J. Am. Chem. Soc. **1987**, *109*, 1790–1792

Ab Initio Study of 2,3-Dilithiopropene

Andrzej Rajca,[*1a,b] **Andrew Streitwieser, Jr.,**[*1b] **and Laren M. Tolbert**[1c]

Contribution from the Departments of Chemistry, University of California, Berkeley, California 94720, and Georgia Institute of Technology, Atlanta, Georgia 30332.

Received May 22, 1986

Abstract: Two local minima and one transition structure have been found in the potential energy surface for 2,3-dilithiopropene with use of the RHF/3-21G level of theory. The relative energies and vibrational harmonic frequency calculations indicate a highly fluxional molecule in which the bonding to lithium is essentially ionic.

Ab initio studies of various di- and polylithiated organic compounds have revealed a plethora of unusual geometries at the stationary points within symmetry constraints at potential energy surfaces.[2] One example is the "planar tetracoordinate carbon" structure for certain dilithiocarbons.[3] 2,3-Dilithiopropene is of interest in connection with recent NMR studies of dilithium tetraphenylallenide.[4,5] These experiments have suggested an allyl-like hydrocarbon framework with two lithiums that are equivalent on the NMR time scale and coupled exclusively to the central carbon. This finding has raised the possibility of a planar tetracoordinate structure as the observed species.[5a]

A previous ab initio study of 2,3-dilithiopropene has been limited to structures with lithiums at the C_s plane of symmetry.[6] We now report the ab initio exploration of the potential energy surface for 2,3-dilithiopropene, including harmonic vibrational frequency calculations at the stationary points.

Table I. $C_3H_4Li_2$: Geometries[a] at the HF/3-21G Level

	1	2	3
CC	1.414 (1.393)	1.419	1.401
C(1)Li(1)	2.107 (2.141)	2.253	2.092
C(2)Li(1)	2.083 (2.093)	1.986	2.003
C(1)Li(2)	2.970		
C(2)Li(2)	2.000		
LiLi	3.750	3.785	3.433
CCC	119.9 (125.9)	121.0	116.6
LiC(2)Li	133.3	144.8	113.2
Li(1)C(1)C(2)C(3)	49.7 (49.1)	72.4	132.2
Li(2)C(3)C(2)C(1)	177.0 (−168.7)	72.4	132.2
H(1)C(1)C(2)C(3)	−27.0 (−28.1)	0.0	4.7
H(2)C(1)C(2)C(3)	−179.4 (179.0)	180.0	−150.9

[a] Bond lengths in angstroms and angles in degrees (allyllithium geometry at the HF/3-21G level, see ref 13).

Table II. $C_3H_4Li_2$: Energies[a]

	1	2	3
3-21G	−130.01059	2.47	6.08
3-21G/ZPVE	−129.95590	2.32	6.09
6-31+G*//3-21G/ZPVE	−130.69162	4.14	6.37

[a] Total energies in Hartrees for **1**; energies for **2** and **3** are relative to **1** in kcal mol^{-1}. [b] Zero-point vibrational energies (ZPVE) are scaled by 0.9.

Computational Details

Geometries corresponding to the stationary points on the potential energy surface were located by spin-restricted Hartree–Fock (RHF) calculations with use of the 3-21G basis set[7] in conjunction with the analytical gradients method of GAUSSIAN82.[8] Previous calculations on closed-shell lithiocarbons have demonstrated that this level of theory gives adequate geometries.[9] Relative energies are also tolerable, but inclusion of polarization and diffuse functions at the anionic centers improves them somewhat, partially because of reduction in the basis set superposition error;[10] geometry reoptimization with these larger basis sets have been shown to give no or very little improvement.[9a] Accordingly, single-point calculations at the 3-21G geometries were performed by employing the 6-31+G* basis set[7] with sp-diffuse and d-functions on carbons. The predominantly ionic character of the carbon–lithium bond makes the relative correlation energy corrections for the structures with different disposition of lithiums very similar.[9,11] Harmonic vibrational frequencies, which were used to characterize saddle points and minima, were evaluated from second derivatives obtained by the finite difference method from the analytical first derivatives.[8] Because vibrational frequencies at the HF/3-21G level are generally overestimated by about 10%,[12] the calculated frequencies of Table III and zero-point vibrational energies (ZPVEs) of Table II are scaled by 0.9.

