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Isomeric Structures of CH_2LiF , the Prototype Carbenoid

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Abstract

Molecular electronic structure theory has been used to investigate the geometrical and energetic characteristics of CH_2LiF , the simplest halolithiocarbenoid. The structures of three isomers were predicted using self-consistent-field (SCF) theory in conjunction with a basis set of better than double zeta plus polarization quality, namely C(9s5p1d/4s2p1d), H(4s1p/2s1p), Li(9s4p/4s2p), F(9s6p1d/4s3p1d). At this level of theory there are three minima on the potential energy hypersurface: I, which may be roughly described as the ion pair $\text{H}_2\text{CLi}^+\cdots\text{F}^-$; II, for which the description $\text{H}_2\text{C}\cdots\text{LiF}$ is suitable and III, where the picture $\text{H}_2\text{C}\cdots\text{FLi}$ (and to a lesser degree $\text{H}_2\text{CF}^-\cdots\text{Li}^+$) is pertinent. Vibrational frequencies have been predicted for each of these structures. The part of the potential surface connecting structures II and I is initially extremely flat, but a transition state connecting them has been located. Explicitly correlated wavefunctions (22,366 configurations) confirm the SCF prediction that I is the lowest energy isomer with II lying at ~ 27 kcal and structure III at ~ 25 kcal.

Introduction

The term "carbenoid" has been suggested^{1,2} for the description of intermediates which exhibit reactions analogous to those of carbenes, without actually being the free divalent carbon species $R_2C:$. Methylene donors R_2CAB via

are thus labeled carbenoids when A and B remain weakly associated with the carbon atom at transition states for what would otherwise be free $R_2C:$ carbene reactions. Haloalkalycarbenoids are of special interest in that the formation (1) of the alkali halide is typically such an energetically favorable process that it may facilitate the generation of highly unstable reactive intermediates.³ In the present paper we wish to further narrow consideration to the halolithiocarbenoids R_2CLiX , which have recently been shown to have some remarkable structural characteristics.

Perhaps the earliest recognition of halolithiocarbenoids as a source of carbenes was the work of Closs and Closs⁴ in 1959. Their syntheses of chlorocyclopropanes from methylene chloride implicated the carbenoid $LiCHCl_2$ as the source of chlorocarbene ($:CHCl$), via

However, Closs and Closs were unable to trap the intermediate carbenoid.³ The first actual preparation and interception of a carbenoid was reported in 1963 by Köbrich and Trapp.⁵ Köbrich's

school then proceeded to synthesize a large number of halolithio-carbenoids, including Closs's intermediate LiCHCl_2 and the other simple molecules LiCHBr_2 , LiCCl_3 , and LiCBr_3 . This research is nicely summarized in Köbrich's 1967 review,⁶ which also describes the reactions of these initial carbenoids.

As Seebach has noted,⁷ the treasury of chemical results¹⁻⁶ available for carbenoids tended initially to diminish interest in their structural properties. However, as early as 1965 Hoeg, Lusk, and Crumbliss,⁸ on the basis of the observed reactions of α -chloroalkyl lithium compounds, proposed an equilibrium

between two isomeric forms. The first actual spectroscopic observation of a carbenoid was reported in 1968 by Andrews and Carver.⁹ Via matrix isolation infrared spectroscopy, Andrews and Carver were able to observe several vibrational frequencies of LiCCl_3 and LiCBr_3 . In a closely related paper appearing in 1975, Andrews and co-workers¹⁰ concluded that a second MCCl_3 isomer exists, namely a dichlorocarbene-metal halide complex. For the structure of this carbenoid isomer, they propose

as being most consistent with the observed vibrational frequencies.

Thus there is some experimental history behind the notion that there are several energetically competitive isomers of carbenoids.

A primary motivation for the present research was the series of theoretical studies of carbenoids by Schleyer and co-workers. Among the halolithiocarbenoids studied by Schleyer have been LiCH_2F ,¹¹ LiCHF_2 ,¹² and LiCCl_3 ,¹³ the latter of course being the topic of numerous experimental studies.⁶⁻¹⁰ One reason for the general interest in these systems is the question of structures and energetics of tetravalent carbon systems having one electropositive and one electronegative substituent. Clearly the absence of definitive experimental structures for these carbenoids makes such theoretical studies very important. However, Schleyer's results have been quite unorthodox. In particular the predicted lowest energy isomer of LiCCl_3 is a triply bridged species with the lithium situated on the "wrong side" of the molecule. Therefore it seemed of value to investigate at least one of these carbenoids at a more sophisticated level of theory.

