# A Theoretical Investigation on the Role of Solvent in Solvolytic Reactions. Part 7.[1] $CH_2LiF$ in Water

**Vera Bellagamba and Roberta Ercoli**
*Istituto di Chimica Fisica, Università di Sassari, V. Vienna 2, I-07100 Sassari, Italy*
**Aldo Gamba and Massimo Simonetta** *
*Dipartimento di Chimica Fisica ed Elettrochimica, Centro CNR, University of Milano, V. Golgi 19, I-20133 Milano, Italy*

The effect of water, a highly polar solvent, on the dissociation of $CH_2LiF$, the simplest prototype of halogenolithiocarbenoids, is studied by MO-SCF theory at the CNDO/2 level of approximation. Ten water units are used to describe the first hydration shell. Different dissociative pathways are examined. $CH_2LiF$ is predicted to dissociate to hydrated $CH_2Li^+$ and $F^-$ ions with formation of intermediates, whose geometries are interpreted in terms of ion pair structures.

In the last few years molecular electronic structure theory has been widely used to investigate the geometry and energetics of $CH_2LiF$, the simplest system which could reasonably be expected to have properties related to those of the larger halogenolithiocarbenoids. The primary motivation of several studies available in the literature is theoretical support for the different energetically competitive isomers of carbenoids proposed by experimentalists to interpret their results (see ref. 2). The lack of definitive experimental structures for these systems makes such theoretical investigations important.

The first geometry optimization of $CH_2LiF$ was performed by Clark and Schleyer,[3] by using SCF theory with a split valence 4-31G basis set. No fewer than three separated local minima on the potential energy hypersurface were identified. The most stable structure (I) has a peculiar 'umbrella' (inverted carbon) shape, and $CH_2Li^+F^-$ ion pair character. The other less stable structures (II) and (III) seemed to be singlet methylene–lithium fluoride complexes, the carbene acting as electron donor and acceptor, respectively. The existence of three minima was confirmed by Vincent and Schaefer[2] on a higher level of theory, *i.e.* with a basis set of better quality than double zeta plus polarization functions. The part of the potential surface connecting structures (II) and (III) was very flat, but a transition state was located. Recently, the potential energy surface of singlet $CH_2LiF$ was further examined using *ab initio* methods including electron correlation and zero point energy corrections.[4] The three non-tetrahedral structures found earlier were confirmed to be minima, but only the lowest energy one (I) should be prone to experimental observation.

Calculations on various stationary points of the potential hypersurface of $CH_2LiF$ in the singlet and lowest triplet states were also performed by the semiempirical LCAO SCF INDO method.[5] These calculations predict a classical $C_s$ structure, at first sight very different from that found by *ab initio* calculations: in particular, the C–F bond length is shorter, owing to the well known behaviour of the method which systematically underestimates bond lengths. However, on qualitative grounds, the INDO structure shows, in accord with the *ab initio* results, significant 'intimate' ion pair character, even if the extent of the charge separation is reduced, as a consequence of the shorter C–F bond length.

The geometries of the distinct isomers of the prototype carbenoid $CH_2LiF$, predicted by high quality *ab initio* calculations,[2,3] can be easily accepted for the isolated molecule in the gas phase. The use of these results to define the structure of the species present in solution[6] and in matrix isolation experiments,[7] where the effect of the environment can be important, is less justified. For this reason we present here a study of the solvolysis of $CH_2LiF$ including the water molecules, along the lines of our research on the effect of solvents on chemical reactions.

Our model describes the solvent effect on the solute and on the energetics of its dissociative paths as primarily due to a restricted number of water molecules simulating the first solvation shell. In particular, for each value of the reaction co-ordinate, representing the separation between the fragments of the dissociating molecule, the geometry of the solvent cage is optimized by minimizing the total energy of the system, calculated by LCAO MO SCF theory at the CNDO/2 level of approximation.[8]

This approach has been used many times in similar situations, and the results were always found to be consistent with expectation and experiments. In the present case there are no experimental data and our confidence in the predictive power of the treatment is based on previous examples. Moreover, the success of the semiempirical CNDO method may be surprising, and we believe that it is due to a compensation of tendencies: on one side CNDO exaggerates bonding forces, but on the other our model, in which only the first shell of solvent is included, describes a loose system.

A study of the geometry of the solvent cages describing the first solvation of the species directly involved in the dissociation of $CH_2LiF$ was required in order to compare the energetics of several possible dissociative pathways.

## Calculations

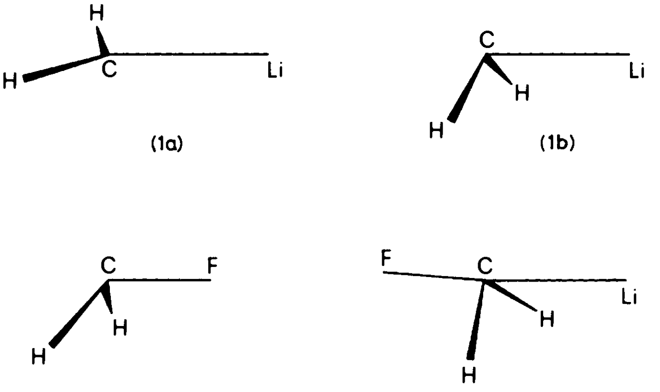
Our model of solvation, its assumptions, and limitations were previously discussed and are described in refs. 1 and 9—11. For each system considered in the present paper, isolated or surrounded by a cage of water molecules, an energy minimization process, which iteratively optimizes the most important geometrical parameters through a quadratic interpolation process, till selfconsistency is achieved,[12] was carried out. The standard parametrization of the CNDO/2 method[8] was used throughout the calculations.

