

Electronic Structure of Monomeric Methyl-lithium

Fabio E. G. Penotti and Joseph Gerratt

Department of Theoretical Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS

David L. Cooper*

Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

Mario Raimondi

Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, 20133 Milano, Italy

In order to investigate the nature of the C—Li bond in alkyl-lithium compounds, *ab initio* calculations have been performed for the monomeric CH₃Li molecule using spin-coupled theory. The eight singly occupied non-orthogonal valence orbitals have been fully optimized without symmetry constraints, and the complete spin space of 14 singlet spin functions has been employed. We found essentially four distorted sp³ hybrids on the carbon atom and three 1s orbitals on the hydrogen atoms. The eighth orbital can be described as the superposition of an s-type orbital on lithium and a p-type orbital on carbon, and it also has some amplitude on the hydrogen atoms. When compared with the situation expected for a normal covalent bond, the build-up of 'overlap charge' in the C—Li bond region appears to be quite limited. However, an examination of the valence contribution to the total electron density shows a residual peak on lithium. In this sense, the C—Li bond can be described as essentially ionic, although it does not correspond to the transfer of a whole electron.

The nature of the C—Li bond in alkyl-lithium compounds remains a matter of some considerable controversy. The lithium atom is more electropositive than magnesium and so the C—Li bond is likely to be more ionic than C—Mg. As a consequence, one would expect a more negative partial charge for a carbon atom bonded to lithium. Although this may seem consistent with the fact that organolithium reagents are generally more reactive as nucleophiles than are Grignard reagents, and organolithium compounds are also extremely strong bases, the situation is complicated by the fact that many of the smaller alkyl-lithium species oligomerize.

Methyl-lithium, for example, exists as a tetramer under standard conditions and takes the form of a tetrahedral arrangement of lithium atoms with a methyl group on each face. It is unlikely to exist as a monomer even in the gas phase, although it has proved possible to isolate monomeric methyl-lithium at low temperature in an argon matrix by the reaction of methyl radicals and lithium atoms.¹ The i.r. spectrum of the monomer was measured under these conditions and the low force constant for H—C—Li bending was rationalized in terms of a high degree of ionic character.

A large number of theoretical papers has been devoted to the nature of the C—Li bond and many of these have concentrated on the monomeric methyl-lithium molecule. Considerations of electron-density maps for CH₃Li, produced *via ab initio* SCF² and SCF-CI³ calculations, seem to indicate a high degree of ionicity. There is, of course, no unique way of defining such an elusive quantity as the 'percentage of ionic character'. Thus it is not very surprising that different authors have produced electron-density maps that are very similar but have given quite different estimates (in the range 55–80%) for the ionic character of the C—Li bond.

In the present work, we use spin-coupled theory⁴ to investigate the electronic structure of the monomeric methyl-lithium molecule. The results are unlikely to shed much light on the oligomerization of CH_3Li or on solvent effects, but we believe that the monomer is a good model system for understanding the character of the C—Li bond in larger alkyl-lithium species.

The spin-coupled wavefunction consists of a single spatial configuration with one orbital for each electron, and it includes all allowed modes of coupling together with the spins of the electrons. The orbitals are fully optimized and, in general, they turn out to be distinct and non-orthogonal. The spin-coupled model incorporates a significant degree of electron correlation. It produces accurate potential curves and properties, and its flexibility allows for all possible modes of dissociation. Additional electron correlation can be included in a non-orthogonal configuration interaction calculation, but this does not alter the essential physical picture.

Calculations

The calculations on CH_3Li used a basis set of roughly double-zeta plus polarization quality. For (C/H) the basis set consisted of (9s5p/4s) Gaussian functions contracted⁵ to [4s2p/2s], without any scaling of the hydrogen exponents. This was augmented with a d polarization function on carbon (five components) with an exponent of 0.78 and a p polarization function on each hydrogen atom with an exponent of 1.0. For lithium, Huzinaga's (9s) basis⁶ was contracted to [4s] using the orbital coefficients from an SCF calculation on the Li atom. The exponent of 0.4 for a p polarization function on lithium was chosen by minimizing the SCF energy of CH_3Li . The following geometry for CH_3Li (C_{3v} symmetry) was adopted: $r(\text{C—Li}) = 3.8$ bohr, $r(\text{C—H}) = 2.065$ bohr and $\Theta(\text{HCH}) = 105.8^\circ$ [so that $\Theta(\text{HCLi}) = 112.9^\circ$]. $\Theta(\text{HCH})$ and $r(\text{C—Li})$ were taken from ref. (2), but were rounded to one decimal place, and $r(\text{C—H})$ is the experimental value for methane. The geometry has not been optimized in the current basis set, although this would be possible, but this is very unlikely to affect any of our conclusions.

