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

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Abstract: Non-empirical free energy calculations on lithium and sodium *gem*-dichloroallyl and dichloromethyl systems show that the dimeric structures are favoured for both species, but to a significantly lesser extent than in the analogous difluoro systems previously studied. The two dichloromethyl systems show geometric and energetic features very close to those found in the larger systems, whose vinylic part is not directly involved in the dimerization process. In both cases about the same dimerization free energies are computed for the lithium and sodium systems (ca. -24 kcal mol^{-1}). Dichloromethyl is then used as a model for dichloroallyl to investigate, for two different dimerization equations, the structural and energetic effects of the interaction with the counterion of a discrete number of water molecules (used as a model for ether). The sign of the energy differences obtained by taking into account this interaction is reversed, and, in the case of lithium, the equilibrium is now clearly in favour of the monomeric species (by ca. 16 or 20 kcal mol^{-1}, depending on the equation considered). The inclination to dimerize of the sodium systems is less clearly set, because smaller approximate ΔG values are estimated (close to zero or ca. 7 kcal mol^{-1}, depending again on the equation considered). This picture contrasts the results previously published for the analogous difluoro compounds, for which approximate ΔG values ranging from -13 to -18 kcal mol^{-1} had been obtained.

INTRODUCTION

Metallated *gem*-dihalo allyl systems behave as ambident nucleophiles toward carbonyl compounds, and exhibit an interesting and variable regiochemistry, which has been explored by Seyferth, Mauzé, and coworkers.[1] An interpretation (or prediction for the monohalo substituted systems) of the regiochemical behaviour had been attempted in our earlier studies, by examining the structural and electronic features of the monomeric systems associated to different counterions.[2] Both experimental[3] and theoretical[4] studies on lithium alkyls suggest that these species are likely to be present in solution as aggregates (dimers or higher oligomers). For the unsubstituted allylic system this possibility is suggested, in the case of a lithium counterion, by the experimental work by Winchester, Bauer and Schleyer: their results indicate that while allyllithium exists, in the usual reaction conditions, as an asymmetric dimer, allylsodium and allylpotassium seem to be present as symmetric monomers.[5] The presence of two halogen atoms bound to the α carbon might in principle alter this situation, by giving rise to interactions which are not present in the unsubstituted systems. In order to get some insight into the reactivity of these dihalo systems, it would be helpful to assess, at least in a qualitative way, which is the more likely aggregation status for the reactant systems. As a first step, the monomers and dimers of the *gem*-difluoro allyl and methyl anions, in association with lithium or sodium counterions, were recently studied by ab initio theoretical methods, in order to estimate their inclination to dimerize.[6] In the present paper the investigation is extended to the metallated dichloro allyl systems, whose regioselectivity has been studied experimentally in this laboratory.[2b,c] The actual reactions are often carried out in tetrahydrofuran (THF), and a significant role in the dimerization process can be thought to be played by the oxygenated solvent, which interacts directly with the cation and can be released to some extent when aggregation takes place. In Paper I these effects were taken into account in an approximate way, through a model study of the simpler metallated difluoromethyl anions: it was concluded that in both lithium and sodium difluoro systems the dimeric forms are favoured with respect to the monomeric, although the interaction with the solvent molecules significantly reduces this preference. The same approach will be followed in the present study, with two main purposes: (i) to compare the effects of the different double substitution on the carbanionic carbon (F vs. Cl); (ii) to define an acceptable model for the investigation of the energy hypersurface relevant to the electrophilic attack by a carbonyl compound, which will be subsequently undertaken as the next step in the study of the regiochemistry of these systems.

