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(27) We must acknowledge that the estimated two orders of magnitude differential actually observed (extrapolated, 310°) corresponds to ca. 5 kcal/mol ($\Delta\Delta G^{\ddagger}$), which quantitatively is half the differential between **1** and **3**.

(28) It is well to bear in mind the premises underlying this conclusion: that **1**, **3**, and **4** have "equivalent" ground state energies (i.e., none is uniquely activated toward reaction by ring strain nor deactivated by conjugative stabilization, etc.), that the reactivity differences observed are not due to some unrecognized factor such as intramolecular nonbonded interactions (which for example we believe leads to the relatively refractory nature of the adduct between 1,3-cyclooctadiene and sulfur dioxide, ref 2). Consideration has been given to these points, and while it is felt that none is of a magnitude to vitiate our conclusions, an uncertainty amounting to several kilocalories per mole should be attached to activation energy comparisons between these sulfones.

(29) A zwitterionic solvation requirement sufficiently rationalizes this observation. On the other hand, the enthalpy-entropy partitioning of the activation free energy may more nearly correlate with whether the transition state occurs early or late on the reaction coordinate rather than with the ordering of bond rupture: P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc.*, **91**, 7131 (1969).

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Augmented Silicon–Carbon Bond Strengths via d–σ Hyperconjugation[1]

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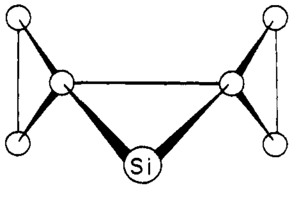
Received December 23, 1974

Abstract: The potentially interesting silacyclopropanes continue to be elusive, as only three stable members of this class of compounds have been reported to date; interestingly, all three are derivatives of 7-siladispiro[2.0.2.1]heptane. Molecular orbital calculations have been carried out on various derivatives of silacyclopropane and 7-siladispiro[2.0.2.1]heptane, together with their carbon analogs. The results suggest that d–σ hyperconjugation may contribute substantially to the strengthening of the silicon–carbon ring bonds in the siladispiroheptane. A similar hyperconjugative interaction should also operate to augment the total silicon–carbon bond strength in the yet unknown cyclopropylidenesilanes.

Ando et al., have recently claimed the formation of 1,1-dimethyl-2-phenylsilacyclopropane, which rearranges to form a benzosilacyclopentene[2] (thus adding one more chapter to the continuing account of unsuccessful attempts to synthesize stable silacyclopropanes).[3] To date, three derivatives of 7-siladispiro[2.0.2.1]heptane (**1**) are the only stable, isolable silacyclopropanes to have been reported.[4] This suggests that there may be some special stability associated with these spirocyclopropyl compounds.[5,6] In particular, we will consider here the possibility of augmented silicon–carbon bond strengths via d–σ hyperconjugation.



1

The interaction of carbon pπ units with acceptor orbitals on silicon has been adduced to explain numerous observations in organosilicon chemistry.[7] The identity of the acceptor orbitals is not altogether well defined; they are most generally considered to be the Si 3d orbitals, but they may be the hyperconjugating σ^* orbitals of the Si–R bonds. Part of the difficulty in distinguishing between the extremes of hyperconjugation and d-orbital participation is that both orbital sets present π-conjugating orbitals of the same local symmetry. The work presented here assumes a set of low-lying silicon 3d orbitals[8] and traces its consequences.

The cyclopropane unit has proved itself as an excellent, conformationally specific donating group relative to vicinal electron-deficient centers.[9] The theoretical basis of this conjugative behavior is well understood.[10] The highest occupied molecular orbitals of cyclopropane are a degenerate set, the Walsh orbitals. Composed almost entirely of peripheral C 2p orbitals, this set endows cyclopropane with good conjugative properties.

Preparatory to a consideration of the siladispiroheptanes, we wish to compare the cyclopropane σ (Walsh) orbitals with the ethylene π orbital in terms of their respective potentials for conjugative interaction with the vacant 3d orbitals of silicon. Any interaction will be governed by symme-

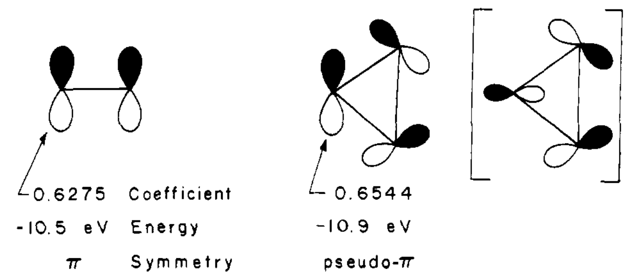
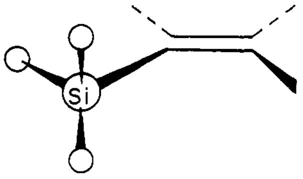


