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Structures and bonding of lithium ethylene complexes

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Abstract

The geometries of the $Li_2C_2H_4$ and $Li(C_2H_4)_n$ ($n = 1, 2, 3$) lithium ethylene complexes have been optimized at the HF/3-21G level. The most stable isomer of each species has been found to have a lithium atom bonded symmetrically to the carbon atoms of each ethylene ligand to form a cyclopropane-like structure or substructure. The ethylene ligands of lithium di- and tri-ethylene are equivalent and parallel to each other, while dilithium ethylene has a C_{2v} structure with its second lithium atom bonded to the metal centre of LiC_2H_4 consistent with recently published infrared data. The lithium ethylene complexes studied have been found to be partially ionic, arising from metal → ligand charge-transfer to the π^* MO of the ethylene ligand through the lithium $2p$ orbital.

Introduction

Organolithium reagents have long been important reagents in organic synthesis [1]. Much theoretical work on lithiocarbon species has thus been carried out over the past decade in order to gain a better understanding of the nature of the Li–C bond [2–9]. In addition, lithium atoms have been found to act as a Lewis acid towards "electron-rich" sites of molecules with unfavourable electron affinity, such as water and ammonia [10–12]. This raises intriguing questions about the possible complexation between lithium atoms and different unsaturated hydrocarbons. An early calculation predicted that interaction of lithium atoms with ethylene was unlikely to give anything but an ethyl-radical-like adduct [13]. The potential energy surface of 1,2-dilithioethane has been investigated theoretically [5,7] but has not been confirmed by experimental data. To investigate the reactivity of alkali metal atoms with unsaturated hydrocarbon molecules and the structures of the possible products, Manceron and Andrews have carried out a series of infrared work on lithium ethylene complexes in solid argon [14]. They found that condensation of ethylene molecules and alkali metal atoms at high dilution in argon produced very different results, depending on the nature of the alkali metal. Heavy alkali metal atoms (Na

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and Cs) yielded only a very weak complex with ethylene virtually unperturbed, but lithium produced $Li_2C_2H_4$ and $Li(C_2H_4)_n$ ($n = 1, 2, 3$) complexes displaying a large degree of perturbation in the ethylene ligand. An examination of the infrared spectra of these complexes containing different isotopes of lithium (^6Li, ^7Li), and various isotopes of carbon and hydrogen in the ethylene ligand (C_2H_4, $^{13}C_2H_4$, C_2D_4 and CH_2CD_2), revealed that the metal centre forms a π-complex with equivalent CH_2 groups in each structure, and that the ethylene ligands are equivalent in lithium di- and tri-ethylene.

Here we would report our theoretical work on the structures of these lithium-ethylene complexes in order to gain some insight into their bonding.

Calculation

Calculations were carried out at the restricted Hartree–Fock (RHF) level using the Gaussian 82 package of programs [15]. The structures were completely optimized within each assumed symmetry using the energy gradient method. The efficient 3-21G split-valence basis set is used. It has been clearly shown that polarization functions and electron correction tend to be less important for organolithium compounds, and the relative energies of isomers are generally well represented at such split-valence basis levels [7]. However, the HF/6-31G* and MP2/6-31G* energies of $Li_2C_2H_4$ at the 3-21G optimized geometry have been computed for comparison purposes.

Results and discussion

The different structures of $Li_2C_2H_4$ studied are shown in Fig. 1. Structures **1**–**5** are the various isomers of 1,2-dilithioethane, the potential surface of which has been examined by Kos et al. [5] at several levels of ab initio theory. Their relative energies are listed in Table 1. The global energy minimum was found to be **1** at all levels of theory studied. It has a *(Li,Li)-trans* configuration but an unusual partially bridged geometry ($\angle LiCC = 73.2°$).