The geometry of the water molecules was kept fixed and, whenever possible, the symmetry of the isolated solute was retained in solution. A considerable number of geometrical parameters were optimized even for the largest systems. Moreover, the calculated minima were checked by repeating the iterative process, both by starting from different points of the variable hyperspace and by increasing the number of the variables.

**Table 1.** Optimized CNDO/2 energies and geometries of Li and/or F substituted methane derivatives and related ions.

| | Symmetry | X | Y | CX (Å) | CY (Å) | XĈY | XĈX | YĈY | $-E$ (a.u.) |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3F$ | $C_{3v}$ | H | F | $1.119\,\frac{(1.105^a)}{(1.076^b)}$ | $1.344\,\frac{(1.385^a)}{(1.412^b)}$ | $109.3\,\frac{(109.9^a)}{(110.7^b)}$ | | | 37.0996 |
| $CH_2F_2$ | $C_{2v}$tetrahedron | H | F | $1.122\,\frac{(1.091^c)}{(1.109^d)}$ | $1.344\,\frac{(1.358^c)}{(1.378^d)}$ | | $110.6\,\frac{(112.1^c)}{(108.8^d)}$ | $106.2\,\frac{(108.2^c)}{(108.7^d)}$ | 64.0941 |
| $CHF_3$ | $C_{3v}$ | H | F | $1.124\,\frac{(1.098^e)}{(1.119^d)}$ | $1.341\,\frac{(1.332^e)}{(1.371^d)}$ | | | $107.4\,\frac{(108.8^e)}{(108.6^d)}$ | 91.0982 |
| $CF_4$ | $T_d$ | F | F | | $1.338\,\frac{(1.317^f)}{(1.366^d)}$ | | | | 118.1113 |
| $CH_3Li$ | $C_{3v}$ | H | Li | 1.133 ($1.092^g$) | 1.878 ($1.989^g$) | 112.8 ($111.5^g$) | | | 9.7169 |
| $CH_2Li_2$ | $C_{2v}$tetrahedron | H | Li | 1.150 ($1.091^h$) | 1.783 ($1.923^h$) | 134.0 | 134.0 ($106.7^h$) | 70.4 ($119.8^h$) | 9.5421 |
| | $C_{2v}$planar | | | 1.155 ($1.110^h$) | 1.757 ($1.744^h$) | | 116.8 ($101.4^h$) | 73.0 ($97.7^h$) | 9.6374 |
| | $D_{2h}$planar | | | 1.177 ($1.073^h$) | 1.709 ($1.807^h$) | | | | 9.3679 |
| $CH_2LiF^{i,l}$ (**3**) | $C_s$ | H | F | 1.180 | 1.350 | 106.1 | 102.4 | | 36.7146 |
| $CLi_2F_2$ | $C_{2v}$ | Li | F | 2.351 ($2.118^h$) | 1.307 ($1.380^h$) | | 42.4 ($114.6^h$) | 101.8 ($105.4^h$) | 63.5273 |
| $CH_2F^{-l}$ (**2**) | $C_s$ | H | F | 1.143 ($1.104^m$) | 1.363 ($1.529^m$) | 105.7 | 102.9 ($107.5^m$) | | 36.1077 |
| $CH_2Li^-$ | $C_{2v}$planar | H | Li | 1.135 (not detected) | 1.688 ($1.853^n$) | 128.1 ($126.6^n$) | | | 8.7830 |
| $CH_2Li^{+l}$ (**1a**) | $C_{2v}$planar | H | Li | 1.118 ($1.085^g$) | 2.105 ($2.139^g$) | | 109.4 ($109.6^g$) | | 8.3763 |
| (**1b**) | $C_s$ | H | Li | 1.138 | 1.914 | 93.2 | 109.1 | | 8.3768 |

[a] Exp.[13] [b] Theor. (4-31G).[14] [c] Exp.[15] [d] Theor. (STO-3G).[16] [e] Exp.[17] [f] Exp.[18] [g] Theor. (4-31G).[19] [h] Theor. (STO-3G).[20] [i] Other optimized parameters: C-Li 1.869 Å, FCLi 175.0°. [l] See Figure 1. [m] Theor. (*ab initio* contracted gaussian basis set 5*s*, 4*p* (POLYATOM).[21] [n] Theor. (4-31G).[22]



(1a) (1b) (2) (3)

