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Ab Initio Theoretical Study of the Monomer-Dimer Equilibrium in Lithium and Sodium *gem*-Difluoro Allyl and Methyl Systems

Carlo Canepa, Paola Antoniotti and Glauco Tonachini*

Istituto di Chimica Organica dell' Università di Torino Via Pietro Giuria, 7 10125 Torino, Italy

Abstract: Non-empirical calculations on lithium and sodium *gem*-difluoroallyl and difluoromethyl systems show that the monomer-dimer equilibrium is shifted in favour of the dimeric species. The two difluoromethyl systems show geometric and energetic features very close to those found in the larger systems. Difluoromethyl is then used as a model for difluoroallyl to allow the investigation of the structural and energetic effects of the interaction of a discrete number of water molecules (used to model ether molecules) with the counterion in both monomers and dimers. Two dimerization processes were investigated, in which the two cations present in the dimers are surrounded by a different number of solvent molecules. The dimerization energies obtained by taking into account the oxygen-cation interactions are significantly reduced, but the equilibrium is still estimated to lie in favour of the dimeric species.

INTRODUCTION

We have recently investigated some structural and electronic features of *gem*-dihalo allyl anions, considering their association with a lithium, sodium or potassium counterion.[1] The results obtained have been used to attempt an interpretation of the regiochemistry of these ambident nucleophilic systems toward carbonyl electrophiles, and a prediction of the regiochemical preferences of the relevant mono-substituted systems. However, the degree of aggregation of these species is unknown, and it would be desirable, before undertaking a theoretical study of such reactions, to assess at least at a qualitative level the possibly different inclination of the metallated nucleophiles toward aggregation. For instance, the unsubstituted allyllithium system has been shown by Winchester, Bauer and Schleyer to exist in the usual reaction conditions as an asymmetric dimer, while allylsodium and allylpotassium seem to be present as symmetric monomers.[2a] But the interactions of the metallic cation with the dihaloallyl anion could be different with respect to those occurring with the unsubstituted allyl anion, and, as a consequence, the inclination of these systems to dimerize could also be different.

Thus, a first purpose of the present investigation was to get information about the position of the equilibrium shown in eq 1 (where M=Li or Na).

$$2\,(CH_2CHCF_2)^-M^+ \rightleftharpoons ((CH_2CHCF_2)^-M^+)_2 \qquad (1)$$

For sake of comparison, a similar equilibrium, involving the simpler difluoromethyl system was also studied (eq 2).

$$2\,(HCF_2)^-M^+ \rightleftharpoons ((HCF_2)^-M^+)_2 \qquad (2)$$

Reactions involving metallated species of this kind are often carried out in tetrahydrofuran (THF). An important role in the dimerization process could thus be played by the oxygenated solvent, which can interact to a significant extent with the cation. Therefore we attempted to estimate the extent to which the structural features and the relative energies of the monomers and dimers can be affected by this interaction through the study of eqs 3 and 4.

$$2\,(HCF_2^-M^+.3H_2O) \rightleftharpoons (HCF_2^-M^+)_2.4H_2O + 2H_2O \qquad (3)$$

$$2\,(HCF_2^-M^+.3H_2O) \rightleftharpoons (HCF_2^-M^+)_2.2H_2O + 4H_2O \qquad (4)$$

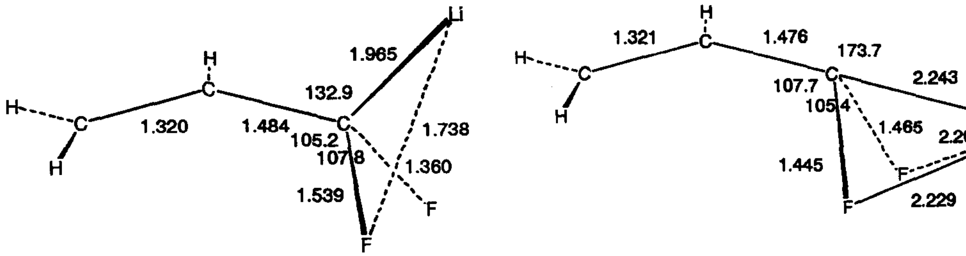
The reliability of the water model when used to simulate ether molecules was explored with computation carried out on the monomers, as discussed below. In these equations lithium is coordinated in the dimers by a different number of oxygen atoms. The possibility of a less extended coordination for lithium (eq 4) was explored on the basis of an indication concerning the dimers and trimers of methyllitium itself, put forward by Schleyer and coworkers.[2b] The main purpose of this study is to assess if the equilibria 3 and 4 are shifted in favour of the dimer, as the experimental data for the unsubstituted allyl system might suggest. Using the same approach, we intend to investigate in a forthcoming paper the related dichloro systems, whose regioselective behaviour was observed in this laboratory to depend on the nature of the alkali metal cation.[1b-d]