In the condensation reaction of ethylene molecules and lithium atoms at high dilution in argon, Manceron and Andrews [14] found that infrared absorption bands attributable to $Li_2C_2H_4$ were observed when the ethylene concentration was lower than 1/400. When hydrogen and lithium had been replaced with their respective isotopes a study of the relevant bands suggested that the complex was $Li_2C_2H_4$, having two inequivalent lithium atoms. This inequivalence of the lithium atoms thus rules out the possible structures **1**–**5** for $Li_2C_2H_4$. Indeed, Manceron and Andrews [14] have shown, on the basis of their infrared study of the C–C stretch, various isotope shifts and model force constant calculations, that only structure **6** can account for the observed spectrum. The geometry of isomer **6** has been optimized in this work and is listed in Table 2. It was found that **6** has the lowest energy of the six isomers of $Li_2C_2H_4$ (Table 1), in agreement with experiment [14]. The eigenvalues of the matrix whose elements are the second derivatives of its energy with respect to its internal coordinates are all positive, indicating **6** to be an equilibrium structure. Hence, **6** is most stable thermodynamically and its existence is not due to kinetic stabilization under specific experimental conditions. The preferential addition of the second Li atom to the first Li atom rather than to the other side of the

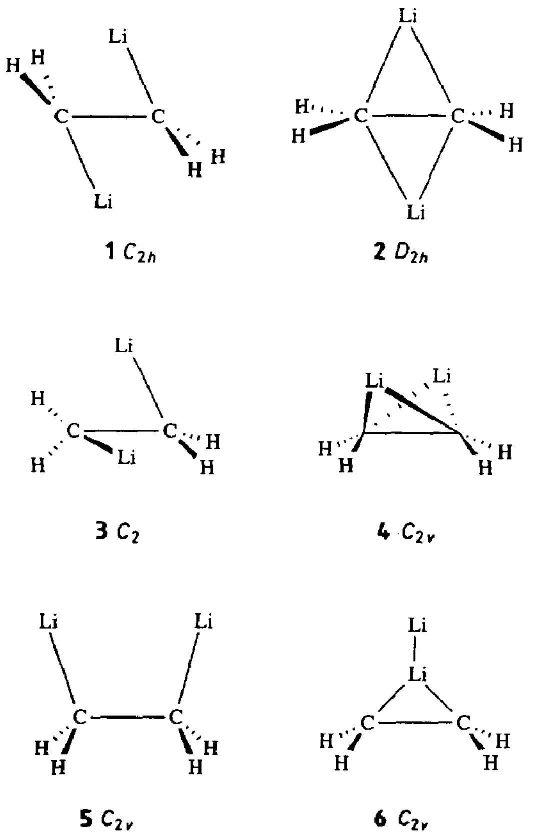


Fig. 1. Structures of $Li_2C_2H_4$.

C–C bond is perhaps due to the fact that the Li and the C atoms of LiC_2H_4 carry large positive (+0.451) and large negative (−0.613) charges, respectively. This probably also explains why no synthesis of α,β-dilithioalkanes has yet been reported.

Results in Table 2 show that the geometry of the free ethylene molecule undergoes no significant changes in forming **6** except that its C–C bond becomes 0.010 Å longer upon complexation. The Li–Li bond distance (2.857 Å) in **6** was found to be somewhat longer than that (2.816 Å at the 3–21G level) of the Li_2 molecule.

Table 1

Relative energies (kcal mol^{-1}) of $Li_2C_2H_4$ isomers

Structure	1	2	3	4	5	6[a]
STO–3G	0.0	3.4	–	25.4	38.5	–
3–21G	0.0	2.3	8.0	8.8	29.3	−20.0
4–31G	0.0	1.3	8.7	9.2	27.0	–
MP2/4–31G	0.0	1.4	–	9.2	24.3	–
6–31G*//3–21G	0.0	4.3	7.1	9.1	27.5	−23.2
6–31G*//4–31G	0.0	3.8	–	8.7	27.0	–
MP2/6–31G*//3–21G	0.0	1.9	8.0	10.4	28.9	−9.2

[a] This work.

