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Two Geminal Delocalizations Affect the Structural Preference of Disilyne and Its Derivatives

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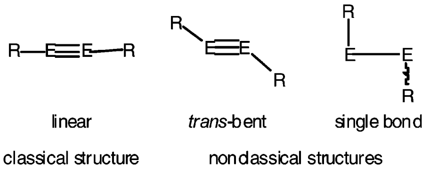
Effects of geminal and vicinal delocalization (hyperconjugative interactions) on the structures of disilyne (HSi≡SiH) and its derivatives were investigated by deleting those hyperconjugative interactions in density functional theory (DFT) calculations. It is concluded that the hyperconjugative interactions are effective for the structural preference of disilyne, and that geminal delocalization are dominant. We found that two geminal delocalizations affect the structural preference of disilyne and its derivatives. One gives trans bending structure and the other gives single bond type structure. Although the status of natural bond orbitals (NBO) and the NBO scheme used for the deletion of hyperconjugative interaction is unclear in general, our present conclusion is true within the NBO method.

Introduction

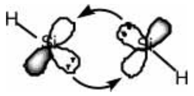
In the chemistry of heavy group analogues of alkyne, the success in the isolation of RPbPbR (R = C_6H_3−2,6-$Trip_2$; Trip = C_6H_2−2,4,6-iPr_3) by Power and co-workers in 2000 represents a breakthrough.[1] The observed geometry has a rather long Pb−Pb interatomic distance (3.188 Å) and a small C−Pb−Pb angle (94.26°). The long Pb−Pb distance and approximately 90° C−Pb−Pb angle is much different from a classical linear structure and from a well-known trans bending structure.[2] The observation indicates that two nonclassical structures are possible for the heavy group analogues of alkyne (Scheme 1). Power and co-workers have proposed, using Pauling's proposed correlation between bond angle and hybridization,[3] that the observed structure of RPbPbR has only a Pb−Pb single bond.[1] The observed unusual geometry of RPbPbR has prompted theoretical chemists to investigate the bonding nature.[4]

The silicon analogue of alkyne, disilyne (RSiSiR), has recently become the focus of interest as targets of synthesis in the silicon chemistry. Despite numerous attempts, methods for obtaining stable disilynes have yet to be developed, with the exception of transient capture.[5] To clarify the interactions leading the two nonclassical structures, trans-bent and single bond type, would give a cue to getting over the difficulty in the synthesis of stable silicon analogues of alkyne. Equilibrium structure of nonsubstituted disilyne is trans bending,[2] and single-bond structure was not found as a minimum of disilyne and its derivatives. A donor−acceptor bonding model has well explained the trans-bent structure same as disilene.[6] The donor−acceptor bonding model is that a triple bond weakened by distortion from a classical linear structure is stabilized by the delocalization of the n_σ lone electron pair of one SiH into the empty p_π* atomic orbital of its partner in a valence bond scheme (Scheme 2). Explaining the donor−acceptor bonding model in a molecular orbital scheme, the distorted structure is stabilized by $\sigma-\pi$ mixing, that is, geminal delocalization (Scheme 3). Despite many examples of vicinal delocalization controlling the preferred structure, examples of geminal delocalization affecting the preferred structure are scarce.[7]

SCHEME 1. Possible Structures of Alkyne and Its Analogues, REER (E = C, Si, Ge, Sn, Pb)



SCHEME 2. Valence Bond Scheme of Donor−Acceptor Bonding Model for Disilyne



Three principal physical factors—exchange, electrostatic, and hyperconjugative interactions—underlie the structural preference. Both hyperconjugation and exchange repulsion are quantum mechanical effects arising from orbital overlap. Hyperconjugation involves electron transfer from an occupied to an unoccupied orbital, leading to the delocalization of charge. In this sense, in the present paper, we use geminal and vicinal hyperconjugations as the synonyms of geminal and vicinal delocalization. Exchange repulsion involves the Pauli exclusion principle, which requires that pairs of electrons do not occupy the same spatial region. In contrast to these two interactions, electrostatic interaction involves classical 1/R repulsion between charges.