METHOD

The energy minima corresponding to the stable structures discussed below were determined by complete optimizations of the geometrical parameters by gradient methods.[3] The computations were done at the RHF level of theory, using the 6-31G(d) basis set.[4] The critical points determined without constraints were characterized by analytical computation and diagonalization of the relevant Hessian matrices (vibrational frequencies calculation). In one case the energy differences were recomputed at the MP2/6-31G(d) level,[5] using the RHF geometries. The calculations were performed using the GAUSSIAN90[6a] and GAUSSIAN92[6b] systems of programs, on a VAX Station 3200 + 3150 cluster and on an IBM RISC-6000/550 computer, respectively. In the Figures accompanying the following section the more important interatomic distances are reported in Ångstrom (if smaller than 2.4 Å), and angles in degrees (the full sets of geometrical parameters are available on request to the authors).

RESULTS

Several stable structures found for the difluoro[1a] and dichloro[1b,c] allyllithium monomers have been published previously. The first information needed in this study concerns the possible existence of peculiar interactions between the halogen atoms and the counterion, such that the dimerization problem can be put for these systems on a different ground with respect to the parent allyl anion system, as studied by Schleyer and coworkers.[2a] The more stable structures of the difluoroallyllithium and sodium monomers (Figure 1a and 1b) can be compared with those of the two relevant dimers (Figure 2 and Figure 3, respectively).



a

b

Figure 1

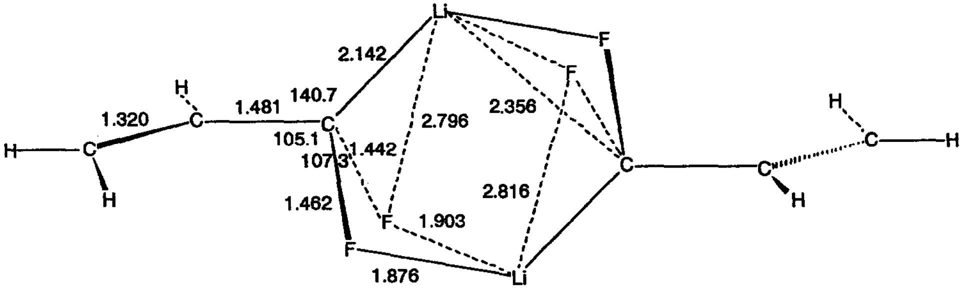


Figure 2

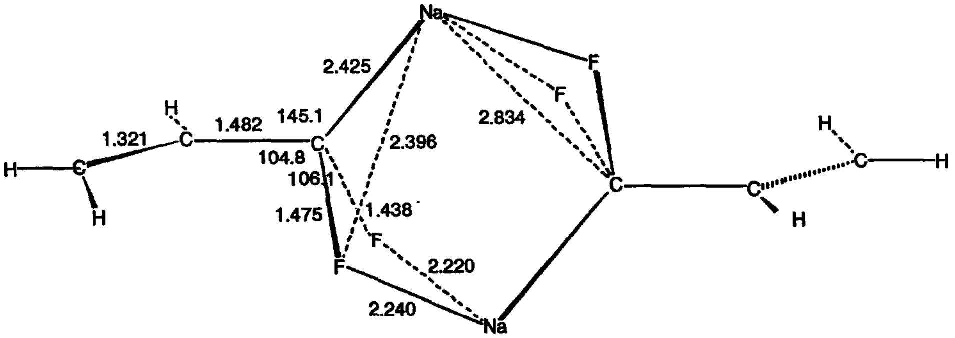
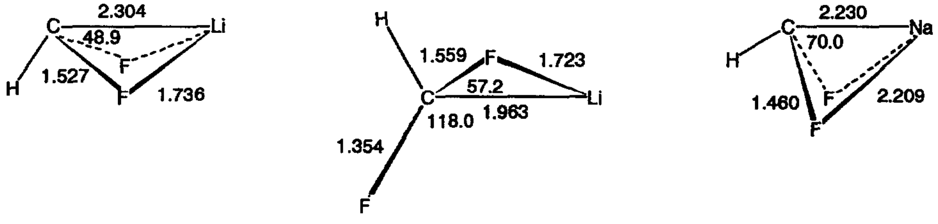


