*Journal of Organometallic Chemistry*, 181 (1979) 399—410
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

# Geometry and Bonding in Substituted Silacyclopropanes*

Paul Ronald Jones and Douglas D. White

*Department of Chemistry, North Texas State University, Denton, Texas 76203, (U.S.A.)*

(Received June 12th, 1979)

## Summary

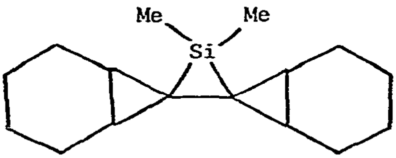
Minimum energy geometries for silirane, **1**; 1,1-difluoro-, **2**; 1,1-difluorotetramethyl-, **3**; 1,1-dimethyl-, **4**; hexamethylsilirane, **5**; 7-siladispiro[2.0.2.1]heptane, **6**; and its 7,7-dimethyl derivative, **7**, have been calculated using the CNDO/2 approximation. Good agreement has been obtained between the predicted structure for **7** and an experimental structure for a related compound. The calculations indicate that the enhanced stability observed for the spirocyclopropyl compounds such as **6** or **7** is due for the most part to increased overlap in the $\sigma$ framework of the silirane ring resulting from increased contributions of the s orbitals of the spiro carbon atoms to the bonding. Hyperconjugation between filled Walsh orbitals of the spirocyclopropyl rings and acceptor orbitals on silicon does not contribute as much to the stabilization of **6** and **7** as does the increased $\sigma$ overlap. The calculations predict that the 1,1-difluorosiliranes, **2** and **3**, should have thermodynamic stability comparable to or greater than the other siliranes, but much higher reactivity due to charge separation.

---

*Reported in part at the 173rd National Meeting of the American Chemical Society, New Orleans, Louisiana, March 1977, Abstr. INOR 20.

## Introduction

Since the first isolation of a "stable" silacyclopropane by Seyferth and Lambert in 1972 [1], a number of other substituted silacyclopropanes have been prepared [2] or proposed an intermediates [3]. Recently the preparation and some reactions of 1,1-difluoro-2,2,3,3-tetramethylsilirane has been reported [4]. Theoretical calculations using the extended Hückel approximation by Mollere and Hoffmann indicated that d-σ hyperconjugation may contribute substantially to the enhanced stability observed for the 7-siladispiro[2.0.2.1] heptane, **6**, compared with silirane or 2,2,3,3-tetramethylsilirane [5]. However, the geometries assumed for these calculations were not specified. Recently Stucky and co-workers, using geometries for the silacyclopropane rings based on an experimental structure for the dispirosilacyclopropane, **8**, examined the bonding in silirane, **1**, hexamethylsilirane, **5**, and 7,7-dimethyl-7-siladispiro[2.0.2.1] heptane, **7**, using the CNDO approximation [6]. They agreed with Mollere and Hoffman that the enhanced stability of the dispirocyclopropylsilacyclopropanes could be attributed to hyperconjugative electron release from the cyclopropyl substituents to vacant silicon orbitals [6].



**8**

To date there has been no systematic study on the effects of substituents on the structure or bonding for a series of substituted silacyclopropanes. Our success in describing toluene radical anion using CNDO/2 minimum energy geometries [7] prompted us to perform such a study.

## Procedure

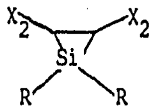
The minimum energy geometries for silirane, **1**, and the substituted siliranes, **2** through **7**, given in Table 1 were calculated using the CNDO/2 approximation [8] with a spd basis set using the d orbital parameterization of Santry and Segal [9]. This parameterization was found to be the most suitable for investigations of the geometry of molecules in ground and electronically excited states [10]. The energy minimization technique has been described by Lloyd and Wood [11]. The *only* restrictions imposed were maintenance of $C_{2v}$ symmetry for the molecules, and the assumption of tetrahedral bond angles and C-H bond lengths for methyl groups. Test calculations showed that deviations from $C_{2v}$ symmetry for the molecules led away from the energy minimum. In addition, variations in the C-H bond lengths for the methyl groups in compounds **4**, **5**, and **7** were found to have a negligible effect on the energy minimum. In an attempt to determine the geometry for 1,1-difluoro-2,2,3,3-tetramethylsilirane, **3**, the minimization procedure for the ring parameters went smoothly. However, when the determination of the location of the ring methyl groups was attempted no energy minimum could be obtained. This is perhaps a result of the dominance of the fluorine atoms' effects on the energy-geometry hypersurface making the calculations insensitive to minor variations in the location of the methyl groups. Nevertheless, because this compound has recently been prepared we have included our results for it in this report. Once the geometries given in Table 1 were determined, the Muliken overlap populations [12], Table 2, and the net atomic charges, Table 3, were calculated.