No introduction to the problem of carbenoid structures would be complete without some discussion of Seebach's recent work.^{7,14,15} Seebach has reported the low temperature (-100°C to -40°C) ^{13}C NMR spectra of tetrahydrofuran solutions of 16 different chloro-, bromo-, and iodo-lithiocarbenoids. The NMR results suggest the existence of more than one species in solution. Considering the four structures

Seebach concludes that 1 and 2 may be ruled out, while 3 and 4 are consistent with the NMR observations. However, there is a serious problem associated with comparing Seebach's NMR spectra to either the theoretical predictions¹¹⁻¹³ or the matrix isolation results of Andrews.^{9,10} Namely, tetrahydrofuran is a donor solvent and lithium is a fine acceptor. Thus the solvent could have a major effect on the structures ultimately observed by Seebach.^{7,14,15} In fact, Seebach's sketches of structure 2, 3, and 4 above explicitly include solvent molecules. The theoretical structures of course refer to the isolated molecules in the vapor phase, and the matrix isolation technique is usually presumed as well to focus on the isolated molecule.

The CH₂LiF Problem

CH₂LiF is the prototype carbenoid, that is the simplest molecule that could reasonably be expected to have properties related to those of the larger halolithiocarbenoids. For this reason CH₂LiF was the molecule chosen by Clark and Schleyer¹¹ for their initial theoretical study of carbenoids. Using self-consistent-field (SCF) theory in conjunction with a split valence 4-31G basis set, Clark and Schleyer identified no less than three separate local minima on the potential energy hypersurface. As noted above, the existence of more than one isomer of CH₂LiF would appear to be consistent with experiments^{7-10,14,15} on the heavier carbenoids.

The three equilibrium structures of Clark and Schleyer for CH₂LiF are reproduced in Figure 1. Structure I is predicted to lie lowest energetically and is interpreted¹¹ as being an intimate ion pair between F⁻ and the very stable lithiomethyl cation, CH₂Li⁺. Clark and Schleyer's less stable structures II and III were designated as singlet methylene-lithium fluoride complexes in which the carbene acts as electron donor or acceptor, respectively.

In light of recent interest in the carbenoid structure problem, it seemed important to us to pursue the electronic structure of CH₂LiF at a considerably more complete level of theory. If the Clark-Schleyer (CS) predictions had been made for more conventional hydrocarbons, their split valence basis, SCF predictions would almost certainly be qualitatively correct. However, for the relatively unconventional structures seen in Figure 1, some caution is in order. For example,

CS describe¹¹ all three geometrical structures as having F^- character, i.e., that of the fluoride ion. But their 4-31G basis set gives a poor representation of the isolated F^- anion.

The carbon and fluorine basis sets used in the present work began with the standard double zeta sets of Huzinaga and Dunning,¹⁶ designated 9s5p/4s2p. To describe the expanded charge distribution in F^- , a third set of p functions (with gaussian exponent 0.05) was appended to the fluorine basis. This was followed by sets of polarization functions on both carbon and fluorine. For this purpose, six cartesian d functions with exponents 0.75 (carbon) and 1.0 (fluorine) were added to the basis. The final designation for the C and F basis sets is thus C(9s5p1d/4s2p1d), F(9s6p1d/4s3p1d). A comparable basis for hydrogen, designated H(4s1p/2s1p), was readily constructed with s function scale factor of 1.2 and p function exponent $\alpha = 1.0$. The lithium atom basis set is the (9s4p/4s2p) set of Dunning and Hay.¹⁷ In summary, one can reasonably conclude that SCF structures predicted with this basis set, of slightly better than double zeta plus polarization (DZ+P) quality, should be quite close to the Hartree-Fock limit structures.

Predicted CH₂LiF Structures

Beginning with the equilibrium geometries of Clark and Schleyer,¹¹ analytic gradient techniques^{18,19} were employed to redetermine these structures using the larger DZ+P basis set described above. In each case, all quadratic force constants were shown to be positive, proving that the three structures shown in Figure 2 are true minima (at this level of theory).

The most readily apparent difference between the two sets of theoretical predictions occurs for the H₂C...LiF moiety, structure II. There Clark and Schleyer predicted a C-Li-F bond angle of 150.3° (see Figure 1) while Figure 2 illustrates that the DZ+P SCF level of theory suggests a collinear arrangement for these three atoms. As will be demonstrated, however, the potential surface with respect to C-Li-F bending is exceedingly flat and even the DZ+P SCF prediction cannot be taken to be definitive.

