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# Molecular and Electronic Structure of Siladiimide and Other Allenic X=Y=X Compounds

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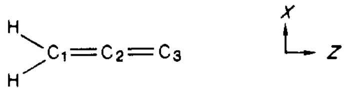
The preferred geometric structures of the allene analogues $CH_2{=}Si{=}CH_2$ (**1**), $NH{=}Si{=}NH$ (**2**), $PH{=}Si{=}PH$ (**3**), $NH{=}C{=}NH$ (**4**), and $NH{=}Si{=}CH_2$ (**5**) are examined at the RHF/6-31G(d) level of theory, and that of **2** is further examined at the MP2/6-31G(d) computational level. The prediction that at the SCF level compounds **1**, **3**, **4**, and **5** prefer orthogonal geometries like allene, while **2** prefers a planar structure, is examined with the aid of localized molecular orbitals, correlated energies, and, in the case of **2**, a detailed analysis of the potential energy surface. The latter is very flat, and at the highest level of theory this molecule is predicted to be nonplanar with a nonlinear N–Si–N angle.

## Introduction

It is well-known that the molecular structure of allene ($CH_2{=}C{=}CH_2$) is twisted in such a way that the two methylene groups are in planes that are orthogonal to each other.[1] This comes about in order to maximize the energy gained from "$\pi$" binding at the central carbon atom. If the three collinear carbons are taken to lie along the *z* axis and the left methylene is taken to lie in the *xz* plane



the $C_1$–$C_2$ $\pi$ bond is formed between the $2p_y$ atomic orbitals on these two atoms. Then, the $2p_x$ orbitals on $C_2$ and $C_3$ must be used to form the $C_2$–$C_3$ $\pi$ bond, so the two $H_2C$ planes are perpendicular to each other. Similar arguments may be applied to other X=Y=X species: 2-silaallene ($CH_2{=}Si{=}CH_2$), for example, takes on a structure which is analogous to that of allene.[2]

In view of the foregoing, it is somewhat surprising that siladiimide (NH=Si=NH) has recently been predicted by Thomson and Glidewell,[3] using restricted Hartree–Fock (RHF) /3-21G[4] wave functions, to be planar with the rather large HNSi bond angle of 150°. Of course, the barrier resisting rotation about the X=Y bond should decrease with the XY pi bond strength. However, while one expects the Si=N $\pi$ bond to be considerably weaker than that for C=C, the Si=C and Si=N $\pi$-bond energies are expected to be similar.[5] Thus, the difference in structures cannot be entirely explained by $\pi$-bond energy differences.

**Table I.** Energies at SCF/6-31G(d) Geometries

| molecule no. | molecule type | tot. energy[a] MP2/6-31G(d) | rel energy[b] SCF | rel energy[b] MP2 | ZPE[b] |
|---|---|---|---|---|---|
| 1 | twisted | −367.17688 | 0.0 | 0.0 | 32.5 |
| | planar | −367.12821 | 26.1 | 30.5 | 30.5 |
| 2 | | −399.29430 | *c* | *c* | 17.2 |
| 3 | twisted | −971.73913 | 0.0 | 0.0 | 12.1 |
| | planar | −971.71596 | 12.7 | 14.5 | 10.6 |
| 4 | twisted | −148.33557 | 0.0 | 0.0 | 22.0 |
| | planar | −148.32482 | 8.5 | 6.7 | 20.4 |
| 5 | twisted | −383.23199 | 0.0 | 0.0 | 24.8 |
| | planar | −383.22705 | 0.5 | 3.1 | 24.5 |

[a] Total energies in hartrees. [b] Relative energies and zero-point vibrational energies (ZPE) ion kcal/mol. [c] See text.

Interest in the equilibrium structure of siladiimide is heightened by recent photochemical studies of matrix-isolated bis(trimethylsilyl) diazide[6a] and di-*tert*-butyldiazidosilane.[6b] In those experiments, the di-*tert*-butyl and bis(trimethylsilyl) analogues of siladiimide were identified as products of the photolyses.

In order to search for a consistent explanation for the structural differences discussed above, the present work considers the geometries of several molecules that potentially contain adjacent $\pi$ bonds. The molecules considered here are 2-silaallene (**1**), siladiimide (**2**) and its phosphorus analogue PH=Si=PH (**3**), carbodiimide NH=C=NH (**4**), and the mixed compound $NH{=}Si{=}CH_2$ (**5**). Carbodiimide, whose $\pi$ bonds should be similar in strength to those of allene,[5] has been the subject of previous investigations[7] and has been predicted to have a structure similar to that of allene, in contrast to that of siladiimide. The phosphorus molecule should have the weakest $\pi$ bonds of the five compounds considered here,[5] and molecule **5** provides a species whose structure could be intermediate between those of 2-silaallene and siladiimide.

