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# BRIDGED AND LINEAR DILITHIOACETYLENES - Two Minima on the Potential Energy Surface?

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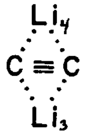
## ABSTRACT

Vibrational frequency calculations at the 6-31G*, 6-31G and STO-3G levels in addition to an STO-3G basis set with only a 1s orbital on lithium reveal that both bridged and linear dilithioacetylenes are minima on the potential energy surface

A number of recent theoretical calculations have indicated that lithiocarbons may violate classical ideas of valence bonding  For example, molecular orbital calculations by Schleyer et al  have indicated that dilithioacetylene may prefer a bridged structure, as shown by **1**, rather than a more conventional linear structure, as shown by **2**[1]



**1**, $D_{2h}$

$\mathrm{Li{-}C{\equiv}C{-}Li}$

**2**, $D_{\infty h}$

Schleyer et al  attribute the unusual stability of **1** to the σ donating ability of lithium and, in part, to 2π aromaticity which arises from the involvement of empty 2p orbitals on lithium. On the other hand, others have suggested that ionic bonding with lithium naturally accounts for the cyclic structure.[2,3]

I was intrigued by these results and wondered, if indeed the cyclic structure has a lower energy than the linear structure, what is the status of the linear isomer  minimum, transition state, or hilltop? Or, conversely, if the linear isomer is of lower energy, what is the status of the cyclic isomer? To answer these questions and to gain insight into the nature of the carbon-lithium bond, I performed RHF-SCF-MO calculations using the computer program HONDO[4] With this program, geometries were optimized and force constants calculated using the 6-31G*[5a], 6-31G[5b,c] and STO-3G[6] basis sets in addition to using an STO-3G basis set without a 2sp shell on lithium (here called the truncated STO-3G basis set)  The truncated basis set should model lithium as a lithium cation and, hence, require ionic bonding between carbon and lithium.

The results of the optimization calculations for **1** and **2** are summarized in Table 1, along with previous results by Schleyer[1] for comparison  The completely

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[†] This work was performed under the auspices of the United States Department of Energy

optimized structures and relative energies at the 6-31G* level are in excellent agreement with Schleyer's results, which were obtained at the 4-31G optimized geometry The similarity of the truncated STO-3G and the much more elaborate 6-31G* results is consistent with substantially, if not wholly, ionic carbon-lithium bonding[7] Streitwieser suggested that the basis set superposition error is significant for these types of compounds,[2] and it seems likely that this effect accounts for the basis set dependence observed for the two isomers of $C_2Li_2$

If the cyclic structure is truly lower in energy than the linear structure, one might assume that the linear structure would be a transition state for the degenerate exchange of $Li_3$ and $Li_4$ in **1** If **2** were such a transition state, the required imaginary normal mode would look something like:

$$\overset{\nearrow}{Li_3} - C_1 \equiv C_2 - \underset{\swarrow}{Li_4} \quad .$$

Such a mode, however, has a component along an axis perpendicular to the $C_\infty$ axis and cannot transform as ±1 with respect to the $C_\infty$ axis, eliminating all nondegenerate representations in the $D_{\infty h}$ group Further consideration indicates that this vibration transforms as $\pi_g$ Because this representation is doubly degenerate, the linear structure cannot be a transition state for the suggested reaction This result is in accord with the symmetry rules of McIver[8]

Having arrived at this result and having obtained the optimized geometries of **1** and **2** with various basis sets, force constant calculations were performed to determine the true nature of **1** and **2** As the results in Table 2 indicate, both **1** and **2** are minima in the potential energy surface at the truncated STO-3G, STO-3G, and 6-31G levels Calculations at the 6-31G* level show that **2** is a bona fide minimum, but that **1** is a transition state The $1b_{1u}$ vibration, which has the imaginary vibrational frequency at the 6-31G* level, corresponds to an out-of-plane motion of the lithium atoms Displacement of **2** along the $1b_{1u}$ mode, followed by geometry optimization, yielded a $C_{2v}$ structure $4\ 7 \times 10^{-7}$ a u. lower in energy than the $D_{2h}$ structure This $C_{2v}$ structure has C-Li and C-C bond distances equal to within 0 001 Å of the corresponding parameters in **2**, but is distorted 6 2° from planarity Subsequent force constant calculations proved this $C_{2v}$ structure to be a true minimum The vibrational frequencies for this structure were very similar to those of **1**, the imaginary vibrational frequency present in **1**, of course, was replaced by a very low positive vibrational frequency. The difference in energy between these two structures is so small as to defy a chemical explanation, hence, its origins remain enigmatic