If methyl fluoride is taken as incorporating the prototype C-F single bond, then its C-F distance²⁰ of 1.385 Å may be considered a standard by which others may be evaluated. In this light, the C-F distance predicted for Structure I, 1.568 Å, is much longer than a normal C-F single bond. However this is not unexpected since structure I is of the qualitative form H₂CLi[⊕]...F[⊖], for which the C-F distance should be longer. It is also noteworthy that this C-F distance of 1.568 Å is significantly shorter (by 0.076 Å) than that predicted by Clark and Schleyer¹¹ at the 4-31G SCF level of theory.

For the structure III, the predicted C-F distance of 1.576 Å is again much longer than that expected for a C-F single bond. Again, however, this result is plausible in light of the qualitative valence

structures $\text{H}_2\text{CF}^{\ominus} \cdots \text{Li}^{\oplus}$ and/or $\text{H}_2\text{C} \cdots \text{FLi}$. In the former case, it is not too unreasonable that the anion H_2CF^- might have a somewhat longer C-F distance than the analogous neutral. Nevertheless, based on the longer C-F distance, we prefer to label structure III as $\text{H}_2\text{C} \cdots \text{F Li}$. As with structure I, the structure III C-F bond distance predicted here is significantly less (by 0.119 Å) than that of Clark and Schleyer.¹¹

In a similar manner, the C-Li bond distances predicted for CH_2LiF may be compared with those obtained for the prototype lithiocarbon CH_3Li . The structure of methyl lithium has been predicted by Streitwieser and co-workers²¹ at a level of theory very nearly comparable to the DZ+P SCF used here to determine structures I, II, and III. They find a carbon-lithium bond distance of 2.021 Å, which is actually longer than the C-Li distance of 1.952 Å predicted for structure I. This certainly confirms our qualitative view of structure I as being $\text{H}_2\text{CLi}^{\oplus} \cdots \text{F}^{\ominus}$. For structure II, however, the predicted C-Li distance is much longer, 2.237 Å, which weighs against a C-Li single bond there. This long C-Li distance confirms the idea that structure II is a singlet carbene-alkali halide complex, i.e., $\text{H}_2\text{C} \cdots \text{LiF}$. Our predicted C-Li distance for structure II is 0.056 Å longer than that of Clark and Schleyer.

Finally the experimental bond distance²² for diatomic lithium fluoride is $r_e = 1.564$ Å, compared with 1.613 Å for structure II, in which the LiF entity is most clearly separated from the methylene group. For structure III the Li-F distance is still only 0.126 Å longer than in the diatomic, supporting our preferred view of structure III as $\text{H}_2\text{C} \cdots \text{FLi}$. For structure I, the Li-F separation is 0.199 Å longer than in diatomic LiF, and there the qualitative picture $\text{H}_2\text{CLi}^{\oplus} \cdots \text{F}^{\ominus}$, discussed above, is more reasonable.

Vibrational Frequencies

At the DZ+P SCF level of theory, cartesian force constants were determined for each of the three structures via central differencing of the analytically-determined gradients. The harmonic vibrational frequencies derived in this manner are summarized in Table I.

The qualitative identifications of the different predicted normal modes in Table I confirm the simple picture for the three different structures given above. For example, we have labeled structure I as $\text{H}_2\text{CLi}^{\oplus} \cdots \text{F}^{\ominus}$ based on its predicted equilibrium geometry, seen in Figure 2. Table I shows that the normal mode at 732 cm^{-1} is predominantly a C-Li stretching frequency, but that neither C-F nor Li-F stretching frequencies were apparent. The closest one comes to the latter two is the CLiF ring deformation at 564 cm^{-1} . Similarly, structure II, labeled $\text{H}_2\text{C} \cdots \text{LiF}$ above, has a clearly identifiable Li-F stretching frequency at 897 cm^{-1} (910 cm^{-1} experimentally²² for diatomic LiF). While the C-Li stretch in structure II is identifiable at 275 cm^{-1} , it is drastically reduced relative to the 732 cm^{-1} prediction of the same frequency for structure I.

