^{7}Li–^{13}C N.M.R. Coupling Constants and the Nature of the Carbon–Lithium Bond: INDO MO Calculations

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Summary INDO molecular orbital calculations suggest that the ^{7}Li–^{13}C n.m.r. coupling constant for the methyl-lithium monomer should be very large; this indicates the predominantly covalent character of the C–Li bond.

THE nature of the carbon–lithium bond, whether covalent or ionic, remains a matter of controversy.[1–5] Most authors have concluded that the bonding in alkyl-lithiums is covalent with significant polar (ionic) character, but the multicentre bonding present in alkyl-lithium tetramers and hexamers complicates the interpretation.[1,3–5] Theoretical analyses of methyl-lithium monomer have come to various conclusions.[2–4] An extreme viewpoint is that of Streitwieser, who insists that methyl-lithium is largely[2a] or wholly[2b] ionic.

^{7}Li–^{13}C N.m.r. coupling constants[1,5] provide important experimental evidence regarding the nature of alkyl-lithium bonding. Ionic bonds should show only relatively small coupling.[6] Alkyl-lithium hexamers and tetramers have $J(^{7}Li–^{13}C)$ values in the 10—15 Hz range.[1,5] Streitwieser argues that 'diradical character,' $H_3C{\downarrow}{\uparrow}Li$, may account for these couplings through spin polarisation,[2a] but no further justification of this suggestion is offered. Recently, Seebach *et al.*[7] have observed ^{7}Li–^{13}C coupling constants of *ca.* 45 Hz for a series of lithium carbenoids, three times larger than any observed before. These large couplings may be due either to the unusual structures of the carbenoids[8] or to the fact that they may be monomeric in tetrahydrofuran (THF) solution.[7] We have therefore used finite perturbation theory within the INDO formalism[9] including the Fermi contact term to investigate the effect of aggregation on ^{7}Li–^{13}C coupling in methyl-lithium. The INDO method has been shown[4b] drastically to overestimate the stability of the methyl-lithium tetramer and to yield significantly different hybridisation at carbon than *ab initio* methods. The INDO method using only the Fermi contact term may not be reliable for the multicentre bonds found in the methyl-lithium tetramer. On the other hand

TABLE. INDO calculated coupling constants (in Hz) for methyl-lithium species.

Species	Geometry	r_{CLi}/Å	r_{CH}/Å	$J(^{7}Li–^{13}C)$	$J(^{1}H–^{13}C)$
CH_3Li, C_{3v}	STO-3G[a]	2·009	1·083	115·9	63·4
	6-31G*[b]	2·001	1·094	115·9	63·6
	MNDO[c]	1·821	1·117	116·1	57·0
$(CH_3Li)_2, C_{2h}$	STO-3G[d]	2·126[f]	1·090[f]	20·0[f]	58·4[f]
	MNDO[c]	2·037[f]	1·130[f]	25·3[f]	56·5[f]
$(CH_3Li)_4, T_d$, staggered	STO-3G[d]	2·230	1·091	6·9,0·4[g]	62·1
	MNDO[c]	2·199	1·136	7·3,0·3[g]	61·4
	X-ray[e]	2·311	0·960	7·7,1·3[g]	51·2
$(CH_3Li)_4, T_d$, eclipsed	STO-3G[d]	2·250	1·095	7·0,0·3[g]	61·1
	MNDO[c]	2·197	1·139	7·3,0·1[g]	59·7
$CH_3Li–NH_3, C_{3v}$	STO-3*G*[b]	2·021	1·084	127	65·6
	MNDO[c]	1·847	1·117	118·9	60·1

[a] J. D Dill, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, 1977, **99**, 6159. [b] T. Clark, unpublished calculations [c] A preliminary parameter set for lithium (W. Thiel and T. Clark, unpublished) was employed. [d] T. Clark, P. v. R. Schleyer, and J. A. Pople, *J. Chem. Soc., Chem. Commun.*, 1978, 137. [e] E. Weiss and G. Hencken, *J. Organomet. Chem.*, 1970, **21**, 265. [f] Mean values for all C–Li and C–H bonds. [g] C–Li coupling involving the lithium atom not bonded to the perturbing carbon.

INDO predicts that the bonding in $(CH_3Li)_4$ should be too favourable, and that the s-character at carbon in the C–Li bonding orbitals should be too large.[4b] Both of these factors should result in a calculated ^{7}Li–^{13}C coupling constant which is too large for the tetramer with respect to the monomer, and therefore should not affect our conclusions. The Table shows calculated ^{7}Li–^{13}C and ^{1}H–^{13}C coupling constants for a series of methyl-lithium oligomers, and for monomeric methyl-lithium complexed with one ammonia molecule. The ^{7}Li–^{13}C coupling constants are essentially independent of the geometry used, the C–Li bond in CH_3Li being 10% shorter for MNDO than for STO-3G or 6-31G*, whereas the calculated $J(^{7}Li–^{13}C)$ values are essentially identical.

Our calculated $J(^{7}Li–^{13}C)$ for $(CH_3Li)_4$ is approximately 50% of the experimental value.[5] The discrepancy is probably the result of the fact that we have used a value of 0·735 a.u.$^{-3}$ for $|\psi_s^{(0)}|^2$ (lithium) obtained by extrapolation from the elements boron to fluorine.[9] If, as has been suggested,[10] the lithium 1s orbital mixes into valence MO's to increase the coupling abnormally, our extrapolated $|\psi_s^{(0)}|^2$ may be too small. *Ab initio* calculations on alkyllithiums in fact show a very substantial contribution from the lithium 1s orbital in the C–Li bonding orbitals (the Li 1s coefficient may be as high as 50% of the Li 2s coefficient).[11] The calculated $J(^{1}H–^{13}C)$ for $(CH_3Li)_4$ is also underestimated, but is correctly predicted to be lower than that in methane.[5]

We have also investigated the effect of solvent coordination on $J(^{7}Li–^{13}C)$. The coupling constants calculated for the $CH_3Li–NH_3$ complex (see Table) are slightly larger than those in CH_3Li, in accord with the observation that $J(^{7}Li–^{13}C)$ and $J(^{1}H–^{13}C)$ are independent of solvent for $(CH_3Li)_4$.[5]

For interpretative purposes the absolute values of the coupling constants are, however, less important. The significance of our results lies in the fact that the calculated $J(^{7}Li–^{13}C)$ for monomeric methyl-lithium is 15 times larger than that obtained for the tetramer, and 4—5 times larger than for the dimer. Assuming proportionality between calculated and experimental ^{7}Li–^{13}C coupling constants, a value of *over 200 Hz* is indicated for monomeric CH_3Li! The coupling in CH_3Li is in fact, calculated to be twice as large as that typically calculated for lithium carbenoids,[11] suggesting that the 45 Hz coupling found[7] for the latter compounds is abnormally low, rather than abnormally high, for monomeric organolithiums. The startling decrease in ^{7}Li–^{13}C coupling on going from CH_3Li to $(CH_3Li)_4$ appears to be the result of two factors. the decrease in C–Li overlap on going from two-centre to multicentre bonding and the large decrease in s-character on lithium upon oligomerisation.[4b]

We conclude that $J(^{7}Li–^{13}C)$ in monomeric methyllithium should be very large, perhaps over 200 Hz. In our view, this indicates the predominantly covalent nature of C–Li bonding, unless a rationalisation consistent with the 'wholly ionic' interpretation can be found.

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