# Infrared Spectrum of the LiC$_2$H$_2$ Molecule in Solid Argon

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**Abstract:** Simultaneous matrix deposition of lithium atoms and acetylene molecules at high dilution in argon on a CsI window maintained at 15 K produced new infrared absorptions attributable to four different species. The main reaction product has a LiC$_2$H$_2$ stoichiometry; isotopic studies ($^6$Li, $^7$Li, C$_2$H$_2$, C$_2$D$_2$, C$_2$HD, and $^{13}$C$_2$H$_2$) of the six observed fundamentals show that the structure of LiC$_2$H$_2$ is likely to be planar, with lithium bridging the $\pi$ system and cis C–H groups with CCH angles estimated to be 140 ± 10°. The considerable weakening of the C–C bond is demonstrated by the position of the C–C stretching fundamental at 1655 cm$^{-1}$ near the value for ethylene, which is explained by electron density sharing between the $\pi$ system of C$_2$H$_2$ and lithium rather than lithium valence electron transfer into an antibonding $\pi^*$ orbital of C$_2$H$_2$. The minor reaction products have different stoichiometries; the Li$_2$C$_2$H$_2$ spectrum is consistent with a more acute CCH angle and a lithium bridging structure. Observations from the propyne–lithium atom reaction are consistent with the products observed for acetylene. All the observed species are unstable on annealing the matrix above 30 K.

The important use of organolithium reagents in organic synthesis[1] and a better understanding of the nature of the C–Li bond have recently stimulated a large amount of theoretical research on lithiocarbon species.[2-9] Furthermore, the ability of lithium atoms to act as a Lewis acid toward an "electron-rich" system of molecules with unfavorable electron affinity, such as water or ammonia,[10,11] raises intriguing questions about possible complexation between lithium atoms and different $\pi$ systems of unsaturated hydrocarbon compounds. In order to investigate the reactivity of alkali metal atoms with unsaturated hydrocarbon molecules and the structure of the possible products, we have undertaken a program of research using matrix isolation spectroscopy. In this first article, an infrared study of lithium atom reactions with acetylene molecules highly diluted in argon is reported; parallel studies with heavier alkali metals are in progress.[12]

## Experimental Section

The cryogenic refrigeration system, vacuum vessel, alkali metal source, and experimental techniques have been described previously.[13] Isotopically enriched samples of lithium metal 99.99% $^7$Li and 95.6% $^6$Li (O.R.N.L.) were used without purification. High purity acetylene (Matheson), argon (Air Products, 99.995%), $^{13}$C$_2$H$_2$ (90% $^{13}$C), and C$_2$D$_2$ (98% D) (Merck, Sharp and Dohme) were used without further purification. C$_2$HD was prepared from calcium carbide and a mixture of 70% D$_2$O (Aldrich 99.8% D) and 30% H$_2$O; the resulting gas was an equilibrium mixture of C$_2$HD$_2$, C$_2$H$_2$, and C$_2$D$_2$, which was vacuum-distilled prior to use.

Gaseous mixtures were deposited at 1.5 mmol/h simultaneously with a monoatomic beam of lithium on a CsI window maintained at 15 K; the concentration of lithium atoms was modified by varying the source temperature between 345 and 405 °C, representing a relative variation of 1–15 in the matrix and an approximate Li/Ar ratio of less than 1/10$^4$

(1) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergammon Press: New York, 1974.
(2) Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. *Tetrahedron Lett.* **1976**, *43*, 3923.
(3) Jemmis, E.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *101*, 2848.
(4) Apeloig, Y.; Clark, T.; Kos, A. J.; Jemmis, E.; Schleyer, P. v. R. *Israel J. Chem.* **1980**, *20*, 43.
(5) Kos, A. J.; Jemmis, E.; Schleyer, P. v. R.; Gleiter, R.; Fischbach, U.; Pople, J. *J. Am. Chem. Soc.* **1981**, *103*, 4996.
(6) Schleyer, P. v. R.; Kos, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 449.
(7) Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. *J. Am. Chem. Soc.* **1983**, *105*, 7617.
(8) Bachrach, S. M.; Streitwieser, A. *J. Am. Chem. Soc.* **1984**, *106*, 2283.
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(10) (a) Meier, P.; Hauge, R.; Margrave, J. *J. Am. Chem. Soc.* **1978**, *100*, 2108. (b) Perchard, J. P.; Loutellier, A.; Manceron, L. *Chem. Phys.*, in press.
(11) Bentley, J.; Carmichael, I. *J. Phys. Chem.* **1981**, *85*, 3821.
(12) Manceron, L.; Andrews, L., unpublished results.
(13) Andrews, L. *J. Chem. Phys.* **1968**, *48*, 972.

at the lower effusion temperature used here. Deposition periods were 12–24 h.

UV–visible irradiations were conducted with a 125-W medium-pressure mercury are focused on the sample with a quartz lens through a quartz window on the side of the vacuum vessel. IR spectra were recorded on a Beckman IR-12 filter grating spectrometer. Frequency accuracy is ±0.5 cm$^{-1}$ with slit widths of 2 cm$^{-1}$ at 2900 or 350 cm$^{-1}$ and 0.8 cm$^{-1}$ at 700 cm$^{-1}$.

## Results

Figure 1 presents spectra for lithium atoms (isotopes 6 or 7) deposited with normal and deuterated acetylene. In addition to the bands of free and aggregated acetylene[14] and weak absorptions due to water and carbon dioxide from the residual atmosphere of the vacuum vessel, one can see numerous product bands in several spectral regions, which were not observed in a sample deposited in the absence of lithium using the same experimental conditions. The frequencies of these absorptions measured with different isotopic precursors are listed in Table I.