In the course of our theoretical study on the structure and stability of unsaturated silicon compounds,[8] we report here the role of geminal and vicinal delocalization (hyperconjugation) in the structural preference of disilyne and its derivatives. In this study, we find two geminal hyperconjugative interactions affecting the structure of disilyne and its derivatives: one gives a trans bending structure and the other gives a single bond type

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SCHEME 3. Molecular Orbital Scheme of Donor−Acceptor Bonding Model for Disilyne

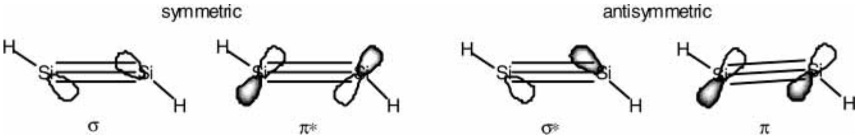


TABLE 1: Destabilization Energy Δ*E* upon Removing the Hyperconjugative Interactions[a]

compound	deletion of hyperconjugation	ΔE^b/kcal mol^{-1}
disilyne	all	89.7
	vicinal	4.9
	geminal	96.5
disilene	all	53.6
	vicinal	8.9
	geminal	49.6
ethylene	all	67.3
	vicinal	56.0
	geminal	24.3
acetylene	all	50.5
	vicinal	38.7
	geminal	23.8

[a] Energies were obtained for the structures optimized at the B3LYP/6-311++G(3df,3pd) without deleting any hyperconjugative interactions. [b] ΔE = (total energy with the deletion of hyperconjugative interactions) − (total energy without the deletion).

structure (Scheme 1). The trans bending structure is well known as an equilibrium structure of disilyne, but the single bond type structure has not been previously reported for disilyne and its derivatives.

Methods and Calculations

Ab initio MO calculations[9a] were performed using the Gaussian 98 software package.[9b] Geometry optimizations were carried out at the B3LYP/6-311++G(3df,3pd) level. In our preceding report on Si−Si double-bond systems,[10] excellent results were obtained using both MP2 and B3LYP.[11] For the calculations of second-row species, the use of basis sets including high-exponent d and f functions was recommended to obtain a reliable geometry,[12] and thus we used 6-311++G-(3df,3pd) basis sets. Effects of hyperconjugative interactions were investigated using calculations with and without selected antibonds in the natural bond orbitals (NBOs).[13]

Results and Discussion

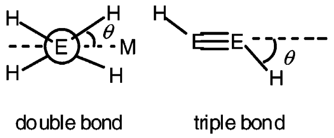
We investigate first whether hyperconjugative interaction controls the structural preference of disilyne. The destabilization energies upon removing the hyperconjugative interactions are given in Table 1. Although hyperconjugative interactions contribute to the stability in any case, we are interested in the effects on the structural preference among linear, trans-bent, and single bond type structures. Pophristic and Goodman have reported that hyperconjugation is dominant in the structural preference of ethane[14] but is not in the structural preference of the silicon analogue, disilane,[15] based on the precise investigation of hyperconjugative, exchange, and electrostatic interactions. Whether hyperconjugative interaction is dominant or not in structural preferences can be monitored by the deletion of all hyperconjugative interactions: the conformation of ethane changes from staggered to eclipsed upon the deletion of all hyperconjugative interactions,[14] while conformational change does not occur upon deleting all hyperconjugative interactions of disilane.[15] In Table 2, the optimized structure of disilyne with deleting all hyperconjugative interactions is shown. For comparison, the results for disilene, ethylene, and acetylene are listed in the table. With full optimization (no deletion), ethylene and acetylene adopt a planar and a linear structure, respectively, whereas disilene and disilyne take trans-bent ones. Structural change occurs for disilene and disilyne upon the deletion of all hyperconjugative interactions: deletion of all hyperconjugative interactions leads to a planar structure of disilene and a linear structure of disilyne. In contrast, the planar structure of ethylene and the linear structure of acetylene are retained after the deletion of all hyperconjugative interactions. It is concluded that hyperconjugative interactions play a dominant role for the nonclassical trans bending structures of disilene and disilyne, in contrast to those of ethylene and acetylene.

