Ab Initio Study of the Molecular Structure and NMR Carbon–Lithium Coupling Constant for Trichloromethyllithium

Terutake Koizumi and Osamu Kikuchi*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

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Ab initio calculations of the molecular structure and NMR C–Li coupling constant for trichloromethyllithium have indicated that the classical C_{3v} form is favorable for trichloromethyllithium observed by NMR spectroscopy.

Trichloromethyllithium (**1**) is an important reagent for organic synthesis,[1)] and its structure has been a subject of much interest. Theoretical calculations[2)] for **1** have included five structures, **1a**—**1e** (Fig. 1); structure **1b**[2a)] or **1e**[2b)] has been shown to be the most stable among them. These results support matrix isolation studies in which a species with C_{3v} symmetry[3a)] or a complex of type $Cl^{-}\cdots Li^{+}\cdots CCl_2$[3b)] has been observed.

On the other hand, the NMR spectra of **1** were measured in THF at −105 °C, and its ^{13}C–^{6}Li and ^{13}C–^{7}Li coupling constants ($^{1}J_{CLi}$) were obtained to be 17 and 45 Hz, respectively.[4,5)] These values are comparable with those of monomeric alkyllithiums.[6)] Although it has been considered based on the multiplicity of the NMR signal caused by C–Li coupling that **1** was observed as a monomer,[4,6)] and **1a**[2a,4)] or **1c**[2a)] has been predicted as the observed structure, previous energetic calculations[2)] are insufficient for rationalizing the observed results. It is important to pay attention to the ionic character of the lithium atom, which seems to be influenced by a donor solvent.[2a,4,6—8)] In previous studies, the truncated basis set for lithium, which includes only the 1s function and corresponds to the lithium cation, was used to model the ionic C–Li bond; reasonable results were obtained for the structure of benzyllithium[9)] and the NMR coupling constants for methyllithium and *t*-butyllithium.[10)] In this study, ab initio molecular orbital calculations[11)] with a truncated basis set for lithium were applied to five structures, **1a**—**1e**, and the structure observed by NMR spectroscopy was predicted on the basis of the relative energies and the $^{1}J_{CLi}$ values.

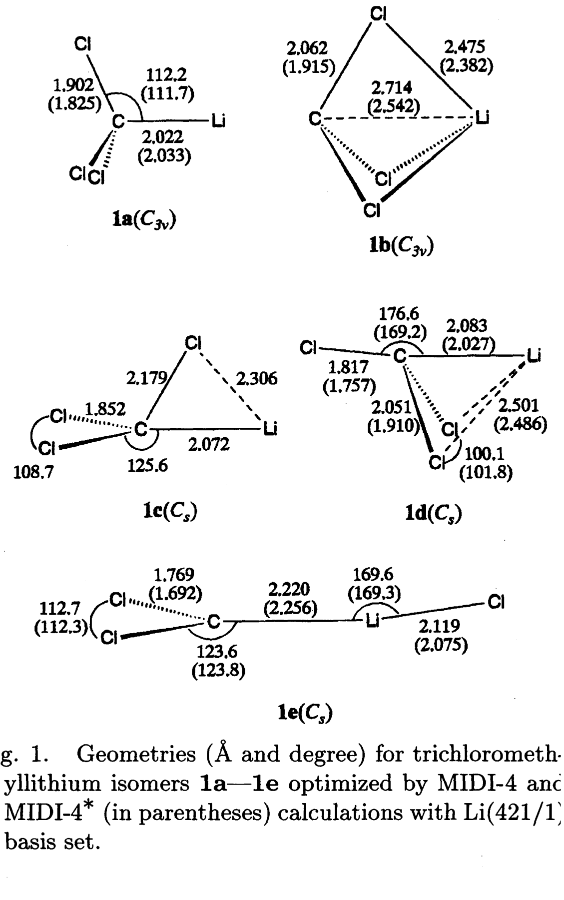

Fig. 1. Geometries (Å and degree) for trichloromethyllithium isomers **1a**—**1e** optimized by MIDI-4 and MIDI-4* (in parentheses) calculations with Li(421/1) basis set.