Interestingly enough, all three heavy atom-heavy atom stretches are roughly identifiable for structure III. The 735 cm^{-1} Li-F frequency is appropriately less than the 897 cm^{-1} predicted for structure II, where the LiF fragment is much more completely separated from the rest of the molecule, as also seen by the shorter Li-F bond distance in structure II. Both of these results suggest that the designation $\text{H}_2\text{C} \cdots \text{LiF}$ is more appropriate for structure II than is $\text{H}_2\text{C} \cdots \text{FLi}$ for structure III. The latter conclusion is of course consistent with the

fact that the nominally "nonbonded" C-Li stretch at 365 cm^{-1} is also identifiable. Note, however, that this "nonbonded" C-Li distance in structure III is only $2.176\text{ \AA}$, which is actually $0.061\text{ \AA}$ less than in structure II. These observations support the notion that there is some $\text{H}_2\text{CF}^{\ominus}\cdots\text{Li}^{\oplus}$ character associated with structure III. The identifiability of the C-F stretch at 531 cm^{-1} in structure III confirms this view. Note, however, that the typical C-F stretching frequency of 1048 cm^{-1} found experimentally²³ for methyl fluoride is nearly twice as large as that predicted for structure III. Thus we remain convinced that the best single qualitative description of structure III is $\text{H}_2\text{C}\cdots\text{FLi}$.

Transition State for the Process II $\rightarrow$ I

The two exceedingly low vibrational frequencies (53 cm^{-1} and 31 cm^{-1}) for structure II suggest that II might undergo an isomerization reaction involving only a small barrier height or activation energy. In fact the out-of-plane (i.e., b_1) C...Li-F bend at 31 cm^{-1} connects structure II with the lower energy structure I. The transition state for this rearrangement was located with DZ+P SCF gradient methods and is seen in Figure 3.

Except for the C-Li-F angle, the structural parameters for the transition state for II $\rightarrow$ I are quite similar to those of structure II itself. Specifically the methylene HCH angle is 106.4° in both cases, while the Li-F distance is only $0.005\text{ \AA}$ longer for the transition state. The C-Li distance at the transition state is decreased by $0.057\text{ \AA}$ relative to II, but is still $0.228\text{ \AA}$ longer than that predicted for structure I. In general then, the transition state for the rearrangement from II to I is quite consistent with Hammond's suggestion²⁴ that for significantly exothermic unimolecular processes, the transition state structure should resemble that of the reactant molecule.

The total energy of the transition state structure shown in Figure 3 is -145.88409 hartrees at the DZ+P SCF level of theory. This is only 1.0 kcal above the total energy of structure II, i.e., the barrier is exceedingly small. When one appreciates that the C-Li-F bond angle has gone from 180° (structure II) to 109.8° , this very small increase in the total energy stands out even more. One must conclude that the potential energy hypersurface is exceedingly flat

with respect to the degrees of freedom linking the H_2C and LiF fragments.

It is entirely possible that structure II would cease to be a relative minimum on the CH_2LiF potential surface at a higher level of theory.²⁵ Given the flatness of the surface, it was considered inappropriate to carry out a single calculation at a higher level of theory, i.e., without a complete redetermination of the transition state geometrical structure. Since the latter was not feasible, we simply conclude that even if structure II is a relative minimum on the CH_2LiF potential surface, this minimum is so shallow with respect to rearrangement to structure I that experimental observation would be exceedingly difficult.

Relative Energies

At the DZ+P SCF level of theory, Table II shows structure I to lie lowest energetically, followed by structure II at 17.1 kcal, followed by structure III at 26.1 kcal. This ordering is the same as that predicted earlier by Clark and Schleyer¹¹ at several lower levels of theory.

However, it was considered important to explicitly consider the effects of electron correlation. Therefore using the same DZ+P basis set, configuration interaction (CI) including single and double excitations was carried out. In these correlated wave functions the three lowest occupied and three highest virtual orbitals (the 1s-like orbitals on C, Li, and F) were not involved in the CI. With these restrictions, all single and double excitations were included variationally, a total of 22,366 configurations for structure I and III (C_s symmetry) and 12,293 configurations for structure II (C_{2v} symmetry). In addition the importance of higher than double excitations, specifically unlinked clusters, was investigated via the Davidson correction.²⁶

The relative energetic positions of the two deep minima I and III are essentially unaffected by correlation considerations. That is, the SCF, CI, and Davidson ΔE (I-III) values are 26.1, 25.1, and 24.5 kcal. However, electron correlation is notably less important for structure II, consistent with the fact that the CH_2 and LiF moieties there are widely separated compared to the other two structures. For this reason, structure III becomes 3 kcal lower in energy than structure II at the highest level of theory.

Concluding Remarks

This theoretical study predicts the existence of two distinct isomers of the prototype carbenoid CH_2LiF . These are structures I and III in Figure 2, and it is hoped that their predicted harmonic vibrational frequencies will aid in the future experimental identification of CH_2LiF . A third structure, labeled II in Figure 2 is predicted to correspond to an extremely shallow minimum (subject to immediate isomerization to the lower energy structure I) on the CH_2LiF potential energy hypersurface.