**Figure 1.** CNDO/2 structures of $CH_2Li^+$ (**1a,b**), $CH_2F^-$ (**2**), and $CH_2LiF$ (**3**) *in vacuo*

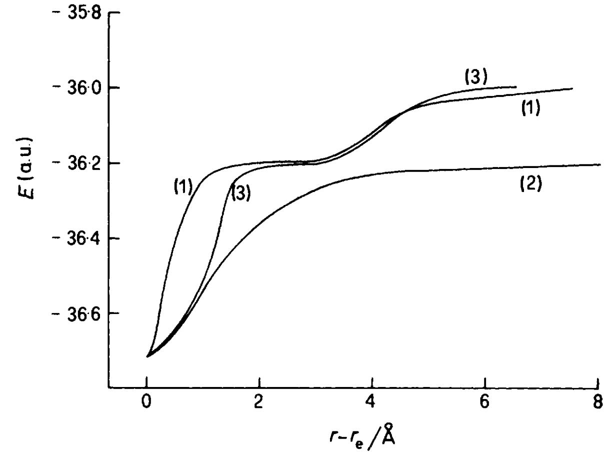


**Figure 2.** CNDO/2 dissociative paths of $CH_2LiF$ *in vacuo* to: (1) $CH_2Li^+ + F^-$; (2) $CH_2F^- + Li^+$; (3) $CH_2 + LiF$

## Results

*$CH_2LiF$ and its Dissociation Products in the Gas Phase.*—The dissociation of $CH_2LiF$ *in vacuo* can occur according to pathways (1)—(3). The minimum energy geometry of the

$$CH_2LiF \longrightarrow CH_2Li^+ + F^- \quad (1)$$
$$CH_2LiF \longrightarrow CH_2F^- + Li^+ \quad (2)$$
$$CH_2LiF \longrightarrow CH_2 + LiF \quad (3)$$

starting carbenoid and its possible dissociation products were obtained by CNDO/2. The optimized structure of $CH_2LiF$ shows $C_s$ symmetry [(**3**) in Figure 1] and it is very similar to that predicted by INDO calculations.[5] The most relevant results are collected in Table 1, where the optimized energies and geometries of a series of organolithium and fluorinated compounds are included, together with the corresponding available *ab initio* and/or experimental results.

Table 1 shows that the C–F bond lengths predicted by CNDO/2 are systematically shorter than the corresponding values obtained by *ab initio* calculations for all the systems considered. However, it is worthy of note that whenever experimental data are available, CNDO/2 C–F bond lengths are in better agreement with them than the *ab initio* values. No such comparison is possible for $CH_2LiF$, for which the optimized C–F distance of 1.35 Å is significantly shorter than the value 1.568 Å, obtained by *ab initio* calculations.[2]

Since evident differences were found between CNDO/2 and

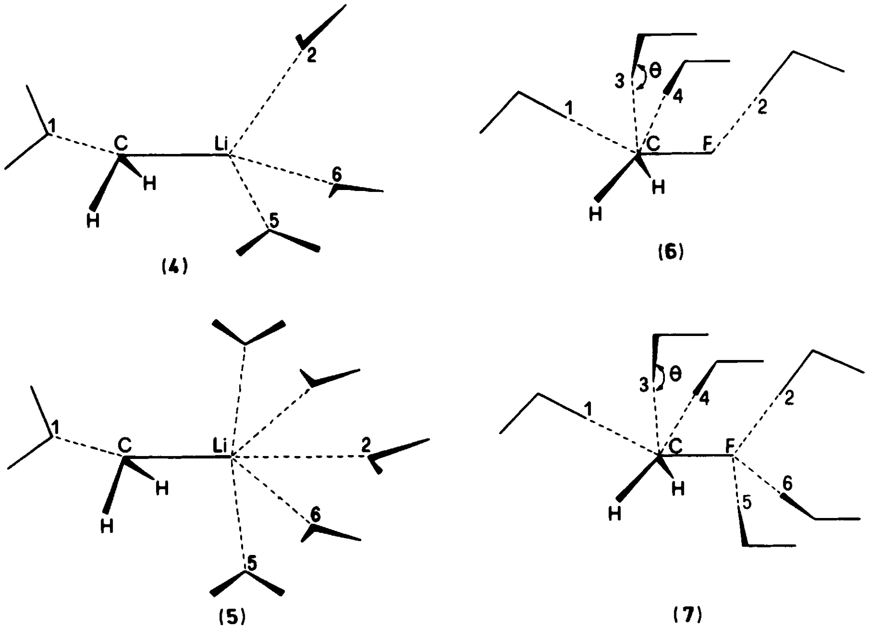


**Figure 3.** CNDO/2 structures for $CH_2Li^+(H_2O)_n$ and $CH_2F^-$ $(H_2O)_n$, $n = 4, 6$. Total energies (a.u.): $CH_2Li^+$, −88.4782 (**4**); −128.3231 (**5**). $CH_2F^-$, −115.8343 (**6**); −155.6502 (**7**)

*ab initio* geometries of some molecules containing Li, we checked the influence of CNDO/2 parameters of Li on the computed structures. Some simple biatomic molecules were chosen for a test, and the Li parameters were fitted to reproduce the experimental distances and dipole moments. The best set of parameters, though, did not produce any significant change in the geometry of $CH_2LiF$. Greater variations were found in the atomic charges, in line with previous theoretical investigations concerning related systems.[23] The standard parametrization[8] was then used throughout the calculations.