All these absorptions can be correlated to four different species (labeled LiA, LiA$_2$, Li$_2$A, and (Li$_2$A)') by means of concentration effects in either lithium or acetylene and UV–visible irradiation. Table II gives an idea of the relative intensity variations, with different Li/C$_2$H$_2$ ratios, of the bands assigned to the different species LiA, LiA$_2$, and Li$_2$A. The LiA and LiA$_2$ species are greatly predominant in experiments run at the lowest lithium effusion rate ($t_{Li}$ = 345 °C) and, therefore, are assigned to species containing only one lithium atom. The LiA$_2$ species is favored by low Li/C$_2$H$_2$ ratios and is barely detectable in experiments conducted at low acetylene concentration (C$_2$H$_2$/Ar = 1/800). Hence, this species has a higher stoichiometry in C$_2$H$_2$, the more probable one being a single lithium atom for two acetylene molecules. The two other species, Li$_2$A and (Li$_2$A)', which are not detected in the experiments run at the lowest Li/C$_2$H$_2$ ratio, grow in a strictly parallel way when increasing this ratio and contain most probably two lithium atoms for one C$_2$H$_2$ molecule; the only difference is their behavior on irradiation which bleaches out all absorptions but the (Li$_2$A)' bands. Surprisingly, annealing does not provide very significant differences between the four species. At most, for very dilute samples in both lithium and acetylene, moderate warming of the matrix up to 25 K produced a small increase of the LiA, Li$_2$A, and (Li$_2$A)' absorptions, indicating that within this temperature range, migration of metal atoms allows further complexation; annealing the matrix to 35 K, however, produced a general decrease for all product absorptions, indicating that further aggregation occurs in the temperature range where diffusion of all the species is possible on a large scale.

(14) Baganskis, N. I.; Bulanin, M. O.; Fedeev, Vu. V. *Opt. Spectrosc.* **1970**, *29*, 687; **1972**, *35*, 525.

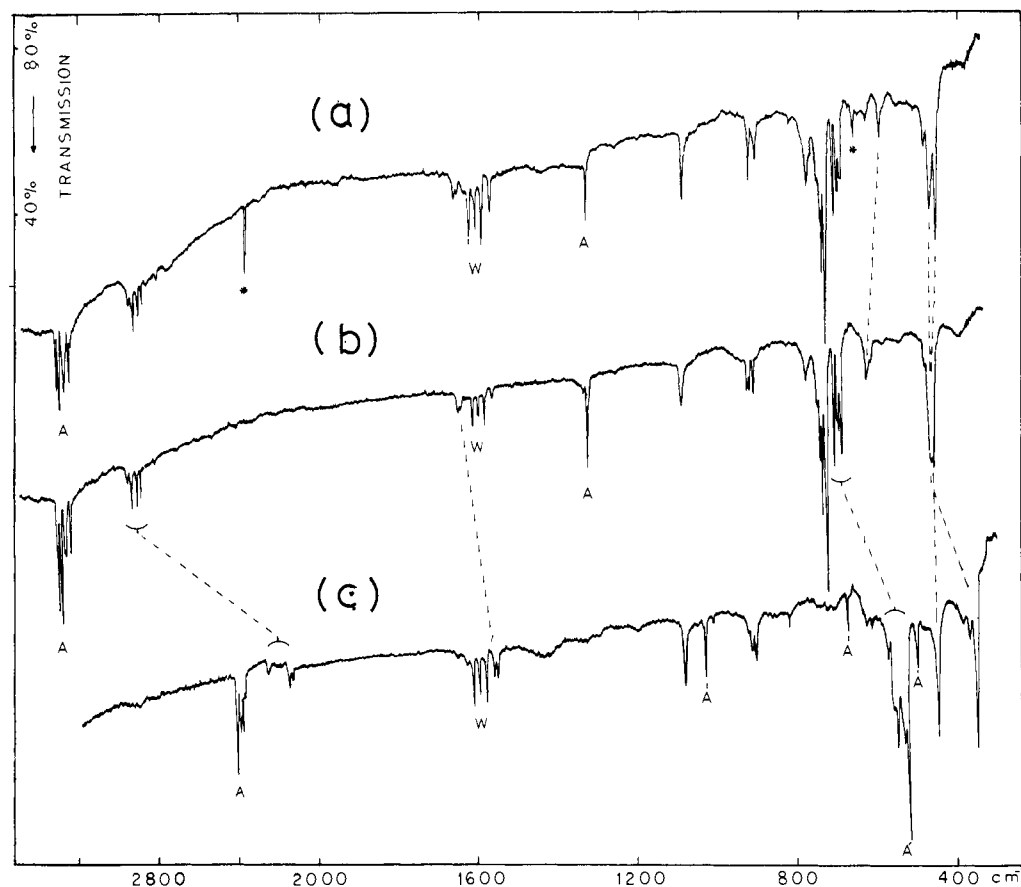**Figure 1.** Infrared spectra of Li atoms and acetylene molecules in an argon matrix (1/800) at 15 K recorded after 22-h deposition: (a) $^7Li + C_2H_2$; (b) $^6Li + C_2H_2$; (c) $^6Li + C_2D_2$. The transmission scale applies to (a). (*) designates $CO_2$ impurity absorption, (A) acetylene monomer and polymer, and (W) water impurity absorption.