Results and Discussion

Geometries of 2,3-dilithiopropenes were optimized at the ab initio HF/3-21G level. The lowest stationary point determined in this work, **1**, which is similar to one found previously,[6] possesses a 2-lithioallyllithium structure; i.e., both lithiums lie on the C_s plane with one (Li(1)) bridging the terminal carbons (130.3° below the CCC plane) while the other (Li(2)) is in the proximity of the central carbon (3.0° above the CCC plane). The hydrogens are bent outward from Li(1); i.e., endo H's are 27° and exo are 0.6° above the CCC plane. The large bending of the endo hydrogens is reminiscent of allyllithium.[10] Placing Li(2) exactly in the CCC plane and reoptimizing the structure raises the energy by only

---

(1) (a) Miller Institute Fellow, 1985–1987. (b) University of California. (c) Georgia Institute of Technology, Atlanta, Georgia 30332.

(2) (a) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. (b) Disch, R. L.; Schulman, J. M.; Ritchie, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6246. (c) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151. (d) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355.

(3) (a) Bachrach, S. W.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 5818. (b) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419. (c) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. (d) Kawa, H.; Manley, B. C.; Lagow, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5313.

(4) Bernard, J.; Schnieders, Ch.; Mullen, K. *J. Chem. Soc., Chem. Commun.* **1985**, 12.

(5) (a) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 2969. (b) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Kost, D.; Klein, J.; Streitwieser, A., Jr.; Schriver, G. W. *Proc. Natl. Sci. U.S.A.* **1982**, *79*, 3922.

(7) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (e) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(8) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon University, 1985.

(9) (a) Kaneti, J.; Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Andrade, J. G.; Moffat, J. B. *J. Am. Chem. Soc.* **1986**, *108*, 1481. (b) Sapse, A.-M.; Raghavachari, K.; Schleyer, P. v. R.; Kaufmann, E. *J. Am. Chem. Soc.* **1985**, *107*, 6483.

(10) Bachrach, S. W.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283.

(11) Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560.

(12) (a) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkley, J. S.; Frish, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum. Chem.* **1981**, *15*, 269. (b) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4.

0002-7863/87/1509-1790$01.50/0

Table III. $C_3H_4Li_2$: Harmonic Frequencies[a] at the HF/3-21G Level

1		2		3	
A″	37.6i	B_1	64.3	A	87.8
A′	138.0	A_1	90.6	B	122.6
A′	324.8	B_2	171.8	A	246.2
A″	350.0	A_2	296.8	B	295.7
A′	403.3	A_1	439.4	A	419.2
A″	500.0	B_1	592.7	B	530.3
A′	563.1	A_2	693.7	A	581.0
A′	599.8	B_1	761.6	B	585.8
A″	702.2	A_2	776.4	A	664.3
A′	745.3	B_1	845.9	A	756.3
A′	808.3	B_2	972.0	B	807.0
A″	996.2	A_1	974.5	A	972.6
A′	997.4	A_1	1112.5	B	1003.7
A′	1190.7	B_2	1194.3	A	1172.5
A″	1239.5	B_2	1449.4	B	1307.6
A″	1461.7	A_1	1471.5	B	1460.6
A′	1483.7	B_2	2713.7	A	1464.8
A″	2785.8	A_1	2730.2	B	2844.5
A′	2802.1	B_2	3010.0	A	2848.2
A″	2956.1	A_1	3012.8	B	2919.6
A′	2959.0			A	2923.7

[a] In cm^{-1}; scaled by 0.9.

24 cal mol^{-1}, which may reflect increased Li–Li electrostatic repulsion.

