Tetrahedron Letters No. 51, pp 4963 - 4966. 0040-4039/79/1215-4963$02.00/0
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ISOMERIC STRUCTURES OF THE CARBENOID, CHF$_2$Li

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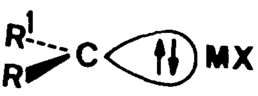
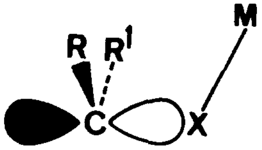
Abstract: The carbenoid, CHF$_2$Li, is suggested by *ab initio* molecular orbital theory to exist in three isomeric forms, none of which corresponds to a classical tetrahedral carbon structure.

Matrix isolation[1] and reactivity[2] studies first suggested that carbenoids can exist as equilibrium mixtures of at least two isomers. Recently, our theoretical work on CH$_2$LiF[3] and on CCl$_3$Li[4] and Seebach's ^{13}C nmr evidence on a variety of lithiated species[5,6] have confirmed that carbenoids can have very unusual structures. We have now investigated an intermediate model case with two halogen atoms, CHF$_2$Li, by means of *ab initio* molecular orbital theory.[7] Carbenoids of this type are among the thermally most stable; CHCl$_2$Li, for instance, dissociates into :CHCl only above -30°C in THF solution.[8]

Three types of carbenoid structures (A-C) have emerged from our calculations.



A



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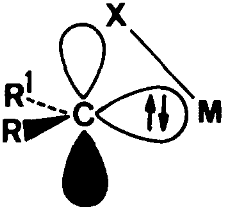
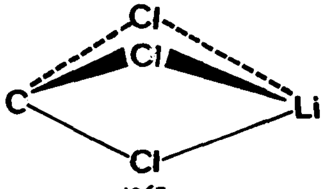


C

In A, the singlet carbene lone pair HOMO interacts with a vacant metal orbital of a metallic halide, MX. In B, the carbene LUMO and a filled halogen orbital are involved. In C, both interactions occur simultaneously. This form is indicated to be the most stable for CH$_2$FLi.[3] For CCl$_3$Li, form B is favoured because of additional interaction between M = Li and R,R^1 = Cl; a remarkable "inside-out" structure with C_{3v} symmetry results:[4]



Full geometry optimizations of CHF$_2$Li isomers (4-31G basis set)[9] starting from structural types (A-C) led to three minima (I-III) on the potential energy surface. Optimization starting from standard geometry (i.e. tetrahedral) CHF$_2$Li also gave II directly. The classical structure is thus not an energy minimum. Single point calculations on the 4-31G optimum geometries were then performed with the 6-31G* basis set[10] (6-31G*//4-31G) and also with second order Møllet-Plesset correction[11] for electron correlation with the 4-31G basis set (MP2/4-31G//4-31G).

At all three levels of theory, structures I and II are comparable in energy (Table). At the lowest level (4-31G//4-31G), isomer I is indicated to be the most stable. This type B species is best described as a CHF$_2^-$Li$^+$ ion pair with significant multicenter bonding. As in CCl$_3$Li,[4] lithium prefers to associate with the "back-side" of the pyramidal CHF$_2^-$ anion. Only the two fluorines, but not the hydrogen, bridge to lithium. Structure II, indicated to be the most stable at the higher theoretical levels (MP2/4-31G//4-31G and 6-31G*//4-31G), is analogous to the ion pair structures of type C found for CH$_2$FLi[3] and for CCl$_3$Li.[4] These type C forms can be considered to involve a halide ion associated with a very stable metallocarbenium ion. Such structures, a consistent feature of our carbenoid investigations, are always either of comparable energy to the most stable isomer or, as for R$_2$CXM carbenoids (R = alkyl, H), are indicated to be the most stable form[12]. For halocarbenoids, equilibria between structures of types B (e.g. I) and C (e.g. II) may be important in determining reactivity.[2] Isomer III, which is considerably less stable than I and II, is a FHC:LiF complex of type A in which the carbene is acting as an electron donor. The equivalent structures for CH$_2$FLi[3] and for CCl$_3$Li[4] have $\underline{C}_s$ symmetry (i.e., the halogen bonded to lithium lies perpendicular to the plane of the 'carbene' moiety). In contrast, optimization of CHF$_2$Li yields an almost coplanar CLi bond (the corresponding *cis* isomer is not an energy minimum). The CLiX bond angle and the HCLiX torsional angle are extremely "soft" parameters in type A species (i.e. relatively large deviations from the optimum values require very small amounts of energy) so that even large differences in such geometrical features are not very significant energetically. We can compare our results with the ^{13}C nmr observations of Seebach *et al*[6] for CH$_3$CBr$_2$Li; the single species detected in THF solution at -100°C had unusually large ^{7}Li-^{13}C and small ^{13}C-^{13}C coupling constants. A structure analogous to II (type C) is consistent with such a spectrum. Extrapolation of our results for CF$_3$Li[12] and for CCl$_3$Li[4] suggests that structures of type C should be increasingly preferred over those of type B for carbenoids involving bromine. We stress that our calculations refer to isolated species in the gas phase. As Köbrich[13] observed enhanced thermal stability of carbenoids in THF solution, the relative energies of the isomers in donor solvents may be significantly different than those indicated by our gas phase results. Calculations assessing solvent effects are in progress.

