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THE ISOMERIC STRUCTURES OF SiH_2LiF

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Summary

The structures of four isomeric forms of the model "silylenoid" SiH_2LiF have been investigated by ab initio molecular orbital theory. The two most stable forms are suggested to be the $SiH_2Li^+F^-$ ion pair and the $H_2Si : FLi$ complex, analogous to the similar structures previously found for carbenoids. Two further species, a $H_2Si : LiF$ complex and the "classical" (tetrahedral) SiH_2LiF, are also local minima on the potential energy surface, but are higher in energy.

The properties and reactions of silylene, SiH_2, and of its derivatives have been well studied [1]. Photochemical or thermal methods are usually used to generate such divalent silicon species. Silylene reactions, however, can also be performed using compounds of the type, R_2SiXM (M = alkali metal, X = halogen) *, analogous to carbenoids, R_2CXM. These "silylenoids" (named in analogy with carbenoids) are of particular interest because their carbon counterparts have been shown by a variety of experimental methods [3—5] and by our theoretical studies on CH_2FLi [6], CHF_2Li [7], and CCl_3Li [8] to exist in a number of very usual structural forms. We have now investigated the model silylenoid SiH_2LiF using ab initio molecular orbital theory in order to compare the results with those of the carbon analog, CH_2FLi [6].

Quantum mechanical methods

All calculations employed the Gaussion 76 series of programs [9]. Geometry optimizations were performed with the STO-3G [10] and 3-21G [11] (33-21G for silicon [12]) basis sets. In order to assess the effect of *d*-orbitals, single

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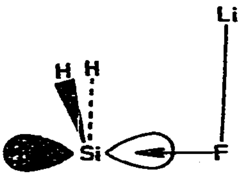
* Dimethylsilylene was first generated by the reaction of $(CH_3)_2SiCl_2$ with sodium/potassium vapour [2a]. More recently [2b] $(CH_3)_2SiCl_2$ has been treated with lithium metal in THF at 0°C to obtain a series of $((CH_3)_2Si)_n$ molecules. The intermediacy of a rhodium silylenoid has been proposed [2c].

point calculations on the STO-3G optimum geometries were performed using the STO-3G* basis set [13] (these calculations are designated STO-3G*// STO-3G). Experience has shown [13,14] that STO-3G* optimum geometries are often close to the STO-3G structures, rather than those obtained with split-valence basis sets. We have therefore used the STO-3G geometries for single point STO-3G* calculations. Further single point calculations on the 3-21G optimum geometries were performed using the larger 6-21G [11] (66-21G for silicon [12]) basis set (6-21G//3-21G) and, again with the 6-21G basis set, employing second order Mϕller-Plesset correction for electron correlation [15] (MP2/6-21G//3-21G). Geometry optimization was by means of Davidon-Fletcher-Powell multiparameter search [16] using analytically evaluated atomic forces *.

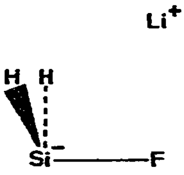
Results and discussion

Starting from classical (tetrahedral) SiH_2LiF and from structures analogous to those found for CH_2FLi [6], four local minima, I—IV, were located on the SiH_2FLi potential energy surface. The STO-3G and 3-21G optimum geometries of I—IV are shown in Fig. 1; the total and relative energies at the different levels of theory are given in Table 1.

Isomer I, which is found to be the most stable at all levels of theory employed, is a particularly interesting silicon structure, as it represents an H_2Li-Si^+F^- ion pair. We have previously proposed [6] that metallocarbenium ions may be reactive intermediates in many carbenoid reactions. The stability of structure I suggests that metallosilicenium ions may also be intermediates in silylenoid reactions. In view of the extremely active search for silicenium ions in solution [18] and the relative ease with which the ion pair forms of carbenoids can be observed by ^{13}C NMR [5a], we suggest that a ^{29}Si NMR study of silylenoids at low temperatures might be extremely rewarding. Such species may be the first silicenium ions (or ion pairs) observed in condensed phases. Due to the high stabilization energy of lithiocarbenium ions [19], structures analogous to I are common to all the carbenoids we have investigated [6—8]. Although lithium is indicated calculationally not to favor a SiH_2^+ center as much as it does CH_2^+, lithium substitution still leads to a very effective stabilization (56.8 kcal mol^{-1} at STO-3G for SiH_2Li^+) [20], which is sufficient to loosen the strong ** Si—F bond in I.