**Table I.** Absorption ($cm^{-1}$) Observed in Isotopic Lithium Atom–Acetylene Matrix Reactions

| $^6Li/C_2H_2$ | $^6Li/C_2D_2$ | $^7Li/C_2D_2$ | $^7Li/C_2H_2$ | $^6Li/^{13}C_2H_2$ | LiC₂HD | | assignment | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $^6Li$ | $^7Li$ | | |
| 2952.5 | 2272 | 2272 | 2952.5 | 2939 | 2930 (CH) | 2930 (CH) | $\nu_s CH$ | LiA |
| 2907.5 | 2161 | 2161 | 2907.5 | 2900 | 2222 (CD) | 2222 (CD) | $\nu_a CH$ | |
| 1655[a] | 1561 | 1561 | 1655[a] | 1597 | 1605[a] | 1605[a] | $\nu_{CC}$ | |
| 714.5 | 576.5 | 576.5 | 714.2 | 708.3 | | | $\delta_a CH$ (in-plane) | |
| 635.0 | 635[a] | a | 600.5 | 631.5 | 645[b] | 617 | $\nu_s LiC$ | |
| | | | | | 632 | 632 | $\delta_s CH$ | |
| 479.7 | 368.2 | 366.5 | 478.5 | 478 | 407 | 405 | $\delta_a CH$ (out-of-plane) | |
| | | | | | | | | |
| 2885[b] | 2139[b] | 2139[b] | 2885[b] | | | | $\nu_a CH^b$ | LiA₂ |
| 1660 | 1569 | 1569 | 1660 | 1604 | | | $\nu_{CC}$ | |
| 706.5 | 572.5 | 572.5 | 706.5 | 697.5 | | | $\delta_a CH$ (in-plane) | |
| 703 | | | 703 | | | | | |
| 490 | 371[a] | 370[a] | 475[a] | | | | $\delta_a CH$ (out-of-plane) | |
| 477[a] | | | | | | | | |
| | | | | | | | | |
| 2935.5 | 2176 | 2176 | 2935.5 | 2918.5 | | 2912 (CH) | $\nu_s CH$ | Li₂A |
| 2890 | 2152 | 2152 | 2890 | 2882.5 | | 2215[b] (CD) | $\nu_a CH$ | |
| 696.5 | 565.5 | 565.5 | 696.0 | 690.5 | | | $\delta_a CH$ (in-plane) | |
| | | | | | | | | |
| 1100 | 1098 | 1092 | 1093 | 1100 | | 1092 | | (Li₂A)′ |
| 932.5 | 929.5 | 926 | 929 | 943.5 | | | | |
| 927 | 927 | | 919 | 930 | | 919 | | |
| 918 | 916.5 | 919 | 914.5 | 924 | | 915 | | |
| 468.5 | 466.0 | 459.5 | 463.0 | 469 | | 460 | | |

[a] Overlapping makes measurement inaccurate. [b] Tentative assignment.

Experiments have been conducted with different isotopic precursors and propyne, which provide several experimental facts to consider in the following discussion:

(1) The LiA (1/1 complex) absorption at 1655 $cm^{-1}$ has definitely a C–C stretching character but shifts more upon deuteration (1561 $cm^{-1}$) than upon $^{12}C/^{13}C$ substitution (1597 $cm^{-1}$), as shown in Figure 2, indicating that the C–C stretching mode is active in this complex but it has a significant coupling with a C–H mode.

(2) For each LiA and Li₂A species, two different signals were observed in the CH stretching region in $C_2H_2$ studies or in the CD stretching region for $C_2D_2$ experiments, but only *one* new band was observed in each region for each LiA and Li₂A species with the scrambled isotopic mixture, as shown in Figure 2, indicating that the two C–H oscillators are equivalent in these species.

(3) For the LiA, LiA₂, and Li₂A species, two absorptions shifting strongly with deuteration are found in the low frequency
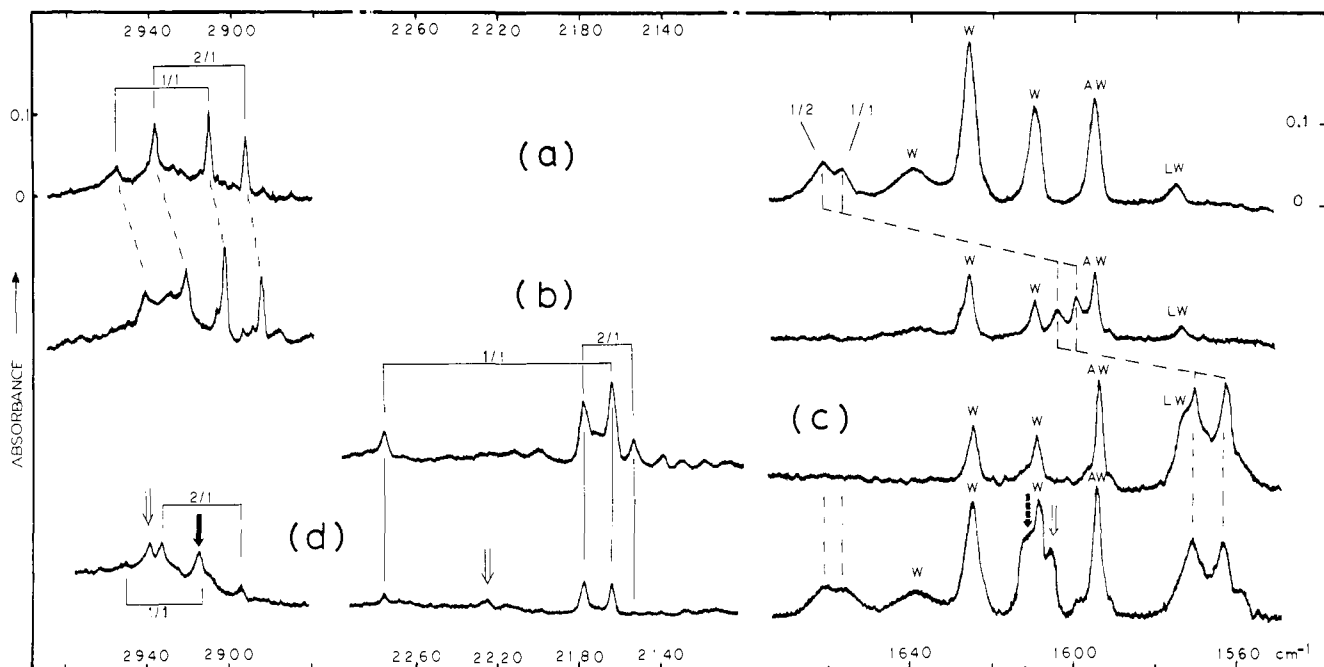
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**Figure 2.** Infrared spectra recorded after deposition of Li atoms with various acetylene isotopic molecules in an argon matrix. The total concentration of acetylene (1/800) and the lithium effusion rate (temperature $\simeq$ 395 °C) were kept constant: (a) Li + $C_2H_2$; (b) Li + $^{13}C_2H_2$; (c) Li + $C_2D_2$; (d) Li + $C_2H_2$ (10%), $C_2D_2$ (50%), $C_HD$ (40%). (W) designates bands due to water impurity, (AW) those due to acetylene complexed water,[15] and (LW) those due to lithium complexed water.[10b] The open arrows indicate new signals assigned to the 1/1 complex, the bold arrow designates the 2/1 complex, and the dotted arrow shows the band assigned to the 1/2 complex.

