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THE CYCLIC STRUCTURE OF MONOMERIC DILITHIOACETYLENE

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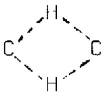
Acetylene ($D_{\infty h}$) and its simple derivatives prefer linearity strongly.[1] Doubly bridged D_{2h} acetylene (1) is calculated to be 196.9 kcal/mole (optimized geometry RHF/STO-3G)[2,3 and 158.9 kcal/mole (RHF/4-31G using the STO-3G geometry)[3b] less stable than the linear form. Our recent findings that lithium is remarkably effective in stabilizing unusual structures,[4] suggested that the bridged form (3) may be preferentially stabilized by lithium substitution.

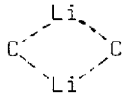
Most organolithium compounds display strong tendencies toward complex formation with n-donor solvents and toward self-aggregation, which persists even in the gas and not just in the condensed phases.[5] Monomeric organolithium compounds are thus difficult to study experimentally; *ab initio* calculations are the best methods currently available for the investigation of such species. We therefore studied computationally the structure and relative energies of *linear (2) and doubly bridged (3) dilithioacetylenes.*



1, D_{2h}

$Li—C\equiv C—Li$

2, $D_{\infty h}$



3, D_{2h}

Initial calculations were carried out at the restricted Hartree-Fock (RHF) level using the *ab initio* SCF-MO Gaussian 70 series of programs.[5] Both structures were fully optimized using both the minimal STO-3G[3a] and the split valence 4-31G[3b,c] basis sets. Single point calculations at the 4-31G geometries were then done with the polarized 6-31G* basis set [3c,7] to assess the influence of adding d-functions to the basis. Single point calculations were also carried out using Møller-Plesset perturbation theory to second order starting with the RHF/4-31G wave function (RMP2/4-31G).[8] This allows us to assess the role of correlation in determining the energy difference. The triplet forms of 2 and 3 and other possible structures of dilithioacetylene were also calculated but found to be significantly less stable than either singlet 2 or singlet 3.

Table. Calculated Energies and Structural Parameters for Linear (2) and Bridged (3) Dilithioacetylene.

Calculational Method	Total Energies (hartrees)		Relative Energies (kcal/mole)		Optimized Structural Parameters (Å)			
	2	3	2	3	2		3	
					C-C	C-Li	C-C	C-Li
RHF/STO-3G	-89.37134[a]	-89.40403[a]	20.5	0.0	1.221	1.815	1.269	1.914
RHF/4-31G	-90.44360[a]	-90.43616[a]	0.0	4.7	1.240	1.886	1.260	2.059
RMP2/4-31G	-90.63990[b]	-90.63747[b]	0.0	1.5	-	-	-	-
RHF/6-31G*	-90.55107[b]	-90.56186[b]	6.8	0.0	-	-	-	-
RHF/STO-3G	-89.21222[c]	-89.21722[c]	3.1	0.0	-	-	-	-

[a] Fully optimized geometries. [b] Calculated using the RHF/4-31G geometry. [c] Excluding all 2p orbitals on lithium and using the RHF/STO-3G optimized structure.

The Hartree-Fock relative energies of 2 and 3 (Table) are basis set dependent but at all levels the energy differences are much smaller than the corresponding differences in the acetylene structures. At the RHF/6-31G* level, which should approximate the situation at the Hartree-Fock limit, 3 is found to be 6.8 kcal/mole more stable than 2. The inclusion of correlation energy apparently favors the bridged structure further. With the 4-31G basis, both RHF and RMP2 theory give 2 to be most stable but the difference is 3.2 kcal/mole lower if correlation is included. Consequently, both inclusion of d-functions and of correlation stabilize 3 more than 2. We therefore predict that monomeric dilithioacetylene has a double bridged, D_{2h} structure (3) in the ground state.

The only experimental data with which this prediction may be compared at present is the structure of lithium carbide.[9] This is known to be polymeric. Although the orthorhombic structure (space group D_{2h}^{25}-Immm) is certainly affected by strong crystal forces, it does show some similarities to 3. Carbon atoms are strongly associated in pairs with neighboring lithium atoms in bridging positions. The observed nuclear separations (R_{CC} = 1.20Å and R_{CLi} = 2.27Å) are in reasonable agreement with our predictions for the isolated molecules 3 (1.26Å and 2.06Å respectively).[10]

The conformational preference of dilithioacetylene can be partially understood by examining the Figure[12] which represents the three highest occupied molecular orbitals 2 and of 3.

