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THE SIGN OF THE LITHIUM—CARBON NUCLEAR SPIN COUPLING CONSTANT IN METHYLLITHIUM TETRAMER

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Summary

Heteronuclear magnetic double resonance experiments are used to show that ${}^1J({}^7\text{Li}—{}^{13}\text{C})$ is positive in methyllithium tetramer. This is consistent with dominance of the coupling mechanism by the Fermi contact interaction.

Introduction

Studies of the signs and magnitudes of nuclear spin coupling constants have proved to be a very valuable way of testing theories of chemical bonding [1], but relatively little work has been done in this area on organometallic derivatives of the more electropositive elements. This is because comparatively few of these elements have isotopes with suitable nuclear properties (ideally, spin quantum number $I = 1/2$ and 100% natural abundance.) However, ^{7}Li has a high natural abundance and $I = 3/2$, and in many derivatives the electrical symmetry at the lithium atom is sufficiently high for the effects of quadrupole broadening to be small, so that coupling constants involving this nucleus have been reported [2]. In this note we describe the first determination of the *sign* of a coupling constant involving lithium.

Results and discussion

For coupling constants between directly bound elements experimental sign determinations have generally provided confirmation of the theoretical treatment by Pople and Santry [1]. There are some discrepancies however, [notably in the case of ${}^1K(\text{HF})$] and experimental measurements are particularly sparse for couplings involving the more electropositive elements. According to Pople and Santry's theory, and also to a more recent [3] treatment, ${}^1K(\text{LiC})$ should be positive, whereas a rationalisation [4] based upon electronegativity differences predicts that this reduced coupling constant should be negative. The magnitude of ${}^1J({}^7\text{Li}—{}^{13}\text{C})$ in methyllithium tetramer has been calculated [5] from Pople and Santry's expression by the Self-Consistent Charge method to be 0.77 Hz, which is in very poor agreement with the experimental value [2] of 15 Hz, and it is clear that further discussion demands a knowledge of the sign.

${}^1\text{H}—\{{}^7\text{Li}\}$ and ${}^1\text{H}—\{{}^{13}\text{C}\}$ heteronuclear double resonance experiments were performed upon a 2% w/v tetrahydrofuran solution of methyllithium tetramer, $(\text{LiCH}_3)_4$ which contained the isotopes ^{7}Li and ^{13}C in abundances of 92.6 and 25% respectively. The tetramer has a tetrahedral structure in which each lithium atom is directly associated with three equivalent methyl groups [2, 6], and at this level of ^{13}C enrichment the proportions of the various species (assuming random distribution) are as follows: 0 ^{13}C, 31.6%; 1 ^{13}C, 42.2%; 2 ^{13}C, 21.1%; 3 ^{13}C, 4.7%; 4 ^{13}C, 0.4%. Thus the major ^{13}C-containing species has one ^{13}C per unit of tetramer and the interpretation of the experiments remains straightforward. Strictly, account should also be taken of the presence of ^{6}Li (abundance 7.4%) but this is only a small effect. The experiments were done at —50° because at higher temperatures intermolecular exchange leads to loss of the Li—C coupling.

Separate overlapping methyl proton resonances were observed for the tetramer itself and for the lithium iodide—methyllithium aggregate which was also present as a consequence of the mode of preparation (from n-butyllithium and methyl iodide.) The tetramer resonance was ca. 4.8 Hz wide at —50° and this width was reduced to 2.9 Hz by irradiation at the ^{7}Li resonant frequency. The quadrupole-induced broadening prevented observation of fine structure arising from spin coupling between the protons and the lithium spin of 3/2, but from the change in line width produced by ^{7}Li irradiation we estimate that ${}^2J({}^7\text{Li}\cdots\text{H})$ is not less than 0.4 Hz. Selective ${}^1\text{H}—\{{}^7\text{Li}\}$ experiments using lines arising from molecules having opposite spin states of ^{13}C, and selective ${}^1\text{H}—\{{}^{13}\text{C}\}$ experiments which produced changes of line-shape only, then gave the results in Table 1. It is unusual for ${}^1J(\text{X}—{}^{13}\text{C})$ and ${}^2J(\text{X}\cdots\text{H})$ to have like signs in the same molecule, but further discussion is not profitable at present because the precise magnitude (small) of ${}^2J({}^7\text{Li}\cdots\text{H})$ is unknown and may well be solvent-dependent.

TABLE 1

RESULTS OF DOUBLE RESONANCE EXPERIMENTS ON METHYLLITHIUM TETRAMER ENRICHED TO 25% IN ^{13}C

${}^1J({}^{13}\text{C}-\text{H})$ + 96.2 Hz	$\delta({}^1\text{H})$ —2.04 ppm
${}^1J({}^7\text{Li}-{}^{13}\text{C})$ + 15 Hz	$\Xi({}^7\text{Li})$ 38 863 887 Hz [a]
${}^2J({}^7\text{Li}\cdots\text{H}) \nless$ + 0.4 Hz	$\Xi({}^{13}\text{C})$ 25 144 613 Hz

[a] $\Xi(\text{K})$ is the resonant frequency of X corrected to a magnetic field in which $(\text{CH}_3)_4\text{Si}$ would give a proton resonance at exactly 100 MHz.

Since ${}^1J({}^{13}\text{C}-\text{H})$ is known to be positive it follows that ${}^1J({}^7\text{Li}-{}^{13}\text{C})$ and hence ${}^1K(\text{LiC})$ are also positive. (Both ^{7}Li and ^{13}C have positive magnetic moments). The suggestion [4] that electronegativity difference exceeding 1.5 lead to negative coupling constants is therefore incorrect in this case (the electronegativity difference between carbon and lithium is 1.5 - 1.6 according to the method of calculation) while the theoretical molecular orbital approach [1, 5] may be qualitatively correct.

The value of ${}^1J({}^7\mathrm{Li}{-}{}^{13}\mathrm{C})$ obtained from the Pople and Santry expression for the Fermi contact term is very small (0.77 Hz) largely because $[\phi_{2s}(0)]^2$ for the lithium atom is very small (only 1/16 of the value for carbon). Even the use of an unreasonably small value for ΔE, and of improbably large values for the *s*-characters of the lithium and carbon hybrid orbitals used for the Li—C bonds is insufficient to give a calculated value for ${}^1J({}^7\mathrm{Li}{-}{}^{13}\mathrm{C})$ which is as much as one fifth of the observed one (15 Hz), so it appears that in methyllithium tetramer $[\phi_{2s(\mathrm{Li})}(0)]^2$ is much larger than in the lithium atom. This could be a result of mixing the 1*s* orbitals of lithium in the valence molecular orbitals [6].

Acknowledgements

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