METHOD

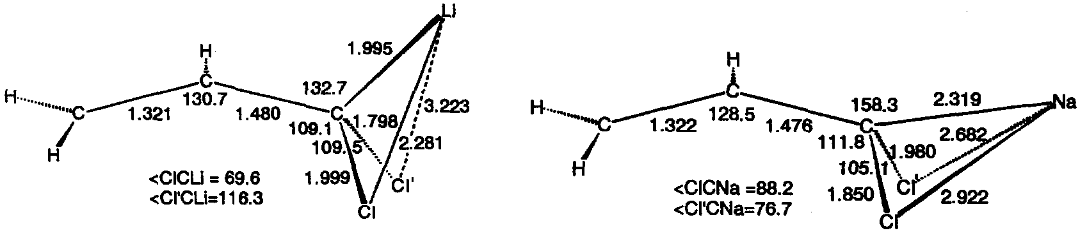
The computations were performed at the same theoretical level of Paper I, using the same basis set. Therefore, the stable structures were determined by complete RHF/6-31G(d)[7] optimization of the geometrical parameters using gradient methods.[8] The critical points determined without constraints were characterized by analytical computation and diagonalization of the relevant Hessian matrices (vibrational frequencies calculation). Some energy differences were recomputed at the MP2 level of theory,[9] using the 6-31G(d) basis set, in correspondence of the RHF optimized geometries. The calculations were performed using the GAUSSIAN88[10a] and GAUSSIAN92[10b] systems of programs, on a VAX Station 3200 + 3150 cluster and on an IBM RISC-6000/550 computer, respectively. In the Figures of the following Section the more important interatomic distances and angles are reported in Ångstroms and degrees, respectively.

RESULTS

The first purpose of this study was to get some information about the position of the equilibrium shown in eq 1 (where M=Li or Na).

$$2\,(CH_2CHCCl_2)^-M^+ \rightleftharpoons ((CH_2CHCCl_2)^-M^+)_2 \qquad (1)$$

The more stable structures of the dichloroallyllithium and sodium monomers (Figure 1a and 1b) as well as those of their corresponding dimers (Figure 2 and 3, respectively) can be compared. The counterion is bound to the CCl_2 terminus of the monomeric allyl system, and mediates the interaction between the two components in the dimers. Thus, while the CCl_2 groups and the cations are involved in bonding interactions, the vinyl groups are projected 'outwards' and do not participate directly. The same structural feature was found in Paper I for the difluoro dimers. (A complete involvement of the allylic moieties is found if the two components of the dimers have a bridged structure, with the counterion interacting with both termini of the system: compare the MNDO structure of the allyllithium dimer reported in ref.5). As a consequence, the CαCβ bond is a slightly shortened single bond, while the CβCγ bond length is close to that of a double bond. Therefore, these geometrical parameters in the two lithium-dichloroallyl components are close to those of the monomers.