IIa



IIb

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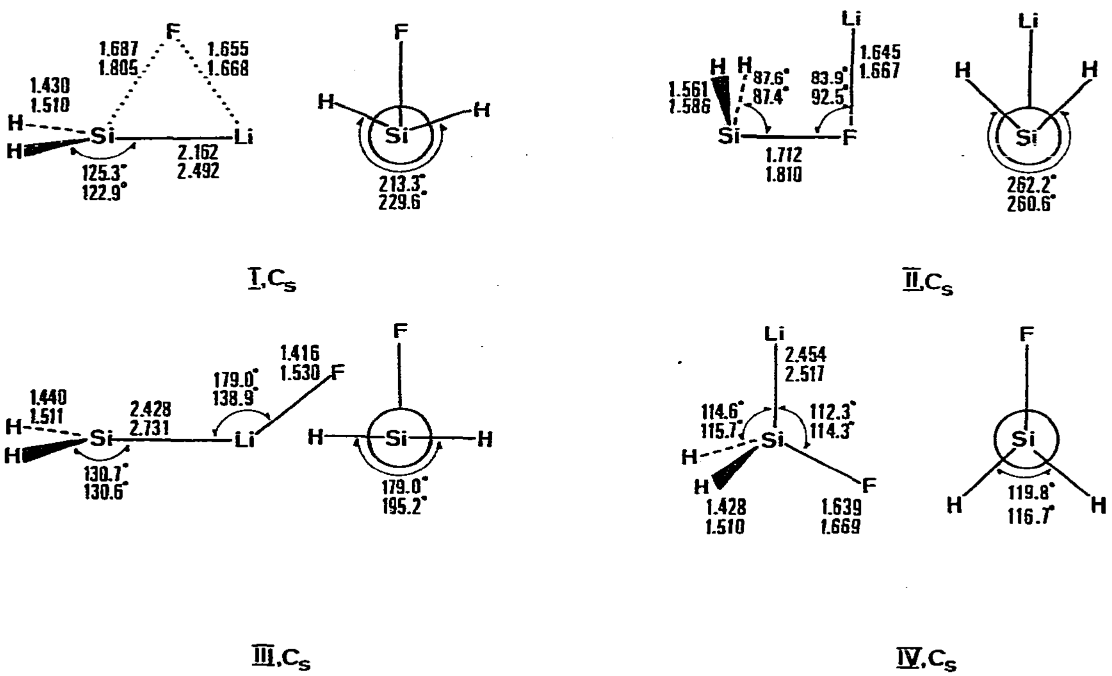
[*] The analytical force evaluation routines [17] were incorporated into the earlier Fletcher-Powell program [16] by Dr. J. Chandrasekhar.

[**] The mean Si—F bond dissociation energy in SiF_4 is 142 kcal mol^{-1} [21].



I, C_s

II, C_s

III, C_s

IV, C_s

Fig. 1. STO-3G (above) and 3-21G (below) optimized geometries for SiH_2LiF. Bond lengths are in Ångstroms and angles in degrees.

Structure II is, at first sight, surprisingly stable relative to the other three isomers (see Table 1). The analogous form of CH_2FLi is the least stable of the three carbenoid-based isomers. Classically, II can be represented as the silylene complex, IIa, or as the ion pair, IIb [6—8].