The dissociation curves of $CH_2LiF$ in the gas phase relative to paths (1)—(3) are shown in Figure 2. The trend of total energy *versus* $r$ was studied in the three cases, $r$ being the distance of C from F, or Li, or the barycentre of LiF. $F^-$, $Li^+$, and LiF were kept in the $C_s$ symmetry plane of the starting molecule. A monotonic trend is observed for all the curves even if in the case of (1) and (3) a flat region is predicted in the range of $r - r_e$ 1—3 Å. One can expect the dissociation energies to be largely overestimated by CNDO/2 calculations: in fact they are 536, 381, and 451 kcal mol$^{-1}$ for reactions (1)—(3), respectively. The geometries of $CH_2LiF$ and the resulting dissociation ions $CH_2Li^+$ and $CH_2F^-$ are shown in Figure 1. Here (**1a** and **b**) denote two isomers of the cation having quite different geometries and closely comparable energies.

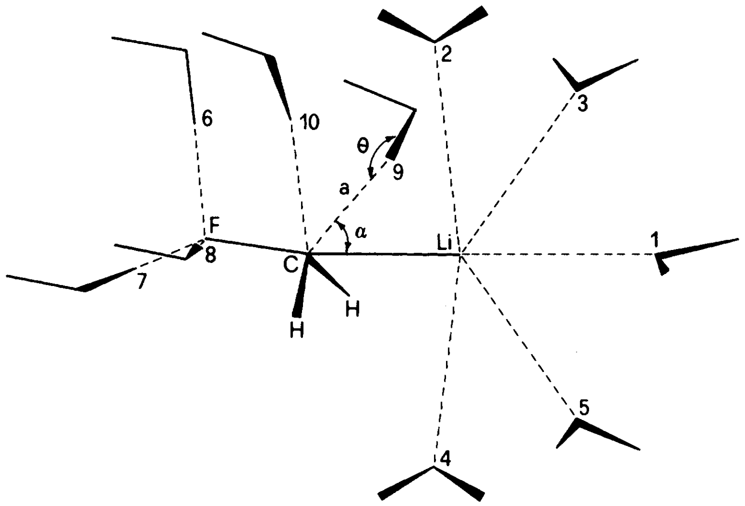
The carbenoid is predicted to dissociate without formation of any intermediates, and the less energetic path (2) leads to the dissociation into $CH_2F^-$ and $Li^+$, a mechanism probably not favoured in solution. In fact, there are some indications that metal carbenium ions may be intermediates in carbenoid reactions, as they readily undergo nucleophilic substitution.[24] The investigation of the role of the solvent on the energetics and the nature of the possible dissociation mechanism is a goal of the present work.

$CH_2LiF$ *and its Dissociation Products in Water* $Li^+(H_2O)_n$, $n$ = 1,2,4,6; $F^-(H_2O)_n$, $n$ = 1,4,6.—Monte Carlo calculations on the structure of the hydration shells of alkali and halogen ions carried out by Clementi and Barsotti[25] show that 4 and 3.85 water molecules are proper co-ordination numbers for the first solvation shell of $Li^+$ and $F^-$, respectively. On the other hand, when $Li^+F^-$ ion pairs are present in solution, the co-ordination number of $F^-$ remains practically unchanged (four water molecules), while that of $Li^+$ varies from four to six for inter-ion distances greater than 5 Å.[26] On the basis of these results we used different numbers of water molecules, with a maximum of six, to build up the solvent cages of $Li^+$ and $F^-$. CNDO total energies (a.u.) for $T_d$ ($n = 4$) and $O_h$ ($n = 6$) solvated systems are −79.8250 and −119.6923 for $Li^+$, and −107.3005 and −147.1265 for $F^-$.

The average radii of the first solvation shells obtained by Monte Carlo calculations[25] are 2.28 and 1.99 Å for Li–O and F–H, respectively. The Li–O distance (2.4—2.5 Å) is slightly overestimated by CNDO calculations, while F–H (1.2—1.4 Å) is largely underestimated, in line with the general trend of these semiempirical methods in computations of intermolecular distances involving $F^-$. The same behaviour is found in *ab initio* calculations using a minimal basis set, and in this case the effect is ascribed to the basis set superposition error.[27,28]

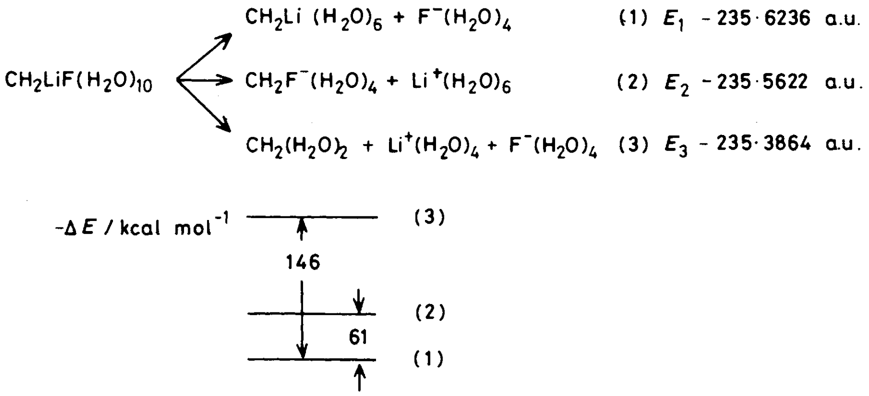
$CH_2Li^+(H_2O)_n$, $n$ = 4, 6.—Four and six water molecules were used to describe the first hydration shell of this ion. In the first case each of the four solvent molecules was originally co-ordinated to each atom of the solute. However, during the optimization process, three solvent units moved to solvate lithium, forming a cage of nearly $C_{3v}$ local symmetry. As two stable isomers [(**1a** and **b**) in Figure 1] were found for the isolated cation, they were both taken into consideration. The resulting solvated systems are qualitatively very similar, and the most stable one (**4**), derived from (**1b**), is shown in Figure 3. Six solvent units were then used to build up the solvent cage, and five of them resulted to co-ordinate lithium with a local $C_{4v}$ symmetry [(**5**) in Figure 3]. The optimized values of the geometrical parameters and atomic charges are available upon request. Total energies are reported in the caption to Figure 3. The geometry of the cation is significantly modified by the solvent cage, and a very small value (1.40 Å) is predicted for the C ··· O distance, prefiguring the formation of a true bond.