## Results and Discussion

*Geometries*. A comparison of the calculated structural parameters for 7,7-dimethyl-7-siladispiro[2.0.2.1]heptane, **7**, with the experimental structural parameters for **8** [6] is shown in Table 1.

Considering that the calculation was not biased in any way, the agreement with experiment is remarkable. The largest discrepencies are found in the C-Si-C bond angle of the silacyclopropyl ring and in the angle between the X-C-X plane and the ring C-C bond, both of which are predicted by the calculations to be smaller than the experimentally observed angles. It has been noted that the crystal structure for **8** shows evidence for intramolecular nonbonded interactions between the bulky 7-spironorcaranyl ring systems [6].

Table 1. Calculated Structural Parameters of Various Substituted Siliranes [a]



| Substituents | | | Bond Lengths, Å | | | | Bond Angles | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cmpd. | R | X | Si-C | C-C | Si-R | C-X | C-Si-C | R-Si-R | X-C-X | C-C-X [b] |
| 1 | H | H | 1.891 | 1.509 | 1.598 | 1.119 | 47.0 | 110.8 | 108.6 | 139.0 |
| 2 | F | H | 1.882 | 1.528 | 1.861 | 1.119 | 47.9 | 106.8 | 108.3 | 137.0 |
| 3 | F | Me | 1.883 | 1.572 | 1.870 | 1.471[c] | 49.4 | 101.8 | 124.6[c] | 158.6[c] |
| 4 | Me | H | 1.903 | 1.507 | 1.894 | 1.119 | 46.7 | 114.0 | 108.2 | 138.5 |
| 5 | Me | Me | 1.915 | 1.545 | 1.905 | 1.473 | 47.6 | 111.3 | 120.4 | 155.2 |
| 6 | H | Cpr[d] | 1.866 | 1.536 | 1.600 | 1.478 | 48.6 | 108.7 | 59.7 | 137.0 |
| 7 | Me | Cpr[d] | 1.882 | 1.530 | 1.896 | 1.478 | 48.0 | 112.5 | 59.7 | 136.8 |
| 8 | Me[e] | Nor[e] | 1.826 | 1.520 | 1.858 | 1.511 | 49.2 | 112.8 | 60.7 | 143.9 |

[a] Calculated minimum energy geometries using the CNDO/2 approximation. [b] Angle between the X-C-X plane and the ring C-C bond. [c] Geometry minimized except for location of methyl groups. See Procedure section. [d] Spirocyclopropyl. [e] Experimental values for compound 7, Ref. 5; Nor = 7-spironorcaryl.

Table 2. Mulliken Overlap Populations for Various Substituted Siliranes

| Cmpd. | R | X | Si-C |  |  | C-C |  |  | C-C | Si-C |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | σ | π | Total | σ | π | Total | %π | %π |
| **1**. | H | H | 0.7946 | 0.1084 | 0.9030 | 0.6590 | 0.0352 | 0.6942 | 5.07% | 12.00% |
| **2**. | F | H | 0.8124 | 0.1092 | 0.9216 | 0.6314 | 0.0322 | 0.6636 | 4.85% | 11.85% |
| **3**. | F | Me | 0.7384 | 0.0929 | 0.8313 | 0.5747 | 0.0149 | 0.5896 | 2.53% | 11.18% |
| **4**. | Me | H | 0.7921 | 0.0998 | 0.8919 | 0.6594 | 0.0361 | 0.6955 | 5.19% | 11.19% |
| **5**. | Me | Me | 0.7203 | 0.0856 | 0.8059 | 0.6117 | 0.0182 | 0.6299 | 2.89% | 10.62% |
| **6**. | H | Cpr[b] | 0.8093 | 0.1379 | 0.9472 | 0.6142 | 0.0263 | 0.6405 | 4.11% | 14.56% |
| **7**. | Me | Cpr[b] | 0.8017 | 0.1254 | 0.9271 | 0.6198 | 0.0281 | 0.6479 | 4.34% | 13.53% |

[a] Geometry not totally minimized. [b] Cpr = spirocyclopropyl.