**Table II.** Comparison of Intensity Ratios for LiA, LiA₂, Li₂A, and (Li₂A)′ Infrared Absorptions Measured with Different Li/$C_2H_2$ Concentration Ratios in the Argon Matrix

| | $^6Li/C_2H_2/Ar$ | | |
|---|---|---|---|
| | $x/4/800$ | $x/1/800$ | $5x/1/800$ |
| $^6Li/C_2H_2$ | $x/4$ | $x$ | $5x$ |
| $I(2935.5)(Li_2A)/I(2907.5)(LiA)$ | 0.60 | 0.75 | 1.30 |
| $I(1660)^a(LiA_2)/I(1655)(LiA)$ | 6.5 | 2.5 | 1.1 |
| $I(696.5)^b(Li_2A)/I(714.5)(LiA)$ | 0.37 | 0.45 | 0.83 |
| $I(703)(LiA_2)/I(714.5)(LiA)$ | 1.55 | 0.55 | 0.38 |
| $I(477)^a(LiA_2)/I(479.7)(LiA)$ | 1.2 | 0.6 | 0.4 |
| $I(468.5a)(Li_2A)'/I(479.7)(LiA)$ | 0.25 | 0.48 | 1.5 |

*a* Overlapping makes measurements uncertain. *b* Highest maximum of a multiplet.

region and are thus due to bending modes. The higher frequency bending mode is very close to the $\nu_5$ ($\delta_a$ CCH) of free acetylene, but it shows a much lower H/D ratio (714/576 = 1.239) than free acetylene (737/544 = 1.355) (see Table III). The lower frequency bending mode has a larger H/D ratio (479.7/368.2 = 1.303 with $^6Li$) and moreover shows a small but noticeable lithium effect (see Figure 3 and Table I).

(4) Although observation in the low-frequency region for the scrambled isotopic experiment is made difficult by the presence of numerous absorptions due to $C_2H_2$, $C_2D_2$, and $C_2HD$ monomer, dimer, and acetylene complexed water,[15] three new signals (not seen in $C_2H_2$, $C_2D_2$; and $C_2H_2$ + $C_2D_2$ experiments) were observed at 632, 617, and 405 cm⁻¹ with $^7Li$. Note that this 632-cm⁻¹ band cannot be confused here with the absorption at 632 cm⁻¹ in $^6Li$ and $C_2H_2$ experiments, which shifts to 600 cm⁻¹ with $^7Li$ and $C_2H_2$.

(5) Experiments run with propyne indicate a very similar reactivity of lithium atoms and the existence of 1/1 and 2/1 lithium propyne complexes with an absorption pattern very similar to the one observed with the acetylene products. Although the results are complicated by the number of parent molecule absorptions, it is possible to correlate features at 2893, 1738, 1015, 907, 722, and 458 cm⁻¹ to a 1/1 species.

(6) Some experiments have been conducted with variable amounts of water outgassing from the oven or with equal amounts

(15) Engdahl, A.; Nelander, B. *Chem. Phys. Lett.* **1983**, *100*, 129.
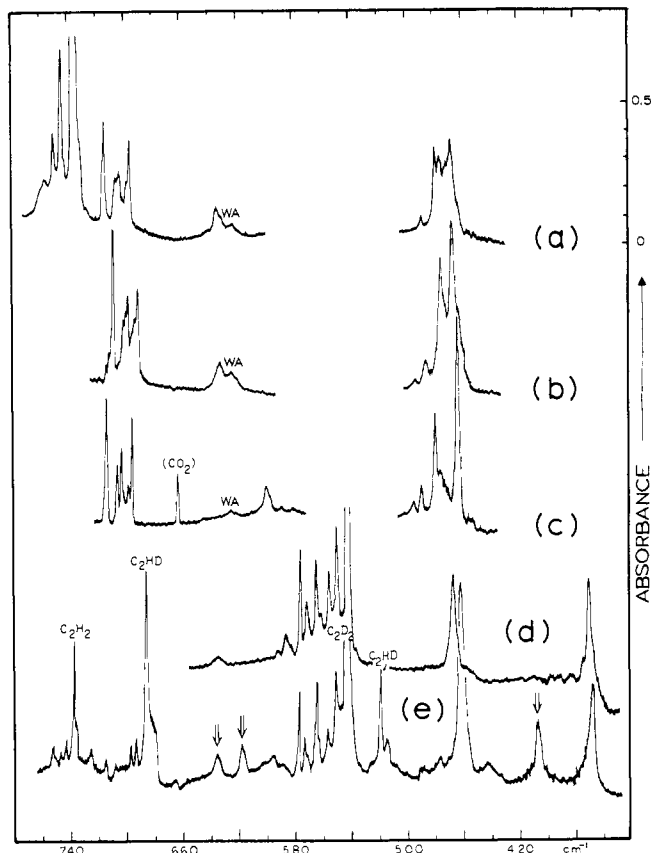
**Figure 3.** Infrared spectra recorded after deposition of Li atoms with various acetylene isotopic molecules in an argon matrix. Total concentration of acetylene (1/800) was kept constant: (a) $^6Li$ + $C_2H_2$; (b) $^6Li$ + $^{13}C_2H_2$; (c) $^7Li$ + $C_2H_2$; (d) $^6Li$ + $C_2D_2$; (e) $^7Li$ + $C_2H_2$ (10%), $C_2D_2$ (50%), and $C_2HD$ (40%). The open arrows indicate absorptions of the LiC₂HD species.