The present theoretical results for CH_2LiF may perhaps be compared most closely with the matrix isolation experiments of Andrews and co-workers^{9,10} on the species X_3CM ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{and Cs}$; $\text{X} = \text{Cl}, \text{Br}$). However, it may be concluded that the experimental geometrical structures of the Andrews molecules are quite different than those of the CH_2LiF molecule. Andrews observes two structures, and identifies these as pseudotetrahedral or methane-like (with C_{3v} symmetry); and $\text{Cl}_2\text{C} \cdots \text{M}^+ \cdots \text{X}^-$, which corresponds to the structure II (extremely shallow minimum) of the present study. We conclude that the substitution of halogen ligands for hydrogen in these hydrocarbons has a large effect on their geometrical and electronic structures.

It is nevertheless intriguing that the equilibrium (3) suggested in 1965 by Hoeg, Lusk, and Crumbliss⁸ (presumably on much less solid evidence than that of Andrews^{9,10}) is reminiscent of the two qualitative valence pictures suggested for structure III. Perhaps one should not rule out entirely the possibility that the matrix environment might effect the equilibrium geometries adopted by these simple carbenoids.

Acknowledgments

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Figure Captions

Figure 1. Predictions of Clark and Schleyer¹¹ for the geometrical structures of three isomers of CH_2LiF . SCF theory was used with a split valence basis set. All bond distances are in Å.

Figure 2. Present SCF predictions of the structures of CH_2LiF isomers. A basis set slightly superior in quality to double zeta plus polarization was employed. Bond distances are in Å.

Figure 3. Transition state connecting structures II ($\text{H}_2\text{C}\cdots\text{LiF}$) and I ($\text{H}_2\text{CLi}^+\cdots\text{F}^-$). The level of theory employed was consistent with Figure 2.

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Table I. Predicted DZ+P SCF harmonic vibrational frequencies (in cm^{-1}) for CH_2LiF . The qualitative labeling

of the normal modes refers to the dominant character and should not be taken to imply exclusivity.

Structure I		Structure II		Structure III	
$\text{H}_2\text{C}^{\oplus}\text{Li}^{\oplus}\cdots\text{F}^{\ominus}$		$\text{H}_2\text{C}\cdots\text{LiF}$		Li $\text{H}_2\text{C}\cdots\text{F}$	
3295	Asym. CH stretch	3298	Asym. CH stretch	3089	Asym. CH stretch
3222	Sym. CH stretch	3216	Sym. CH stretch	2994	Sym CH stretch
1542	CH_2 scissor	1514	CH_2 scissor	1495	CH_2 wag & scissor
1278	CH_2 wag	897	Li-F stretch	1273	CH_2 twist
1203	CH_2 twist	737	CH_2 wag	1137	CH_2 scissor & wag
732	Li-C stretch	412	CH_2 rock	735	Li-F stretch
564	$\text{C} \begin{array}{c} \nearrow \text{Li} \\ \downarrow \end{array}$	275	Li-C stretch	531	C-F stretch
446	CH_2 rock	53	in-plane (b_2) $\text{C}\cdots\text{Li-F}$ bend	365	$\text{Li}\cdots\text{C}$ stretch
443	$\leftarrow \text{C} \begin{array}{c} \nearrow \text{F} \\ \downarrow \end{array} \text{Li}$	31	out-of-plane (b_1) $\text{C}\cdots\text{Li-F}$ bend	290	CH_2 rock

Table II. Predicted absolute (in hartrees) and relative (in kcal) energies for three isomers of the prototype carbenoid CH_2LiF . All results were obtained with a double zeta plus polarization (DZ+P) basis set of one-electron functions.

	$\text{H}_2\text{CLi}^{\oplus}\cdots\text{F}^{\ominus}$	$\text{H}_2\text{C}\cdots\text{LiF}$	$\begin{array}{c} \text{Li} \\ \\ \text{H}_2\text{C}\cdots\text{F} \end{array}$
	<u>Structure I</u>	<u>Structure II</u>	<u>Structure III</u>
Self-Consistent-Field			
Absolute	-145.91292	-145.88562	-145.87132
Relative	0	17.1	26.1
Configuration Interaction			
Absolute	-146.22060	-146.17852	-146.18066
Relative	0	26.4	25.1
Davidson Corrected			
Relative	0	27.5	24.5

Figure 1

XBL814-3752

I, C_3

II, C_{2v}

III, C_s

Figure 2

XBL814-3753

Transition State

XBL8111 - 4354

Figure 3

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