## Computational Approach

The structures of all molecules treated in this work have been predicted at the RHF/6-31G(d)[8] level of computation, by using the analytical gradient procedures in GAUSSIAN82.[9] All structures (expected to be reasonably well represented at this level) were verified as minima or transition states (with zero or one imaginary

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(1) (a) Maki, A. G.; Toth, R. A. *J. Mol. Spectrosc.* **1965**, *17*, 136. (b) Buenker, R. J. *J. Chem. Phys.* **1968**, *48*, 1368. (c) André, J. M.; André, M. C.; Leroy, G. *Chem. Phys. Lett.* **1969**, *3*, 695. (d) Schaad, L. J. *Tetrahedron* **1970**, *26*, 4115. (e) Weimann, L. J.; Christoffersen, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 2074. (f) Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103. (g) Krogh-Jespersen, K. *J. Comp. Chem.* **1982**, *3*, 571. (h) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479. (i) Rauk, A.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 3781. (j) The latter four papers discuss the role of non-closed-shell configurations in planar allenic compounds with regard to the linearity of the X–Y–X angle. Only Lam and Johnson used multiconfigurational wave functions, and they did not optimize geometries.

(2) (a) Barthelat, J. C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1979**, *10*, 3785. (b) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419. (c) Gordon, M. S.; Koob, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 2939. (d) Krogh-Jespersen, K. *J. Comput. Chem.* **1982**, *3*, 571. Note that these authors found a second planar form of 2-silaallene whose C–Si–C angle is less than 180° and which is lower in energy than the $D_{2h}$ structure. This is not expected to affect the main conclusions drawn in this paper. (e) Lien, M. H.; Hopkinson, A. C. *Chem. Phys. Lett.* **1983**, *80*, 114.

(3) Thomson, C.; Glidewell, C. *J. Comput. Chem.* **1983**, *4*, 1.

(4) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 1980. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Chem. Phys.* **1982**, *104*, 2997.

(5) (a) Schmidt, M. W.; Truong, P.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217. Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(6) (a) Ziegler, S. S.; Welsh, K. M.; West, R. W.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 4392. (b) Welsh, K. M.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 6689.

(7) (a) Gordon, M. S.; Fischer, H. *J. Am. Chem. Soc.* **1968**, *90*, 2471. (b) Hart, B. T. *Aust. J. Chem.* **1973**, *26*, 461, 477. (c) Moffat, J. B. *J. Mol. Struct.* **1979**, *52*, 275.

(8) Note that 3-21G(d) was used for compound **5**, since it is part a separate study of $SiCNH_m$ compounds: Truong, P.; Truong, T. N.; Gordon, M. S. Manuscript in preparation. (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(9) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. "GAUSSIAN82", Carnegie-Mellon University, Pittsburgh, PA, 1983.

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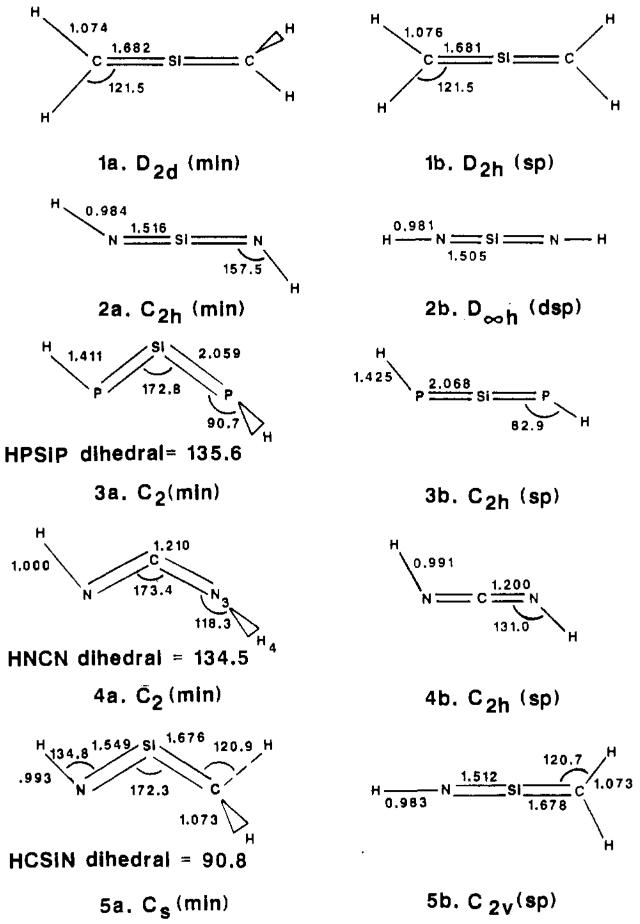