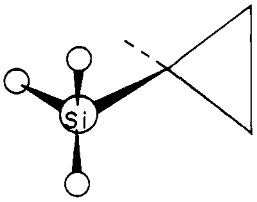
Figure 1. The highest occupied orbitals of ethylene and cyclopropane; properties influencing conjugative potential.

try, overlap, and energy factors. A comparison of these factors for the case of **2** and **3** is outlined in Figure 1. In the



d←pπ

2

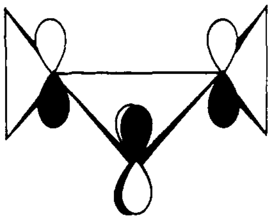


d←σ

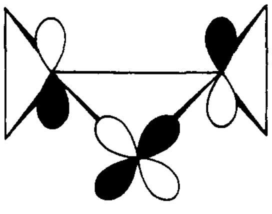
3

orientations shown, one of the Walsh orbitals has the same π-type nodal property as the ethylenic π orbital. The energy of the ring σ orbital is slightly lower than that of the ethylenic π orbital, as determined from their photoelectron spectra.[11] But on the other hand, the larger ring orbital coefficient at the site of interaction should provide better overlap with the silicon d orbitals in the case of the cyclopropyl substituent.

Compound **1** belongs to the symmetry point group C_{2v}. Linear combinations of the cyclopropane orbitals of interest generate semidelocalized orbitals transforming as b_1 and a_2, respectively. In turn, each of these interacts with a d orbital of appropriate symmetry, as shown in **4** and **5**.[12]



4 (b_1)



5 (a_2)

Figure 2 presents a comparison of Mulliken overlap populations in a set of model compounds, calculated by the extended Hückel method.[8] Note that, while the C–C overlap population in silacyclopropane is greater than that in the hydrocarbon, the Si–C population is considerably smaller (**6** and **7**). The incorporation of the spirocyclopropyl groups results in the slight diminishing of the C–C overlap population in the heterocycle **1**. By contrast, however, the Si–C overlap population is enhanced by 15–16% over its original value and now even exceeds that of the analogous homonuclear bond in the carbocycle **10**. This special enhancement of the overlap population suggests expectations of augmented silicon-carbon bond strength in this compound. It is due to the delocalization of σ-bonding electrons from the spirocyclopropyl units into the d orbitals of the adjacent silicon atom, as reflected in the overlap populations of the respective substituent rings. (It was also manifested as increased d orbital occupation relative to that in the unsubstituted silacyclopropane.) Similar, though attenuated, effects are found in a comparison of the two tetramethyl derivatives **8** and **9**.[5]

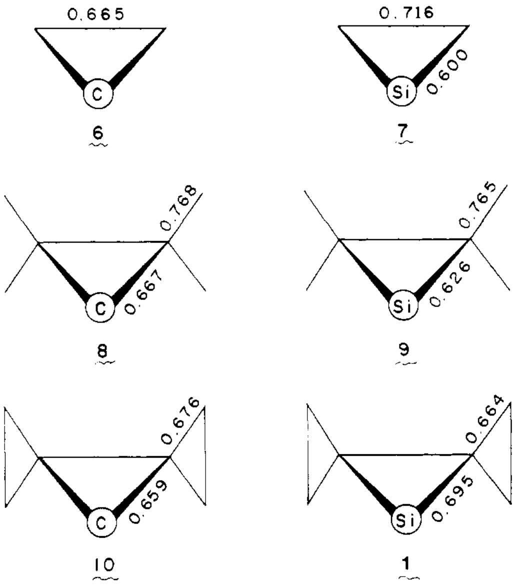


Figure 2. Comparison of overlap populations calculated for cyclopropanes and silacyclopropanes.

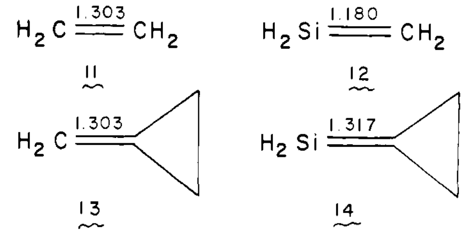


Figure 3. Comparison of overlap populations calculated for olefins and alkylidenesilanes.