Figure 3

In our previuos study on the difluoroallyllithium monomer,[1a] bridged structures similar to that of allyllithium[7] had not been found: the only structure where the cation was interacting with both the α and γ termini is rather distorted and located at ca. 19 kcal mol^{-1} above the lowest energy minimum. In the monomers **1a** and **1b** the counterion is bound only to the a carbon and interacts significantly with one fluorine atom. In the dimers **2** and **3** the counterion is bound to the CF_2 terminus of each allylic component, and mediates their interaction. Thus, while the CF_2 groups of each moiety and the cations are involved in bonding interactions, the vinyl groups are projected outwards with respect to this central part of the dimer, and do not participate directly in bonding between the two moieties. Structures **2** and **3** contrast in this respect the MNDO structure of the allyllithium dimer reported in ref. 2a, where its two components have a lithium-bridged structure, and a participation of both termini of the allyl system in bonding interactions is consequently found. As a consequence of the lack of cation bridging between Cα and Cγ, the CαCβ bonds in **1a** and **1b** are a slightly shortened single bonds, while the CβCγ bond lengths are close to that of a double bond (for instance, at this computational level the single and double CC bond lengths in propene are 1.503 Å and 1.318 Å, respectively). These structural features are maintained in the dimers, which have geometrical parameters close to those of the monomers. The main structural differences between the dimer "components" and the monomers are related to the increased coordination around the metal cations. Thus, in the dimers, where the cation interacts with two carbon and two fluorine atoms, the Cα-M distance increases and the C-F bond lengths vary consequently.

The result that the vinylic parts are virtually unmodified in the dimerization process, as described by eq 1, poses the question if trends to dimerization can be assessed by studying simplified systems where the non interacting vinyl groups are replaced by hydrogen atoms. Therefore, the next step was the comparative study of the monomer-dimer equilibrium in the H-CF$_2$M systems (eq 2). For the Li monomers, two stable structures have been found. One energy minimum (Figure 4a) corresponds to a C_s structure in which lithium interacts with both fluorine atoms. The second structure (in which the lithium-carbon distance is smaller) belongs to the C_1 point group (Figure 4b), and is similar to the difluoroallyllithium monomer **1a**, in which only one fluorine atom interacts significantly with lithium. This minimum is located at 3.9 kcal mol^{-1} below the C_s minimum.



a **b** **c**

Figure 4

The sodium monomer optimized in the C_s symmetry (Figure 4c); its geometrical parameters are rather close to those of the difluoroallylsodium monomer **1b**. Optimization of the dimers produced the structures shown in Figure 5a and 5b, which are reminiscent of the difluoroallyl dimers **2** and **3**.

The comparison of the geometrical parameters of the allylic and methylic dimers confirms that the two vinyl groups affect in a negligible way the structure of the central part of the dimers. The comparison of the dimerization energies for the lithium and sodium difluoroallyl vs. difluoromethyl systems (reported in Table 1) provides a complementary information: they differ by ca. 1 kcal mol^{-1}, thus encouraging the choice of the simpler model system for further study. Electron correlation was introduced in eq 2, through MP2/6-31G(d) computations, and was found to favour the dimers by 6.3 (Li) and 3.8 (Na) kcal mol^{-1}. In ref. 2b, where the dimerization of methyllithium was studied, a smaller effect of electron correlation was estimated, at the same theoretical level. It is unfortunate that the extension of this kind of computations to eqs 1, 3 and 4 turned out to be unaffordable.