**Figure 1.** RHF/6-31G(d) structures. Bond lengths are in Å; angles are in deg. In all cases, the X=Y=X angle is 180°. The notations "min" and "sp" refer to minimum and saddle-point structures, respectively.

frequency, respectively) by diagonalizing the analytically determined matrix of energy second derivatives at the same computational level. The potential energy surface of siladiimide was probed further by using second-order perturbation theory (MP2[10]) and the same basis set, followed by full MP4/6-31G(d,p)[10] calculations at selected structures. The inner shells were not correlated in the perturbation theory calculations. In order to assist in analyzing the molecular structures, Boys localized molecular orbitals[11] (LMO's) were obtained from the canonical MO's using the program GAMESS.[12]

## Results and Discussion

The RHF/6-31G(d) structures for the molecules of interest are given in Figure 1. As noted above and by Thomson and Glidewell,[3] 2-silaallene is predicted to have a twisted ($D_{2d}$) structure, with the planar $D_{2h}$ geometry being a saddle point. Carbodiimide is similar, with a minimum energy $C_2$ geometry and a planar $C_{2h}$ saddle point. In contrast, siladiimide is indeed predicted to be trans planar, with a HNSi bond angle of 157.5°. Any attempt to optimize either an orthogonal or a W-shaped cis planar structure for this compound leads to a completely linear geometry (**2b**). The latter has a pair of imaginary frequencies corresponding to the degenerate bend of the hydrogens. On the other hand, the phosphorus analogue (**3**), for which one expects a very weak $\pi$ bond, has the typical twisted allenic structure, with a trans planar saddle point. The mixed structure (**5**) is also interesting. In this compound, the twisted structure is predicted to be a minimum on the potential energy surface, while optimization of the planar structure leads to a saddle point with a linear nitrogen (**5b**).

For the minimum energy structures, the normal modes with the smallest vibrational frequencies reflect the relative pi bond strengths. For example, the two lowest frequencies in carbodiimide are 557 and 558 cm$^{-1}$. These correspond to the nearly degenerate CNC linear bend. The corresponding frequencies are 153 cm$^{-1}$ in 2-silaallene and 113 and 114 cm$^{-1}$ in **3**. On the other hand, siladiimide does not fit into this general trend. Even though the SiN $\pi$ bond should be stronger than that in SiP and about the same as that in SiC, the smallest frequencies in siladiimide are 24 and 88 cm$^{-1}$. These again correspond to the degenerate linear bend.

The relative isomer energies listed in Table I provide a *qualitative* comparison of the compounds of interest. These are computed at the SCF level and are thus expected to be only qualitatively correct. The computation of accurate barriers would require MCSCF level wave functions,[1f-j] whereas the prime interest here is in the preferred conformations.

The SCF/6-31G(d) energy difference between planar and orthogonal 2-silaallene is 26.1 kcal/mol. This is within a few kilocalories per mole of previously published estimates[2] and is 20 kcal/mol smaller than that predicted for allene.[1] The corresponding energy differences in **3** and **4** are 12.5 and 7.8 kcal/mol, respectively. It is striking that the smallest energy difference occurs in carbodiimide, even though CN is expected to have the strongest $\pi$ bond. For the mixed compound, structures **5a** and **5b** have virtually the same energy, even though **5a** is a minimum and **5b** is a saddle point on the potential energy surface. Since the minimum energy SCF structure of siladiimide is planar and the other possible structures investigated optimize to a linear geometry, an energy difference analogous to those discussed above is not available. However, it is noteworthy that the linear geometry **2b** is only 0.2 kcal/mol higher in energy than **2a**.

The MP2 total and relative energies are also listed in Table I. The effect of correlation is generally small and changes the relative isomer energies in a direction opposite to that of the zero point vibrational energy (ZPE) correction (also listed in Table I). This is not the case for **4** for which the addition of correlation and ZPE corrections reduces the energy difference from 7.8 to 3.8 kcal/mol. For **5** the correlation corrections favor the twisted structure by nearly 3 kcal/mol.