a

b

Figure 1

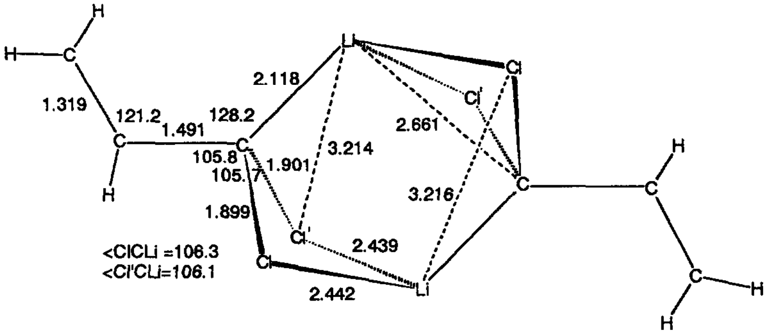


Figure 2

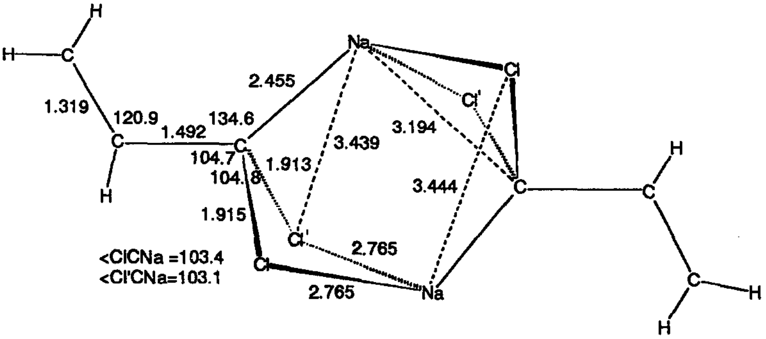
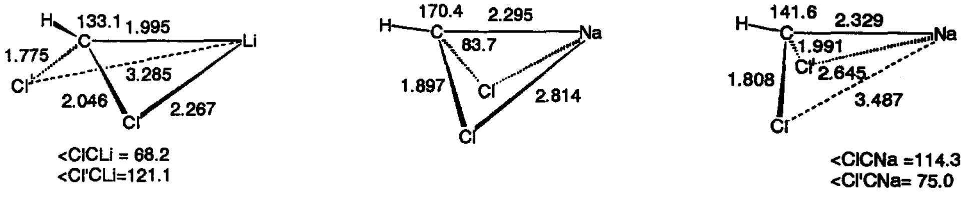


Figure 3

As in Paper I, such a result poses the question if trends to dimerization of Li *vs.* Na systems can be assessed by studying the simpler dihalomethyl systems, in which 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-CCl_2M systems (where M=Li or Na, eq 2).

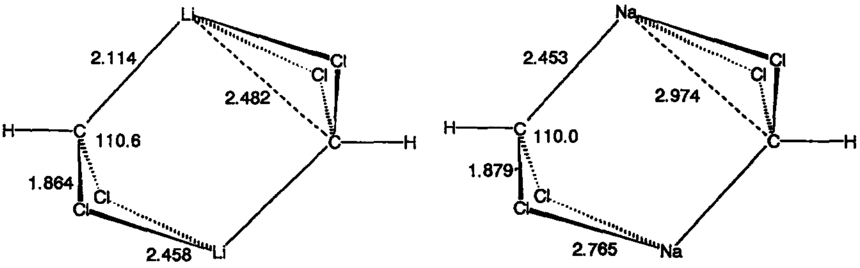
$$2\,(HCCl_2)^-M^+ \rightleftharpoons ((HCCl_2)^-M^+)_2 \qquad (2)$$

Only one stable structure of the Li monomer was found, belonging to the C_1 point group (Figure 4a). Its geometry is similar to that of **1a**, in which only one chlorine atom interacts significantly with lithium. Another structure of C_s symmetry was found to correspond to a saddle point, and its structure is not reported. In contrast with lithium, the sodium monomer optimized in the C_s symmetry (Figure 4b) is an energy minimum; however another minimum exists (of C_1 symmetry), which is slightly more stable (Figure 4c). Both have geometrical parameters rather close to those of the dichloroallylsodium monomer **1b**; only the Cl atom in **4c** seems to have lost its interaction with Na to a large extent. Optimization of the dimers produced the structures shown in Figures 5a and 5b, respectively.



a **b** **c**

Figure 4



a **b**

Figure 5

Comparison of the geometrical parameters of the dimers (in **2** and **5a**; in **3** and **5b**) confirms that the two vinyl groups affect in a negligible way the the central part of these structures. The more significant differences are found in the M-C distances indicated by dashed lines, which are shorter in the methylic systems. As done in Paper I, the basis set superposition error (BSSE)[11] was computed: the results reported in Table 1 show an overestimation of the dimerization energies by ca. 11%. Comparison of these BSSE-corrected figures provides an information, complementary to that obtained from the geometries, that encourages the choice of the simpler model system for further study: indeed, the moderate structural differences between dichloroallyl and dichloromethyl systems are found to affect the energy differences to a limited extent (Table 1).

The free energy ΔG of the process was also calculated, by use of the standard formulae[12] (at T=183 K). The entropy contribution is significant, reducing by ca. 9 kcal mol^{-1} the values of the BSSE-corrected energy differences. These two corrections to the ΔE values closely parallel those computed in Paper I for the fluorinated systems. It can also be noted that the two sets of ΔG values relevant to the dichloroallyl and dichloromethyl systems compare well, the differences being less than 1 kcal mol^{-1} for Li and ca. 2 kcal mol^{-1} for Na. Up to this point, the lithium and sodium systems are described as inclined toward dimerization about to the same extent. These results contrast those obtained at the same stage in Paper I: indeed, in the case of the fluorinated systems, those associated to Li^{+} appeared to be more inclined to dimerize than those associated to Na^{+} by ca. 5 kcal mol^{-1}.