Structures and Energies. The MIDI-4 and MIDI-4* basis sets[12a,12b,12c)] were employed for calculating the structures and energies of **1a**—**1e**. The latter basis set includes the d-type polarization functions on carbon and chlorine atoms. For lithium, two types of basis functions were used: Li(421/1), in which the p-type polarization functions are added to the MIDI-4 basis set[12)] and Li(31), a truncated MIDI-4 basis set which includes only the 1s function.[12d)] The geometries were optimized under the restriction of a given symmetry for each structure. Single-point calculations for the optimized geometries were performed using the second-order Møller–Plesset perturbation theory (MP2)[13)] within the frozen-core orbital approximation. The total and relative energies are listed in Table 1, and the charge densities are listed in Table 2. The structures calculated with the Li(421/1) and Li(31) basis sets are

Table 1. Total Energies (hartree) and Relative Energies (kcal mol^{-1}, in Parentheses) for Trichloromethyllithium Isomers

	HF/MIDI-4	HF/MIDI-4*	MP2/MIDI-4*
Li(421/1) basis set			
1a	−1422.134231 (5.76)	−1422.234952 (12.83)	−1422.788100 (4.36)
1b	−1422.143412 (0.00)	−1422.240518 (9.33)	−1422.795044 (0.00)
1c	−1422.141706 (0.90)	a)	a)
1d	−1422.138357 (3.17)	−1422.239410 (10.03)	−1422.793328 (1.08)
1e	−1422.137301 (3.83)	−1422.255390 (0.00)	−1422.788399 (4.17)
Li(31) basis set			
1a	−1422.130212 (0.20)	−1422.230420 (2.90)	−1422.791904 (0.00)
1b	−1422.121028 (5.96)	−1422.222284 (8.00)	−1422.782248 (6.06)
1c	−1422.130528 (0.00)	−1422.235034 (0.00)	−1422.780253 (7.31)
1e	−1422.108200 (14.01)	−1422.230495 (2.85)	−1422.769682 (13.94)

a) Optimization gave the structure **1e**.

Table 2. Charge Densities for Trichloromethyllithium Isomers

	MIDI-4			MIDI-4*		
	Li	C	Cl	Li	C	Cl
			Li(421/1) basis set			
1a	0.927	−0.561	−0.122	0.877	−0.248	−0.210
1b	0.650	0.073	−0.241	0.662	0.091	−0.251
1c	0.840	−0.361	−0.060a) −0.359			
1d	0.812	−0.312	−0.245a) −0.010	0.785	−0.136	−0.261a) −0.128
1e	0.674	−0.132	0.060a) −0.661	0.667	0.022	−0.003a) −0.684
			Li(31) basis set			
1a	1.006	−0.627	−0.126	1.007	−0.353	−0.218
1b	1.001	0.076	−0.359	1.002	0.090	−0.364
1c	1.006	−0.467	−0.069a) −0.401	1.006	−0.046	−0.052a) −0.855
1e	1.007	−0.138	0.066a) −1.002	1.008	−0.009	0.002a) −1.003

a) Values for two equivalent chlorine atoms.