Table 3. Calculated Net Atomic Charges for Various Substituted Siliranes

| Cmpd. | R | X | Si | Ring C | R | X |
|---|---|---|---|---|---|---|
| **1** | H | H | +0.324 | -0.105 | -0.117 | +0.030 |
| **2** | F | H | +0.682 | -0.127 | -0.309 | +0.047 |
| **3** | F | Me | +0.591 | -0.047 | -0.314 | +0.032 |
| **4** | Me | H | +0.145 | -0.094 | -0.094 | +0.012 |
| **5** | Me | Me | +0.108 | -0.028 | -0.169 | +0.038 |
| **6** | H | Cpr[b] | +0.285 | -0.052 | -0.117 | +0.027 |
| **7** | Me | Cpr[b] | +0.118 | -0.045 | -0.176 | +0.021 |

[a] Geometry not totally minimized. [b] Cpr = spirocyclopropyl.

Such steric interactions, which should not be as significant in the less crowded spirocyclopropyl systems, **6** and **7**, would be consistent with the larger experimental values for **8** as compared with our calculated values for **6** and **7**. The overall good agreement between calculated and experimental structural parameters gives us reasonable confidence in the predicted geometries.

It is of interest to examine the trends in the structural features of the silirane systems with variation of ring substituents. As can be seen in Table 1, replacing the hydrogen atoms on silicon, compound **1**, with fluorines, compound **2**, results in a decrease in the Si-C bond length and an increase in the C-C bond length in the ring. Substitution with methyl groups on silicon has the opposite effect. Substitution of hydrogens on the ring carbons, **1** or **4**, with spirocyclopropyl groups, **6** or **7**, results in a decrease in the Si-C bond length and a concomitant increase in the C-C bond length in the ring. These variations are all consistent with a formulation of the bonding in the silirane ring as the in-plane interaction between an "$sp^2$" hybridized silylene fragment with ethylene $\pi$ orbitals, Figure 1. Such a formalism has been discussed in detail by Hoffmann and co-workers in their description of bonding of three-membered rings containing sulfur [13]. It should be

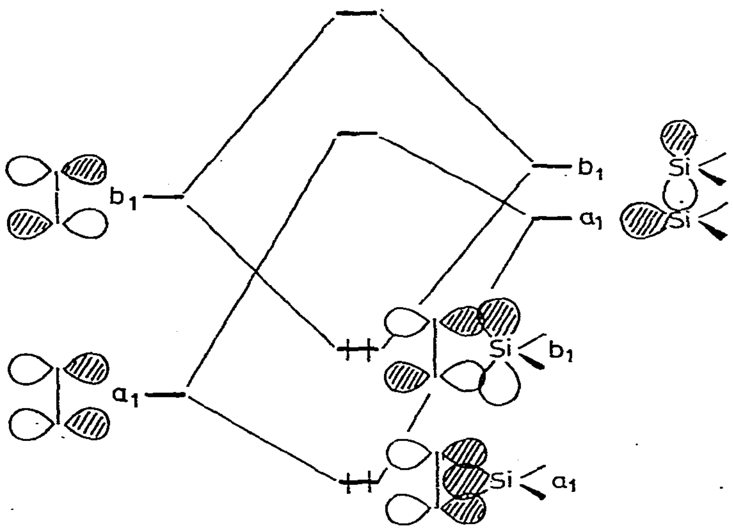


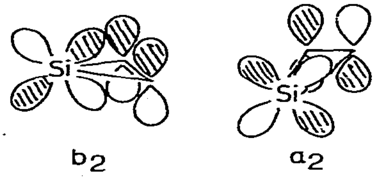
Figure 1. Qualitative orbital diagram for the formation of a silirane from the interaction of a silylene fragment with an ethylene.

emphasized that this formalism is a construct which permits qualitative understanding of the bonding in the silirane rings and in no way represents a chemical process leading to the compounds. In this construct, the predominant bonding interactions in the three-membered ring arise from donation of $\pi$ electron density from the ethylene fragment to acceptor orbitals on silicon of $\underline{a}_1$ symmetry along with donation of electron density from orbitals of $\underline{b}_1$ symmetry on silicon to the $\pi^*$ orbitals of the ethylene fragment. Both of these interactions weaken the C-C bond in the silirane ring from its original ethylenic strength.

The extent of the interaction between the silylene and ethylene fragments is predominantly affected by the energy match of the interacting $\underline{a}_1$ and $\underline{b}_1$ orbitals of the fragments. Making the assumption that the $\underline{a}_1$ and $\underline{b}_1$ orbitals of the silylene fragment are higher in energy than the $\pi$ and $\pi^*$ orbitals, respectively [14], one would expect substituents which stabilize the orbitals on the silylene fragment to improve the bonding in the silirane ring. Consistent with this expectation, the electronegative fluorine substituents on silicon in **2**, stabilize the silylene $\underline{a}_1$ and $\underline{b}_1$ orbitals, improve their interaction with the ethylene orbitals, and give a longer (weaker) C-C bond and a shorter (stronger) Si-C bond in the silirane ring. The electron releasing methyl groups on silicon in 4 show the opposite effect. When spirocyclopropyl groups are substituted for hydrogens on the ring carbons the bonding interaction between the silylene and ethylene fragments are again improved as evidenced by the increase in the C-C bond length and the decrease in the Si-C bond length which are predicted.