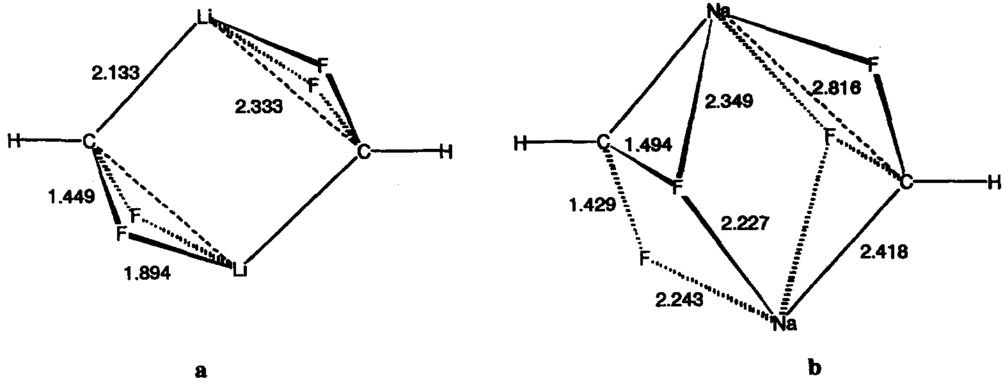


Figure 5

Table 1. Total^a and Relative^b Energies

		E	ΔE	ΔE(BSSE)^c	ΔG^d
Li difluoroallyl					
monomer	**1a**	-321.621907	0.0	0.0	0.0
dimer	**2**	-643.334961	-57.2	-51.0	-43.2
Li difluoromethyl					
monomer (C_s)	**4a**	-244.729657	3.9	-	-
monomer (C_1)	**4b**	-244.735798	0.0	0.0	0.0
dimer (C_s)	**5a**	-489.561037	-56.1	-50.8	-41.9
Na difluoroallyl					
monomer	**1b**	-476.007137	0.0	0.0	0.0
dimer	**3**	-952.097546	-52.3	-44.8	-37.5
Na difluoromethyl					
monomer (Cs)	**4c**	-399.118630	0.0	0.0	0.0
dimer (C_i)	**5b**	-798.321911	-53.1	-45.7	-37.3

(a) Hartree; (b) eq 1; kcal mol^{-1}; (c) BSSE correction included; (d) computed at T=183 K.

Considering the limitations of the basis set employed, an estimate of the basis set superposition error (BSSE)[8] was advisable. The correction to the BSSE (also reported in Table 1) lowers the estimate of the dimerization energy by ca. 10%. Using this set of corrected energies, the free energy ΔG of the process was estimated (at T=183 K) by the use of standard formulae (see for instance ref 9a). The entropy contribution amounts to 7.8 and 7.7 kcal mol^{-1} for the lithium difluoroallyl and methyl systems, respectively, and to 7.3 and 7.7 kcal mol^{-1} for their sodium analogues. Although the absolute values are lowered, they are corrected in an almost parallel fashion and the differences between the allyl and methyl systems, as well as between the Li and Na systems, are kept. In conclusion, the two sets of data relevant to the difluoroallyl and difluoromethyl systems compare well, the differences being of the order of 1 kcal mol^{-1}. At this stage, the lithiated systems are described as more inclined to dimerize, by ca. 5 kcal mol^{-1}.

The next step was to address the question about the possible role of oxygenated solvent molecules in affecting the picture obtained so far, from both a structural and energetic points of view. We limited ourselves to the explicit consideration of the interaction of the difluoromethyl systems with a small number of solvent molecules, without attempting to estimate the energy contribution given by the reorganization of the solvent itself around the solute. Moreover, feasibility forced us to model the ether molecules by H_2O molecules in the geometry optimizations of the dimeric structures. To test if this simplification is acceptable, the optimum geometries and energies of the difluoromethyllithium monomer interacting with one molecule of dimethyl ether (Figure 6a) was compared with the results obtained in parallel calculations where water was used to simulate the ether (Figure 6b). The same test was performed on the sodium monomer (Figure 7a and 7b).