$CH_2F^-(H_2O)_n$, $n$ = 4, 6.—In this case also four and six water



(8)

**Figure 4.** CNDO/2 structure (8) for $CH_2LiF(H_2O)_{10}$ at C–F 1.364 Å



**Scheme.**

molecules were used to describe the first solvation shell of the anion. The optimized structures (6) and (7) are shown in Figure 3. Three water molecules are co-ordinated to the carbon atom in both cases, while fluorine was solvated by one and three water molecules in (6) and (7), respectively, with a local $C_{3v}$ symmetry in the latter case. Total energies are reported in the caption to Figure 3. The geometry of the solute is slightly modified by the presence of the solvent cage; charge transfers from the solute to the solvent, even if overestimated by the semiempirical calculations, appear to be of moderate level (atomic charges of solvated $CH_2LiF$ are shown in Table 3).

$CH_2LiF(H_2O)_{10}$.—Lacking any experimental data or information on the first hydration shell of this system, ten water molecules were chosen on the basis of the following factor: the number of the solvent units has to be close to that of the corresponding hydration shell of $CH_3F$, namely 10—12. This number was proposed on the basis of structural assumptions and thermodynamic evidence,[29] and it corresponds to the sum of the solvation numbers of the dissociated species. Moreover, in this way the size of the calculations is retained at a reasonable level.

The structure corresponding to the absolute minimum, depicted in Figure 4, represents the undissociated but solvated $CH_2LiF$. The solute shows slight but not negligible relaxation owing to the effect of the highly polar solvent. In fact, the main bond distances of the isolated $CH_2LiF$ (CF 1.35, CLi 1.87 Å) are stretched to 1.364 and 2.03 Å, respectively. The solvent units are located regularly around the solute, forming a cage which describes the first hydration shell. Five of them surround the Li atom, and three are co-ordinated to fluorine, while the remaining ones have a hydrogen bond with carbon. The global system has $C_s$ symmetry, and the values of the optimized geometrical variables and energies are collected in the first row of Tables 2 and 3.

The CNDO/2 energy balances related to the possible dissociative mechanisms in solution are shown in the Scheme. With regard to the solvation numbers of the ions resulting from the dissociations, the reported values (*i.e.* four for $CH_2F^-$ and six for $Li^+$, six for $CH_2Li^+$ and four for $F^-$) are preferred in terms of CNDO/2 energies. On the other hand, for any distributions of the ten solvent molecules between the dissociated species, the cleavage of $F^-$ is always energetically favoured with respect to that of $Li^+$, which in turn is preferred to that of $Li^+F^-$.

The view[2-4] that $CH_2LiF$ is an ion pair formed by the fluorine anion and the lithiomethyl cation[19] supports this choice. In fact, while carbenoids exhibit some reactions as

**Table 2.** CNDO/2-optimized geometrical variables for $CH_2LiF(H_2O)_{10} \rightarrow CH_2Li^+F^-(H_2O)_{10}$ dissociation at different values of the C–F distance[a]

| CF | CLi | CH | $\mathrm{C\hat{F}Li}$ | $\mathrm{H\hat{C}Li}$ | $\mathrm{H\hat{C}H}$ | Li(1) | Li(2) | CLi(2) | F(6) | CF(6) | F(7) | CF(7) | (7)FCLi | $a$ | $\alpha$ | $\mathrm{(9)C\hat{L}iF}$ | C(10) | $\mathrm{Li\hat{C}(10)}$ | $\theta$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.364[b] | 2.03 | 1.16 | 170 | 80 | 102 | 2.58 | 2.57 | 103 | 1.54 | 104 | 1.54 | 105 | 104 | 1.91 | 79 | −38 | 1.91 | 79 | 174 |
| 2.0[c] | 2.03 | 1.17 | 133 | 73 | 102 | 2.58 | 2.57 | 103 | 1.41 | 79 | 1.35 | 123 | 77 | 2.06 | 83 | −49 | 1.43 | 194 | 180 |
| 3.0[c] | 2.01 | 1.16 | 137 | 77 | 102 | 2.59 | 2.58 | 105 | 1.49 | 60 | 1.42 | 102 | 71 | 2.17 | 80 | −49 | 1.38 | 171 | 158 |
| 4.0[d] | 1.97 | 1.16 | 153 | 79 | 103 | 2.63 | 2.60 | 111 | 1.32 | 59 | 1.39 | 128 | 91 | 1.27 | 59 | 0 | 1.37 | 174 | 128 |
| 5.0[d] | 1.99 | 1.16 | 145 | 79 | 103 | 2.63 | 2.59 | 111 | 1.29 | 23 | 1.37 | 123 | 78 | 1.29 | 37 | 0 | 1.38 | 172 | 126 |
| 6.0[d] | 1.99 | 1.16 | 151 | 79 | 104 | 2.62 | 2.57 | 110 | 1.35 | 98 | 1.35 | 102 | 121 | 1.34 | 4 | 0 | 1.41 | 173 | 128 |
| ∞ | 2.01 | 1.15 |  | 85 | 104 | 2.61 | 2.55 | 110 | 1.33 |  | 1.33 |  |  | 1.33 |  |  | 1.40 | 163 | 128 |