The spin-coupled calculations were carried out assuming core-valence separation. The eight valence electrons were described by eight non-orthogonal orbitals and the four core electrons, essentially $\text{C}(1s^2)$ and $\text{Li}(1s^2)$, were accommodated in two doubly occupied SCF molecular orbitals. Since the two core orbitals are doubly occupied, the valence orbitals can be taken to be orthogonal to both without loss in generality, and this effectively reduces the spin-coupled calculation to an eight-electron problem. The valence orbitals were fully optimized without constraints on their symmetry properties or on the overlaps between them. For a singlet state with eight electrons there are 14 modes of spin coupling, and all of these were included.

Results

The energies and dipole moments calculated in this work for the $^1\text{A}_1$ electronic ground state of CH_3Li are collected in table 1. There is, of course, no experimental value for the dipole moment, but a reliable estimate of 5.40 D^\dagger comes from a calculation with a basis set near the Hartree-Fock limit and with configuration interaction involving 13 322 Slater determinants.³ When compared with the SCF calculation, the electron correlation taken into account by the spin-coupled method lowers the energy by almost 166 kJ mol^{-1} and brings the calculated dipole moment significantly closer to the best theoretical estimate. The calculation of an accurate dipole moment for CH_3Li almost certainly requires a more extensive basis set than has been used here.

Valence orbitals φ_5 , φ_6 , φ_7 and φ_8 are shown in fig. 1-4. These are contour plots in a σ_v mirror plane (containing the C—Li bond and a C—H bond) and in a plane

[†] $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$.

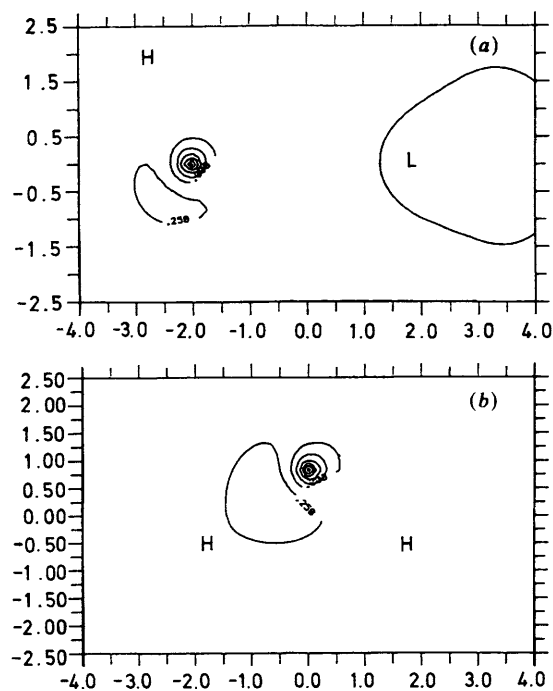


Fig. 1. Valence orbital φ_5 of CH_3Li shown as contour plots in a σ_v mirror plane containing the C—Li bond and a C—H bond (a) and in a plane containing the other two C—H bonds (b). Two other orbitals are symmetry-related to this one. Values are in atomic units.

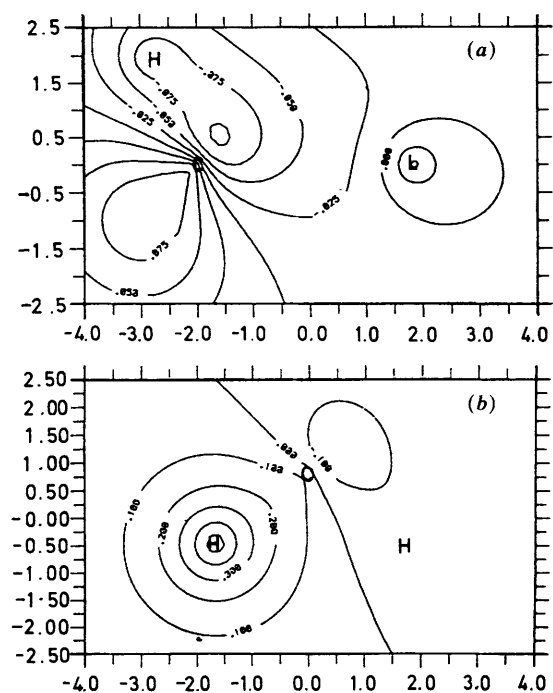


Fig. 2. Valence orbital φ_6 of CH_3Li . Two other orbitals are symmetry-related to this one. The views correspond to those in fig. 1.