The frequency calculations reveal that structure **1** is in fact a transition structure (one imaginary frequency, 37.6i cm^{-1}, Table III). The low magnitude of this frequency indicates an extremely flat potential energy surface in the neighborhood of the point corresponding to **1**. Indeed, reoptimization with the hydrocarbon framework constrained to the geometry of **1** and with the lithiums allowed to move freely on the potential energy surface lowers the energy by only 0.3 cal mol^{-1} relative to **1**. Li(2) moves by 3° off the C_s plane (plane of symmetry for the hydrocarbon framework) toward one of the terminal carbons while Li(1) remains at the C_s plane (within 0.001°). The C(2)–Li distances increase slightly (less than 0.001 Å), but the LiLi separation is not increased compared to that of **1**. The resulting structure is not strictly a global minimum because the hydrocarbon framework was fixed as that of **1**. Nevertheless, the minute energy changes involved indicate that the global minimum has an energy hardly less than that of **1** and a structure that cannot be much different. Because the potential energy surface is so flat in this region, it made little sense to determine the true global minimum. The use of a different basis set could change the lithium positions somewhat, but undoubtedly without significant change in relative energy. This nondirectional character of the C–Li bonds suggests high ionic character. Indeed, when the 3-21G lithiums (that includes 2s and 2p functions) are replaced by lithium cations[13,14] (effectively no 2sp shell) the resulting structure is virtually the same. That is, optimization with the hydrocarbon framework fixed at the geometry of **1** locates Li(2) 3° off the C_s plane and Li(1) at the C_s plane (within 0.003°), an arrangement very close to that with standard 3-21G lithiums.

Two additional structures, **2** and **3**, were located as well (Tables I and II). The harmonic frequency calculations determine them to be local minima on the potential energy surface. The existence of normal modes with very low frequencies points again to the flatness of the potential energy surface (Table III). The C_{2v}-symmetric structure **2** is 2.47 kcal mol^{-1} above **1**. The C_2-symmetric structure **3** (6.08 kcal mol^{-1} above **1**) is obtained upon reoptimization of the C_{2v}-symmetric "planar tetracoordinate carbon" structure **4** (19.77 kcal mol^{-1} above **1**). The terminal methylenes in **1** and **3** are somewhat pyramidal (5.4° and 4.3°, respectively).[6,15]

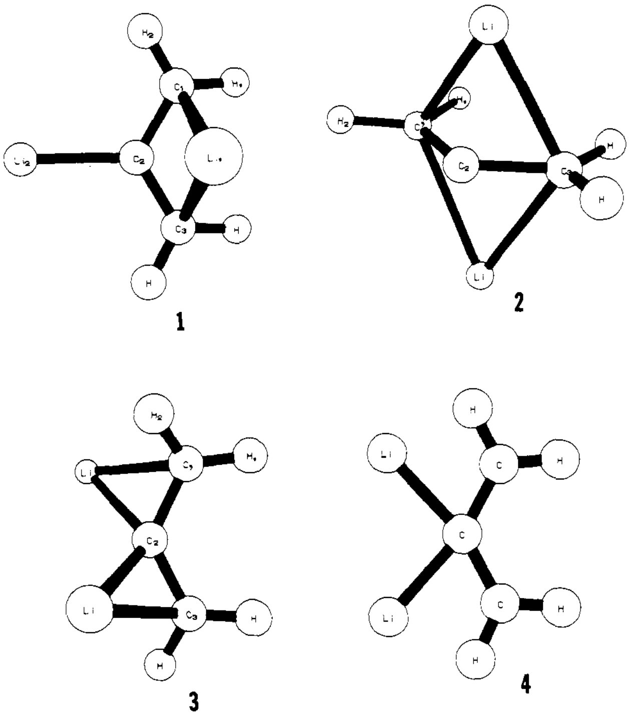

Figure 1. Structures of 2,3-dilithiopropene.

A 1,1-dilithiocyclopropane structure with planar tetracoordinate C(1), which was optimized within the C_{2v}-symmetry constraint, is 49.17 kcal mol^{-1} above **1**. Note that this is even above **4**. Previous optimizations at the HF/STO-3G level have shown that the tetrahedral C(1) structure for 1,1-dilithiocyclopropane is 7.15 kcal mol^{-1} above the planar one.[3b] Thus, we conclude that 1,1-dilithiocyclopropane is thermodynamically unstable with respect to the cyclopropane ring opening leading to 2,3-dilithiopropenes.