Table 1. Total^{a} and Relative^{b} Energies

		E	ΔE	ΔE(BSSE)^{c}	ΔG^{c,d}
Li dichloroallyl					
monomer	**1a**	-1041.721711	0.0	0.0	0.0
dimer	**2**	-2083.503048	-37.4	-32.9	-23.9
Li dichloromethyl					
monomer	**4a**	-964.843151	0.0	0.0	0.0
dimer	**5a**	-1929.746002	-37.5	-33.3	-24.3
Na dichloroallyl					
monomer	**1b**	-1196.110626	0.0	0.0	0.0
dimer	**3**	-2392.277991	-35.6	-31.7	-23.2
Na dichloromethyl					
monomer (C_s)	**4b**	-1119.229884	0.0	0.0	0.0
monomer (C_1)	**4c**	-1119.230070	-0.1	-	-
dimer	**5b**	-2238.521088	-38.5	-34.6	-25.3

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

As done in Paper I, the effect of electron correlation on the dimerization energies was estimated only for eq 2 through MP2/6-31G(d) computations. The dimerization energies so obtained are -51.2 and -47.8 kcal mol^{-1}, for lithium or sodium, respectively. Correlation effects thus appear to favour the dimers by 13.7 or 9.3 kcal mol^{-1}. However, these values are not corrected for the BSSE, which is in general expected to be larger, at this computational level, than that detected at the RHF level.[13]

It was necessary at this point to determine to what extent the oxygenated solvent molecules can affect the picture obtained so far. The interaction between the solvent molecules and the systems under study was shown in Paper I to be important from the energetic point of view. We were forced by the limitations of our resources to model the ether molecules by H_2O molecules. This simplification appeared to be acceptable when studying the difluoro systems. Nevertheless the same test carried out in Paper I was repeated here, by studying the interaction of the dichloromethyl lithium or sodium monomer either with one molecule of dimethyl ether or with one water molecule. The complexes of dimethyl ether and water with dichloromethyllithium and dichloromethylsodium are shown in Figures 6 and 7, respectively. The structures shown in Figures 6b and 7b were obtained by constrained optimizations (the nature of these constrains is discussed in Paper I), because unconstrained optimization of the water complexes gives rise to unavoidable spurious interactions of the water