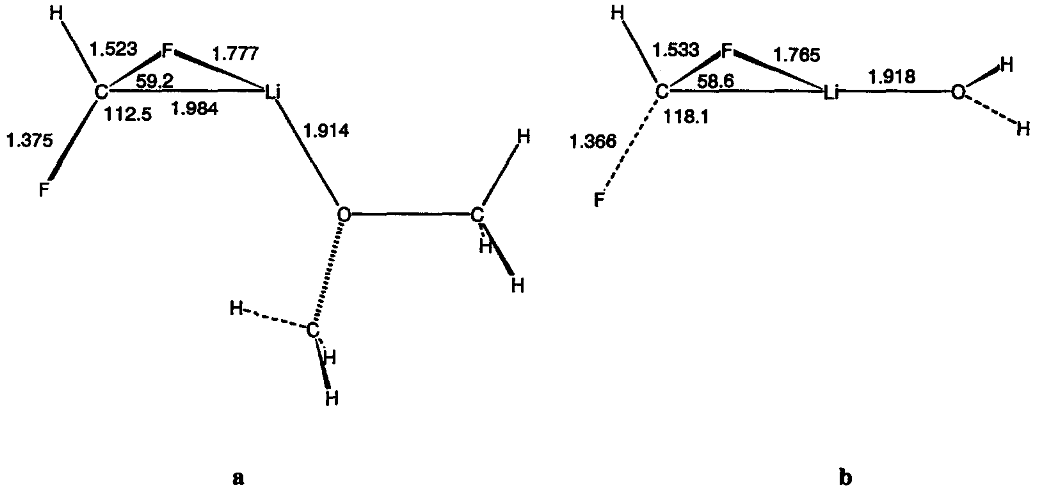


Figure 6

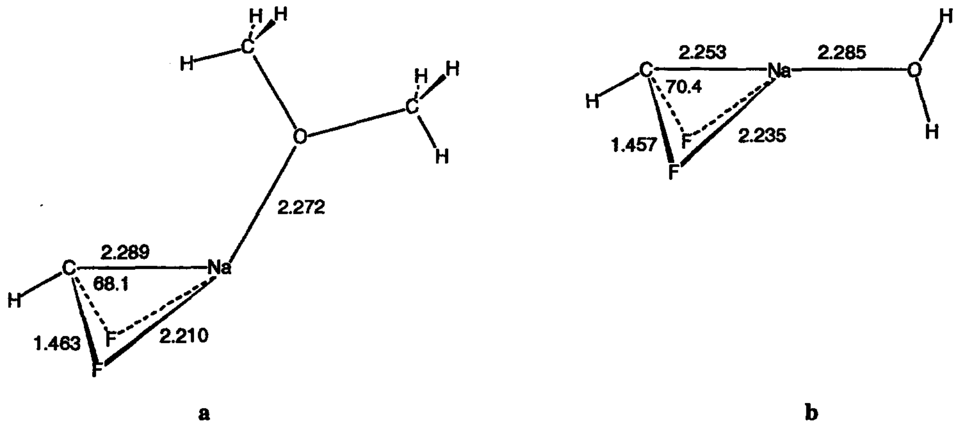


Figure 7

Unconstrained optimization of the water complexes would be doomed to give rise to spurious interactions of the water hydrogens with high-electron density centers (negative carbon, fluorine). Strong hydrogen bonds of this kind cannot obviously be present in the case of ether molecules, although some interactions of the methyl hydrogens with the negative centers are observable in **6a** and **7a**. Therefore, a geometrical constraint on the orientation of the water hydrogens had to be imposed, in order to obtain a water-based model as close as possible to the ether-based model (the bisector of the HOH angle was constrained to be collinear to the cation-oxygen axis: the water molecule was free to rotate around this axis but not to bend with one or the other of the two hydrogens toward negative charge carrying center in the HCF_2 moiety). The structures of the complexes of a water molecule with difluoromethyllithium and sodium **6b** and **7b** were thus obtained through constrained optimizations. From a geometrical point of view, the more important feature observed is the virtually unchanged Li-O distance. The complexation energies are reported in Table 2. In the case of water ΔG values could not be rigorously computed because of the mentioned constraints; however, in the case of dimethyl ether, ΔG values differ from ΔE values by less than 0.7 kcal mol^{-1} .

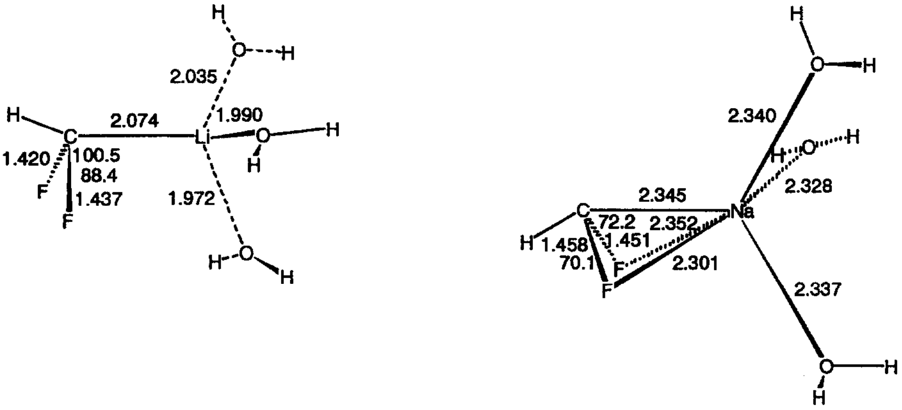
Table 2. $R_2O{\cdot}MCF_2H$ Complexes: Interaction Energies[a]

		E	ΔE^b	$\Delta E(BSSE)^c$
$Me_2O{\cdot}LiCF_2H$	**6a**	-398.835390	-21.9	-18.5
$H_2O{\cdot}LiCF_2H$	**6b**	-320.781893	-22.2	-19.2
$Me_2O{\cdot}NaCF_2H$	**7a**	-553.208876	-16.0	-13.7
$H_2O{\cdot}NaCF_2H$	**7b**	-475.156158	-16.8	-14.3

(a) kcal mol^{-1}; $E(OMe_2)$=-154.064744 Hartree; (b) without BSSE correction; (c) with BSSE correction; in the case of dimethyl ether the $\Delta G(BSSE)$ values have also been computed: ΔG=-19.2 for **6a** and ΔG=-14.4 for **7a**.