TABLE 2: Optimized Geometries with Deleting All Hyperconjugative Interactions[a]

compound	deletion of hyperconjugation	r(E−E)	θ^b	structure
disilyne	no	2.100	55.1	*trans*-bent
	all	2.012	0.0	linear
disilene	no	2.161	17.5	*trans*-bent
	all	2.127	0.0	planar
ethylene	no	1.324	0.0	planar
	all	1.433	0.0	planar
acetylene	no	1.196	0.0	linear
	all	1.289	0.0	linear

[a] Results obtained at the B3LYP/6-311++G(3df,3pd) with tight option. Bond length r(E−E) and deformation angle θ are given in Å and in degrees, respectively. E = C, Si. [b] Deformation angle θ is a half of H−E−E−H dihedral angle for double-bond compounds. For triple-bond compounds, θ is subtraction of H−E−E bond angle from 180°. See Scheme 4 of text.

SCHEME 4. Deformation Angle, *θ*, of Double (left) and Triple (right) Bond Compounds (E = C, Si)



Recently, Pophristic and Goodman have reported that hyperconjugation is dominant in the structural preference of ethane[14] by deleting hyperconjugative interactions. This view is against the generally accepted picture of steric hindrance between vicinal C−H bonds in the eclipsed conformation. Bickelhaupt and Baerends criticized the work of Pophristic and Goodman and have concluded that it is perfectly valid for organic chemists to adhere to the explanation by steric hindrance (exchange interaction).[16] The main reason causing the controversy lies in the fact that both exchange and hyperconjugative interactions prefer the staggered conformation of ethane and make barriers at the eclipsed conformation. To solve the cause of the barrier in ethane is to clarify the degree of dominance between hyperconjugative and exchange interactions. In case of the molecule of our present chemical interest, disilyne, the effect of steric repulsion is expected to be similar in three structures (linear, trans-bent, and single bond type) because the two hydrogen atoms of HSiSiH are located so that the repulsion between SiH bonds is avoided. Therefore, the degree of dominance between hyperconjugative and exchange interactions

TABLE 3: Structural Dependence on Hyperconjugative Interactions of Disilene and Disilyne[a]

compound	deleted hyperconjugation	r(Si−Si)	θ^b	structure
disilene	vicinal	2.279	22.4	trans-bent
	geminal	2.078	0.0	planar
disilyne	vicinal	2.172	58.1	trans-bent
	vicinal	2.722	89.1	twisted
	geminal	1.976	0.0	linear

[a] Results at the B3LYP/6-311++G(3df,3pd) with tight option. Bond length r(Si−Si) and deformation angle θ are given in Å and in degrees, respectively. [b] Deformation angle θ is a half of H−Si−Si−H dihedral angle for disilene. For disilyne, θ is subtraction of H−Si−Si bond angle from 180°. See Scheme 4 of text.

for the structural preference of disilyne is not the question of the present paper. Bickelhaupt and Baerends did not deny the method used by Pophristic and Goodman to investigate the effects of hyperconjugative interactions on the structural preference, and they mentioned that hyperconjugation is the cause of the barrier in ethane being "true" within the NBO method of electronic-structure analysis.[16] Accordingly, our conclusion obtained for the present unsaturated silicon compounds is also "true" within the NBO method.

There are two types of hyperconjugative interactions: vicinal and geminal. Individual hyperconjugative interactions, which can influence structural preferences, are defined as charge (electron) transfers between selected bonding and antibonding orbitals. The geminal hyperconjugative interactions of disilene (disilyne) are charge transfers within single SiH_2 (SiH) groups and within Si−Si bonds. The vicinal hyperconjugative interactions of disilene (disilyne) are charge transfer between two SiH_2 (SiH) groups.

