, Angle Strain, and Delocalizability

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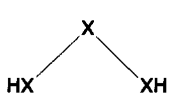
Abstract: Bond-to-bond delocalization of σ-electrons in silanes and phosphanes was analyzed. σ-Electrons in the Si–Si and P–P bonds were numerically shown to delocalize more than those in the C–C bonds and less than π-electrons in C=C bonds. The delocalization between the geminal bonds is antibonding as was previously reported for the C–C bonds. As the bond angle is acute, the antibonding property increases in the silanes and decreases in the phosphanes. This implies that the three-membered ring is more strained in the silanes and less strained in the phosphanes. The concept of antibonding delocalization was substantiated. The correlation between the antibonding property of the geminal delocalization and angle strain was confirmed.

Introduction

We have been studying delocalization of σ-electrons from bonds to bonds.[1,2] An interesting result is the conformational dependence of the delocalization between geminal bonds.[1] The geminal delocalization contributes as significantly as the vicinal delocalization to the stereoelectronic effects including the anomeric[3] and gauche[4] effects. Furthermore, delocalization has been found to be antibonding between geminal C–C bonds,[2] in sharp contrast to the preceding belief that delocalization accumulates bonding electrons in the interaction regions. The antibonding delocalization is depressed as the bond angle is acute.[2] The attenuated antibonding property was proposed[2] to relax the angle strain of cyclopropane. Thus, the theoretical studies of the bond-to-bond delocalization of σ-electrons have given new insight into molecular properties of the first-row element compounds.

In this paper, we investigate properties of σ-electrons in the silanes and phosphanes **1**–**3**-SiH_2, **1**–**3**-PH, **4**-SiH, and **4**-P,



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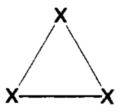

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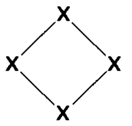

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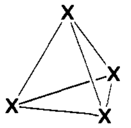

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including interactions between geminal σ-bonds, angle strains, and delocalizabilities of σ-electrons. Our attention is focused especially on the antibonding property of the geminal delocalization and its effects on angle strain. The new findings in the previous work[2] may be fundamental but were based solely on the C–C bonds in the alkane and the strain of cyclopropane. Its generality remains to be confirmed by other chemical phenomena.

The silanes and the phosphanes are suitable for the present purpose since the three-membered ring is more strained in the silanes and less strained in the phosphanes, compared with the alkanes. A number of papers dealing with strain in cyclosilane rings have appeared.[5–9] George et al.[10] proposed to regard the reaction energy of homodesmotic rather than isodesmic reactions as ring strain energy. The estimated values (37.5–40.3,[5] 39–41,[6] 38.9,[7] and 36[8] kcal/mol) for the three-membered ring silane **2**-SiH_2 are by nearly 10 kcal/mol greater than the strain energy (27.5 kcal/mol)[11] of the cycloalkane **2**-CH_2. Cyclophosphanes have been studied both theoretically and experimentally.[12–19] Baulder et al.[13] investigated the equilibrium of the permethyl derivatives of the three-, four-, and five-membered cyclophosphanes, and estimated the strain energies on the assumption that there is no strain in the P_5 ring. The strain energy of the three-membered ring **2**-PCH_3 is very low (7.8 kcal/mol). The calculated value of **2**-PH from the homodesmotic reaction is similarly small (6.7 kcal/mol).[14] For P_4, the strain energy has been estimated to be 21.7–24.6 kcal/mol.[15] This is much lower than the calculated value of tetrahedrane (140–150 kcal/mol).[20]

Method

The methods of the calculations and analysis employed here have been described in the previous paper.[2] Electronic structures of molecules were calculated by ab initio molecular orbital methods. The Slater determinant for the electronic structures was expanded into various electron configurations:

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(1) Inagaki, S.; Iwase, K.; Mori, Y. *Chem. Lett.* **1986**, 417. Inagaki, S.; Mori, Y.; Goto, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1098.