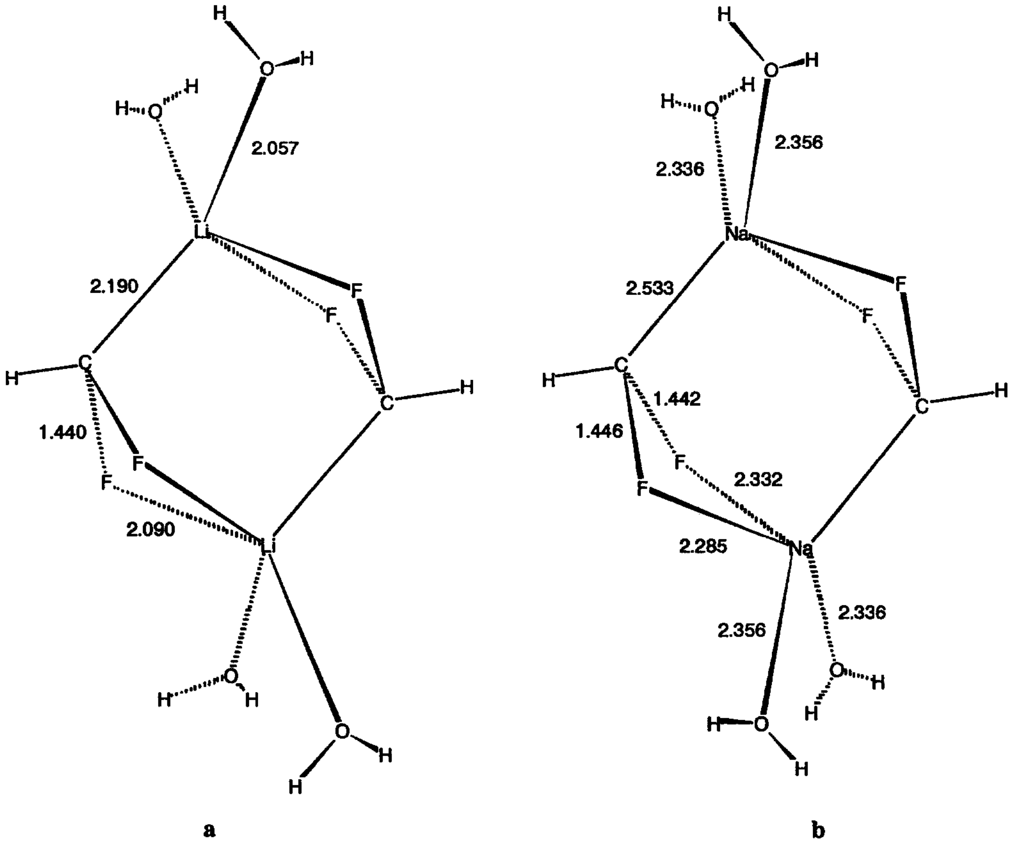
The values obtained for the interaction energy with dimethyl ether and water are very close, within 1 kcal mol^{-1}. The main energetic effect, which can be supposed a priori to be related to the M^+---O interaction, appears to be sufficiently well reproduced. Therefore, both structural and energetic data suggest that modelling the ether molecule by water can be reasonable (possible steric effects cannot of course be reproduced).

On the basis of these explorative calculations, an estimate of the relative tendency to dimerize of the lithium and sodium systems was attempted, through the study of the "water model"-based equilibria shown in eqs 3 and 4. The optimized monomers, where the cation is surrounded by three water molecules, are shown in Figure 8 (a further constraint was introduced in these computations by freezing the three OLiC angles at their optimized 3-21G values, obtained for the $HCF_2{\cdot}3OMe_2$ system).