Which hyperconjugative interaction mainly affects the structural preference of disilene and disilyne, geminal or vicinal? Energetically, geminal hyperconjugative interactions stabilize the structures at the B3LYP/6-311++G(3df,3pd) geometry in both disilene and disilyne much more than vicinal ones (Table 1). Geometry optimization was performed both by deleting all vicinal hyperconjugative interactions and by deleting all geminal hyperconjugative interactions. The result is summarized in Table 3. Since NBO changes during optimization, it is not adequate to perform the optimization with the deletion of selected delocalization. However, any orbital change during optimization does not affect the classification of geminal and vicinal delocalization. Therefore, the optimization procedure of the deletion with all geminal (or vicinal) delocalization is reliable. The optimization of disilene with the deletion of all geminal hyperconjugations resulted in a planar structure with a shortened Si−Si bond (2.078 Å), whereas the structure with the deletion of all vicinal hyperconjugations is trans bending, which is the same as the structure of no deletion of hyperconjugative interactions. For disilyne, the deletion of all geminal hyperconjugations resulted in a linear geometry with a shortened Si−Si bond (1.976 Å), whereas the deletion of all vicinal hyperconjugations gives the trans bending structure, the same as the structure of no deletion of hyperconjugative interactions. It is concluded from the present calculations with deleting geminal and vicinal hyperconjugative interactions separately that, both in disilene and disilyne, geminal delocalization leads to the trans-bent structures. It was found from natural bond orbital analysis that geminal delocalization that resulted in the highest stabilization in the trans-bent disilene and disilyne are the $\sigma_{SiSi}-\pi^*_{SiSi}$ and $\pi_{SiSi}-\sigma^*_{SiSi}$ delocalizations, which contribute to the donor−acceptor bonding, as proposed by Carter, Goddard, Malrieu, and Trinquier.[6] The fact that the geminal delocalization of $\sigma_{SiSi}-\pi^*_{SiSi}$ and $\pi_{SiSi}-\sigma^*_{SiSi}$ is dominant in the structural preference of the trans bending structure is not a new finding in the present study, but we could confirm that the B3LYP deletion calculations analyzes the molecule of our interest in a satisfactory fashion. Since NBO changes during optimization, it is not adequate to perform the optimization with the deletion ofselected, for example, $\sigma_{SiSi}-\pi^*_{SiSi}$ and $\pi_{SiSi}-\sigma^*_{SiSi}$, geminal delocalization. What we obtained in the present calculations is that main interactions to stabilize the trans-bent structure of nonsubstituted disilyne are $\sigma_{SiSi}-\pi^*_{SiSi}$ and $\pi_{SiSi}-\sigma^*_{SiSi}$ delocalization, and nonsubstituted disilyne does not take *trans*-bent structure without geminal delocalization.

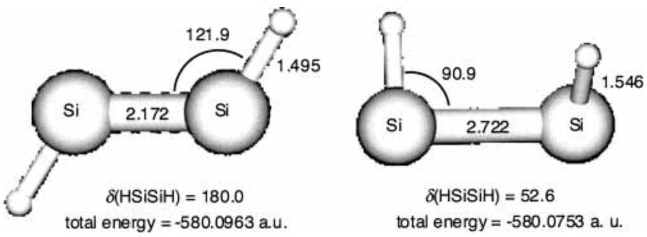
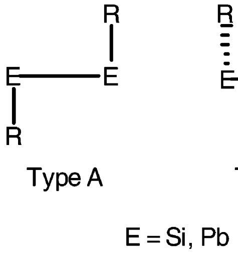


Figure 1. Optimized structures of disilyne obtained by the deletion of all vicinal delocalization at the B3LYP/6-311++G(3df,3pd) level. Bond lengths are given in Å. Bond and dihedral angles are given in degrees.