(1/400) of acetylene and oxygen as molecular dopants in order to check any probability of complex containing these impurities, but no new features arose from these experiments. It is re-

**Table III.** Frequencies (cm$^{-1}$) of Fundamentals of Acetylene in the Gas Phase and in the Argon Matrix (Indicated in Parentheses)[a]

| mode | $C_2H_2$ | $C_2D_2$ | $^{13}C_2H_2$ | $C_2HD$ | mode |
|---|---|---|---|---|---|
| $\Sigma g(\nu_1)\nu_s CH$ | 3374 | 2701 | | 3336 (3341) | $\nu_{CH}\Sigma$ |
| $\Sigma g(\nu_2)\nu_{CC}$ | 1974 | 1762 | | 1854 (1842?) | $\nu_{CC}$ |
| $\Sigma u(\nu_3)\nu_a CH$ | 3295[b] (3303)[b] 3283 (3289) | 2439 (2443) | 3279 (3287) | 2584 (2589) | $\nu_{CD}$ |
| $\pi g(\nu_4)\delta_s CCH$ | 612 | 505 | 603 | 519 (521) | $\delta_{CCD}\pi$ |
| $\pi u(\nu_5)\delta_a CCH$ | 730 (737) | 537 (544) | 727 (734) | 683 (684.5) | $\delta_{CCH}$ |

[a] Gas-phase data: Lafferty, W. J.; Thibault, R. J. *J. Mol. Spectrosc.* **1965**, *16*, 15. Scott, J. F.; Rao, K. N. *J. Mol. Spectrosc.* **1966**, *20*, 438. Strey, G.; Mills, I. M. *Ibid.* **1976**, *59*, 103 and references therein. Matrix data: this work and ref 14 and 15. [b] Fermi resonance doublet.

**Table IV.** Harmonic Frequencies Calculated with a Planar Cis Geometry[a]

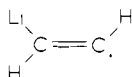| mode | $LiC_2H_2$ | | $LiC_2D_2$ | | $Li^{13}C_2H_2$ | | $LiC_2HD$ | | mode |
|---|---|---|---|---|---|---|---|---|---|
| | obsd | calcd($\Delta\nu$) | obsd | calcd($\Delta\nu$) | obsd | calcd($\Delta\nu$) | obsd | calcd($\Delta\nu$) | |
| $(B_2)\nu_a CH$ | 2907.5 | 2907.5 (0) | 2161 | 2135 (−26) | 2900 | 2899 (−1) | 2930 | 2932 (+2) | $\nu_{CH}(A')$ |
| $(A_1)\nu_s CH$ | 2952.5 | 2954.5 (+2) | 2272 | 2260 (−12) | 2939 | 2941 (+2) | 2222 | 2199 (−23) | $\nu_{CD}(A')$ |
| $(A_1)\nu_{CC}$ | 1655 | 1656.5 (+1.5) | 1561 | 1560.5 (−0.5) | 1597 | 1597 (0) | 1605 | 1604.5 (−0.5) | $\nu_{CC}(A')$ |

[a] The CCH angle is assumed to be equal to 140°; $F_{CH}$ = 4.66, $F_{CC}$ = 10.36, $F_{CC,CH}$ = 0.05, $F_{CH,CH}$ = 0.03 aJ Å$^{-2}$.

markable, though, that adding an equal amount of oxygen cut the product yield by an order of magnitude, indicating a much higher reactivity of lithium atoms for molecular oxygen, which has been studied previously.[16]

## Discussion

The infrared absorptions observed for several lithium–acetylene species provide information on structure and bonding in these new molecules.

**LiA Species.** Six fundamentals have been observed for the LiA complex. The most significant experimental result is the ob-



servation of single C–H and C–D stretching modes for the Li-C$_2$HD species, one intermediate between the two C–H stretching modes for LiC$_2$H$_2$ and the other intermediate between the two C–D stretching modes for LiC$_2$D$_2$. This indicates that the two C–H bonds in LiC$_2$H$_2$ are chemically equivalent and rules out a vinyl radical structure analogous to that proposed for the Al or Au + C$_2$H$_2$ species.[17] Thus, the two signals observed for this species in the C–H stretching region at 2952.5 and 2907.5 cm$^{-1}$ (with C$_2$H$_2$) have symmetric and antisymmetric character. The high-frequency absorption is assigned to a symmetric motion for two reasons: (i) the observed shifts with $^{12}$C/$^{13}$C substitution are −13.5 cm$^{-1}$ on the high-frequency motion and −7.5 cm$^{-1}$ on the low-frequency one, indicating that the high-frequency stretch is coupled with another motion of the same symmetry, which is obviously the C–C stretch (see Figure 2) and (ii) the observed deuterium shift is clearly less for the high-frequency mode (−680 cm$^{-1}$ (−23%)) than for the low-frequency one (−747 cm$^{-1}$ (−26%)) and therefore is consistent with a larger expected coupling with the C–C stretch in the case of the C$_2$D$_2$ species.

Structurally, the equivalence of the two C–H oscillators in the complex means that the new molecule has kept, at least, a 2-fold symmetry axis or a symmetry plane bisecting or including the CC bond. Strictly speaking, the structures in Scheme I are consistent with this experimental fact.

Structure **1** can be rejected for several reasons, although it has some resemblance to the structure computed by Chandrasekhar et al.[18] and deduced by Lineberger et al. for C$_2$H$_2^-$ in the gas phase[19] and to the most stable Na + C$_2$H$_2$ product observed in the argon matrix ESR studies:[20]

Scheme I



Scheme II



(i) The positions of the two observed bending motions (714 and 480 cm$^{-1}$) are very unlikely for a rocking or wagging mode of a CH$_2$ group, and no band is found in the scissoring CH$_2$ region; moreover, none of the G-matrix elements for each of these motions would have a lithium contribution as shown by the experimental results for the low-frequency bending mode.

(ii) The positions of the two CH motions, the symmetric mode above the antisymmetric mode, would also be in opposition to all the data for comparable structures.

The models **2** and **3** have the major disadvantage of not predicting an active symmetric C–H stretching mode without involving a fluctuation of electron density between the $\pi$ system and lithium, provided through a change in the C–H distance or the partial C–C stretching character of the C–H symmetric stretching, two propositions which appear unlikely since the $\nu_{sym}$ C–H mode is more intense than the $\nu_{C-C}$ mode. Moreover, structure **2** would not have any direct lithium contribution in the hydrogen bending modes. The structure which meets best all the conditions mentioned above is **5**.