a b

Figure 8

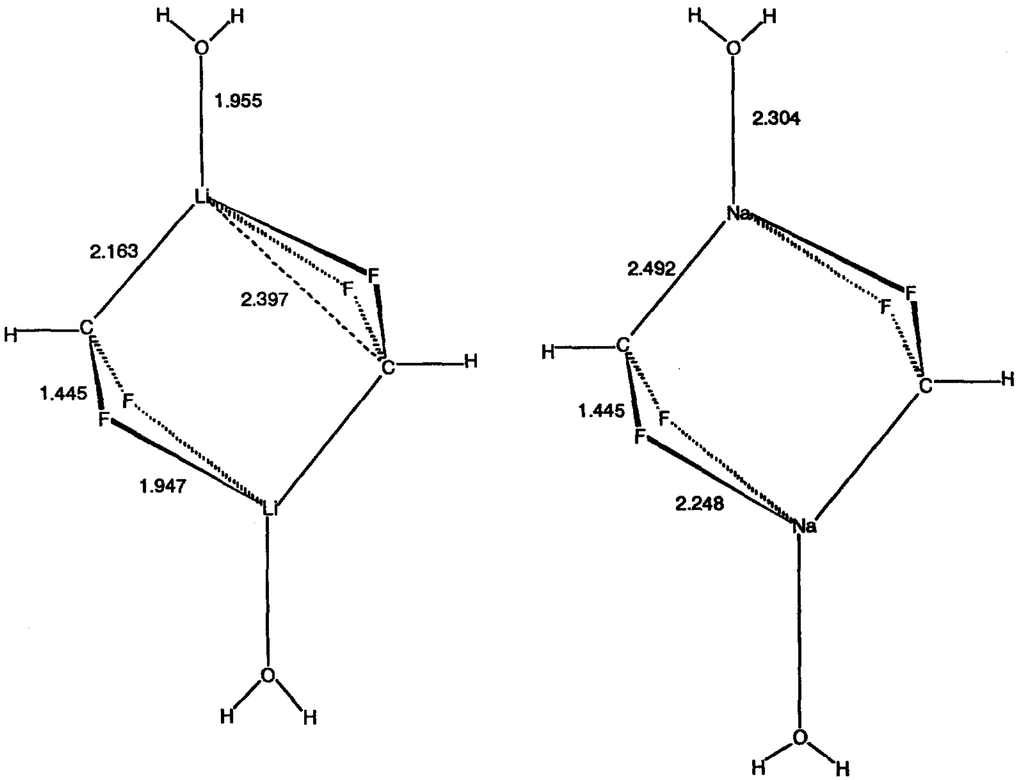


a b

Figure 9

Comparing the computations involving one and three H_2O molecules, the expected lack of additivity can be noted: in the latter case the stabilizing interaction per H_2O molecule can be estimated to be about two thirds of the value found in the case of a single H_2O molecule. Then, in correspondence to each of the monomers **8a** and **8b**, two dimeric structures were determined, in which lithium or sodium are surrounded by a different number of water molecules. In one case four H_2O molecules are kept to coordinate the cations in the dimers, and two are released (eq 3): the optimized structures are shown in Figure 9a and b, for Li and Na, respectively.

In the other case, only two H_2O molecules still interact with the cations in the dimers, while four are released (eq 4); the optimum structures of these dimers are reported in Figure 10a and 10b.



a **b**

Figure 10

The dimeric structures are little affected by the change in coordination of the cations, as can be observed by comparing the structures **9** and **10** to the structures **5a** and **5b**. The dimerization energies are reported in Table 3, together with an estimate of the BSSE correction. Comparing with Table 1, it can be seen that the energy differences relevant to eqs 3 and 4 are greatly reduced with respect to those of eq 2.

On the basis of our previous discussion, the "water model" can be deemed to have the capability of providing energy differences in satisfactory agreement with those computed by using the more demanding "ether model". However, if an estimate of the free energies relevant to the processes of eqs 3 and 4 were desired, this model would be weak in two respects. A first drawback rises because the constraints imposed on the orientation of the water molecules, giving rise to some non-zero elements in the gradient vector, would prevent a rigorous computation of the vibrational contribution to the ΔS term (as well as the zero point energy term in ΔH). One possible approach to this first problem (though an unpleasing one because of its crudity) could simply consist in calculating the translational contribution only (ΔS_{trans}), assumed a priori to be the more significant contribution. Tackling the entropy contribution problem through this shortcut may be suggested by the entropy data relevant to eq 2 and to the complex formation of Table 2. These data show that the $-T\Delta S_{trans}$ term represents a major share of the total $-T\Delta S$ term (T=183 K): (i) 6.1 over 7.7 kcal mol^{-1} (Li) and 6.3 over 7.3 kcal mol^{-1} (Na) for eq 2; (ii) 6.1 over 6.0 kcal mol^{-1} (Li) and 6.2 over 5.6 kcal mol^{-1} (Na) for the complexation of the monomers by dimethyl ether. A second drawback might consist in the computation of the entropy term for a not sufficiently realistic system, if the model system is built with water molecules. But a simple way of coping with this second problem, available within the approximation just discussed, could consist in the comparison of the $-T\Delta S_{trans}$ contributions relevant to the release of water and, for instance, of THF. In conclusion, we end up with an overall calculation consisting in the use of the "water model" to estimate the energy difference term in eqs 3 and 4, which is then converted to a "ΔH" term by adding RT or 3RT, respectively. This is followed by a calculation of ΔS_{trans}, in one case for water and in the other case for THF: two approximate "ΔG" values are obtained by this procedure, and are reported in Table 3 (last two columns).