During the search of minima by deleting all vicinal hyperconjugations in disilyne, we found a twisted structure different from trans-bent (Figure 1). This suggests that two geminal hyperconjugative interactions affect the structure of disilyne when there is no vicinal hyperconjugative interaction. The twisted structure is less stable by 13.2 kcal/mol than the trans-bent structure. Therefore, the twisted structure itself does not exist as an equilibrium structure of nonsubstituted disilyne (HSiSiH). The twisted structure of disilyne obtained by deleting all vicinal hyperconjugations has significantly stretched Si−Si (2.722 Å) and Si−H (1.546 Å) bonds, and twisted H−Si−Si−H dihedral (52.6°) and strongly bent Si−Si−H bond (90.9°) angles. A Si−Si−H bond angle of approximately 90° is the other characteristic of this new structure, in addition to the twisting. This structure is regarded as single-bond type from the elongated Si−Si distance and the 90° Si−Si−H bond angle. Recently, a structure with a 90° bending angle was theoretically[4a] and experimentally[1] reported for a lead analogue, RPbPbR, but has not been reported for silicon analogues, RSiSiR. From the natural orbital analysis, the structure is mainly stabilized by a geminal delocalization between σ^*_{SiH} and the almost pure p-character of the orbitals at silicon (2p(Si) and Si−Si p(σ)). The existence of two geminal hyperconjugative interactions affecting the structure of disilyne suggests that vicinal $\sigma_{SiH}-\sigma^*_{SiH}$ delocalization may contribute the preference for a trans-bent structure rather than a twisted structure. The twisted structure has approximately 90° Si−Si−H angle and thus vicinal $\sigma_{SiH}-\sigma^*_{SiH}$ delocalization is expected to be less at the twisted structure than at the trans-bent structure because of small orbital overlap between σ_{SiH} and σ^*_{SiH}. In addition, to obtain the linear structure of disilyne derivatives, it seems that substituents at silicon are required to have strong vicinal hyperconjugative interactions exceeding stabilization by two geminal hyperconjugative interactions.

Although the B3LYP deletion calculation works well in our system, to confirm the effects of newly found geminal delocalization on the structural preference of disilyne derivatives, we have searched for the disilyne derivatives having approximately 90° bending angle with the normal optimization method. Several derivatives with π-accepting and π-donating

SCHEME 5. Two Types of Structures with 90° Bond Angles



substituents, **1**−**4**, were investigated (**1**:$(H_2BSi)_2$; **2**: $(H_2AlSi)_2$; **3**: $(H_2NSi)_2$; **4**: $(H_2PSi)_2$). Geometry was fully optimized and no deletion of hyperconjugative interactions was performed. Optimized structures were confirmed to have no negative frequency modes by harmonic vibration frequency calculations. The obtained structures have approximately 90° bending angles for these derivatives and are classified into single bond type structures. As structures with 90° bending angles, two types are possible, trans (type A) and twisted (type B) as shown in Scheme 5. Experimentally, the structure of RPbPbR was found to be type A (trans) in Scheme 5, while theoretically, both types A and B were found to be equilibrium structures of RPbPbR depending on the substituents at lead. The optimized structure of the amino-substituted disilyne, **3**, is type A, and those of **1**, **2**, and **4** are type B (Figure 2). Silicon−silicon bond distances are elongated in all derivatives compared with that of HSi≡SiH. R−Si−Si (R=BH_2, AlH_2, NH_2, PH_2) bond angles are approximately 90°. It is well known that in disilene, π-donating substituents such as NH_2 lead to strongly bent structures and π-accepting substituents such as BH_2 induce planar structures.[6l,8b] However, in disilyne, both π-donating (NH_2- and PH_2-substituted disilynes) and π-accepting (BH_2- and Al_2-substituted disilynes) substituents lead to the single bond type structure with 90° bending angles.