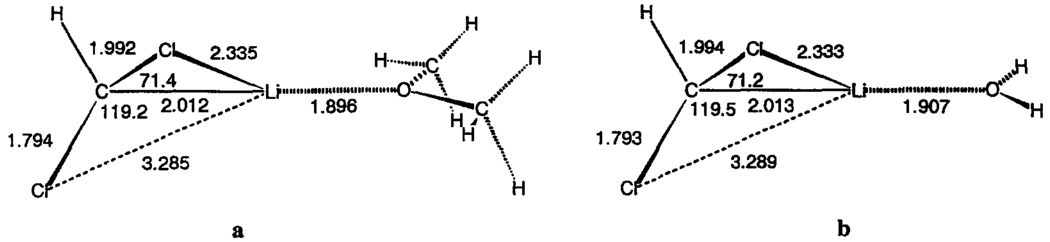


Figure 6

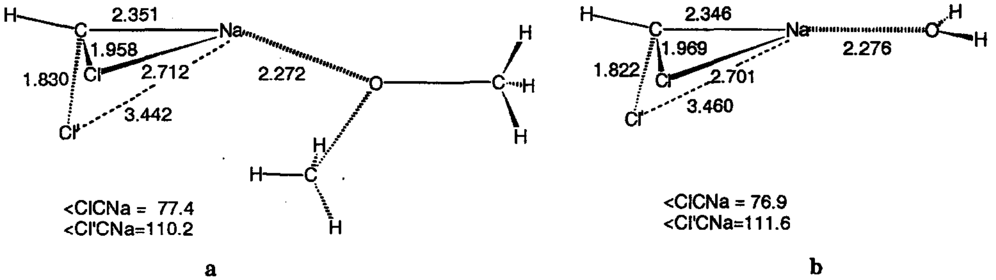


Figure 7

hydrogens with high-electron density centers. From a geometrical point of view, the more important feature that can be observed is the virtually unchanged Li-O or Na-O distance. The complexation energies are reported in Table 2.

Table 2. $R_2O{\cdot}MCCl_2H$ Complexes: Interaction Energies[a]

		E	ΔE[b]	$\Delta E(BSSE)$[c]
$Me_2O{\cdot}LiCCl_2H$	6a	-1118.945157	-23.4	-20.6
$H_2O{\cdot}LiCCl_2H$	6b	-1040.891249	-23.4	-20.9
$Me_2O{\cdot}NaCCl_2H$	7a	-1273.322021	-17.2	-14.2
$H_2O{\cdot}NaCCl_2H$	7b	-1195.269087	-17.7	-15.3

(a) kcal mol^{-1}; $E(OMe_2)$=-154.064744 H; (b) without BSSE correction; (c) with BSSE correction.

It can be noted that oxygen interacts more strongly with lithium than with sodium (by ca. 6 kcal mol^{-1}). This feature can be expected to affect the description of the dimerization process in the presence of ether (or water) molecules with respect to that obtained above for eq 1. The values obtained for the interaction with dimethyl ether and water are very close. Therefore, both structural and energetic data suggest that modelling the ether molecule by water can be reasonable.

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 following model equilibria (where M=Li or Na):

$$2\,(HCCl_2^-M^+.3H_2O) \rightleftharpoons (HCCl_2^-M^+)_2.4H_2O + 2H_2O \quad (3)$$

$$2\,(HCCl_2^-M^+.3H_2O) \rightleftharpoons (HCCl_2^-M^+)_2.2H_2O + 4H_2O \quad (4)$$

The structure of the monomer, in which the metal cation is interacting with three water molecules, is shown in Figure 8a for Li, and in Figure 8b for Na. The constraints on the orientation of the water hydrogens were applied also to these optimizations. It can be noted that both cations, while tetra-coordinated by the negative carbon and the three oxygen atoms, have completely lost their interactions with the two chlorine atoms.[14]