The potential energy surface for lithium shifts in the C_s plane (structure **1**) is also rather flat. For example, when the Li(2)–central carbon bond axis is fixed at 45° or 70° above the CCC plane and the structures are fully optimized within the C_s symmetry constraint, the relative energies are 2.24 and 2.74 kcal mol^{-1}, respectively. The other Li(1)–carbon axis is 122.9° and 119.0°, respectively, below the CCC plane. Therefore, one may anticipate a low barrier (about 3 kcal mol^{-1} at 3-21G) for intramolecular lithium exchange in structure **1**, possibly via structure **2** (lithiums 107.6° above and below the CCC plane). Zero-point vibrational energies are about 34 kcal mol^{-1} for all structures **1**, **2**, and **3**. Single-point calculations with the 6-31+G* basis set using 3-21G geometries increase the relative energy of structure **2** to 4.14 kcal mol^{-1} after zero-point energy correction (Table II). This result suggests that the barrier for Li exchange in **1** within the C_s plane may be somewhat higher, perhaps about 5 kcal mol^{-1}.

The nature of the barrier-to-lithium exchange is clearly indicated by the electrostatic map for the CH_2CCH_2 dianion (RHF/3-21G at the geometry of **2**) calculated for the plane containing the C(2) and orthogonal to the CCC plane (Figure 2). This map gives the electrostaic potential for the dianion with correction for the polarization by a single cation.[16] Figure 2 includes a circle of radius 2.0 Å centered at C(2); the normal C–Li bond distance is 2.0 Å (Table I), and the circumference of this circle indicates the closest normal approach of Li to C. Within these constraints the maximum electrostatic potential is that at the point marked by "M". Neither lithium, however, can occupy this site because it is too close to two of the methylenic hydrogens. In the lowest energy structure **1** one lithium moves above the CCC plane to the position marked "1". Putting the second lithium at the equivalent C_{2v} position, however, apparently involves too much

---

(13) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344.

(14) Lithium cations were modeled with use of Gaussian functions with exponents of 950.0 and 900.0 to contract the valence orbitals in the lithium basis; see also ref 13 and 6.

(15) Pyramidality at carbon is estimated as 360° minus sum of bond angles around carbon; see ref 6.

(16) Francl, M. M. *J. Phys. Chem.* **1985**, *89*, 428.

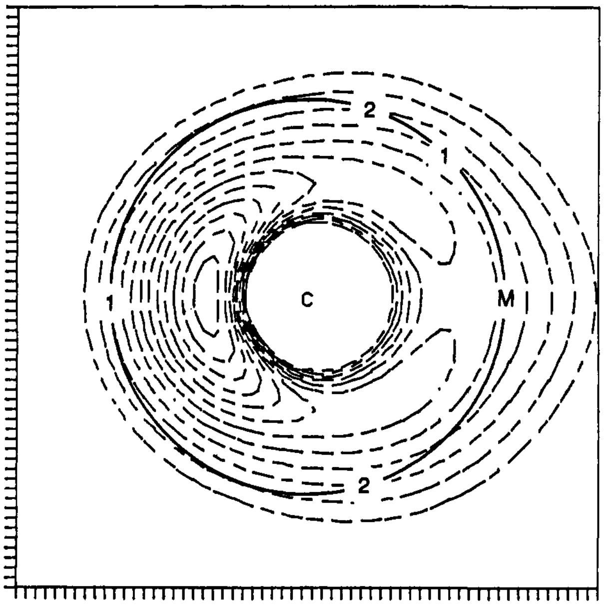

Figure 2. Electrostatic map for CH_2CCH_2 dianion calculated at the RHF/3-21G level at the geometry of **2** and with polarization correction for a single positive charge. The plane of the plot is orthogonal to the CCC plane and contains the C(2). This is the plane where the lithiums in structures **1** and **2** are located. The C(2) is indicated by "C" and the full line is a circle of radius 2.0 Å centered at this atom. Because the C(2)–Li distances in **1** and **2** are about 2 Å the electrostatic potential at this circumference circle is a guide to the disposition of the lithiums within the plane of the plot. The contours are plotted from –0.74 to –0.41 by 0.03 hartree.