The only molecule which does not exhibit this correlation between Si-C and C-C bond lengths is hexamethylsilirane, 5. An examination of the geometric parameters for 5 given in Table 1 reveals that the ethylene portion of the molecule is closer to the geometry of a free olefin than in any of the other molecules for which energy minimums were obtained. In terms of the bonding formulation discussed above, these results imply that the dimethylsilylene fragment in 5 interacts with the ethylene fragment of the molecule to a much lesser extent than in the other siliranes, consistent with the known ease with which hexamethylsilirane decomposes to dimethylsilylene and tetramethylethylene [2, 15].

Our results do not support the suggestion that the enhanced stability of the 7-siladispiro[2.0.2.1]heptane derivatives over other siliranes may be due to increased $\sigma \rightarrow d$ hyperconjugative interaction between the spirocyclopropyl groups and acceptor orbitals on silicon [5, 6]. This stabilization amounts to an interaction of $\pi$ symmetry between the $\sigma$ bonds of ring carbon substituents and acceptor orbitals on silicon illustrated in Figure 2. Such an interaction should result in an increase in the C-X bond length as the transfer of electron density from these bonds to orbitals of $\underline{a}_2$ and $\underline{b}_2$ symmetry on the silylene fragment occurs [16]. However, the calculated C-X bond



$b_2$ $a_2$

Figure 2. Silirane ring orbitals of $\pi$ symmetry.

length in the spirocyclopropyl compounds 6 or 7 is only slightly longer than the corresponding C-X bond length in hexamethylsilirane. Indeed, available experimental data do not support the postulation of extensive σ→d hyperconjugation in the spirocyclopropylsiliranes. The experimentally determined C-C bond length in the spirocyclopropyl group of 8 is equal, within experimental error, to the C-C bond length of 1.512(3) Å determined for unsubstituted cyclopropane [17]. These considerations seem to mitigate against a σ→d hyperconjugative interaction as the major stabilizing effect for the 7-siladispiro[2.0.2.1]heptane systems. Support for this conclusion is found in the examination of the Mulliken overlap populations for the substituted siliranes.

Overlap Populations. Table 2 lists the Mulliken overlap populations obtained for the minimum energy geometries of the siliranes in this study. Also included in the table are the percentages of these overlap populations which arise from orbitals of π symmetry with respect to the silacyclopropane rings. It is the variations in this π component of the overlap populations which would reflect changes in the extent of the σ→d hyperconjugative interactions in the compounds.

In general, the variations in the total overlap populations are consistent with the variations in geometries calculated for the siliranes. Increased Si-C populations are linked with decreased C-C populations. Either fluorine substituents on silicon or spirocyclopropyl substituents on the ring carbons enhance the strength of the ring Si-C bond. The weakest Si-C interaction in the ring is found for hexamethylsilirane, 5. While the variations in the total overlap populations are consistent with the properties of the known siliranes, it can also be seen in Table 2 that there is not a large variation in the percentage of the overlap populations due to the π components. A small increase does indeed show up for the Si-C bonds in the spirocyclopropyl compounds, 6 and 7. However, in comparing 5 to 6 or 7, the major increase in the Si-C overlap populations occurs in the σ overlap, arising mainly in the molecular orbitals of $\underline{a}_1$ and $\underline{b}_1$ symmetry illustrated in Figure

1. For example, in going from hexamethylsilirane, 5, to 7,7-dimethyl-7-siladispiro[2.0.2.1]heptane, 6, the Si-C $\sigma$ overlap population increases from 0.7203 to 0.8017, an increase of 0.0814, while the Si-C $\pi$ overlap population increased from 0.0856 to 0.1254, an increase of only 0.0398. While some stabilization is achieved through increased $\pi$ type hyperconjugative interactions, the major increase is in the $\sigma$ overlap.

It is well known that the geometry of cyclopropane results in an increase in the *p* character of the C-C bonds in the ring, and a concomitant increase in the *s* character of the bonds to the ring substituents. This effect is manifested physically in the large $J_{^{13}\text{C-H}}$ coupling constants in cyclopropane rings [16] and in the enhanced stability of the cyclopropyl carbanion relative to aliphatic carbanions [19]. Our calculations suggest that this increase in the *s* character enhances the overlap in the $\sigma$ framework of the silirane ring and is the major electronic effect contributing to the enhanced stability in the 7-siladispiroheptanes. If this is correct, one would anticipate that strongly electron-donating substituents on the ring carbons should afford siliranes of comparable stability to the spirocyclopropyl derivatives.