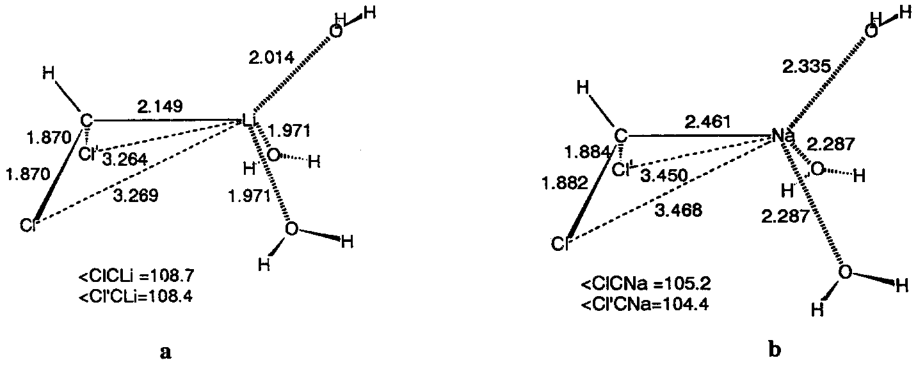


Figure 8

The complexation energies are -51.9 and -43.4 kcal mol^{-1} for 8a and 8b, respectively. These data can be compared with those reported in Table 2: it can be seen that there is no additivity in the interaction energies. As was already observed in Paper I, 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 of 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 b. The dimerization energies relevant to eqs 3 and 4 are reported in Table 3. They are unfavourable to dimerization in all cases, more so for the lithium systems (compare the ΔE data relevant to **6b**, **7b**, **8a** and **8b**) and for eq 4, in correspondence of which more oxygen-cation interactions go lost. Moreover, it can be observed that all of the energy difference terms are much more positive than in the case of the difluoro systems discussed in Paper I.[15] The constraints imposed on the water hydrogens prevent from computing a vibrational entropy contribution to the ΔG. Nevertheless a translational contribution (ΔS_{trans}) can be estimated: this was the dominant term in the ΔS calculated for eq. 2, due to a substantial cancellation of the vibrational and rotational terms. The computations follow the scheme outlined in Paper I: a "ΔH" term is computed by adding to the ΔE values either RT or 3RT, for eqs 3 or 4 respectively (Δn=1, 3).

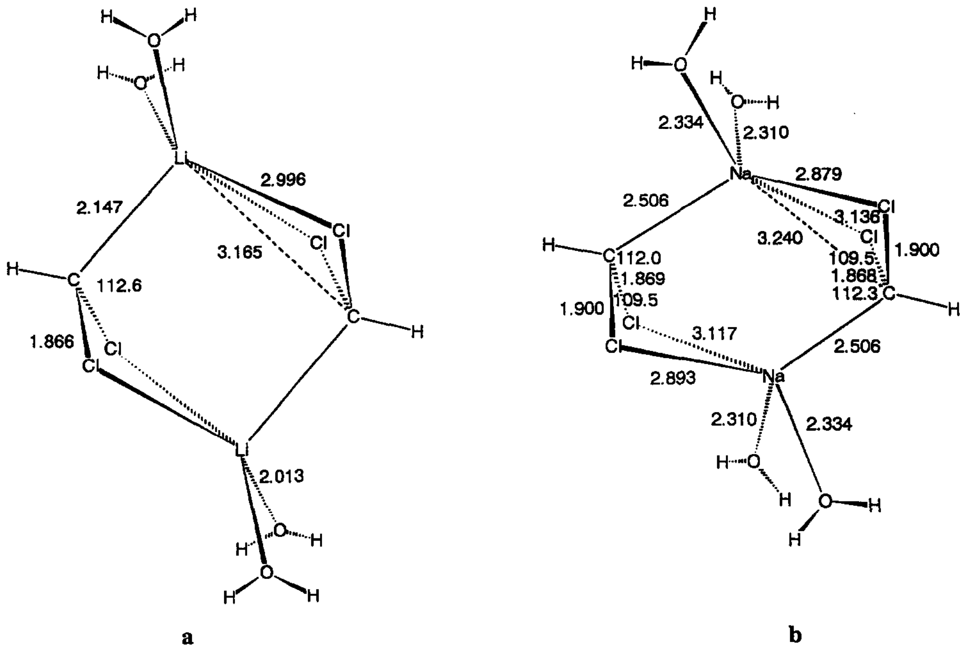


Figure 9

Then a ΔS_{trans} term is computed for water, in one case, and for THF, in a second case. Although the entropic contribution works in favour of the dimerization process (more significantly in the case of eq 4), for the lithium systems these approximate ΔG values are large and positive.

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

		E^b	ΔE	ΔE(BSSE)	$\Delta G^{c,d}$	$\Delta G^{c,e}$
$3H_2O$·Li-monomer	**8a**	-1192.958142	0.0	0.0	0.0	0.0
$4H_2O$·Li-dimer	**9a**	-2233.873772	13.2	20.5	15.9	14.8
$2H_2O$·Li-dimer	**10a**	-2081.826015	29.7	35.1	19.5	17.0
$3H_2O$·Na-monomer	**8b**	-1347.331283	0.0	0.0	0.0	0.0
$4H_2O$·Na-dimer	**9b**	-2542.642278	-0.8	5.2	0.5	-0.6
$2H_2O$·Na-dimer	**10b**	-2390.589849	18.7	23.0	7.4	4.9

(a) kcal mol^{-1}; (b) Hartree; (c) ΔH computed as ΔE +Δn·RT; T=183 K; (d) -TΔS translational contribution computed for water; (e) -TΔS translational contribution computed for THF.