(2) Inagaki, S.; Goto, N.; Yoshikawa, K. *J. Am. Chem. Soc.* **1991**, *113*, 7144.

(3) Lemieux, R. U.; Koto, S. *Tetrahedron* **1974**, *30*, 1933. Szarek, W. A.; Horton, D. *ACS Symp. Ser.* **1979**, No. 87. Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983. Gorenstein, D. G. *Chem. Rev.* **1987**, *87*, 1047.

(4) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102 and references cited therein.

(5) Schleyer, P. v. R. *NATO ASI, Ser. C* **1986**, *189*, 69. Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364.

(6) Sax, A. F. *Chem. Phys. Lett.* **1986**, *127*, 163; *129*, 66.

(7) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60.

(8) Grev, R. S.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 6569.

(9) Schoeller, W. W.; Dabisch, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1706; *Inorg. Chem.* **1987**, *26*, 1081.

(10) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(11) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

(12) Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 492 and references cited therein.

(13) Baudler, M.; Hahn, J.; Clef, E. *Z. Naturforsch.* **1984**, *39b*, 438.

(14) Schiffer, H.; Ahlrichs, R.; Häser, M. *Theor. Chim. Acta* **1989**, *75*, 1.

(15) Pauling, L.; Simonetta, M. *J. Chem. Phys.* **1952**, *20*, 29.

(16) Ahlrichs, R.; Brode, S.; Ehrhardt, C. *J. Am. Chem. Soc.* **1985**, *107*, 7260.

(17) Schoeller, W. W.; Staemmler, V.; Rademacher, P.; Niecke, E. *Inorg. Chem.* **1986**, *25*, 4382.

(18) Yoshifuji, M.; Inamoto, N.; Ito, K.; Nagase, S. *Chem. Lett.* **1985**, 437.

(19) Gleiter, R.; Böhm, M. C.; Baudler, M. *Chem. Ber.* **1981**, *114*, 1004.

(20) (a) Baird, N. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1967**, *89*, 3966. (b) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. (c) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.

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$$\Psi = C_G\Phi_G + \sum_T C_T\Phi_T \qquad (1)$$

In the ground configuration G (Figure 1), a pair of electrons occupy a bonding orbital of a bond or a nonbonding orbital of a lone pair. The bond orbitals are expressed by linear combinations of hybrid orbitals on bonded atoms. The bond orbitals and the lone-pair orbitals were optimized in order to represent the electronic structure of molecules by G as much as possible.[2] The electron delocalizability or the extent of electron delocalization from bonds to bonds was estimated by the coefficient ratio C_T/C_G,[21] where T denotes the electron-transferred configuration. The bonding–antibonding properties of the interactions between the *i*- and *j*th bond orbitals were estimated by the interbond population IBP_{ij}:[2]

$$\mathrm{IBP}_{ij} = 2\sum_p n_p c_{pi} c_{pj} s_{ij} \qquad (2)$$

where n_p is the occupation number of the *p*th molecular orbital, c_{pi} being the expansion coefficient of the *i*th bond orbital for the *p*th MO. The delocalization was estimated by the interbond population $\mathrm{IBP}_{\sigma\sigma^*}$ between bonding and antibonding orbitals. The overlap repulsion was similarly estimated by $\mathrm{IBP}_{\sigma\sigma}$ between the bonding orbitals. In the analysis of the bond-to-bond delocalization of electrons, we used the STO-3G basis set which enabled us to define the hybrid atomic orbitals and the bonding and antibonding orbitals of clear chemical image.