Unfortunately, no theoretical study on the 1–1 complex has been published to date. The only available study on a lithium–acetylene species is the work of Apeloig et al.[4] on the preferred structure of dilithioethylene (Scheme II). Their conclusion is that the more stable isomer of Li$_2$C$_2$H$_2$ has a $C_{2v}$ geometry with two lithium atoms bridging the C–C bond and the C$_2$H$_2$ group in a "cis" planar position. Although structural parameters computed for Li$_2$C$_2$H$_2$ cannot be transposed exactly to LiC$_2$H$_2$, this calculation does reinforce the conclusion that **5** is a more probable structure than **4** for LiC$_2$H$_2$.

It is practically impossible to estimate the structural parameters(three bond lengths, one bond angle) by a best fitting of the observed isotopic ratios on the bending modes; however, two other important experimental facts provide some information on the CCH angle:

(i) The two modes $\nu_{sym}$C–H and $\nu_{C-C}$ are strongly coupled but less than in the free C$_2$H$_2$ molecule. For instance, the $\nu_{C-C}$ shifts with deuteration from 1655 to 1561 cm$^{-1}$ (−5.7%) whereas in free acetylene it shifts from 1974 to 1762 cm$^{-1}$ (−10.7%).
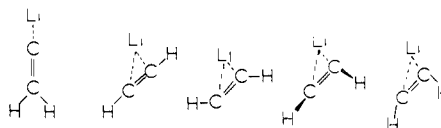
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(17) Kasai, P. H.; McLeod, D.; Watanabe, T. *J. Am. Chem. Soc.* **1977**, *99*, 3521; **1983**, *105*, 6704.
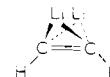
(18) Chandrasekhar, J.; Kahn, R. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 493.

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**Table V.** Calculated Harmonic and Observed Frequencies for the Two Out-of-Plane Bending Modes of the LiC$_2$H$_2$ Molecule[a]

| $C_{2v}$ | $^6$Li$^{12}$C$_2$H$_2$ | | $^7$Li$^{12}$C$_2$H$_2$ | | $^6$Li$^{12}$C$_2$D$_2$ | | $^7$Li$^{12}$C$_2$D$_2$ | | $^6$Li$^{13}$C$_2$H$_2$ | | $^6$Li$^{12}$C$_2$HD | | $^7$Li$^{12}$C$_2$HD | | $C_s$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | obsd | calcd | obsd | calcd | obsd | calcd | obsd | calcd | obsd | calcd | obsd | calcd | obsd | calcd | |
| B$_1$ | 479.7 | 479.3 | 478.5 | 477 | 368.2 | 372.5 | 366.5 | 369.5 | 478 | 476.7 | 407 | 407.0 | 405 | 404.5 | A″ |
| A$_2$[b] | | 686.7 | | 686.7 | | 537.3 | | 537.3 | | 680.9 | 632 | 632.0 | 632 | 631.9 | A″ |

[a] The parameters used are $R_{CH}$ = 1.09 Å, $R_{CC}$ = 1.32 Å, $R_{CLi}$ = 2 Å, CLiC = 40°, and CCH = 140°; the force constants are taken equal to $F\psi_1\psi_1$ = $F\psi_2\psi_2$ = 0.1935, $F\psi_1\psi_2$ = 0.065 aJ. [b] Not IR active.

(ii) The intensity ratio between $\nu_{sym}$ C–H and $\nu_{antisym}$ C–H allows, in the very crude model of bond dipole moment,[21] an estimation of the angle between the two C–H bonds, assuming no intensity alteration by charge transfer or rehybridization effect.

We have computed the harmonic frequencies for the CC, CH, and CD stretching modes for the different isotopic species by using the deduced intensity ratio $I(\nu_{sym}$C–H$)/I(\nu_{antisym}$C–H$)$ for different values of the CCH angle. Table IV presents the results obtained with a value of 140° which gives the best compromise between the observed decrease in the coupling between $\nu_{CC}$ and $\nu_{sym}$C–H in comparison with acetylene on the one hand and the observed $I(\nu_{sym}$C–H$)/I(\nu_{antisym}$C–H$)$ ratio on the other hand. Harmonic frequencies have been calculated with the Wilson method,[21] assuming no significant coupling with the other low–frequency modes of the molecule. This simple model shows good agreement for the different isotopic substitutions on the C–C stretching mode. In the case of the C–H/C–D stretching mode, without any anharmonicity correction, the C–D stretching modes fall far below the experimental data when the C–H values are fitted by the model; we believe, however, that even in this case, the comparison between calculated and observed frequencies is physically meaningful if we take as a reference for the anharmonicity the difference found for the $\nu_{antisym}$C–H and C–D modes. The $I$-$(\nu_{sym}$C–H$)/I(\nu_{antisym}$C–H$)$ ratio which thus can be inferred is equal to cos$^2$ ($\alpha$/2)/sin$^2$ ($\alpha$/2) × (0.89)$^2$ = 0.5 (where $\alpha$ represents the angle between the two C–H oscillators and 0.89 is a correction factor obtained from the eigenvectors because this mode is weakened by a partial C–C stretching character). The calculated value is in good agreement with the measured $I(\nu_{sym}$C–H$)/I$-$(\nu_{antisym}$C–H$)$ ratio of 0.4 ± 0.1. If the bond angle were much more or much less than the estimated value, a larger $F_{CH,CC}$ interaction constant would be required to counterweigh the decreased off-diagonal G-matrix element between the C–C and C–H stretching fundamentals. For instance, a bond angle of 120° or 160° would require −0.75 or +0.8 aJ Å$^{-2}$ interaction force constants to fit the data, which seem unreasonably large in this case. Therefore an uncertainty of ±10° seems reasonable; the uncertainty coming from the intensity ratio measurement itself is ±3°.

It is also worth noting that this simple model, by a computation of the eigenvectors, allows an estimate of the relative intensity variation of $\nu_{C-C}$ by deuteration (see Figure 2). With C$_2$H$_2$ this mode has a 25% C–H character, whereas with C$_2$D$_2$ the C–D character increases to 41%, yielding a 2.7-fold intensity enhancement, close to the 3.2 factor experimentally estimated.