IIa and IIb might have been expected to be inferior relative to their carbon counterparts. Silylene should be a great deal less electrophilic than methylene [22], and so complex IIa, in which the silylene moiety is acting as an acceptor, might well be less favourable than its carbenoid counterpart. A silyl anion, as in IIb, is also likely to be less favourable than a carbanion because of the more electropositive nature of silicon [23]. The fluorsilyl anion, SiH_2F^- is not a very favourable species, the STO-3G energy for the reaction $SiH_3F + SiH_3^- \rightarrow SiH_2F^- + SiH_4$ being only —9.3 kcal mol^{-1}. The most obvious factor contributing to the stability of II is, however, the negative charge on the two hydrogens, which leads to interaction with lithium and bridging. Fig. 2 shows the calculated atomic charges and overlap populations in II and in the equivalent form of CH_2LiF, IIc [6]. The positive charge on silicon results in considerable Li—H bonding and in a stronger Si—F bond. The Li—F bond is also considerably stronger in II than in IIc, suggesting a more significant contribution from structure IIa in the silicon compound, again reflecting the electropositive nature of silicon. The bonding in II is best described as in structure IIa with considerable stabilization via Li—H bridging. In contrast, the hydrogen in the equivalent form of CHF_2Li does not form such bridges [7]. However, C—H—Li bridging usually is an important factor in determining organolithium structures [24];

TABLE 1

TOTAL (au) AND RELATIVE (kcal mol^{-1}, in parenthesis) ENERGIES FOR SiH_2FLi ISOMERS I–IV

Isomer	STO-3G//STO-3G	STO-3G*//STO-3G	3-21G//3-21G	6-21G//3-21G	MP2/6-21G//3-21G
I	−392.17648 (0.0)	−392.26712 (0.0)	−394.92161 (0.0)	−396.82757 (0.0)	−397.01378 (0.0)
II	−392.14358 (+20.6)	−392.23658 (+19.2)	−394.92072 (+0.6)	−396.82645 (+0.7)	−397.01178 (+1.3)
III	−392.12147 (+40.0)	−392.15434 (+70.8)	−394.86247 (+37.1)	−396.77060 (+35.7)	−396.95855 (+35.9)
IV	−392.14181 (+21.8)	−392.25353 (+8.5)	−394.89470 (+16.9)	−396.80115 (+16.6)	−396.98382 (+18.8)

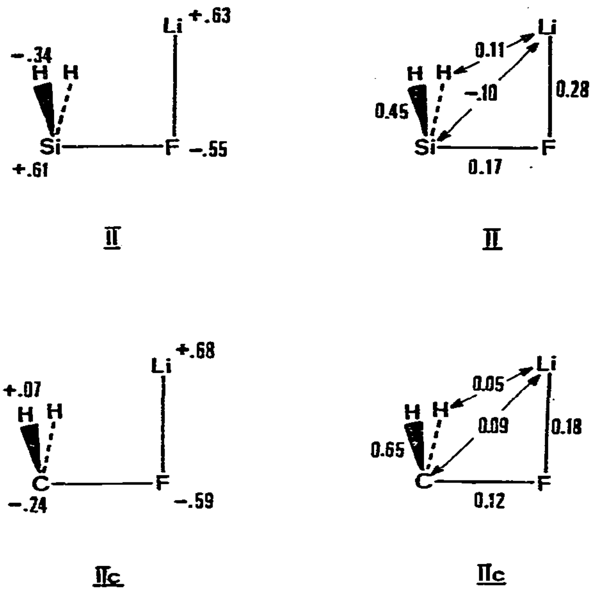


Fig. 2. Atomic charges (left) and overlap populations (right) for II (at 3-21G) and the equivalent form of CH_2LiF, IIc (at 4-31G).

Si—H—Li bridging may be even more important.

Structure III is a H_2Si : LiF complex in which silylene is acting as the donor. This form, analogous to one of the isomers of CH_2FLi, is found consistently to be about 40 kcal mol^{-1} less stable than the most stable form of SiH_2FLi at all levels of theory (Table 1). The large variation in the SiLiF angle between the STO-3G and 3-21G optimum structures (Fig. 1) is not disturbing as we have previously noted [8] that large deformations of the corresponding angles in the equivalent carbenoid structures require very little energy.

Structure IV, although seemingly the most ordinary of the four isomers, is the most unusual in view of our previous experience with carbenoids. In none of the carbenoids so far investigated is the classical ("tetrahedral") form an energy minimum. For SiH_2LiF, IV is relatively unstable (see Table 1) but has an activation barrier (3-21G) of 4.3 kcal mol^{-1} for conversion to I (the reaction path was calculated using the F—Si—Li angle as the reaction coordinate and optimizing the remaining geometry parameters within C_s symmetry).