We employed the molecular geometries optimized by ab initio molecular orbital calculations with the Hartree–Fock method using the 6-31G* basis set. The experimentally determined structures of the silanes are limited to disilane[22] and the highly substituted derivatives of the three- and four-membered ring molecules.[23] The 6-31G* Si–Si bond length (2.35 Å)[7] of disilane is one of the calculated values[8,9] close to the experimental result (2.33 Å).[22] The calculated P–P bond length (2.214 Å)[24] of diphosphane $PH_2–PH_2$ is similarly in good agreement with the observed value (2.219 Å).[25] The 6-31G* geometries of **2**–**4**-SiH_2 have been reported by Nagase et al.[7] The geometry of **4**-P was reported by Raghavachari et al.[26] We optimized the other geometries of **1**–**3**-PH using the GAUSSIAN 82 program.[27]

Results and Discussion

The results are summarized in Table I. The interaction between the bonding orbitals is repulsive since both orbitals are occupied by two electrons. The repulsion between the geminal bonds should be one of the primary causes of the angle strain. As the bond angle decreases, the orbital overlap and, consequently, the antibonding property between the geminal bonds increase. This was confirmed by the calculated $\mathrm{IBP}_{\sigma\sigma}$ values. The antibonding property is overwhelmingly high in the three-membered ring **2**, and higher in the four-membered ring **3** than in the open-chain molecule **1**.

The repulsive interaction between the occupied bonding orbitals is weak in both the silanes and the phosphanes, relative to that in the alkanes. This is compatible with the low strain of the three-membered ring phosphane **2**-PH, but incompatible with the high strain of the silane **2**-SiH_2. We previously[2] failed to explain the comparable strain energies of **2** and **3**-CH_2 in terms of the repulsion. The unexpectedly low strain of **2**-CH_2 was then proposed[2] to come from the geminal delocalization between C–C bonds. The delocalization was surprisingly antibonding. The antibonding property in **2**-CH_2 is lower than that in the open-chain unstrained propane **1**-CH_2, while the delocalization in **3**-CH_2 is as antibonding as the latter.

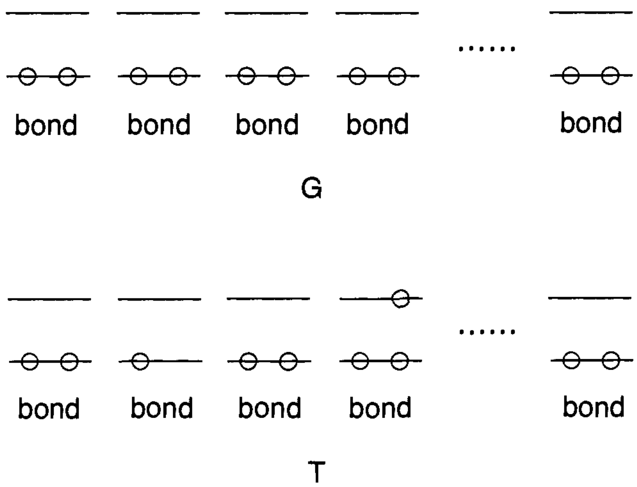

Figure 1. Electron configurations for analysis of bond-to-bond delocalization of electrons.

Table I. Electronic Structures of the Silanes and Phosphanes **1**–**4**

	HO[a]	C_T/C_G[b]	$\mathrm{IBP}_{\sigma\sigma^*}$[c]	$\mathrm{IBP}_{\sigma\sigma}$[d]
1-SiH_2	$sp^{2.8}$	0.109	–0.006	–0.004
2-SiH_2	$sp^{3.6}$	0.077	–0.021	–0.087
3-SiH_2	$sp^{3.2}$	0.107	–0.013	–0.024
4-SiH	$sp^{3.6}$	0.094	–0.022	–0.061
1-PH	$sp^{7.2}$	0.096	–0.005	–0.002
2-PH	$sp^{14.3}$	0.005–0.010	0.002–0.003	–0.058
3-PH	$sp^{9.6}$	0.077	–0.007	–0.013
4-P	$sp^{19.1}$	0.002	0.001	–0.047
1-CH_2[e]	$sp^{2.9}$	0.054	–0.011	–0.022
2-CH_2[e]	$sp^{4.1}$	0.011	–0.002	–0.128
3-CH_2[e]	$sp^{3.4}$	0.055	–0.016	–0.044
4-CH	$sp^{4.5}$	0.029	–0.011	–0.105

[a] Hybrid orbital for the X–X bond. [b] Absolute value of coefficient ratio of electron-transferred configuration to the ground configuration indicating the electron delocalizability. [c] Interbond population between geminal bonding and antibonding orbitals. [d] Interbond population between geminal bonding orbitals. [e] Reference 2.