From the natural bond orbital analysis, stabilization by the geminal delocalization between σ^*_{SiR} and Si−Si p(σ) was found in **2** and **3** (2 and 4 kcal/mol for **2** and **3**, respectively). In other derivatives, **1** and **4**, the geminal delocalization between σ^*_{SiR} and the almost pure p-character of the orbital at silicon gives less contribution (less than 1 kcal/mol) to the stability. In compound **1**, major hyperconjugative interactions to stabilize the structure are vicinal interaction between Si−Si p(σ) and empty p_π* of B, and remote interaction between partially occupied p_π* of Si and B. The stabilization energies are 15 and 30 kcal/mol, respectively. In compound **4**, major hyperconjugative interactions to stabilize the structure are vicinal interactions between σ_{SiP} and empty p_π* of Si, and remote interactions between σ_{PH} and empty p_π* of Si. The stabilization energies are 32 and 28 kcal/mol, respectively. Although in compounds **2** and **3**, stabilization by the geminal delocalization between σ^*_{SiR} and Si−Si p(σ) was found, vicinal and remote interactions also stabilize the system. In **2**, stabilization by the vicinal interactions between σ_{SiAl} and empty p_π* of Si is the largest. The stabilization energy is 43 kcal/mol. Interactions with empty p_π* of Si prefers the twisted structures with 90° R−Si−Si−R dihedral angles of **1**, **2**, and **4**. However, in **3**, the interaction between σ_{NH} and empty p_π* of Si as in **4** seems to be small because of small N−H distance and thus large Si−H distance. In **3**, the contribution by vicinal interactions to the stabilization is comparable to geminal interactions. The stabilization energy of vicinal hyperconjugative interactions between Si−Si p(σ) and σ^*_{NH} is 5 kcal/mol and that between a silicon lone pair with s character and σ^*_{NH} is 5 kcal/mol. The vicinal interaction between a silicon lone pair and σ^*_{NH} prefers the planar structure. It would be informative to find the structures with the XH_2 groups (X = B, Al, N) rotated by 90° from the optimized structures, since major vicinal and remote interactions in the optimized structures of **1**−**3**, which affect the preference of twisted and planar structures, are reduced by the rotation. However, we could not obtain any equilibrium structures with the XH_2 groups rotated by 90° from the optimized structures. When the XH_2 groups are kept frozen at the rotated structure and other geometric parameters are optimized, although obtained structures are not minimum, the derivatives with BH_2 and NH_2 give usual trans-bent structures and that with AlH_2 gives double bridged structure.

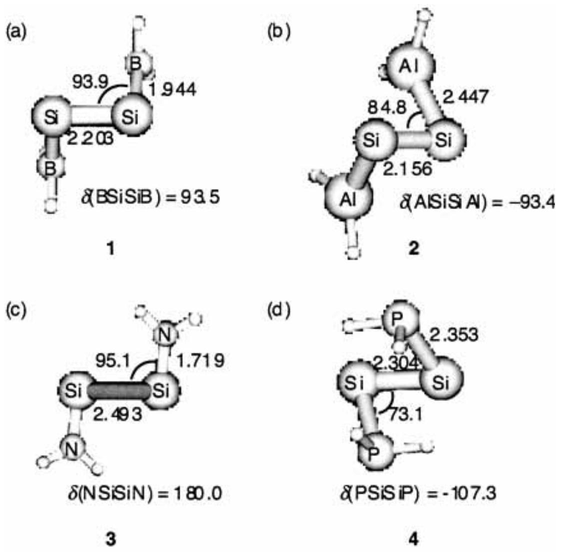


Figure 2. Optimized structures of several disilyne derivatives, RSiSiR at the B3LYP/6-311++G(3df,3pd) level: (a) **1**: R = BH_2, (b) **2**: R = AlH_2, (c) **3**: R = NH_2, and (d) **4**: R = PH_2. Bond lengths are given in Å. Bond and dihedral angles are given in degrees.

Power and co-workers proposed, using Pauling's proposed correlation between bond angle and hybridization,[3] that the observed structure of RPbPbR has only a Pb−Pb single bond, that the 6p (π) atomic orbitals at the lead atoms are empty, and that the Pb−Pb and Pb−C bonds are formed from the remaining two valence p(σ) orbitals of each Pb atom without significant hybridization with the 6s orbital. The latter orbital accommodates a lone pair of electrons found at each Pb. Frenking and co-workers have theoretically confirmed the proposal of Power and co-workers for the bonding nature of RPbPbR.[4a] The proposal can be extended to disilyne derivatives. Actually, from the natural bond orbital analysis, it is valid for disilyne derivatives that the 3p(π) orbital of silicon is empty. As a result, the amino-substituted disilyne is a four-center 4π-system where four lone-pair electrons delocalize in four orbitals. The four-center 4π-system prefers the trans configuration (type A of Scheme 5).[17] Although the phosphino group has lone-pair electrons, compound **4** has a type B structure. This seems to be due to the weak interaction between silicon and phosphorus as in diphosphinodisilene.[8b] This is the other explanation for the trans-bent planar structure of **3**.