In the case of sodium a preference for the monomer is clearly indicated only in the case of eq 4, while in correspondence of eq 3 values close to zero are obtained.

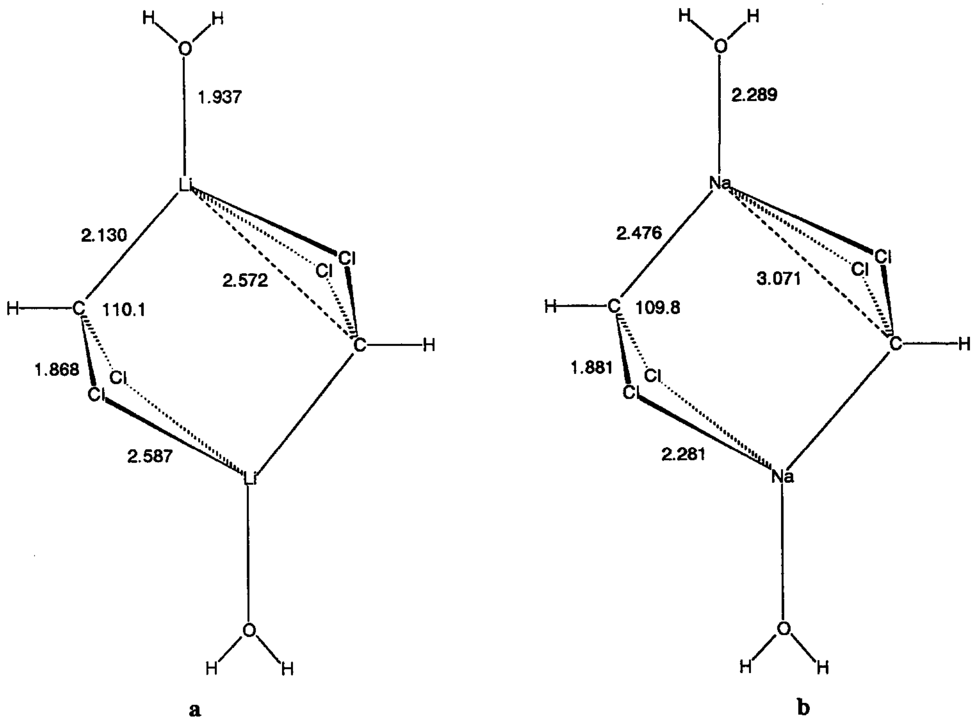


Figure 10

CONCLUSIONS

The lithium and sodium *gem*-dichlorocarbenoids studied in this paper show negative dimerization free energies when no oxygenated solvent molecules are taken into account in the calculations. In the ΔG computed for the dimerization process, the negative energy term is dominating over the entropic contribution. These ΔG values are about the same for the lithium and sodium systems, and show that these molecules are less inclined to dimerize than their fluorinated counterparts studied in Paper I. Constrained water molecules were then used to simulate ether solvent molecules in a 'supermolecule' approach. The dimerization energies obtained in these computations are reversed in sign, indicating that the monomer is preferred. Although the translational entropy term works now in favour of the dimers, as already observed in Paper I, in the case of lithium it is outweighed by the energy term: therefore, an approximate estimate of the free energy difference is clearly still in favour of the monomers. The inclination to dimerize is less clearly set for sodium, because an approximate ΔG value close to zero is otained for eq 3, while for eq 4 a result similar to lithium is obtained, although the monomer is favoured by a smaller positive ΔG value. This result is in sharp contrast with the data collected in Paper I, in which the translational entropy term was larger than the energy term, thus dictating a preference of the difluoro system for the dimeric form.