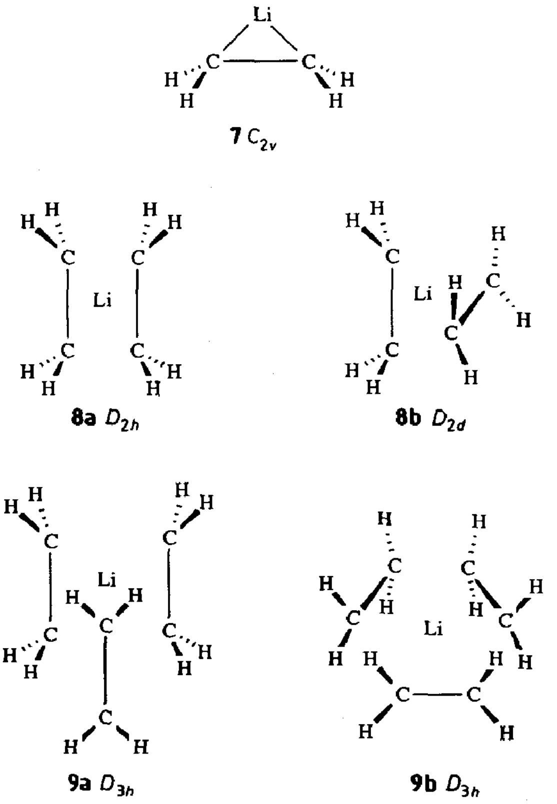
Table 2

Optimized bond lengths (Å), bond angles (deg.) and energies (a.u.) of ethylene and lithium ethylene complexes

	C_2H_4	**6**	**7**	**8a**	**8b**	**9a**	**9b**
R[a]	–	2.519	1.966	2.173	2.216	2.268	2.557
Li–C	–	2.604	2.092	2.276	2.317	2.365	2.641
C–C	1.315 (1.330)[b]	1.325	1.428	1.353	1.354	1.342	1.324
C–H	1.074 (1.076)	1.074	1.078	1.074	1.074	1.073	1.074
CCH	121.9	121.8	119.4	121.5	121.3	121.7	121.3
HCH	116.2 (116.6)	116.5	115.0	116.3	116.7	116.3	117.3
ϕ[c]	–	91.1	104.7	95.0	94.7	93.5	91.4
Li–Li	–	2.857	–	–	–	–	–
E_t	−77.60099	−92.38206	−84.96376	−162.58047	−162.56765	−240.19697	−240.16391

[a] Distance from Li to mid-point of C–C bond. [b] Observed values are in parentheses. [c] LiCCH dihedral angle.

Some of the structures of $Li(C_2H_4)_n$ (n = 1, 2, 3) studied are depicted in Fig. 2 and their optimized geometries are listed in Table 2. The largest geometric change in the ethylene ligand caused by the complexation occurs in LiC_2H_4. As the number of



7 C_{2v}

8a D_{2h}

8b D_{2d}

9a D_{3h}

9b D_{3h}

Fig. 2. Structures of $Li(C_2H_4)_n$ (n = 1, 2, 3).

the ethylene ligands increases, the C–C bond and the LiCCH dihedral angle decrease towards those values of the free ethylene molecule, along with progressive elongation of the Li–C bond. However, the C–H bond and the CCH angle of the ethylene remain almost unchanged on complex formation, except in LiC_2H_4 in which the C–H bond lengthens by 0.004 Å and the CCH angle decreases by about 2°.

The C–C bond elongation caused by the complexation may arise from metal → ligand charge-transfer to the π^* MO or by ligand → metal electron withdrawal from the ethylene π-system to form a three-membered metallocycle. Population analysis shows that the carbon $2p_\pi$ orbital's population increases from 1.000 in C_2H_4 to 1.207 in LiC_2H_4, and the charge distributions change from -0.425 (C) and $+0.213$ (H) for C_2H_4 to -0.614 (C), $+0.194$ (H) and $+0.451$ (Li) for LiC_2H_4. Hence, the lengthening of the C–C bond is due to a charge-transfer from Li to the π^* MO of the ethylene ligand. Such charge-transfer interaction between Li and C_2H_4 is expected to decrease as the number of ethylene molecules increases. This accounts for the variation in molecular dimensions of the $Li(C_2H_4)_n$ complexes noted above.