Both vicinal hyperconjugative interaction and orbital-phase symmetry of the four-center 4π-system of **3** do not make the bond angle of Si−Si−N 90°. Since several interactions including both geminal and vicinal delocalization affect the structures of molecules, present results are not enough to explain the structural preference of new structures in these disilyne derivatives by newly found geminal delocalization between σ^*_{SiR} and the almost pure p-character of the orbital at silicon. However, it is suggested that the geminal delocalization between σ^*_{SiR} and the almost p-character of the orbitals at silicon can be one candidate to affect the structural preference of disilyne.

Conclusions

It is concluded that the hyperconjugative interactions are effective for the structural preference of disilene and disilyne, and that geminal delocalization are dominant. We found that two geminal delocalizations affect the structures of disilyne and its derivatives. One is the $\sigma_{\mathrm{SiSi}}-\pi^*_{\mathrm{SiSi}}$ and $\pi_{\mathrm{SiSi}}-\sigma^*_{\mathrm{SiSi}}$ delocalization, corresponding to the Carter−Goddard−Malrieu−Trinquier model and leading to the trans-bent structures of disilene and disilyne. The other is the geminal delocalization between σ^*_{SiH} and the almost pure p-character of the orbitals at silicon, leading to a new structure of disilyne derivatives, wherein the R−Si−Si angle is approximately 90°. Although the status of natural bond orbitals (NBO) and the NBO scheme used for the deletion of hyperconjugative interaction is unclear in general, our present conclusion is true within the NBO method.

The new structure with an approximately 90° R−Si−Si angle was found for the derivatives with both π-donating and π-accepting substituents. To obtain a linear structure of disilyne derivatives, substituents at silicon are required to have strong vicinal hyperconjugative interactions exceeding stabilization by two geminal hyperconjugative interactions. Synthesis of the silicon analogue of alkyne, disilyne, is one of the most challenging targets in silicon chemistry. Our calculations would give a hint for the synthesis of stable disilyne derivatives.

References and Notes

(1) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524−3525.

(2) (a) Lischka, H.; Köhler, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 6646−6649. (b) Binkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603−609. (c) Kalcher, J.; Sax, A.; Olbrich, G. *Int. J. Quantum Chem.* **1984**, *25*, 543−552. (d) Köhler, H.-J.; Lischka, H. *Chem. Phys. Lett.* **1984**, *112*, 33−40. (e) Clabo, D. A.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *84*, 1664−1669. (f) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 364−367. (g) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 118−125. (h) Colegrove, B. T.; Schaefer, H. F., III *J. Phys. Chem.* **1990**, *94*, 5593−5602. (i) Grev, R. S.; Deleeuw, B. J.; Schaefer, H. F., III *Chem. Phys. Lett.* **1990**, *165*, 257−264. (j) Colegrove, B. T.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1991**, *113*, 1557−1561. (k) Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* **1991**, *66*, 413−416. (l) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J.-L. *J. Chem. Phys.* **1992**, *97*, 7984−7989. (m) Nguyen, M. T.; Sengupta, D.; Vanquickborne, L. G. *Chem. Phys. Lett.* **1995**, *244*, 83−88. (n) Stegmann, R.; Frenking, G. *J. Comput. Chem.* **1996**, *17*, 781−789. (o) Grev, R. S.; Schaefer, H. F., III *J. Chem. Phys.* **1992**, *97*, 7990−7998, and references therein. (p) Apeloig, Y.; Karni, M. *Organometallics* **1997**, *16*, 310−312. (q) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489−2491. (r) Karni, M.; Apeloig, Y.; Schröder, D.; Zummack, W.; Rabezzana, R.; Schwarz, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 331−335. (s) Grützmacher, H.; Fässler, T. F. *Chem. Eur. J.* **2000**, *6*, 2317−2325. (t) Jutzi, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3797−3800. (u) Kobayashi, K.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 234−236.