The proposed importance of the geminal delocalization was here found to be successfully applied to tetrahedrane **4**-CH. The geminal delocalization ($\mathrm{IBP}_{\sigma\sigma^*} = -0.011$) is as antibonding as in **1**-CH_2 (–0.011). The strain relaxation is not anticipated. This is consistent with the calculated high strain energy (140–150 kcal/mol),[20] which is greater by 30–40 kcal/mol than four times that of **2**-CH_2. We discuss the high strain of the three-membered ring silane and the low strain of the phosphane ring in terms of the geminal delocalization in the following.

Cyclopolysilanes. The antibonding property of the geminal delocalization is low in the unstrained trisialane **1**-SiH_2 (–0.006), but is enhanced in the three-membered ring cyclotrisilane **2**-SiH_2 (–0.021). This forms striking contrast with the alkanes, where the antibonding property is attenuated in cyclopropane.[2] The delocalization rather imposes than relaxes the strain in the three-membered ring silane. In fact, the strain energies of **2**-SiH_2 (37.5–40.3,[5] 39–41,[6] 38.9,[7] and 36 kcal/mol[8]) calculated from the homodesmotic reactions are by nearly 10 kcal/mol greater than that of cyclopropane.

Furthermore, the antibonding property in **2**-SiH_2 is remarkably greater than that in the four-membered ring **3**-SiH_2 (–0.013), while the relative magnitudes are reverse in the alkanes. The delocalization should enlarge the difference in the strain energy between **2** and **3**-SiH_2. The three-membered ring is remarkably (by 20 kcal/mol or more) more strained from the four-membered ring (12.9–18.9,[5] 16.7,[7] 17–18,[6] and 16[8] kcal/mol) in the silanes.

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[21] Inagaki, S.; Kawata, H.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3724.

[22] Beagley, B.; Conrad, A. R.; Freeman, J. M.; Monaghan, J. J.; Norton, B. G.; Holywell, G. C. *J. Mol. Struct.* **1972**, *11*, 371.

[23] Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. Chen, Y.-S.; Gaspar, P. P. *Organometallics* **1982**, *1*, 1410. Kratky, C.; Schuster, H. G.; Hengge, E. *J. Organomet. Chem.* **1983**, *247*, 253. Schäfer, A.; Weidenbruch, M.; Peters K. von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302. Dewan, J. C.; Murakami, S.; Snow, J. T.; Collins, S.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1985**, 892. Matsumoto, H.; Minemura, M.; Takatsuna, K.; Nagai, Y.; Goto, M. *Chem. Lett.* **1985**, 1005.

[24] Sen, K. D.; Ohta, K.; Morokuma, K. *J. Mol. Struct.* **1984**, *109*, 287.

[25] Kuczkowski, R. L.; Schiller, H. W.; Rudolph, R. W. *Inorg. Chem.* **1971**, *10*, 2505. Durig, J. R.; Carreira, L. A.; Odom, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 2688.

[26] Raghavachari, K.; Haddon, R. C. *Chem. Phys. Lett.* **1985**, *122*, 219.

[27] Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. *GAUSSIAN 82*; Carnegie-Mellon University: Pittsburgh, PA, 1982.