Manceron and Andrews [14] studied the infrared spectra of the $Li_2C_2H_4$ and $Li(C_2H_4)_n$ ($n = 1, 2, 3$) lithium ethylene complexes in solid argon. They tried to reproduce the few observed vibrational frequencies from calculations based on simplified harmonic models involving interaction between the C–C stretching and the CH_2 bending vibrational modes. Among the various force constants of ethylene, the perturbation of the C–C bond force constant, F_{CC}, by complexation is found to be the largest, decreasing monotonically from LiC_2H_4 to $Li(C_2H_4)_3$ in line with our calculated C–C bond distances. Manceron and Andrews also compared their estimated F_{CC} values of $Li(C_2H_4)_n$ ($n = 1, 2, 3$) with the C–C bond force constants and bond lengths of a number of hydrocarbons reported in the literature, and obtained approximate C–C bond distances for these complexes, viz., 1.44 ± 0.02, 1.42 ± 0.02 and 1.39 ± 0.02 Å, respectively. However, the corresponding values obtained in this work are 1.428, 1.353 and 1.342 Å. In view of the crudeness of Manceron and Andrews' estimation, it is felt that our C–C bond lengths are more realistic.

In the past decade, much work has been directed at elucidating the unusual structures of organolithium compounds [7], and at finding out whether the Li–C bond [8,9] is ionic or covalent. Our charge distribution and overlap population analyses indicate that the $Li(C_2H_4)_n$ complexes are ionic, $Li^{\delta+}(C_2H_4)_n^{\delta-}$, and that their Li(2$p$)–C overlap is about 75% of the total Li–C overlap. This is consistent with the point advanced years ago by Schleyer et al. [7] that the Li–C bond, although largely ionic has a significant covalent component which acts through the lithium p orbitals.

With the energy data given in Table 2 and those for Li (−7.38151 a.u.) and Li_2 (−14.76925a.u.), the stability of $Li_2C_2H_4$ and $Li(C_2H_4)_n$ toward the simplest possible dissociations, represented by equations 1, 2 and 3, can be examined:

$$Li_2C_2H_4 \rightarrow 2Li + C_2H_4 \qquad (1)$$

$$Li_2C_2H_4 \rightarrow Li_2 + C_2H_4 \qquad (2)$$

$$Li(C_2H_4)_n \rightarrow Li + nC_2H_4 \qquad (3)$$

The reaction energies (energy sum of products − energy of reactant) are 11.3, −11.8, −1.9, −9.9, 7.8 and −12.9 kcal mol⁻¹ for **6**, **7**, **8a**, **8b**, **9a** and **9b**, respectively, while the dissociation of $Li_2C_2H_4$ into Li_2 and C_2H_4 requires 7.4 kcal mol^{-1}. Thus, thermodynamically, **6** and **9a** are stable but **7**, **8a**, **8b** and **9b** unstable toward the dissociations 1 and 3, and reaction 1 is less favoured than reaction 2. Reaction energy, total energy and the Li–C bond length all indicate that **8a** and **9a** are more stable than **8b** and **9b**, respectively. However, for the series LiC_2H_4, $Li(C_2H_4)_2$ and $Li(C_2H_4)_3$, their relative stability trend expected in terms of the Li–C bond length is not reproduced by the reaction energies. In order to obtain more realistic complexation energies, the correlation energy (reactions 1–3 are not isodesmic), the zero-point vibrational energy and the basis set superposition error [16] should be taken into consideration, but these are beyond the scope of our limited computing facilities.

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