[a] Distances in Å and angles in degrees; the numbers denoting atoms and $\alpha$, $\theta$, and $a$ are shown in Figures 4, 6, and 7. [b] See Figure 4. [c] See Figure 6. [d] See Figure 7.

nucleophiles, their designation as 'carbanions', which implies a $CH_2F^- Li^+$ structure,[30-32] is inappropriate.

Our aim is to detect the possible formation of intermediates during the initial stage of the process, and to define their structures. The dissociation of solvated $CH_2Li^+$ will be the subject of a further study.

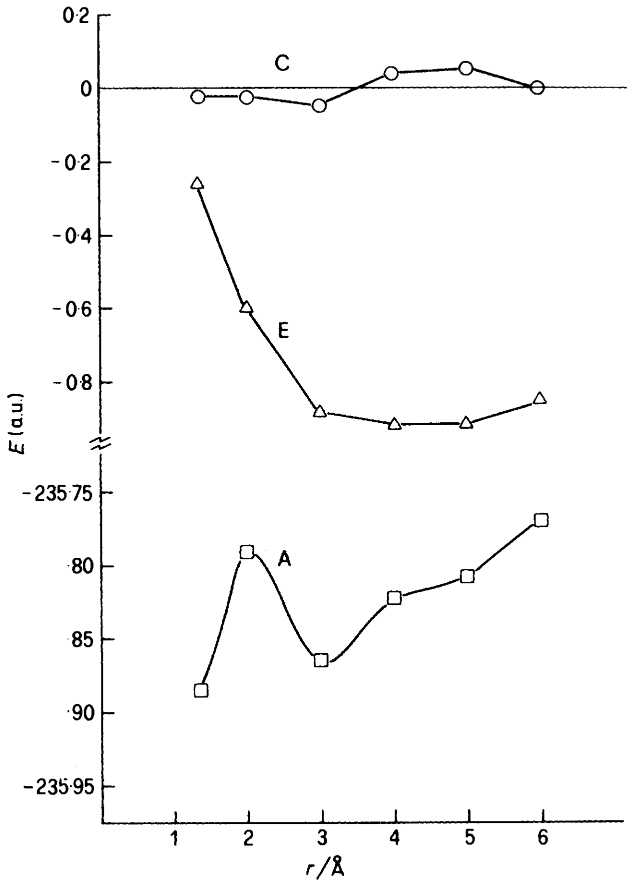
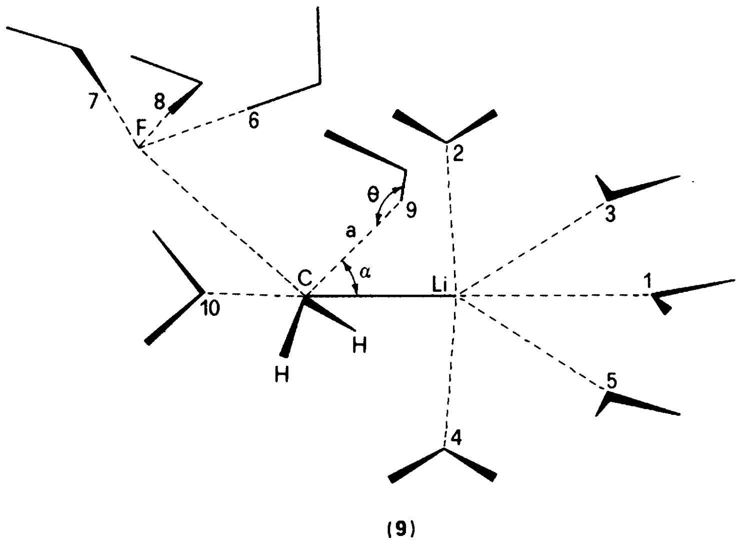


**Figure 5.** Trends of total energy (A), solute–solvent energy (E), and solvent cage interaction energy (C) for $CH_2LiF(H_2O)_{10}$