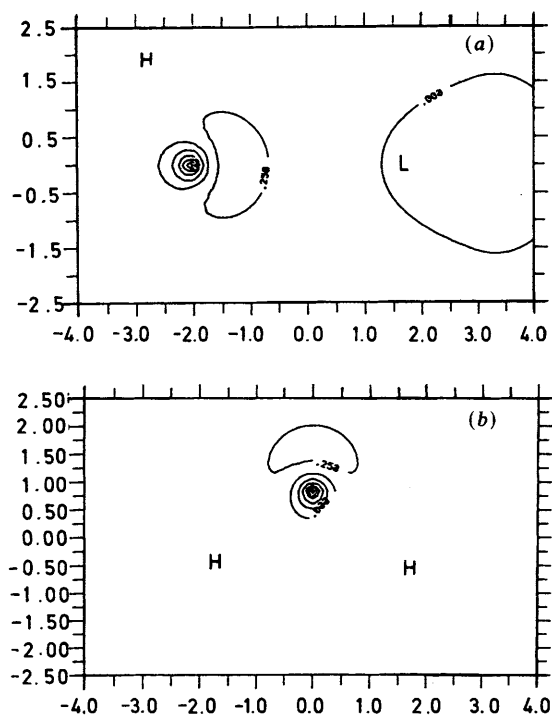


Fig. 3. Valence orbital φ_7 of CH_3Li . This orbital is invariant under all the symmetry operations of the C_{3v} point group. The views correspond to those in fig. 1.

containing the other two C—H bonds. Three of the spin-coupled orbitals (φ_1 , φ_3 , φ_5) are easily recognized as slightly distorted sp^3 hybrids on carbon. They are transformed into one another under successive \hat{C}_3 rotations. The same is true of orbitals φ_2 , φ_4 and φ_6 , which take the form of slightly distorted H(1s) orbitals. These carbon and hydrogen orbitals are remarkably similar to those we found previously for methane.⁷

The two remaining orbitals constitute the C—Li bond. Orbital φ_7 is the remaining lobe of the sp^3 hybrid and is very similar in size and shape to φ_5 . This is despite the fact that the C—Li bond approaches twice the length of the C—H bonds. Orbital φ_8 appears to be the superposition of an s-type orbital on lithium and a p-type orbital on carbon, and it also has some amplitude on the hydrogen atoms. Although heavily delocalized onto the methyl group, orbital φ_8 still has its maximum amplitude on lithium. As the C—Li interatomic distance increases, this orbital becomes pure Li(2s) and the molecule dissociates to neutral Li and CH_3 fragments, as it should.

The dominant mode of spin coupling corresponds to singlet coupling of the electron spins associated with each approximately sp^3 hybrid and the orbital to which it points. Nonetheless, there are significant contributions from the other modes, and the coefficient of the 'perfect-pairing' spin function is only 0.85 in the Kotani scheme. For a discussion of different spin functions, and of the relationships between them, see for example the book by Pauncz.⁸

In order to test the validity of the spin-coupled description, a non-orthogonal configuration interaction calculation was performed. Ionic structures in spin-coupled theory are those in which one or more orbitals is doubly occupied. The 'full-valence VB' calculation used the spin-coupled configuration and all possible ionic configurations which may be generated using the occupied spin-coupled orbitals. Allowing for the

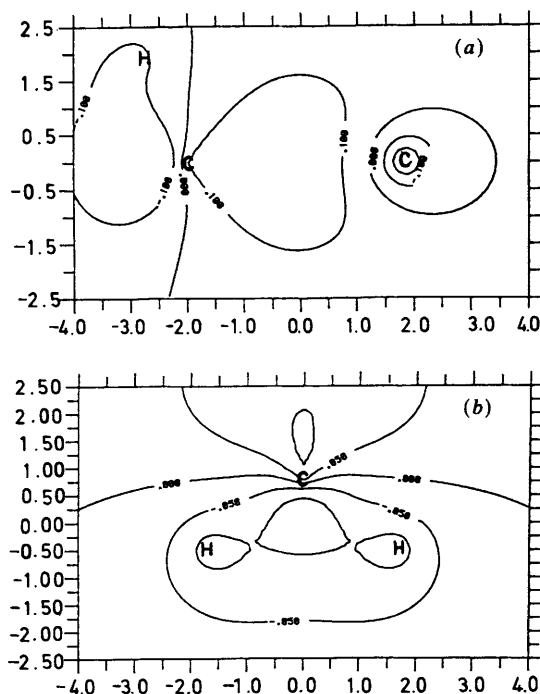


Fig. 4. Valence orbital ϕ_8 of CH_3Li . This orbital is invariant under all the symmetry operations of the C_{3v} point group. The views correspond to those in fig. 1.