(3) Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 256.

(4) (a) Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2052−2055. (b) Danovich, D.; Ogliaro, F.; Karni, M.; Apeloig, Y.; Cooper, D. L.; Shaik, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4023−4026. (c) Grunenberg, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4027−4029.

(5) (a) Sekiguchi, A.; Zigler, S. S.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4241−4242. (b) Sekiguchi, A.; Gillette, G. R.; West, R. *Organometallics* **1988**, *7*, 1226−1227. (c) Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217−252. (d) Pietschnig, R.; West, R.; Powell, D. R. *Organometallics* **2000**, *19*, 2724−2729.

(6) (a) Krogh-Jespersen, K. *J. Phys. Chem.* **1982**, *86*, 1492−1495. (b) Nagase, S.; Kudo, T. *J. Mol. Struct. (Theochem.)* **1983**, *103*, 35−44. (c) Cowley, A. H. *Polyhedron* **1984**, *3*, 389−432. (d) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386-392. (e) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419−509. (f) Olbrich, G. *Chem. Phys. Lett.* **1986**, *130*, 115−119. (g) Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140−4142. (h) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303−5315. (i) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916−5921. (j) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1989; Chapter 17, pp 1015, and references therein. (k) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130−2137. (l) Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8589−8590. (m) Trinquier, G.; Malrieu, J.-P. *J. Phys. Chem.* **1990**, *94*, 6184−6196. (n) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125−170. (o) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667−3679. (p) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231−273. (q) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939−2951. (r) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463−3503. (s) Chen, W.-C.; Su, M.-D.; Chu, S.-Y. *Organometallics* **2001**, *20*, 564−567.

(7) Inagaki, S.; Ishitani, Y.; Kakefu, T. *J. Am. Chem. Soc.* **1994**, *116*, 5954−5958.

(8) (a) Takahashi, M.; Tsutsui, S.; Sakamoto, K.; Kira, M.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **2001**, *123*, 347−348. (b) Takahashi, M.; Sakamoto, K. *Organometallics* **2002**, *21*, 4212−4216. (c) Takahashi, M.; Sakamoto, K.; Kira, M. *Int. J. Quantum Chem.* **2001**, *84*, 198−207. (d) Takahashi, M.; Kira, M.; Sakamoto, K.; Müller, T.; Apeloig, Y. *J. Comput. Chem.* **2001**, *22*, 1536−1541. (e) Veszprémi, T.; Takahashi, M.; Ogasawara, J.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 2408−2414. (f) Veszprémi, T.; Takahashi, M.; Hajgató, B.; Ogasawara, J.; Sakamoto, K.; Kira, M. *J. Phys. Chem. A* **1998**, *102*, 10530−10535.

(9) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.

(10) Veszprémi, T.; Takahashi, M.; Hajgató, B.; Kira, M. *J. Am. Chem. Soc.* **2001**, *123*, 6629−6638.

(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(12) (a) Bauschlicher, C. W., Jr.; Partridge, J. *Chem. Phys. Lett.* **1995**, *240*, 533−540. (b) Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791−2800.

(13) *NBO 4.0 module of the Gaussian 98*; Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin: Madison, 1996.

(14) Pophristic, V.; Goodman, L. *Nature* **2001**, *411*, 565−568.

(15) Pophristic, V.; Goodman, L.; Wu, C. T. *J. Phys. Chem. A* **2001**, *105*, 7454−7459.

(16) Bickelhaupt, F. M.; Baerends, E. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4183−4188.

(17) (a) Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1982**, 709−710. (b) Inagaki, S.; Kawata, H.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3724−3732. (c) Inagaki, S.; Iwase, K.; Goto, N. *J. Org. Chem.* **1986**, *51*, 362−366. (d) Inagaki, S.; Ohashi, S. *Theor. Chem. Acc.* **1999**, *102*, 65−71.