For the alkanes, there is no appreciable difference (nearly 1 kcal/mol) in the strain energies between the three- and four-membered rings (27.5 and 26.5 kcal/mol, respectively).[11]

The antibonding property of the geminal delocalization remarkably increases from the unstrained silane **1**-SiH$_2$ (–0.006) to tetrasilatetrahedrane **4**-SiH (–0.022). The antibonding property in **4**-SiH is comparable to that of the three-membered ring silane **2**-SiH$_2$ (–0.021) of high strain energy. This is consistent with the high strain energy (140.9 kcal/mol) of **4**-SiH.[7]

Cyclopolyphosphanes. The antibonding property of the geminal delocalization is low (–0.005) in triphosphane **1**-PH. In this aspect, σ-electrons in the P–P bonds behave as in the Si–Si bonds. For acute bond angles, the P–P bonds are different from the Si–Si bonds. In the three-membered rings of cyclotriphosphane **2**-PH and tetraphosphatetrahedrane **4**-P, the delocalization is slightly bonding, while strongly antibonding for the corresponding silanes and still antibonding for the alkanes. The angle strain of **2**-PH and **4**-P should be appreciably relaxed by the bonding property of the geminal delocalization. The strain energy of the three-membered ring **2**-PCH$_3$ is very low (7.8 kcal/mol)[13] relative to that of cyclopropane (27.5 kcal/mol).[11] For P$_4$, the strain energy (21.7–24.6 kcal/mol)[15] is much lower than the calculated values of tetrahedrane (140–150 kcal/mol).[20]

In the four-membered ring phosphane, the antibonding property of the geminal delocalization is comparable to the open-chain structure. The angle strain relaxation due to the geminal delocalization is not expected for the four-membered ring. In fact, the four-membered ring has been found to be strained (observed, 6.0 kcal/mol for **3**-PCH$_3$;[13] calculated, 4.3 kcal/mol for **3**-PH[14]) as much as the three-membered ring, in spite of a wider P–P bond angle. This feature has been observed for the hydrocarbons,[2] but not for the silanes.

Ring-Strain Theories

Successful application to ring strains of cyclopolysilanes and cyclopolyphosphanes substantiated the new concept of antibonding delocalization between geminal σ-bonds and its close relation to angle strain proposed in a previous paper.[2] Various components of ring strain have been presented so far, e.g., bond angle deformation, orbital hybridization, torsional effects, 1,3-nonbonded repulsion, σ-aromaticity, bond dissociation energy, and so on.[5,28] Schleyer[5] proposed that angle deformation effects dominate in silicon rings. Our theory shows a new aspect of angle strain, but neither supports nor rules out the other existing theories except for σ-aromaticity.[29] The C_T/C_G values show that electrons delocalize to a greater extent in the silicon three-membered ring (0.077) than the phosphorus one (0.005–0.010). Assuming that the electron delocalization is an indispensable feature of the aromaticity as has been believed, the remarkable difference in the electron delocalizability should be regarded as higher aromaticity or strain relaxation of the silicon ring relative to the phosphorus one. However, this is inconsistent with high strain of the silicon ring relative to the phosphorus ring. The bonding–antibonding properties as well as the extent of the delocalization should be taken into account, as described above and in the previous arguments[2] against the σ-aromaticity in cyclopropane.

σ-Electron Delocalizabilities

While delocalization of π-electrons has been one of the main subjects in organic chemistry and studied extensively, little has been known about σ-electron delocalization. However, there are some fields of chemistry where delocalizability of σ-electrons plays an important role. In polysilane chemistry, one striking feature is the observation that many of their properties, e.g., photoionization and UV spectra, can be interpreted by assuming the high delocalizability of the Si–Si σ-electrons,[30] just like π-electrons in hydrocarbons. The present method of the analysis provide us with quantitative information about the delocalizabilities of σ-electrons between the geminal X–X (X = C, Si, P) bonds. The absolute C_T/C_G values indicated that σ-electrons in the Si–Si (0.109) and P–P (0.096) bonds delocalize more than in the C–C bonds (0.055). In passing, the delocalizability (0.138) of π-electrons in butadiene is a little higher.