Net Atomic Charges. Despite its low stability, hexamethylsilirane has been isolated and characterized [2]. Based on our calculations, it would appear that 1,1-difluorosilirane ought to have comparable or increased thermodynamic stability. However, the main problem encountered in the isolation of siliranes has not been their thermodynamic stability, but rather their very high reactivity [2]. In this light, it is of interest to examine the charge distributions in the substituted siliranes. While not including the clearly significant steric effects on reactivity, the charge distributions can provide some information on the relative susceptibilities of the various siliranes to nucleophilic or electrophilic attack. A compilation of the net atomic charges for the siliranes is given in Table 3.

Consistent with the fact that the known siliranes undergo nucleophilic attack at silicon [2], all of the siliranes for which the geometries were calculated have a net positive charge on silicon. This positive charge is diminished by methyl substitution on silicon, *cf.* 1 and 4 or 6 and 7, and to a lesser extent by cyclopropyl substitution on the ring, 1 and 6 or 4 and 7. Fluorine substitution at silicon, as might be expected, greatly enhances the net positive charge on silicon. Compounds 2 and 3 show the greatest charge separation between the ring carbons and silicon.

Thus, our calculations predict that 1,1-difluorosiliranes should have comparable or greater thermodynamic stability relative to other siliranes, but much higher reactivity. The high polarity, Table 3, and low bond order, Table 2, of the ring Si-C bond in 1,1-difluorotetramethylsilirane, 3, raise the interesting possibility that its facile "two-atom" insertion reactions and remarkable reactions with aldehydes and ketones [4] are dipolar additions rather than free radical in nature. We are currently investigating the theoretical basis for the dichotomous behavior of hexamethylsilirane and 1,1-difluorotetramethylsilirane on thermolysis.

Acknowledgement: The authors acknowledge the financial support of the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund. D.D.W. is grateful to the Phillips Petroleum Company for a graduate fellowship.

## REFERENCES

1. R. L. Lambert, Jr. and D. Seyferth, J. Am. Chem. Soc., 94 (1972) 9246.
2. D. Seyferth, J. Organomet. Chem., 100 (1975) 237; D. Seyferth and D. C. Annarelli, J. Am. Chem. Soc., 97 (1975) 2273.
3. M. Ishikawa and M. Kumada, J. Organomet. Chem., 81 (1974) C3.
4. D. Seyferth and D. P. Duncan, J. Am. Chem. Soc., 100 (1978) 7734.
5. P. D. Mollere and R. Hoffmann, J. Am. Chem. Soc., 97 (1975) 3680.
6. G. L. Delker, Y. Wang, G. D. Stucky, R. L. Lambert, Jr., C. K. Haas, and D. Seyferth, J. Am. Chem. Soc., 98 (1976) 1779.

7. A. M. Ihrig, P. R. Jones, I. N. Jung, R. V. Lloyd, J. L. Marshall, and D. E. Wood, J. Am. Chem. Soc., 97 (1975) 4477.

8. J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

9. D. P. Santry and G. A. Segal, J. Chem. Phys., 47 (1967) 158.

10. P. Zahradnik and J. Leska, Collect. Czech. Chem. Commun., 42 (1977) 2060.

11. R. V. Lloyd and D. E. Wood, J. Am. Chem. Soc., 96 (1974) 659, and references therein.

12. R. S. Mulliken, J. Chem. Phys., 23 (1955) 1833, 1841, 2338, 2343.

13. R. Hoffmann, H. Fujimoto, J. R. Swenson, and C-C. Wan, J. Amer. Chem. Soc., 95 (1973) 7644.

14. See for example $SiH_2$, P. C. Jordan, J. Chem. Phys., 44 (1966) 3400; $SiF_2$, C. Thomson, Theoret. Chim. Acta, 32 (1973) 93, and B. Wirsam, Chem. Phys. Letters, 22 (1973) 360.

15. D. Seyferth, D. P. Duncan, and S. C. Vick, J. Organomet. Chem., 125 (1977) C5; D. Seyferth and S. C. Vick, ibid., 125 (1977) C11.

16. W. J. Hehre, Accounts. Chem. Research, 8 (1975) 369.

17. R. J. Butcher and W. J. Jones, J. Mol. Spect., 47 (1973) 64.

18. J. N. Shoolery, J. Chem. Phys., 31 (1959) 1427.

19. D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press Inc., New York, p. 49, (1965).