A clue to the apparently anomolous behavior of siladiimide, and to some extent carbodiimide, may be obtained by examining the localized orbitals of the planar structures of these two compounds, as well as those of **3b**. Particularly revealing are the Mulliken populations in the lone pairs of these three species. In the phosphorus molecule, 1.962 of the 2.0 electrons in each lone pair are located on the phosphorus. In contrast, the corresponding values on the nitrogen lone pairs in carbodiimide and siladiimide are 1.677 and 1.619, respectively. Thus, the nitrogen lone pairs donate more than 0.3 electron to the adjacent carbon or silicon. Furthermore, while the centroid of the phosphorus lone pair is located outside of the SiP bond region (that is, away from the silicon) the centroid of the nitrogen lone pairs is actually inside the bond region, 0.2 (0.4) bohr toward the C (Si) in carbodiimide (siladiimide). Thus, in the planar structure the nitrogen lone pairs are able to delocalize into the adjacent bond region, thereby stabilizing the structure, whereas this does not occur when the lone pairs are located on phosphorus. Because of its relatively weak $\pi$ bonds, this lone-pair delocalization is apparently sufficient to make the planar geometry a competitive structure in siladiimide. While the minimum energy geometry in carbodiimide is still the twisted one, because of its stronger $\pi$ bonds, the energy difference is smaller than that which one would otherwise expect, again due to the lone-pair delocalization effect. It should be noted in this regard that Schade and Schleyer have recently pointed out the reluctance of phosphorus to delocalize its lone pairs.[13] Rotation to the orthogonal conformer has no effect on the extent of localization of the phosphorus lone pairs, but the population on

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(10) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.
(11) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1963**, *32*, 300.
(12) (a) Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog, Program QG01 1981. (b) Schmidt, M. W.; Boatz, J. A.; Baldridge, K. K.; Koseki, S.; Gordon, M. S.; Elbert, S. T.; Lam, B. *QCPE* **1987**, *7*, 115.
(13) Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1399.
(14) Farnell, L.; Radom, L. *Chem. Phys. Lett.* **1982**, *91*, 373.

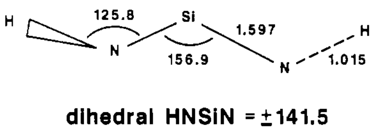

**Figure 2.** MP2/6-31G(d) structure for siladiimide. Bond lengths are in Å; angles are in deg.

**Table II.** Potential Energy Surface (kcal/mol) for HNSiNH[a]

| | energy for dihedral angle | | | | | |
|---|---|---|---|---|---|---|
| HNSi angle | 180° | 160° | 140° | 120° | 100° | 90° |
| 180 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| 170 | 0.1 | 0.1 | 0.2 | 0.2 | 0.3 | 0.3 |
| 160 | 0.0 | 0.1 | 0.2 | 0.4 | 0.6 | 0.8 |
| 150 | 0.1 | 0.2 | 0.3 | 0.6 | 1.1 | 1.3 |
| 140 | 0.8 | 0.8 | 0.9 | 1.1 | 1.6 | 2.0 |
| 130 | 2.5 | 2.4 | 2.2 | 2.2 | 2.6 | 2.9 |
| 120 | 5.7 | 5.5 | 4.9 | 4.4 | 4.3 | 4.6 |
| 110 | 11.0 | 10.5 | 9.4 | 8.3 | 7.7 | 7.8 |
| 100 | 18.4 | 17.8 | 16.2 | 14.6 | 13.6 | 13.5 |

[a] Angles in degrees.

the nitrogens in the nitrogen lone pairs increases to 1.829 when **2** is rotated to a structure with a bond angle of 120° and a dihedral angle of 90°.

The rather small energy difference between planar and linear siladiimide is suggestive of a very flat conformational potential energy surface in this molecule. To investigate this further, the SiN and NH bond lengths were reoptimized as a function of the HNSi bond angle and the HNNH dihedral angle, maintaining the linearity of the NSiN angle. The results of these calculations are displayed in Table II, where the energy (relative to the global minimum) is given as a function of the HNSi angle for several values of the dihedral angle ranging from 90 to 180°. As expected, a large portion of the surface is very flat. For each value of the dihedral angle the energy variation is less than 3 kcal/mol for angles between 130 and 180°. Viewed in another manner, for angles from 120 to 180°, the energy variation is less than 1 kcal/mol for the full range of dihedral angles investigated. Note that for bond angles between 140 and 180° the lowest energy geometry is planar, whereas for bond angles below 140° the orthogonal structure is preferred. Thus, in this compound there appears to be an almost equal balance between $\pi$-bond energies (favoring the traditional allenic structure) and nitrogen lone-pair delocalization (favoring a planar structure).