The geometrical parameters taken into account in the energy minimization process at each value of the dissociation co-ordinate $r$ = C–F are collected in Table 2, together with their optimized values. The trend of total energy *versus* $r$ is shown in Figure 5A. Two minima are located at $r$ 1.36 and 3.0 Å respectively, and the related barrier amounts to 61 kcal mol$^{-1}$. The geometries of the cage of water molecules surrounding the solute at the two minima and at $r$ = 6.0 Å are shown in Figures 4, 6, and 7. From Table 2 it appears that the solvent cages at $r$ 1.36, 4, 5, and 6 Å retain $C_s$ symmetry. In contrast, at $r$ = 2 and 3 Å any symmetry is lost, owing to the displacement of one solvent molecule (labelled 9) towards the $C_s$ plane. Moreover, local symmetry constraints were imposed throughout the calculations both to water molecules 7 and 8, co-ordinated to fluorine, and to the five water molecules 1—5 solvating Li ($C_{4v}$). The positions of the latter (1—5) are slightly affected during the dissociation process, as well as the geometry of $CH_2Li^+$ itself. The structures at different $r$ values differ for the positions of water molecules 6—10. The data in Table 2 report the lowest energy points, and we point out that each represents one among several structures of comparable energy in the range of the considered variables. For $r$ = 2 Å or larger, the oxygen atom of the water molecule labelled 10 in the Figures points towards the methylene carbon, and at $r$ 3 Å the C • • • O distance is *ca.* 1.4 Å, suggesting that a true bond could be formed.

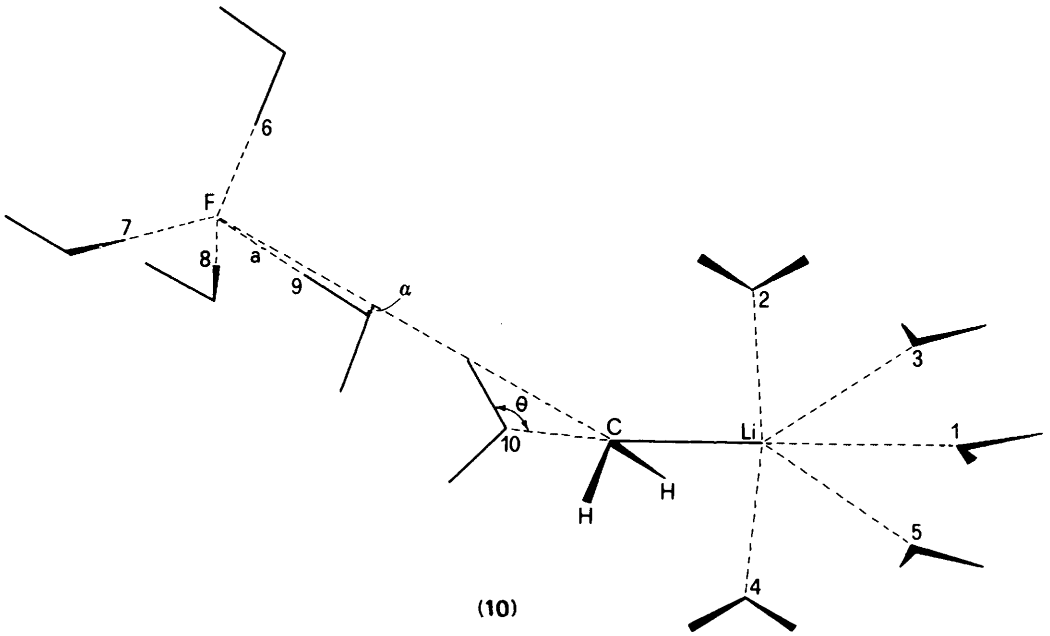
The geometry of the relative minimum at $r$ = 3 Å is compatible with the structure of a tight (intimate) ion pair. Two water molecules try to enter the region between the two counterions. At higher $r$ values the structure of a loose (solvent separated) ion pair appears, and at $r$ *ca.* 6 Å $F^-$ and $CH_2Li^+$ are completely solvent separated, as shown in Figure 7, but the character of the ion pair is preserved by means of the hydrogen bond between two water molecules, belonging to the shell of $F^-$ (9) and $CH_2Li^+$ (10), respectively.

The partitioning of the total energy of hydrated $CH_2LiF$ in terms of solute–solvent and solvent–solvent interactions is reported in Table 3. The meaning of the different terms is explained in the footnotes of Table 3. Unlike similar analyses performed on different organic substrates dissolved in water,[33,34] here the role of the interaction among solvent units seems to be fairly important. In fact, the energy contribution of the cage to the total energy varies on increasing $r$, and the interaction among water molecules is stabilizing at lower $r$ values and repulsive at higher $r$ (column C of Table 3). In view



(9)

**Figure 6.** CNDO/2-optimized structure (9) for $CH_2LiF(H_2O)_{10}$ at C–F 3 Å



(10)

