Structures of α-Lithiomethanol and α-Lithiomethylamine; an *Ab Initio* Study

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Summary $LiCH_2OH$ and $LiCH_2NH_2$ are suggested by *ab initio* molecular-orbital theory to possess a number of isomeric forms; in the lowest energy structures the hydroxy- or amino-group bridges the C–Li bond and extra stabilisation results.

THE great synthetic utility of organolithium reagents has been extended by the introduction of α-lithio-ether[1,2] and α-lithiated alkylamine-related[1,3] reagents. In view of the unusual structures exhibited by lithium carbenoids (α-lithiated methyl halides),[4–7] we have used *ab initio* molecular-orbital theory† to investigate the structures and energies of

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† All calculations employed the Gaussian 76 series of programs (J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. Pople, W. J. Hehre, and M. P. Newton, Q.C.P.E. Program No. 368, Indiana University). Optimisations were performed using analytically evaluated atomic forces (H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, 1975, **63**, 3632) in a modified Davidon–Fletcher–Powell multiparameter search routine (W. C. Davidon, *Comput. J.*, 1968, **10**, 406; R. Fletcher and M. D. Powell, *ibid.*, 1963, **6**, 163; D. Poppinger, *Chem. Phys. Lett.*, 1975, **34**, 332). Post-SCF (MP2) calculations employed the frozen core approximation (ref. 10). The MP2/6-31G*//3-21G energies not reported in the Table are: CH_4 −40·33242, CH_3Li −47·16207, CH_3F −139·33544, CH_3OH −115·34538 and CH_3NH_2 −95·50459 a.u.

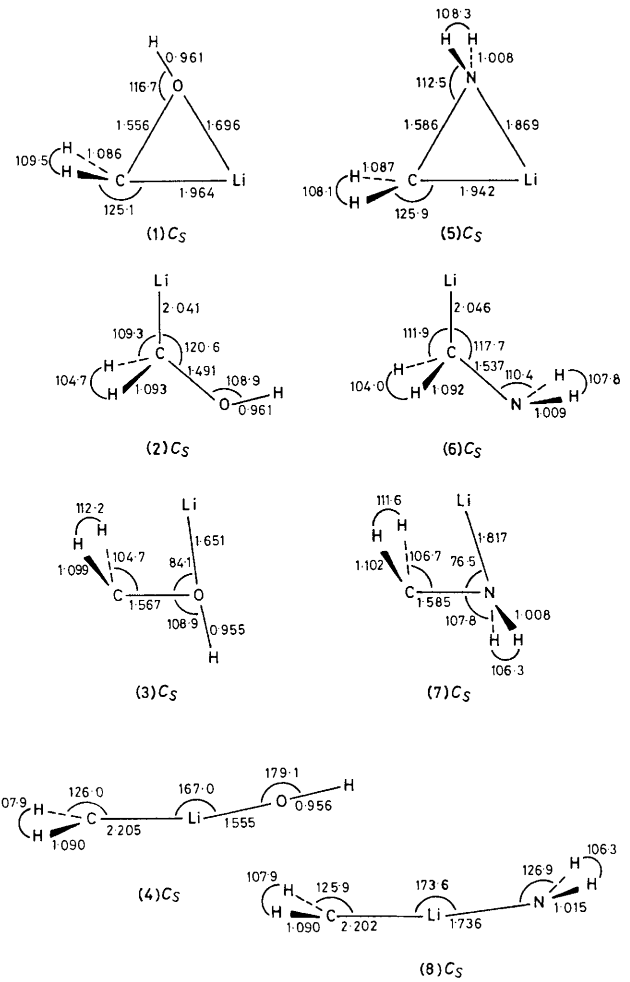

FIGURE. 3-21G Optimised geometries (bond lengths in Å, angles in °) for the isomeric forms of $LiCH_2OH$ and $LiCH_2NH_2$.

the model compounds, $LiCH_2OH$ and $LiCH_2NH_2$. Starting points for optimisation at the 3-21G[8] basis level were based on standard geometries or on the isomeric structures of $LiCH_2F$.[4] The Figure shows the final geometries calculated for compounds (**1**)—(**8**). All the isomers were optimised within the given symmetry constraints except (**1**) and (**5**), which were also obtained starting from structures with C_1-symmetry. Diagonalisation of the force constant (Hessian) matrix showed that compounds (**1**)—(**8**) are all minima on the potential energy surfaces. The 3-21G optimised energies (3-21G//3-21G), those obtained from single point 6-31G*[9] calculations on the 3-21G geometries (6-31G*//3-21G), and from similar calculations including the second-order Møller–Plesset correction[10] for electron correlation (MP2/6-31G*//3-21G) are shown in the Table.

The bridged species (**1**) and (**5**) are the most stable structures for $LiCH_2OH$ and $LiCH_2NH_2$, respectively. They correspond to the most stable isomer of $LiCH_2F$;[4] the orientations of the OH and NH_2 groups are those expected from the description of the bonding we have proposed for the carbenoids.[5] The methylene moieties in $LiCH_2F$, (**1**), and (**5**) act simultaneously as electron donors and electron acceptors in the complexes with LiF, LiOH, and $LiNH_2$. The C–Li bonds in such complexes are short, whereas the bonds to F, O, or N are long, which illustrates the $LiCH_2^+X^-$ ion-pair character of these structures.