Due to the lack of available data, we have taken the bond lengths and CLiC angle estimated for the dilithioethylene by Apeloig et al.[4] to justify the assignment of the three other observed fundamentals to a lithium symmetric stretch and the two antisymmetric bending modes expected for a planar cis structure (see Scheme III). With a CLiC angle of 40°, a simple estimate of the different isotopic effects on the lithium symmetric stretch (S$_4$) yields $^6$Li/$^7$Li and $^{12}$C/$^{13}$C isotopic ratios of 1.060 and 1.0085 (1.057 ± 0.002 and 1.0055 ± 0.0015 experimentally) using the harmonic approximation for a CLiC group. In a similar manner the isotopic ratios measured with H/D and $^{12}$C/$^{13}$C substitution on the high-frequency bending modes are 1.239 ± 0.002 and 1.0090 ± 0.0015, near the 1.219 and 1.013 values obtained in the harmonic approximation for the S$_8$ motion assuming no coupling with another same symmetry mode. Note that the other in-plane

**Scheme III**
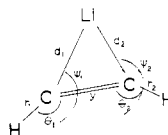


Symmetry Coordinates

(A$_1$) S$_1$ = y
S$_2$ = 1/$\sqrt{2}$(r$_1$ +r$_2$)
S$_3$ = 1/$\sqrt{2}$($\theta_1$ +$\theta_2$)
S$_4$ = 1/$\sqrt{2}$(d$_1$ +d$_2$)

(A$_2$) S$_5$ = 1/$\sqrt{2}$($\psi_1$ −$\psi_2$)

(B$_1$) S$_6$ = 1/$\sqrt{2}$($\psi_1$ +$\psi_2$)

(B$_2$) S$_7$ = 1/$\sqrt{2}$(r$_1$ −r$_2$)
S$_8$ = 1/$\sqrt{2}$($\theta_1$ −$\theta_2$)
S$_9$ = 1/$\sqrt{2}$(d$_1$ −d$_2$)

bending mode (S$_3$, not observed) would have isotopic ratios of 1.362 (H/D) and 1.003 ($^{12}$C/$^{13}$C), whereas the isotopic ratios for the antisymmetric lithium stretch (S$_9$, not observed) would be 1.024 ($^6$Li/$^7$Li) and 1.027 ($^{12}$C/$^{13}$C). Of course, anharmonicity and coupling with other motions are the main source of discrepancy. The out-of-plane antisymmetric bending mode (S$_6$) is alone in its symmetry class and thus constitutes a better test for the model; furthermore, additional information is provided by the LiC$_2$HD species ($C_s$ symmetry) for which the two out-of-plane bending modes are IR active and observed, allowing estimation of the diagonal and nondiagonal force constants and therefore an estimation of the frequency of the (S$_5$) out-of-plane mode in the LiC$_2$H$_2$ or LiC$_2$D$_2$ species (see Table V).

The results obtained with propyne can also be understood in the framework of a planar bent bridged lithium species, although structural information is more difficult to deduce, owing to the lack of symmetry. The C≡C stretching mode, already active in the free propyne, shifts down from 2137 to 1738 cm$^{-1}$ for LiC$_3$H$_4$ (−18%, compared to −16.2% with acetylene) but is less intense than with LiC$_2$H$_2$ where the C≡C stretching mode gains IR intensity from interaction between the symmetric C≡C and C—H stretching modes. Absorptions at 2893, 722.5, and 458 cm$^{-1}$ fall very close to the positions of the $\nu_a$C—H (2907.5), $\delta_a$B$_2$ (714.5), and $\delta_a$B$_1$ (480 cm$^{-1}$) modes of LiC$_2$H$_2$ and are thus likely to be assigned to the C—H stretch and the in-plane and out-of-plane bending modes of the remaining C≡C—H group in the analogous LiC$_3$H$_4$ species.

**LiA$_2$ species.** Four absorptions have been observed for LiA$_2$ (see Table I), which are only slightly shifted from the positions of the LiA frequencies. Moreover, experiments concentrated in both C$_2$H$_2$ and C$_2$D$_2$ do not show any new signal, indicating that the two C$_2$H$_2$ groups are inequivalent in the LiA$_2$ species. Therefore, we believe that the structure of the LiA$_2$ species is analogous to a LiA complex "solvated" by another acetylene molecule. It is well-known that the acetylenic C–H bond has a specific acidic character compared to other hydrocarbon compounds[22] and that acetylene itself dimerizes very easily to for a T-shaped pair, where one acetylene molecule is hydrogen bonded to the π system of another molecule.[14] Hence, it seems very likely that in the LiA$_2$ species, the LiA subunit and the other acetylene molecule are hydrogen bonded. Now the question arises: is the proton donor the LiA subunit or the solvating acetylene molecule? Although spectroscopic proof ruling out one of these two possibilities is not available, we believe that a decrease of the acidic character of the C–H bond in the LiA unit favors the second possibility. This statement is based on two observations:

(i) Only one signal, weakly shifted from the LiA antisymmetric stretch, is observed in the $\nu_{CH}$ region. Similarly, the bending modes

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**Table VI.** Comparison of Frequencies (cm$^{-1}$) of Some Motions of the H—C≡C—H Group in Cyclopropene and LiC$_2$H$_2$ Molecules

| mode | (A$_1$) $\nu_s$C—H | (B$_2$) $\nu_a$C—H | $\nu_{C≡C}$ | (B$_2$) H—C≡C—H $\delta_a$ in-plane | (A$_1$) H—C≡C—H $\delta_s$ in-plane | (A$_2$) H—C≡C—H $\delta_s$ out-of-plane | (B1) H—C≡C—H $\delta_a$ out-of-plane |
|---|---|---|---|---|---|---|---|
| C$_3$H$_4$[a] | 3158 | 3126 | 1656 | 1011 | 905 | 920 | 570 |
| LiC$_2$H$_2$ | 2953 | 2908 | 1655 | 714 | | 687[c] | 480 |

[a] Reference 26; in cyclopropene the CCH angle is 150°.   [b] In the LiC$_2$H$_2$ molecule the CCH angle is estimated 140 ± 10°.   [c] Estimated value.

observed for the LiA$_2$ system are only weakly shifted from the LiA position, showing no evidence for a decoupling of the two CH oscillators in the LiA subunit.