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REFERENCES

1. Seyferth, D.; Murphy, G. J.; Woodruff, R. A. *J. Organometal. Chem.* **1974**, *66*, C29-32; Seyferth, D.; Murphy, G. J.; Mauzé, B. *J. Am. Chem. Soc.* **1977**, *99*, 5317-5330; Seyferth, D.; Simon, R. M.; Sepelak, D. J.; Klein, H. A. *J. Am. Chem. Soc.* **1983**, *105*, 4634-4639; Mauzé, B.; Doucouze, A.; Miginiac, L. *J. Organometal. Chem.* **1981**, *215*, 1-8; Doucouze, A.; Mauzé, B.; Miginiac, L. *ibid.* **1982**, *236*, 139-148; Mauzé, B.; Ongoka, P.; Miginiac, L. *ibid.* **1984**, *264*, 1-7; Ongoka, P.; Mauzé, B.; Miginiac, L. *ibid.* **1985**, *284*, 139-147.
2. (a) Tonachini, G.; Canepa, C. *Tetrahedron* **1989**, *45*, 5163-5174; (b) Angeletti, E.; Baima, R.; Canepa, C.; Degani, I.; Tonachini, G.; Venturello, P. *Tetrahedron* **1989**, *45*, 7827-7834; (c) Canepa, C.; Cobianco, S.; Degani, I.; Gatti, A.; Venturello, P. *Tetrahedron* **1991**, *47*, 1485-1494; (d) Canepa, C.; Tonachini, G.; Venturello, P. *Tetrahedron* **1991**, *47*, 8739-8752.
3. West, P.; Waack, R. *J. Am. Chem. Soc.* **1967**, *89*, 4395-4399; West, P.; Waack, R.; Purmort, J. I. *ibid.* **1970**, *92*, 840-845.
4. Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, and references therein.
5. Winchester, W.R.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 177-179.
6. Canepa, C.; Antoniotti, P.; Tonachini, G. *Tetrahedron* **1994**, *50*, 8073-8084; hereafter referred to as Paper I.
7. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257; Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.
8. Schlegel, H. B. in *Computational Theoretical Organic Chemistry*, Csizsmadia, I. G.; Daudel, Eds. Deidel Publ. Co., 1981, p.129-159; Schlegel, H. B. *J. Chem. Phys.* **1982**, *77*, 3676-3681; Schlegel, H. B.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1984**, *80*, 1976-1981; Schlegel, B. *J. Comput. Chem.* **1982**, *3*, 214-218.
9. Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618; Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229-236; Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem. Symp. 14*, 91.
10. (a) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Ragavachari, K.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, **1988**; (b) Frish, M.J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, **1992**.
11. See for instance: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, **1985**; Bachrach, S. M.; Streitwieser, A. Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283. See also the discussion in: van Lenthe, J. H.; van Duijneveldt-van de Rijdt, C. C. M.; van Duijneveldt, F. B. in *Ab Initio Methods in Quantum Chemistry II*, K. P. Lawley ed., Wiley & Sons **1987**, p.521, and references therein.
12. These formulae, as implemented in the GAUSSIAN system (ref. 10), are based on the perfect gas, harmonic oscillator, and rigid rotor approximations.
13. Compare, for instance, a recent result obtained in a study on the dimerization of hydrogen peroxide: Mó, O.; Yáñez, M.; Rozas, I.; Elguero, J. *J. Chem. Phys.* **1994**, *100*, 2871-2877.
14. In the lithiated difluoro monomer interacting with three water molecules (8a, Paper I), the cation had almost completely lost its interaction with the two fluorine atoms: one fluorine atom (bond length with carbon: 1.420 Å) was 2.718 Å far from lithium, while the other fluorine atom (bond length with carbon: 1.437 Å) was at a distance of 2.491 Å from lithium. These distances can be compared with the value of ca. 1.73 Å , corresponding to a full Li-F interaction (see Figure 4, Paper I). In contrast, this was not the case for the sodium monomer (8b, Paper I), in which the Na-F distances were maintained rather short: 2.301 and 2.352 Å (close to the value of 2.209 Å in 4c, Paper I).
15. However, when comparing eq 2 and eq 3 in the case of the difluoro compounds, the same trends were observed.

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