The classical isomers (**2**) and (**6**) are found to be minima on the potential energy surfaces, but both are about 14 kcal mol^{-1}‡ less stable than the isomers (**1**) and (**5**), respectively. The widening of the Li–C–O and Li–C–N angles reduces repulsion between the C–Li bonding orbital and the heteroatom in-plane lone-pair. Similar classical structures are not usually found to be minima for carbenoids.[2–6]

Isomers (**3**) and (**7**), both about 20 kcal mol^{-1} less stable than the isomers (**1**) and (**5**), respectively, are complexes in which methylene acts as an electron acceptor.[4,5] As for the carbenoid structures, Li–H bonding is significant.

The carbene complexes (**4**) and (**8**) in which methylene acts as an electron donor are analogous to the CH_2:LiF complex found earlier.[4] This association of methylene and LiX becomes progressively less stable as the electronegative group is varied from F to OH to NH_2. The MP2/6-31G* energies of these forms of CH_2LiF, CH_2LiOH, and CH_2LiNH_2 are 29 (estimated from the data in ref. 4), 50, and 71 kcal mol^{-1}, respectively, relative to the most stable geometry in each case. As for $LiCH_2F$,[4] it is likely that the higher energy isomers of $LiCH_2OH$ and $LiCH_2NH_2$ are separated from the isomers (**1**) and (**5**) by very low isomerisation barriers. Therefore, structures (**2**)—(**4**) and (**6**)—(**8**) may be, at best, metastable. Furthermore, because of the typically flat potential surfaces around such minima, optimisation at higher basis levels or with inclusion of electron correlation may lead to significantly different geometries without affecting the relative energies.

The MP2/6-31G*//3-21G energies[11] for the isodesmic bond-separation reactions, equations (1)—(3), illustrate the stabilisation gained by substitution of an electronegative and an electropositive group at the same carbon atom. In all cases, the energies of the most stable $LiCH_2X$ forms are employed. Earlier evaluations of these equations using standard[12] or partially optimised[13] $LiCH_2X$ geometries were

TABLE. Total (a.u.) and relative (kcal mol^{-1}, in parentheses) energies for $LiCH_2OH$ and $LiCH_2NH_2$.

Molecule	3-21G//3-21G	6-31G*//3-21G	MP2/6-31G*//3-21G
(**1**)	−121·21151 (0·0)	−121·86697 (0·0)	−122·18993 (0·0)
(**2**)	−121·16836 (27·1)	−121·84384 (14·5)	−122·16787 (13·8)
(**3**)	−121·17505 (22·9)	−121·83203 (21·9)	−122·15870 (19·6)
(**4**)	−121·14409 (42·3)	−121·80844 (36·7)	−122·11026 (50·0)
(**5**)	−101·48281 (0·0)	−102·03778 (0·0)	−102·34732 (0·0)
(**6**)	−101·44492 (23·8)	−102·01456 (14·6)	−102·32455 (14·3)
(**7**)	−101·44541 (23·5)	−102·00432 (21·0)	−102·31855 (18·1)
(**8**)	−101·38703 (60·1)	−101·94886 (55·8)	−102·23368 (71·3)

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‡ 1 cal = 4·184 J.

intended to identify specific electronic effects on model systems and did not reveal the true magnitude of the energetic trends. These stabilisation energies can be compared

$$CH_3Li + CH_3F \rightarrow CH_4 + CH_2LiF \qquad (1)$$
$$\Delta E \; -13{\cdot}4 \text{ kcal mol}^{-1}$$

$$CH_3Li + CH_3OH \rightarrow CH_4 + \underset{(\mathbf{1})}{CH_2LiOH} \qquad (2)$$
$$\Delta E \; -9{\cdot}3 \text{ kcal mol}^{-1}$$

$$CH_3Li + CH_2NH_2 \rightarrow CH_4 + \underset{(\mathbf{5})}{CH_2LiNH_2} \qquad (3)$$
$$\Delta E \; -8{\cdot}2 \text{ kcal mol}^{-1}$$

with those for CH_2F^-, CH_2OH^-, and $CH_2NH_2^-$, equations (4)—(6), derived from data calculated using the diffuse orbital-augmented 4-31+G and 6-31+G* basis sets[14] and MP2 correction for electron correlation (MP2/6-31+G*//4-31 + G).

$$CH_3^- + CH_3F \rightarrow CH_4 + CH_2F^- \qquad (4)$$
$$\Delta E \; -9{\cdot}3 \text{ kcal mol}^{-1}$$

$$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH^- \qquad (5)$$
$$\Delta E \; -3{\cdot}7 \text{ kcal mol}^{-1}$$

$$CH_3^- + CH_3NH_2 \rightarrow CH_4 + CH_2NH_2^- \qquad (6)$$
$$\Delta E \; + 1{\cdot}5 \text{ kcal mol}^{-1}$$

All $LiCH_2X$ stabilisation energies [equations (1)—(3)] are larger than the corresponding CH_2X^- stabilisation energies [equations (4)—(6)], *e.g.* $LiCH_2NH_2$ is more stabilised (9·7 kcal mol^{-1}) than $CH_2NH_2^-$. The enhanced stabilisation of $LiCH_2X$ relative to CH_2X^- is noteworthy because lithium compounds are generally stabilised *less* than the corresponding anions (*e.g.*, for the ethynyl, vinyl, and ethyl systems).[15] In the classical structures (**2**) and (**6**)[12,13] the methyl stabilisation energies are very much reduced. We are examining the degree to which stabilising effects due to bridging are specific for lithium, and the influence of dimerisation and solvation on the structures and energies of this species.

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