(ii) The $\nu_{CC}$ stretching mode observed for the LiA$_2$ species (at 1662 cm$^{-1}$) is selectively strongly activated compared to the other modes of this species (note the differences in the intensity ratios in Table II) following the trend already observed for acetylene dimer.[14]

**Li$_2$A and (Li$_2$A)' Species.** The Li$_2$A species is responsible for the three absorptions listed in Table I. The main information is provided by the two CH stretching modes which maintain a symmetric and antisymmetric character, as illustrated by the mixed Li$_2$C$_2$HD species (see Table I and Figure 2). But, in opposition to the LiA species, the symmetric stretching mode shows a much weaker coupling with the C–C stretch. This could be due to a smaller CCH angle, to the lowering of the $\nu_{CC}$ frequency, or more probably both. If we assume a $C_{2v}$ geometry similar to the preferred structure computed by Apeloig et al.,[4] the intensity ratio between the two C–H stretching modes ($I\nu_s/I\nu_a = 1.8 \pm 0.3$) gives, with the bond dipole model, a CCH angle of 127 ± 2°, close indeed to the calculated value of 120°.

The (Li$_2$A)' species shows a behavior strictly parallel to the Li$_2$A species except upon UV–visible irradiation, which does not dissociate (Li$_2$A)'. One cannot exclude completely, however, a different stoichiometry based on a similar Li/C$_2$H$_2$ ratio. This species is characterized by two strong broad bands at 1100 cm$^{-1}$ ($\Delta\nu_{1/2} = 15$ cm$^{-1}$) and 468.5 ($\Delta\nu_{1/2} = 8$ cm$^{-1}$), showing a small lithium-7 shift (−6.5 and −5.5 cm$^{-1}$) and an even smaller deuterium shift (−1.5 and −2.5 cm$^{-1}$) but no measurable carbon-13 shift. Further work with more concentrated samples and various experimental conditions will be done to provide more data concerning the other fundamentals of this intriguing molecule.

**Bonding.** The reaction of metal atoms with acetylene in inert matrices has already provided three classes of products: (1) "radical-like" structure with Al, Au, and Ag atoms,[17] (2) weakly $\pi$ bonded with Ni or Cu in concentrated matrices,[23] and (3) ion pair with sodium,[20] the C$_2$H$_2^-$ anion rearranging to a vinylidene structure. We have shown that the LiC$_2$H$_2$ product cannot belong to the first class; consequently, one wonders if lithium can form a $\pi$-bonded complex or transfer its electron to give the ion pair. An answer to this question can be obtained from the following facts:

(i) Similar experiments with acetylene and heavier alkali metals, which should transfer their valence electron more readily than lithium, produced a totally different reaction product; weak ethylene bands were observed[12] and no absorptions were detected for a 1/1 metal–C$_2$H$_2$ complex or M$^+$C$_2$H$_2^-$ species.
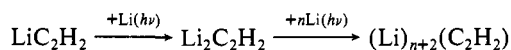
(ii) Adding an electron in an antibonding $\pi^*$ orbital of acetylene is energetically unfavorable and would give (without any large rearrangement) a trans bent structure[18,24] as observed for the first excited electronic state of acetylene where a $\pi$ electron is trans-

ferred to a $\pi^*$ orbital,[25] rather than a cis bent structure as found for the LiC$_2$H$_2$ complex.

In the last five years, a large amount of research has been published emphasizing the unusual structures for organolithium compounds (ref 7 and references therein) or arguing for the ionic or covalent character of the C–Li bonds.[8,9] It seems that the large difference in behavior between atomic lithium and other alkali atoms toward the $\pi$ system of acetylene and the structure of the lithium acetylene complex itself can be better understood if we keep in mind the point advanced years ago by Schleyer and co-workers that the carbon lithium bond, although largely ionic, contains a significant covalent character supplied through lithium p orbitals. Such a stabilization would, of course, be much less energetically favorable with heavier alkali metals, which have lower ionization energies and function substantially as electron donors. It is, therefore, clear that the Li atom is bonded to the $\pi$ system of acetylene in the LiC$_2$H$_2$ molecule.

It is interesting to compare the frequencies measured for the LiC$_2$H$_2$ molecule with the comparable motions of the H—C≡C—H group of cyclopropene[26] presented in Table VI with the LiC$_2$H$_2$ values. This gives a point of comparison for the magnitude of the perturbation of the system by the lithium atom, suggesting an attraction of the in-plane electron density toward the lithium atom, weakening the C≡C bond to almost the value of a double bond system ($F_{CC} \simeq 10.5$ aJ Å$^{-2}$ compared to 9.9 aJ Å$^{-2}$ for ethylene[27]), to form a kind of three-centered/three-electron system between the lithium and the two carbon atoms.

Another intriguing consideration is the photoinduced dissociation of the complex; an explanation could be based on the fact that photoclustering is a very easy process for lithium atoms in an argon matrix.[28–30] Lithium self-aggregation ($D$(Li–Li) = 25 kcal/mol)[31] could be preferred to further addition to give back less perturbed acetylene:

$$\text{LiC}_2\text{H}_2 \xrightarrow{+\text{Li}(h\nu)} \text{Li}_2\text{C}_2\text{H}_2 \xrightarrow{+n\text{Li}(h\nu)} (\text{Li})_{n+2}(\text{C}_2\text{H}_2)$$

Further works are now in progress to characterize complexation of lithium atoms with other $\pi$ systems such as ethylene and benzene.

**Registry No.** Li, 7439-93-2; C$_2$H$_2$, 74-86-2; $^7$Li, 13982-05-3; $^6$Li, 14258-72-1; $^{13}$C, 14762-74-4; D$_2$, 7782-39-0.

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