**Figure 7.** CNDO/2-optimized structure (**10**) for $CH_2LiF(H_2O)_{10}$ at C–F 6 Å

**Table 3.** Total energy, solvent cage energy, and different contributions[a] to solvation energy of $CH_2LiF$, and charges

| C–F (Å) | $E_A$ | $E_B$ | $E_C$ | $E_D$ | $E_E$ | $q_C$ | $q_{Li}$ | $q_F$ | $q_H$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.364 | −235.8869 | −198.9240 | −0.01 | −36.7038 | −0.26 | −0.11 | +0.02 | +0.23 | −0.01 |
| 2.0 | .7897 | .9217 | −0.01 | .2635 | −0.60 | −0.07 | +0.04 | −0.63 | −0.02 |
| 3.0 | .8635 | .9278 | −0.02 | .0583 | −0.88 | −0.09 | +0.01 | −0.51 | −0.01 |
| 4.0 | .8241 | .8883 | +0.02 | .0296 | −0.91 | −0.07 | −0.02 | −0.58 | 0.00 |
| 5.0 | .8089 | .8835 | +0.03 | .0161 | −0.85 | −0.08 | 0.00 | −0.57 | 0.00 |
| 6.0 | .7706 | .9130 | 0.00 | .0073 | −0.85 | −0.09 | +0.02 | −0.58 | +0.02 |
| ∞ | .6236 | .9083 | +0.04 | | | −0.11 | +0.06 | −0.59 | +0.04 |

[a] Energies and charges in a.u.; $E_A$, total energy of $CH_2LiF(H_2O)_{10}$; $E_B$, energy of the solvent cage at the geometry optimized for calculating $E_A$; $E_C = E_B - 10[E(H_2O)]$ solvent–solvent interaction energy; $E_D$ = energy of $CH_2LiF$ *in vacuo* with the geometry of the solvated system; $E_E = E_A - E_B - E_D$ solute–solvent interaction energy.

of this the trend of solute–solvent interaction energy ($E_E = E_A - E_B - E_D$, column E in Table 3) is different from that of total energy $E_A$, as shown in Figure 5, and it seems that solute–solvent interactions preferably stabilize ion pair structures. The curves depicted in Figure 5ACE show the role of total energy and of solute–solvent and solvent–solvent interactions in stabilizing the different species present in solution, *i.e.* undissociated $CH_2LiF$ and different kinds of ion pairs.

## References

1 Part 6, A. Gamba, B. Manunza, C. Gatti, and M. Simonetta, *Theor. Chim. Acta*, 1983, **63**, 245.
2 M. A. Vincent and H. F. Schaefer III, *J. Chem. Phys.*, 1982, **77**, 6103.
3 T. Clark and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1979, 883.
4 B. T. Luke, J. A. Pople, P. v. R. Schleyer, and T. Clark, *Chem. Phys. Lett.*, 1983, **102**, 148.
5 I. A. Abronin, R. Zafradnik, and G. M. Zhidomirov, *J. Struct. Chem.*, 1980, **21**, 1.
6 G. Köbrich, *Angew. Chem., Int. Edn. Engl.*, 1967, **6**, 41.
7 I. Andrews and T. G. Carver, *J. Phys. Chem.*, 1968, **72**, 1743.
8 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970.
9 P. Cremaschi, A. Gamba, and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2*, 1977, 162.
10 A. Gamba, M. Simonetta, G. B. Suffritti, I. Szele, and H. Zollinger, *J. Chem. Soc., Perkin Trans. 2*, 1980, 493.
11 P. Demontis, R. Ercoli, A. Gamba, G. B. Suffritti, and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2*, 1981, 488.
12 M. J. D. Powell, *Computer J.*, 1964, **7**, 155.
13 C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864.
14 R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
15 M. K. Lo and W. H. Flygare, *J. Mol. Spectrosc.*, 1968, **25**, 365.
16 M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 4064.
17 J. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, 1952, **20**, 605.
18 C. W. W. Hoffman and R. L. Livingston, *J. Chem. Phys.*, 1953, **21**, 565.
19 E. D. Jemmis, J. Chandrasekhar, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1979, **101**, 527.
20 J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, 1976, **98**, 5419.
21 J. Burdon, D. W. Davies, and G. del Conde, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1205.
22 T. Clark, H. Körner, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1980, **21**, 743.
23 G. B. Erusalimskii, V. I. Baranovskii, and A. I. Panin, *J. Struct. Chem.*, 1977, **18**, 243.
24 G. Köbrich, K. Flory, H. R. Merkle, and W. Trapp, *Angew. Chem.*, 1965, **77**, 730.
25 E. Clementi and R. Barsotti, *Chem. Phys. Lett.*, 1978, **59**, 21.

26 J. Fromm, E. Clementi, and R. O. Watts, *J. Chem. Phys.*, 1975, **62**, 1388.
27 W. Kołos, *Theor. Chim. Acta*, 1979, **51**, 219.
28 W. Kołos, *Theor. Chim. Acta*, 1980, **54**, 187.
29 D. N. Glew and E. A. Moelwyn-Hughes, *Discuss. Faraday Soc.*, 1953, **15**, 150.
30 H. Siegel, *Top. Curr. Chem.*, 1982, **106**, 55.
31 K. G. Taylor, *Tetrahedron*, 1982, **38**, 2752.
32 R. A. Moss and M. Jones, 'Reactive Intermediates', Wiley-Interscience, New York, 1981, vol. 2, pp. 79*ff.*
33 P. Demontis, A. Gamba, G. B. Suffritti, and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2*, 1981, 488.
34 E. Fois, A. Gamba, G. B. Suffritti, M. Simonetta, I. Szele, and H. Zollinger, *J. Phys. Chem.*, 1982, **86**, 3722.

*Received 5th March* 1984; *Paper* 4/360