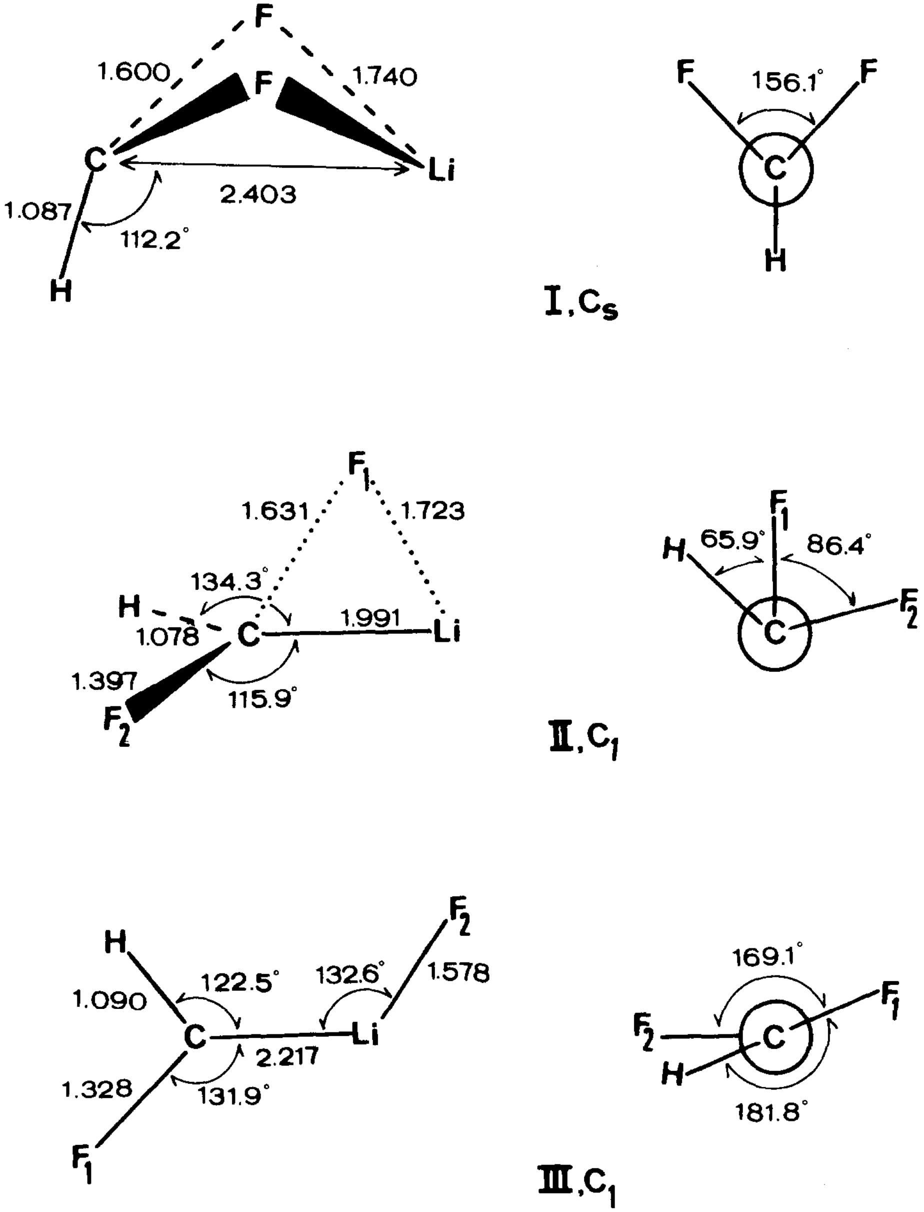


Figure. 4-31G optimum structures, and Newman projections along the CLi vector for the three isomers of CHF$_2$Li. Bond lengths are in Ångstroms and angles in degrees.

This work was supported by the Fonds der Chemischen Industrie. We thank Prof. D. Seebach for communicating his work prior to publication, and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

Table. Total (a.u.) and Relative (kcal mol^{-1}, in parentheses) Energies for CHF_2Li Isomers.

Isomer	4-31G//4-31G	MP2/4-31G//4-31G	6-31G*//4-31G
I	-244.45200 (0.0)	-244.79391 (+0.5)	-244.72656 (+4.2)
II	-244.44954 (+1.7)	-244.79474 (0.0)	-244.73333 (0.0)
III	-244.42564 (+16.7)	-244.76540 (+11.5)	-244.71567 (+11.1)

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(Received in Germany 2 October 1979)