Table 3. Dimerization Energies[a] of the Difluoromethyl Systems (eqs 3 and 4)

		E[b]	ΔE	ΔE(BSSE)	ΔG[c,d]	ΔG[c,e]
$3H_2O\cdot$Li-monomer	**8a**	-472.834613	0.0	0.0	0.0	0.0
$4H_2O\cdot$Li-dimer[f]	**9a**	-793.674665	-16.8	-7.8	-12.6	-13.6
$2H_2O\cdot$Li-dimer[g]	**10a**	-641.635698	-5.9	0.6	-15.1	-17.5
$3H_2O\cdot$Na-monomer	**8b**	-627.210618	0.0	0.0	0.0	0.0
$4H_2O\cdot$Na-dimer[f]	**9b**	-1102.433248	-21.0	-12.8	-17.5	-18.5
$2H_2O\cdot$Na-dimer[g]	**10b**	-950.386386	-5.1	1.5	-14.3	-16.7

(a) kcal mol^{-1}; (b) Hartree; (c) ΔH computed as $\Delta E + \Delta n \cdot RT$; T=183 K; (d) $-T\Delta S$ translational contribution computed for water; (e) $-T\Delta S$ translational contribution computed for THF; (f) dimerization energy computed on the basis of eq 3; (g) dimerization energy computed on the basis of eq 4.

Inspection of this Table shows that the BSSE-corrected energy difference term indicates, in the case of eq 3, the sodium system as slightly more inclined to dimerize; the reverse is true for eq 4, where the figures are even positive, although small, indicating the monomer as the favoured species. However, the $-T\Delta S_{trans}$ term favours the dimerization process, as expected: for eq 3 this means that dimerization is even more favoured, while for eq 4 the energy result just mentioned is reversed. The $-T\Delta S_{trans}$ contribution is the same (within the first decimal figure) for the lithium or sodium systems, either in the computation with water (-5.1 kcal mol^{-1} in the case of eq

3, and -16.9 in the case of eq 4) or in that with THF (-6.1 kcal mol^{-1}, eq 3, and -19.2, eq 4). Therefore, within each process, it does not alter the relative inclination to dimerize, as was set for each equation by the enthalpy term. However, given that either dimerization process is available to the two systems **8a** and **8b**, the more favourable one can be chosen by each system. Therefore, these results suggest that dimerization will take place through eq 3 in the case of Na, and through eq 4 in the case of Li, with a preference for a less extended coordination (compare ref. 2b) which is dictated by the $-T\Delta S_{trans}$ term. As a consequence the sodium system is also described as slightly more inclined to dimerize than its lithium analogue, but the lack of knowledge of the relative importance of the entropy contributions we were forced to neglect suggests to use some caution in interpreting these small "free energy" differences. The qualitative information that both systems are likely to dimerize is related to the temperature chosen (T=183 K reflects the usual experimental conditions for the allylic systems).[1b-d] Raising the temperature would favour the dimerization process mainly through the translational entropy term; for instance, at 298 K the $-T\Delta S_{trans}$ contribution is computed to be -9.1 kcal mol^{-1} in the case of eq 3, instead of -5.1 kcal mol^{-1}.

CONCLUSIONS

Both lithium *gem*-difluoro allyl and methyl systems show a significant inclination to dimerize. Constrained water molecules (three in the monomers and four or two in the dimers) were used to simulate ether solvent molecules and were allowed to interact with the cation in a supermolecule approach. Two dimerization processes have been considered, differing in the coordination of the cations in the dimer (eqs 3 and 4). The dimerization energies obtained in these computations are significantly reduced, and for eq 4 they turn out to be in favour of the monomers. The contribution of the translational entropy to the free energy difference has been estimated, and the resulting picture presents the two systems as still inclined to dimerize through both eq 3 and eq 4 processes. In the case of sodium dimerization will take place preferably through the process shown in eq 3, while in the case of lithium the process of eq 4 is more favourable. In eq 4 the preference for the dimer is totally due to the translational entropy term contribution.

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