Exclusion of silicon d orbitals from the basis set did not obliterate the Si–C bond-strengthening effects; the Si–C overlap populations in **1** were still enhanced by 5–6% over those in **7**. This residual effect can be ascribed to the acceptor capacity of the Si–H antibonding orbitals. Likewise, calculations on model 7,7-difluoro-7-siladispiro[2.0.2.1]heptane (with or without d orbitals on silicon) indicated considerable involvement of the Si–F antibonding orbitals as acceptor orbitals capable of hyperconjugating with the high-lying Walsh orbitals of the spirocyclopropyl substituents.

Another class of elusive compounds which has commanded much interest consists of the silicon analogs of olefins. Here, too, d–σ hyperconjugation may afford a mechanism for augmenting the total silicon-carbon bond strength. Whereas a comparison of ethylene (**11**) with methylenecyclopropane (**13**) reveals essentially no difference in the total overlap population between the doubly bonded carbons, the silicon-carbon overlap population in cyclopropylidenesilane (**14**) is 11–12% greater than that in methylenesilane (**12**) (Figure 3). A similar effect has been predicted for cyclopropylidenephosphorane.[13]

In conclusion, it may be worthwhile to note one further result from the calculations; the contribution of the spirocyclopropyl units to the total energy of **1** appears to exceed their contribution to the total energy of **10** by approximately 17 kcal/mol. The enhancement of their stabilizing effect can again be interpreted in terms of hyperconjugation between occupied levels in the substituent rings with low-lying vacant orbitals associated with silicon. Although total energies calculated by the extended Hückel method are not particularly reliable, the qualitative argument which emerges could possibly be invoked to explain why alkyl substitution appears to impart special thermodynamic stability to many small ring systems (e.g., thiiranes,[14] ethylenehalonium ions,[15] diaziridinones,[16] and α-lactones[17]), all of which possess potential acceptor orbitals positioned for hyperconjugation with the alkyl substituents. Further investigation of the generality of this effect is planned, using more appropriate semiempirical molecular orbital methods.

Acknowledgment. The authors gratefully acknowledge the partial support of this work by the National Science Foundation (GP 28137).

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Studies of Interactions of Adjacent Carbon–Metal σ Bonds by Photoelectron Spectroscopy[1]

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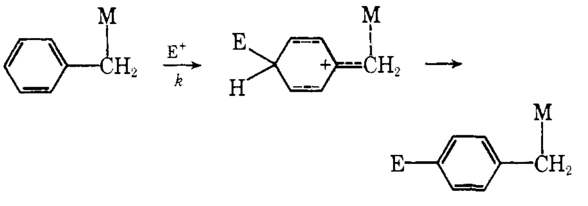
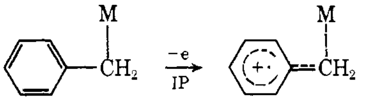
Abstract: The uv photoelectron spectra of 1,2- and 1,3-bis(trimethylstannyl)- and bis(trimethylsilyl)alkanes were determined along with several reference tetraalkyltin compounds. The ionization energies reveal a 2.6-eV interaction between adjacent carbon-tin bonds in $Me_3SnCH_2CH_2SnMe_3$ and an approximately 1.2-eV interaction in *trans*-2,3-bis(trimethylstannyl)norbornane. In the latter compound, the torsional angle between C–Sn σ bonds is 120° as compared with a possible 180° in the former. This σ–σ interaction is compared with σ–π, n–π, and π–π interactions.

The similarity of strained or polarized bond orbitals to n or π orbitals in delocalization phenomena has recently become more clearly demonstrated.[2-6] For example, σ–π conjugation of C–metal bonds can be as large as n–π conjugation of the $-\ddot{N}H_2$ lone pair in its effect upon aromatic electrophilic substitution[7] rates (eq 1) or ionization potentials (eq 2). Thus, expressing the electron donation by the group Y in PhY as the usual σ^+(Y) values, the values σ^+(p-OMe) = −0.78 and σ^+(p-benzylmercuryl-CH_2–) = −1.1 were determined by either the rate of reaction 1[7] or ionization potentials 2.[2] The magnitudes and stereoelectronic requirements for π–π, n–π, and σ–π conjugations are now rather well understood.[2-6]

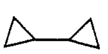


(1)



(2)

The decrease in hydrocarbon ionization potentials with chain length[8,9] and the low ionization potentials of polysilanes[10] indicate that σ delocalizations are to be expected. It remains to choose well-defined pairs of single σ bonds with which to delineate the behavior of σ–σ conjugation of either bent C–C bonds or C–metal bonds or their combinations. Spectroscopic studies have revealed large σ–σ interactions in the compounds shown:



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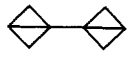
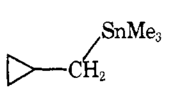


B[12]



C[13]