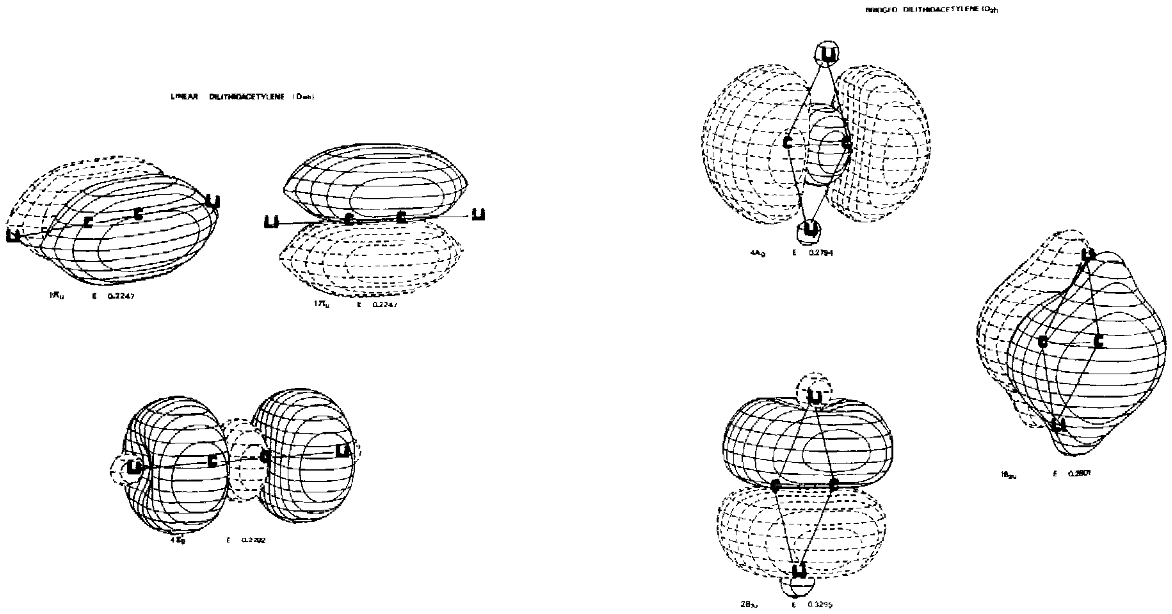


Figure. Corresponding molecular orbitals of linear (2) and of bridged (3) dilithioacetylene.

The cyclic nature of 3 and the availability of 2p orbitals on lithium allow the 1b$_{2u}$ orbital to benefit from 2π electron aromaticity and furnish increased C-Li bonding in the 2b$_{3u}$ orbital. Both of these MO's are lower in energy than the corresponding 1π$_u$ orbitals of 2. The energy of the 4σ$_g$ orbital of 2 remains almost unchanged when correlated with 4a$_g$ of 3, but 3σ$_g$ of 2 (not shown) is higher in energy than 3a$_g$ of 3. When the 2p orbitals on lithium are eliminated from the calculation, 3 is still 3.1 kcal/mole (RHF/STO-3G) more stable than 2 indicating that sigma effects also are important and may actually be dominant. This conclusion is also supported by RHF/STO-3G calculations which indicate that HBe-C=C-BeH prefers linearity strongly, although beryllium is a better π-acceptor than lithium.[10b]

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References

1. H. G. Viehe, "Chemistry of Acetylenes", Dekker, New York, 1969.
2. RHF/STO-3G geometry for 1 is R_{CC} = 1.307Å and R_{CH} = 1.260Å.
3. (a) W. J. Hehre, R. F. Stewart and J. A. Pople, J. Chem. Phys., 51, 2657 (1969); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, ibid., 54, 724 (1971); (c) For lithium the 5-21G basis set was used, J. D. Dill and J. A. Pople, ibid., 62, 292 (1975).
4. E.g., planar tetracoordinate carbon, J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v.R. Schleyer, and J. A. Pople, J. Amer. Chem. Soc., in press; and perpendicular ethylenes, Y. Apeloig, P. v. R. Schleyer, J. S. Binkley and J. A. Pople, ibid., 98, 4432 (1976).
5. B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, New York, 1974.
6. W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newtown and J. A. Pople, Program No. 236 Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.
7. P. C. Hariharan and J. A. Pople, Theoret. Chim. Acta, 28, 213 (1973).
8. C. Møller and M. S. Plesset, Phys. Rev., 46, 618 (1934); J. A. Pople, J. S. Binkley and R. Seeger, Int. J. of Quantum Chem., S10, accepted for publication.
9. V. R. Juza, W. Wehle, and H. U. Schuster, Zeits. für Anorg. und Allge. Chem., 352, 252 (1967), and references therein.
10. (a) At the STO-3G level, both Li_2O_2[11] and Li_2N_2 also prefer D_{2h} geometries. (b) M.-B. Krogh-Jespersen, unpublished calculations.
11. See J. Peslak, J. Molec. Struct., 12, 235 (1972), L. Andrews, J. Chem. Phys., 50, 4288 (1969); D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, ibid., 39, 2463 (1963).
12. Because of the diffuse nature of the lithium 2p orbitals, ±0.03a.u. contour levels were used. For additional details on the construction of the drawings, see W. L. Jorgensen and L. Salem, "The Organic Chemists Book of Orbitals," Academic Press, New York, N. Y., 1973.