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Preliminary communication

THE AROMATIC CHARACTER OF SILACYCLOPROPENES

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Summary

Minimum energy geometries for silacyclopropene, 1,1-difluoro-, 1,1-dimethyl-,2,3-dimethyl-, and tetramethylsilacyclopropene have been calculated using the CNDO/2 approximation. The calculations predict a remarkably small ring C-Si-C bond angle of about 43.6°. The average ring C-C bond length is predicted to be 1.380 Å , slightly shorter than the C-C bond length in aromatic rings. Substantial stabilization of the compounds arises from π interaction between the C-C double bond and acceptor orbitals on silicon giving significant aromatic character to the molecules.

Since the first report of evidence for the existence of a silacyclopropene [1] and the isolation of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene, a stable silacyclopropene [2], there has been a great deal of activity in the investigation of these novel systems [3]. The remarkable stability and unusual properties of these compounds led us to investigate their structure and bonding using the CNDO/2 method which was successful in describing toluene radical anion [4] and which correctly predicted the structures of various substituted silacyclopropanes [5]. The current activity in the study of silirenes coupled with the lack of any structural or bonding information for these molecules prompts us to communicate the preliminary results of our calculations.

The minimum energy geometries for the series of silirenes given in the Table were calculated using the CNDO/2 approximation and the method previously described [4]. The only restrictions on the bond lengths and bond angles were the maintainance of $\underline{C}_{2\underline{v}}$ symmetry for the molecules and tetrahedral bond angles and C-H bond lengths for the methyl groups. Test calculations showed that deviations from $\underline{C}_{2\underline{v}}$ symmetry led away from the energy minimum. This procedure gave the results shown in the Table.

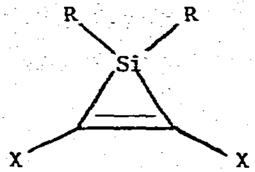

Table. Comparison of Selected Structural and Bonding Parameters for Some Substituted Silirenes [a]

Cmpd.	R	X	C-C,Å	< C-Si-C,°	Overlap Populations C-Si	$\%\pi^b$	C-C	$\%\pi^b$
1	H	H	1.369	43.3	0.9935	19.4	0.9810	21.2
2	F	H	1.377	43.8	1.0085	19.2	0.9608	21.4
3	Me	H	1.366	43.1	0.9867	18.8	0.9867	21.5
4	H	Me	1.397	44.1	0.9817	19.6	0.9122	19.9
5	Me	Me	1.393	43.8	0.9715	18.8	0.9200	20.2

[a] Calculated from the CNDO/2 minimum energy geometries.

[b] Percentage of the Mulliken overlap populations arising from orbitals normal to the ring plane.

The calculations predict a remarkably small average C-Si-C bond angle of 43.6° which is rather insensitive to ring substituents. The low value for the angle is, however, intermediate between experimentally determined values of 49.2° for the C-Si-C angle in a substituted silacyclopropane [6] and 41 ± 1° for the C-Ge-C angle in 1,1-dimethylgermirene [7].

More remarkable is the predicted ring C-C bond length with an average value of 1.380 Å. It has been suggested that the bonding in silacyclopropane rings may be conceptualized as the interaction of an sp^2 hybridized silylene species with an olefin, an analogy with transition metal π complexes [6]. If this analogy extended to silacyclopropene systems one would anticipate a ring C-C bond length intermediate between those typical for carbon-carbon double and triple bonds, 1.337 and 1.204 Å respectively. But, our predicted C-C bond length for the silacyclopropene system is longer than that for a typical C=C bond and, in fact, approaches the value of 1.395 Å observed in aromatic rings. Interestingly, our average calculated C-C bond length for the silacyclopropene ring agrees exactly with C-C bond length calculated for aromatic cyclopropenyl cation [8].

We have also determined the Mulliken overlap populations [9] for the silacyclopropenes in their minimum energy geometries. Pertinent values for the ring Si-C and C-C bonds are given in the Table. Also given is the percentage of the overlap populations arising from orbitals of π symmetry with respect to the ring plane. It is noteworthy that the calculations predict nearly equivalent π character for both the C-Si and C-C bonds, suggesting an aromatic type of π electron delocalization. The main orbital contributing to this π delocalization on silicon is indicated to be the d orbital of appropriate symmetry for bonding overlap with the π orbital of the C-C double bond. Consistent with increased donation to silicon in the silirenes the net atomic charge on silicon, which is positive in the siliranes [5], is found to be reduced in the corresponding silirenes. For example in hexamethylsilirane, silicon is calculated to have a net atomic charge of + 0.108 while in tetramethylsilirene, compound 5, the net atomic charge on silicon is reduced to + 0.059.

Thus our calculations suggest that the remarkable stability of silacyclopropene ring systems may be attributed to their pseudo-aromatic character. Detailed analyses of the structure and bonding in these and related systems are in progress.

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