The "tetrahedral" forms of carbenoids are unstable because of the repulsion between the highly polarized carbon—metal bond and one of the halogen lone pairs. Fig. 3(a) shows the π^*_{CF} orbital resulting from the antibonding combination of the C—Li σ bonding orbital with the appropriate fluorine lone pair orbital in standard (idealised) geometry CH_2LiF *. This orbital can be stabilized by lengthening of the C—F bond and by closing the Li—C—F angle to values smaller than 90°, where the C—F π repulsion is greatest. At smaller Li—C—F angles the electrostatic attraction between lithium and fluorine increases. This

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* The molecular orbital plots employed the STO-3G wave functions and were made using a modified version of Jorgensen's program [25].

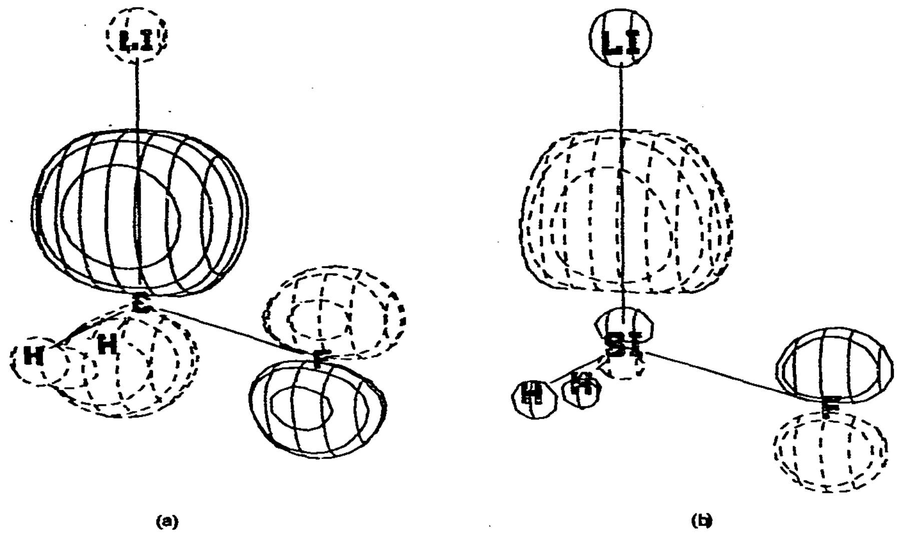

Fig. 3. Highest occupied molecular orbitals of standard geometry CH_2LiF and SiH_2LiF. The small *s*-type contributions on lithium and the inner *p*-type orbital on silicon are due to the 1*s* and 2*p* core orbitals, respectively.

attraction is large enough in magnitude to overcome the inherent π repulsion barrier at 90°. The "tetrahedral" CH_2LiF species shown in fig. 3(a) therefore collapses to a structure analogous to I on optimisation [6]. Fig. 3(b) shows the corresponding π^*_{SiF} orbital in standard geometry SiH_2LiF. The π repulsion is less than that in CH_2LiF. Due to the smaller electronegativity difference, the Si—Li bond is less polarized than C—Li. Also the Si—F bond is longer than C—F. However, the Li—F distance is also larger in SiH_2LiF and the electrostatic attraction smaller. The net result is a small barrier (4.3 kcal mol^{-1}) between IV and I at a Li—Si—F angle close to 90°. This barrier arises because the increase in Li—F bonding is not sufficient to overcome the maximum in Si—F π repulsion at a Li—S—F angle of 90°.

Conclusions

Our calculations indicate the silylenoid, SiH_2FLi, and its carbenoid counterpart, CH_2FLi, to have similar isomeric structures. The changes in relative stabilities of the SiH_2FLi isomers and the fact that the classical form is a local minimum result from the more electropositive nature of silicon, relative to carbon. Our calculations suggest silylenoids to be promising candidates for the direct observation of silicenium ions in solution, at least as ion pairs.

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