$(CH_2LiF)_2$: the Effect of Dimerization on the Structure and Dissociation Energy of Carbenoids

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Ab initio molecular orbital theory suggests that the non-tetrahedral structural features of the prototype carbenoid, CH_2LiF, are retained in its dimer; however, dissociation of singlet methylene is thermodynamically much more favourable from the dimer than from the monomer.

Ab initio molecular orbital calculations[1–3] on a series of carbenoid monomers (and similar species)[4] have revealed the $R_2CM^+X^-$ ion pair nature [*e.g.* (**1**)] of the most stable isomers. These simple, tetrasubstituted methane derivatives prefer structures which deviate fundamentally from tetrahedral geometries. ^{13}C N.m.r. studies[5,6] appear to provide general support for these predictions although the nature of the organolithium species in solution is uncertain.[7] Since the magnitude of ^{13}C–^7Li coupling constants has been shown to be strongly dependent on the degree of association,[8] the large values (*ca.* 45 Hz) found for carbenoids in tetrahydrofuran solution[5,6] suggest that dimers are present. Furthermore, each

Table 1. Mulliken population analyses for (1)—(4) (3-21G//3-21G).

		CH_2LiF (1)	$(CH_2LiF)_2$ (2)	$CH_2LiF:LiF$ (3)	$(LiF)_2$ (4)
Charges					
	Li1	0.571	0.555	0.477	0.569
	Li2	—	—	0.627	—
	F1	−0.448	−0.468	−0.446	−0.569
	F2	—	—	−0.554	—
	C	−0.446	−0.433	−0.426	—
	H	0.162	0.173	0.161	—
Overlap populations					
	Li1F1	0.212	0.102	−0.070	0.264
	C1Li1	0.306	0.321	0.516	—
	C1F1	0.195	0.150	0.225	—
	C1H1	0.695	0.686	0.682	—
	Li1F2	—	0.221	0.280	—
	Li2F2	—	—	0.287	—
	LiLi	—	−0.111	−0.317	—

carbon couples to only one lithium nucleus.[5,6] We have used *ab initio* molecular orbital theory† to investigate the structure and energy of the prototype dimer, $(CH_2LiF)_2$, in order to assess the effect of dimerisation on the electronic and structural characteristics of carbenoids and related species in which a metal and an electronegative group are attached to the same carbon.

As found earlier,[1] optimisations using the 3-21G basis set[9] give structure (**1**) as the most stable CH_2LiF isomer. The dimer (**2**) was optimised within C_{2h} symmetry constraint. Previous experience[10,11] indicates that (**2**) would be the most stable dimer structure; the size of the system discouraged consideration of other alternatives. The 3-21G//3-21G dimerisation energy of CH_2LiF, 56.2 kcal/mol,‡ is between the values calculated for lithium fluoride (87.3 kcal/mol) and methyl-lithium (46.3 kcal/mol) at the same level.[11]

The CH_2LiF units in the dimer (**2**) have essentially the same geometries as in the monomer (**1**). The C–Li bonds remain relatively strong, but the Li1–F1 distance, in particular, is lengthened. The Li1–F2 distance (1.701 Å) is close to that (1.684 Å) calculated for $(LiF)_2$ (**4**). As in (**1**), the CH_2LiF units in (**2**) are inclined towards fluorine, so that all four bonds to carbon lie in one hemisphere. These geometries should facilitate methylene transfer, the typical reaction of carbenoids, to a double bond approaching from the rear of the C–F bond. The bridging position of fluorine above the C–Li bond is also common to (**1**) and (**2**). Further, a comparison of the Mulliken population analyses (Table 1) shows that the electronic nature of the carbenoid is not significantly changed by dimerisation. We conclude that the CH_2Li^+ F^- ion pair nature found for the monomer[1] remains unaffected by dimerisation, and that calculations on monomers are a valid method for the investigation of carbenoids and related species.

† All calculations used the Gaussian 76 series of programs (J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, Quantum Chemistry Program Exchange, Program No. 368, Indiana University, 1976). Geometry optimisations used analytically evaluated atomic forces (H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, 1975, **63**, 3632) in a Davidon–Fletcher–Powell multiparameter search routine (D. Poppinger, *Chem. Phys. Lett.*, 1975, **34**, 332). The 3-21G//3-21G total energies of (**1**), (**2**), (**3**), and (**4**) are −145.09508, −290.27977, −251.57377, and −212.84747 a.u., respectively. For other 3-21G reference energies and geometries [*e.g.*, r_{CLi} (CH_3Li) 2.001, r_{CF}(CH_3F) 1.404, and r(LiF) 1.520 Å], see R. A. Whiteside, M. J. Frisch, J. S. Binkley, D. J. DeFrees, H. B. Schlegel, K. Raghavachari, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Archive, 2nd edn., 1981; available from J. A. Pople.

‡ 1 cal = 4.184 J.