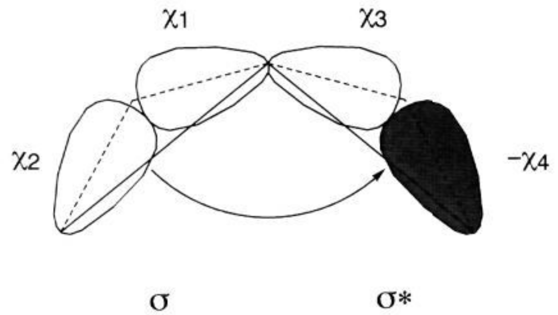

Figure 2. Notation of the hybrid and bond orbitals involved in the geminal delocalization.

Bonding–Antibonding Properties of Geminal Delocalization

The three-membered ring silane is highly strained. Cyclotriphosphane is less strained. These features have been shown to be in agreement with the bonding–antibonding property of the geminal delocalization. The antibonding property of the silane is remarkably high in the three-membered ring. In the phosphanes, the geminal delocalization is not antibonding but bonding. We discuss the striking contrast in the following.

The resonance integral for the geminal delocalization or between the bonding and antibonding orbitals of the geminal bonds is decomposed into the hybrid orbital term: $h_{\sigma\sigma^*} = cc^*(h_{13} - h_{14} + h_{23} - h_{24})$ (see Figure 2), where c and c^* are the coefficients of the hybrid orbitals in the bonding and antibonding orbitals, respectively. Since h_{14} and h_{23} are identical $(-h_{14} + h_{23} = 0)$, $h_{\sigma\sigma^*} = (h_{13} - h_{24})$. We previously[2] proposed that the nonzero value of h_{13}, in spite of $s_{13} = 0$, is responsible for the antibonding delocalization. The antibonding property increases with the relative weight (h_{13}/h_{24}). The s-character of the hybrid orbitals is high (22%) in the three-membered silane and low (7%) in the phosphanes. The resonance integral h_{13} comes mainly from the s-components of the hybrid orbitals. For the pure orbitals, $h_{13} = 0$. The value h_{13}/h_{24} is great in the silane and small in the phosphanes. The high antibonding property results in the silane, while the geminal delocalization is bonding in the phosphanes.

Conclusion

Investigations of bond-to-bond delocalization of σ-electrons[1,2] has given new insight into electronic structures of molecules. In a previous paper,[2] we proposed that the delocalization of σ-electrons is antibonding between the geminal C–C bonds, and that the antibonding property reduced for acute bond angles should account for the well-known but unexpectedly low angle strain of cyclopropane. Similar analysis and hypothesis were here applied to σ-electrons in the silanes and phosphanes: **1–3**-SiH$_2$, **1–3**-PH, **4**-SiH and **4**-P. The high strain of cyclotrisilane **2**-SiH$_2$ and the low strain of cyclotriphosphane **2**-PH were shown to be attributable to the highly antibonding and bonding properties of the geminal delocalization, respectively. The present study substantiated the concept of antibonding delocalization, and con-

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(28) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

(29) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669. Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

(30) *Homoatomic Rings, Chains and Macromolecules of Main Group Elements*; Rheingold, A. L., Ed.; Elsevier Scientific Publishing Co.: New York, 1977.

firmed the significance of the geminal delocalization in the angle strains proposed previously.

The present study neither supports nor rules out most of the other existing ring strain theories, e.g., bond angle deformation, orbital hybridization, torsional strain, 1,3-nonbonded repulsion, and bond dissociation energy.[5,28] However, the concept of the σ-aromaticity,[29] originally proposed for the stability of cyclopropane, cannot accommodate the high strain of cyclotrisilane and the low strain of cyclotriphosphane. The analysis of the bond-to-bond delocalization of σ-electrons showed high electron delocalizability in the three-membered silicon ring relative to that in the phosphorus ring. Electrons are numerically shown to delocalize more in unstrained silanes and phosphanes than in alkanes, as expected.

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