I have been unable to locate any experimental data with which to compare these calculations I hope, therefore, that these results may be of use to experimentalists attempting to determine the gas phase structure of $C_2Li_2$ and

Table 1 Results of ab initio Calculations for **1** and **2**

| Basis Set | Total Energy (Hartrees) **1** | **2** | **1** Relative to **2** |
|---|---|---|---|
| STO-3G[a] | -88 96012[b,c] | -88 95271[b,c] | -4 6 |
| STO-3G[d] | -89 21722[e] | -89 21222[e] | -3 1 |
| STO-3G[e] | -89 40403 | -89 37134 | -20 5 |
| 4-31G[e] | -90 43616 | -90 44360 | +4 7 |
| 6-31G | -90 52094[f] | -90 52964[g] | +5 5 |
| 6-31G* | -90 56194[h] | -90 55113[i] | -6 8 |
| RMP2/4-31G[e] | -90 63747 | -90 63990 | +1 5 |

[a] STO-3G basis set with only a 1s orbital on lithium [b] From Reference 3 [c] Geometry optimization yielded R(C-C) = 1 201 Å R(C-Li) = 1 814 Å for **1** and R(C-C) = 1 190 Å, R(C-Li = 1 668 Å for **2** [d] STO-3G basis set with only 1s and 2s orbitals on Li [e] From Reference 1 [f] Geometry optimization yielded R(C-C) = 1 263 Å and R(C-Li) = 2 065 Å [g] Geometry optimization yielded R(C-C) = 1 246 Å and R(C-Li) = 1 895 Å [h] Geometry optimization gave R(C-C) = 1 250, R(C-Li) = 2 027 [i] Geometry optimization gave R(C-C) = 1 235 Å, R(C-Li) = 1 904 Å

Table 2 Calculated Vibrational Frequencies Using the Indicated Basis Set ($cm^{-1}$)

| | **1** ($D_{2h}$) | | | | | |
|---|---|---|---|---|---|---|
| | $1b_{1u}$ | $1b_{3u}$ | $1b_{1g}$ | $1a_g$ | $1b_{2u}$ | $2a_g$ |
| STO-3G[a] | 164 | 159 | 237 | 853 | 1021 | 2422 |
| STO-3G | 151 | 299 | 285 | 750 | 809 | 2024 |
| 6-31G | 55 | 96 | 129 | 557 | 666 | 1967 |
| 6-31G* | 101 | 153 | 246 | 557 | 693 | 2015 |

| | **2** ($D_{\infty h}$) | | | | |
|---|---|---|---|---|---|
| | $1\pi_u$ | $1\pi_g$ | $1\Sigma_g^+$ | $1\Sigma_u^+$ | $2\Sigma_g^+$ |
| STO-3G[a] | 156[b] | 239[b] | 900 | 1155 | 2623 |
| STO-3G | 97[b] | 151[b] | 720 | 872 | 2304 |
| 6-31G | 121[b] | 227[b] | 618 | 776 | 2129 |
| 6-31G* | 103[b] | 172[b] | 610 | 766 | 2154 |

[a] Uses the normal STO-3G basis set for C, but places only a 1s shell on lithium [b] This mode is doubly degenerate

note the following Because vibrational frequencies calculated from SCF calculations are typically 10-15% too large,[9] determination of structures based solely on the the coincidence of experimental and theoretical vibrational frequencies is difficult Nevertheless, the $D_{2h}$ and $D_{\infty h}$ structures ought to be distinguishable by infrared and Raman spectroscopy. According to all but the 6-31G* calculations, the $D_{2h}$ species has three IR active bands ($1b_{1u}$, $1b_{2u}$, and $1b_{3u}$) and three Raman active bands ($1b_{1g}$, $1a_g$, and $2a_g$) The $D_{\infty h}$ structure has two IR bands, ($1\pi_u$, $1\Sigma_u^+$), and three Raman bands ($1\pi_g$ and two nondegenerate $\Sigma_g^+$) If, as the 6-31G* calculations suggest, the bridged $C_2Li_2$ structure possesses $C_{2v}$ symmetry, there will be five IR active bands ($3A_1$, $B_1$, $B_2$) and all six vibrational modes will be Raman active

In conclusion, these calculations suggest that the $C_2Li_2$ potential energy surface has at least two minima With basis sets lacking d orbitals, a $D_{\infty h}$ and a $D_{2h}$ minima were characterized At the 6-31G* level, the $D_{\infty h}$ structure is a minimum, but the $D_{2h}$ structure is a transition state A $C_{2v}$ structure was located at the 6-31G* level which was 4 7 x $10^{-7}$ a u lower in energy than the $D_{2h}$ structure

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