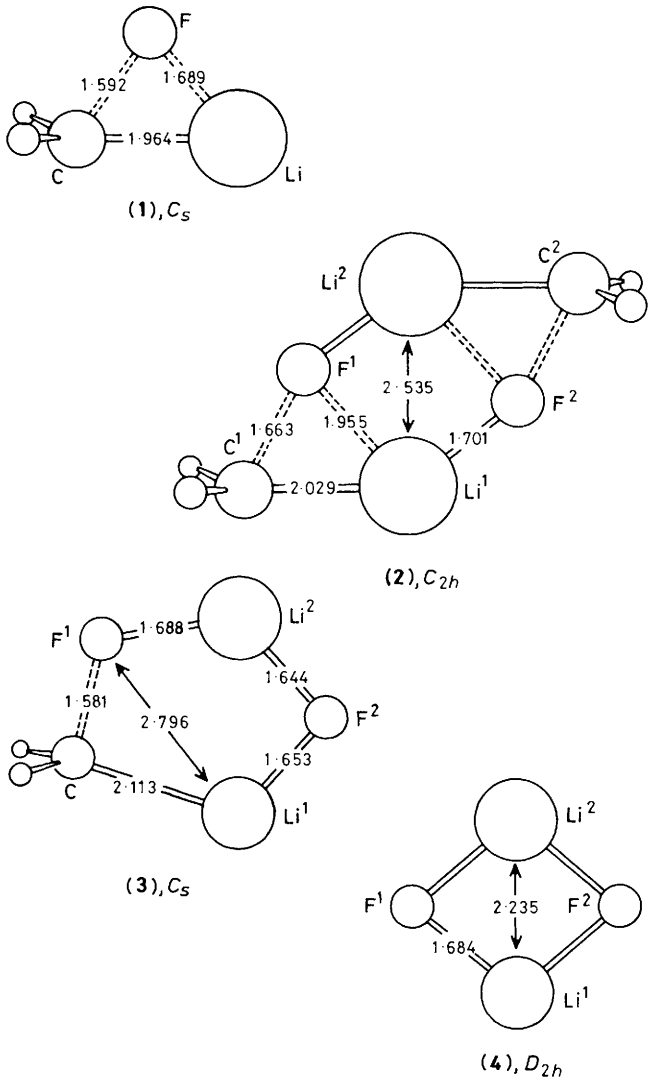

Figure 1. Optimised geometries (3-21G//3-21G) for (**1**)—(**4**). The angles between the C–Li bonds and the H–C–H bisectors in (**1**), (**2**), and (**3**) are, 194.0, 191.7, and 155.3°, respectively. The tetrahedral value is 125.3°.

Dimerisation, however, does modify the nature of CH_2LiF in one important way. Since (**2**) contains a pre-formed $(LiF)_2$ unit, the dissociation of a singlet methylene should be facili-

tated. Calculations on the CH_2LiF–LiF complex (**3**) reveal significant differences in the energies for reactions (1), (2), and (3)

$$CH_2LiF\ (\mathbf{1}) \rightarrow LiF + CH_2\ (^1A_1) \quad \Delta E\ 55.9\ \text{kcal/mol} \qquad (1)$$

$$(CH_2LiF)_2\ (\mathbf{2}) \rightarrow CH_2LiF{:}LiF\ (\mathbf{3}) + CH_2\ (^1A_1) \quad \Delta E\ 34.0\ \text{kcal/mol} \qquad (2)$$

$$CH_2LiF{:}LiF\ (\mathbf{3}) \rightarrow (LiF)_2 + CH_2\ (^1A_1) \quad \Delta E\ 46.7\ \text{kcal/mol} \qquad (3)$$

The structure of (**3**) is also of interest. While most of the Li–F distances approximate that in $(LiF)_2$, (**4**), the separation between Li1 and F1 has increased dramatically and their interaction is repulsive (Table 1). In effect, a CH_2 has been inserted into a Li–F bond in (**4**). The C–Li bond is longer and the C–F bond shorter than in (**2**) [and (**1**)]. The geometry around carbon in (**3**) is more nearly tetrahedral. The further dissociation of (**3**) [reaction (3)] is almost as unfavourable as for the monomer [reaction (1)].

Dimerisation therefore should facilitate considerably the dissociation of singlet carbenes from carbenoids. Nevertheless, the dissociation energy of reaction (2) is still much larger than that indicated in solution, under conditions where other carbenoids, but not CH_2LiF, are observable.[5,6] Dissociation of (**2**) [or (**1**)] exposes additional solvation sites on lithium, and this would further reduce the reaction energies. On the other hand, the carbenoids may exist in certain solvents as higher aggregates (*e.g.* as tetramers) from which CH_2 might be split off even more easily. If so, Köbrich's observation that carbenoids are more stable in tetrahydrofuran[12] may reflect the general tendency of organolithium compounds to exhibit lower aggregation numbers in that solvent.[7,13]

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