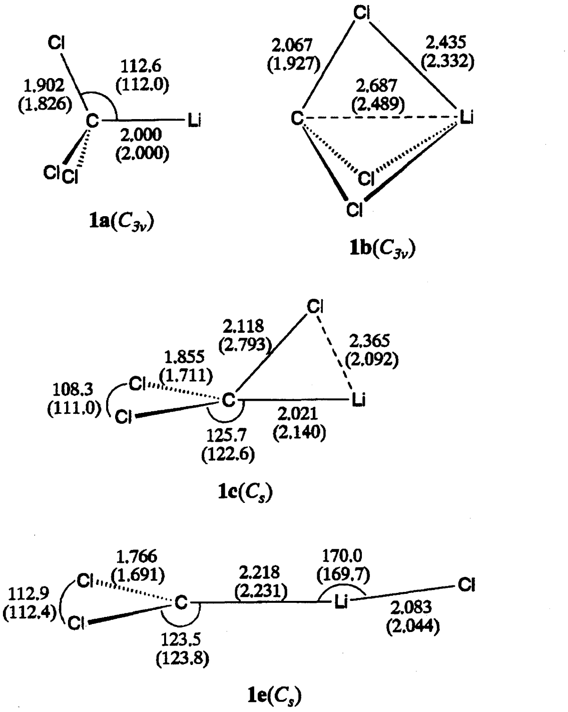

Fig. 2. Geometries (Å and degree) for trichloromethyllithium isomers **1a**—**1c** and **1e** optimized by MIDI-4 and MIDI-4* (in parentheses) calculations with Li-(31) basis set.

shown in Figs. 1 and 2, respectively.

At the Li(421/1) level of the calculation, optimization of structure **1c** with the MIDI-4* basis set gave **1e**; **1b** (MIDI-4) or **1e** (MIDI-4*) is the most stable structure at the Hartree–Fock (HF) level. These trends resemble those reported in previous studies.2) The electron correlation at the MP2 level stabilizes structure **1b**.

At the Li(31) level of the calculation, the optimized geometries are similar to those in Fig. 1, except for structure **1d**, which was led to **1a** by optimization, and structure **1c**, which was determined as a stable species using both the MIDI-4 and MIDI-4* basis sets. An interesting aspect of Table 1 is that the relative energy of **1a**, which has the carbanion character according to the charge densities listed in Table 2, is largely stabilized in the Li(31) calculations, and that **1a** is most stable at the MP2 level. Clark and Schleyer2a) have reported that structure **1a** was calculated to be a minimum when solvated with one NH_3 molecule. Since the use of a truncated basis set for lithium produces an effect on the molecular structure,9) which is parallel to the coordination of solvent molecules,14) **1a** is possibly the structure observed in solution.

C–Li Coupling Constant. The $^1J_{\mathrm{CLi}}$ value was calculated by using self-consistent perturbation theory,15) in which only the Fermi contact term was taken into account as the perturbation. This method well reproduced the experimental trend for methyllithium.10) The calculated $^1J_{\mathrm{CLi}}$ values are listed in Ta-

Table 3. Calculated ^{13}C–^{7}Li Coupling Constants (Hz) for Trichloromethyllithium Isomers

	Li(421/1) basis set		Li(31) basis set	
	MIDI-4	MIDI-4*	MIDI-4	MIDI-4*
1a	67.1	64.0	50.2	46.4
1b	19.1	4.1	−2.3	0.2
1c	36.1	a)	33.9	b)
1d	20.8	23.5	a)	a)

a) Optimization gave another structure; see the text. b) Not obtained because of bad convergence; see the text.

ble 3. The $^1J_{\text{CLi}}$ value for structure **1e** was not obtained because of a bad convergence, which seems to be caused by a UHF instability.[16)]

Table 3 shows that the $^1J_{\text{CLi}}$ values decrease as the number of chlorine atoms bridging to the carbon–lithium bond increases; that is, **1a**>**1c**>**1d**>**1b**. This result rules out structure **1b** from the species observed by NMR spectroscopy, as mentioned in a previous study.[2a)] The $^1J_{\text{CLi}}$ value for **1a** at the MIDI-4* level with the truncated basis set for lithium, 46.4 Hz, is in good agreement with the experimental value, 45 Hz.[4a,4d)] By the same level of calculation, the $^1J_{\text{CLi}}$ value for monomeric *t*-butyllithium, 37.4 Hz,[17)] which is in good agreement with the experimental value, 31.5 Hz,[6)] was obtained. It is concluded from the calculated energies and the coupling constants that **1a**, the classical C_{3v} form, is the most probable for the structure of **1** observed by NMR spectroscopy.

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5) The equation $^1J(^{13}\text{C}-^7\text{Li})=(\gamma(^7\text{Li})/\gamma(^6\text{Li}))\cdot{}^1J(^{13}\text{C}-^6\text{Li})$ $((\gamma(^7\text{Li})/\gamma(^6\text{Li}))=2.641))$ is obtained; see Ref. 4 and Ref. 6.

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