The extremely flat potential energy surface for siladiimide suggests that correlation corrections to the energy might play an important role. Thus, the structure of this molecule was fully reoptimized with MP2/6-31G(d) wave functions in $C_2$ symmetry. The final structure, verified as a minimum by diagonalizing the matrix of energy second derivatives, is displayed in Figure 2. In contrast to the SCF structures, the molecule is found to have a nonlinear N=Si=N angle, with noncoplanar hydrogens, at the MP2 level of theory. For completeness, the SCF structure was reoptimized in $C_2$ symmetry, starting from the MP2 geometry, and the NSiN bond returns to linearity. So, the bending of this angle is a correlation effect. A similar effect has been observed for propadienone.[14]

The structure shown in Figure 2 is 2.1 kcal/mol below that optimized with a NSiN angle constrained to 180°. Higher level computations have only a small effect on this energy difference. At the MP2/6-31G(d) optimized geometries, MP4/6-31G(d,p) calculations increase the relative stability of the twisted structure (Figure 2) to 3.1 kcal/mol. Thus, even though the potential energy surface remains very flat (and therefore the foregoing qualitative analysis of the SCF structural preferences probably remain valid), introduction of correlation corrections produces a nonplanar structure more in keeping with that of allene, albeit with a nonlinear N=Si=N moiety.

It is interesting that the semiempirical calculations performed by Welsh and co-workers[6b] on the *N*,*N*-dimethylated structure has some resemblance to that shown in Figure 2, with a dihedral angle of 3° and an NSiN angle of 172°.

In conclusion, our calculations indicate that this species may adopt a classical allene-like structure (although with a nonlinear NSiN angle) or a trans planar structure. There is very little energy difference between these, so it seems likely that crystal packing forces will play a large role in determining the structure of substituted diimides in the solid state.

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# Low-Spin Tetracyanoferrate(II) and -(III) Complexes of Meso-Type 1,2-Diamines: Synthesis and Steric Effects on Chelate-Ring Conformation and Rate of Ligand Dehydrogenation

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Tetracyano(1,2-diamine)ferrate(II) and -(III) complexes were synthesized by using (1*R*,2*S*)-*cis*-cyclohexanediamine (*cis*-chxn), (2*R*,3*S*)-butanediamine (*meso*-bn), and (2*R*,3*R*)-butanediamine (*R*-bn) as 1,2-diamines. $^1$H and $^{13}$C NMR spectra confirmed that the *cis*-chxn and *meso*-bn complexes alternated their chelate-ring conformations from $\delta$ to $\lambda$ rapidly on the NMR time scale in solution at room temperature, while the *R*-bn complex assumed a predominantly $\lambda$ conformation. The oxidation product of the *meso*-bn complex, tetracyano(2,3-butanediimine)ferrate(II), was isolated and characterized. All Fe$^{III}$ complexes underwent a disproportionation reaction accompanied by diamine dehydrogenation, yielding tetracyanoferrate(II) complexes of diamine, monoimine, and diimine in basic aqueous solutions. The third-order rate constants (M$^{-2}$ s$^{-1}$) for the disproportionation were as follows: *cis*-chxn, 4.62 × 10$^4$; *meso*-bn, 2.34 × 10$^4$; *R*-bn, 1.28 × 10$^4$. The difference in rate constants is attributed to the strain energy of the chelate ring due to steric repulsion between the axial alkyl group and other protons within the chelate.

## Introduction

The chemistry of tetracyano(diamine)ferrate complexes is complex despite their rather simple structure because a redox reaction takes place at the central metal ion (Fe$^{II}$, **1**; Fe$^{III}$, **2**) and ligand oxidation also takes place to yield diimine complexes **3**.[1–4] The Fe$^{III}$ complexes (**2**) undergo a disproportionation, yielding **1** and **3**. We have synthesized tetracyanoferrate(II) and tetra-

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(1) Goedken, V. L. *Chem. Commun.* **1972**, 207.
(2) Goto, M.; Takeshita, M.; Sakai, T. *Inorg. Chem.* **1978**, *17*, 314.

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