Table 1. Energies and dipole moments calculated for CH_3Li

	energy/hartree	μ/D
m.o. SCF	-47.02200	6.07
spin-coupled	-47.08178	5.59
full-valence VB	-47.10535	5.58

All the calculations use the same geometry and basis set.

different modes of spin coupling, this generates a total of 1764 VB structures. The total energy and dipole moment are listed in table 1. None of the ionic configurations makes a large contribution to the final wavefunction. However, the additional energy lowering is not negligible (53 kJ mol^{-1}) simply because of the large number of very small contributions. The dipole moment is scarcely affected by the inclusion of all these ionic configurations and we can reasonably claim that their inclusion does not alter the essential physical picture.

Discussion

A recent study of CH_3Li using topological partitioning of the total electron density⁹ suggests considerable ionic character. Similarly, Streitweiser *et al*² have interpreted low values of the electron density between C and Li as an indication of weak covalent

character, and they advocate strong ionic character approaching 80%.^{2,10,11} However, Lipscomb and co-workers have argued that the integrated densities might not be a reliable criterion, simply because of the bond-length dependence.³ They estimated only 55–60% ionic character.

Using essentially the same basis set and geometry as in the present work, Hiberty and Cooper have projected SCF, GVB and CASSCF wavefunctions for CH₃Li onto classical VB structures.¹² These structures were built from orbitals which were constrained to be perfectly localized, in the sense of using basis functions only from one atomic centre. The GVB (4/PP) wavefunction corresponds to an energy slightly poorer (by 13 kJ mol⁻¹) than that from our spin-coupled calculation, whereas the CASSCF description (with 8 electrons in 8 orbitals) is very similar to our full-valence VB wavefunction. The SCF, GVB and CASSCF calculations gave very similar estimates for the weights of ionic structures constructed in this way, with a value of 76% in the CASSCF case. A similar projection of the spin-coupled or full-valence VB wavefunctions would also give estimates approaching 80%.

The valence contribution ρ_v to the total electron density from the spin-coupled calculation exhibits a residual peak on lithium, indicating that ionization is by no means complete. However, ρ_v drops to very low values in the region between lithium and carbon. The build-up of 'overlap charge' in the C—Li bond region appears to be quite limited, when compared with the situation expected for a normal covalent bond. Thus, the spin-coupled calculations suggest that the C—Li bond can be described as essentially ionic, although it does not correspond to the transfer of a whole electron.

We thank Prof. A. Streitwieser for suggesting this problem, and Philippe Hiberty for helpful discussions.

References

- 1 L. J. Andrews, *J. Chem. Phys.*, 1967, **47**, 4834.
- 2 A. Streitwieser Jr, J. E. Williams, S. Aleksandratos and J. M. McKelvey, *J. Am. Chem. Soc.*, 1976, **98**, 4778.
- 3 G. D. Graham, D. S. Marinick and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1980, **102**, 4572.
- 4 For recent reviews see: (a) D. L. Cooper, J. Gerratt and M. Raimondi, *Adv. Chem. Phys.*, 1987, **69**, 319; (b) D. L. Cooper, J. Gerratt and M. Raimondi, *Int. Rev. Phys. Chem.*, 1988, **7**, 59.
- 5 T. H. Dunning Jr, *J. Chem. Phys.*, 1970, **53**, 2823.
- 6 S. Huzinaga, *J. Chem. Phys.*, 1965, **42**, 1293.
- 7 F. Penotti, D. L. Cooper, J. Gerratt and M. Raimondi, *J. Mol. Struct. (Theochem.)*, 1988, **169**, 421.
- 8 R. Pauncz, *Spin Eigenfunctions* (Plenum, New York, 1979).
- 9 J. P. Ritchie and S. M. Bachrach, *J. Am. Chem. Soc.*, 1987, **109**, 5909.
- 10 A. Streitwieser Jr, *Acc. Chem. Res.*, 1984, **17**, 353.
- 11 A. Streitwieser Jr, D. L. Grier, B. A. B. Kohler, E. R. Vorpapel and G. W. Schriver, in *Electron Distributions and the Chemical Bond*, ed. M. Hall and P. Coppens (Plenum, New York, 1982).
- 12 P. C. Hiberty and D. L. Cooper, *J. Mol. Struct. (Theochem.)*, 1988, **169**, 437.

Paper 8/02187B; Received 1st June, 1988