Li–Li repulsion. The positions marked "2", where the lower electrostatic potential is offset by reduced Li–Li repulsion, correspond to the actual location of the lithiums in structure **2**. Alternatively, in structure **1** one lithium remains at the position "1" close to the electrostatic potential maximum and the second lithium locates at the carbon lone pair position "1" far from the first lithium and yet at an electrostatic potential equivalent to position "2". These two factors show why structure **2** is of higher energy than **1**. Of course, additional variations are to be expected from the perturbation of the electrostatic potential caused by polarization by the second lithium. The electrostatic potential map for the dianion itself, however, is qualitatively similar to that corrected for a single positive charge in Figure 2; hence, the polarization correction for a second positive charge is expected to have no significant effect on the conclusions. The important point is that the essential features of the structures are excellently represented by the simplest type of electrostatic energy analysis. This result is in line with a recent study of methyl lithiomethyl sulfone[17] in which structures were also well understood in terms of simple electrostatic considerations. Finally, moving Li from position "1" to position "2" in Figure 2 requires traversing a barrier of reduced electrostatic potential—the obvious source of the barrier for lithium exchange.

Although the above discussion documents the high ionic character of the carbon–lithium bonds, we cite further aspects of the electronic structure of 2,3-dilithiopropene. Orbital interactions for structures **1**, **2**, and **3** between the lithiums and the hydrocarbon framework are essentially unimportant because all occupied MOs are overwhelmingly localized on the carbons and hydrogens and only lower virtual valence orbitals are on the lithiums. This trivial manifestation of the predominantly ionic character of the CLi bond is confirmed by the Natural Population (NP) procedure of Reed and Weinhold[18] (Table IV). Calculated total NPs for the lithiums are between 2.13 and 2.20 electrons, in essential agreement with both NPs and integrated spatial electron populations for other organolithium compounds.[3a,10,19,20] The lithiums or, approximately, the lithium cations exert a small influence on the charge distribution within the hydrocarbon framework; for example, increased lithium coordination of the C(2) as in structures **2**, **1**, and **3** leads to larger negative charge associated with this carbon. Incidentally, the energy of the subjacent HOMO, which is predominantly the free-electron pair at C(2), is lowered in the same order. The other two occupied neighboring MOs (HOMO and SSHOMO) correspond virtually to the nonbonding and bonding allylic π-MOs, respectively. The energetics of these three highest occupied MOs does not reflect trends in the total energies for **1**, **2**, and **3**. The C(2) atom, which formally bears the free electron pair, has less negative charge than the terminal carbons, thus indicating an important polarization of the π-electron density within the allylic framework, reminiscent of vinyl anion.[21]

Table IV. $C_3H_4Li_2$: Natural Populations (Electrons) and Energies for the Three Highest Occupied Molecular Orbitals (Hartrees) at the HF/3-21G Level

	1	2	3
C(1)	6.92	6.98	6.89
C(2)	6.57	6.53	6.61
Li(1)	2.19		
Li(2)	2.13	2.14	2.18
HOMO	–0.1991	–0.2297	–0.1953
SHOMO	–0.2704	–0.2473	–0.2804
SSHOMO	–0.3613	–0.3970	–0.3491
Σ	–0.8307	–0.8741	–0.8249

Conclusion

The symmetry-breaking lithium shift in the 2-lithioallyllithium C_s-symmetric structure **1**, which occurs at an extremely flat fragment of the potential energy surface, exemplifies once again an effect originating in the ionicity of the carbon–lithium bond.[2a] The η^3-bridging lithium has a tendency to remain close to the C_s plane of symmetry in clear analogy with the C_s-symmetric structure for allyllithium.

The two local minima on the potential energy surface considered above are characterized by exceedingly small curvatures; some of the vibrational normal modes involving displacements of lithiums possess underlying frequencies on the order of only 100 cm^{-1}.

The barrier for lithium shifts leading to the exchange of the lithiums is estimated as no more than about 5 kcal mol^{-1}. The calculations apply to unsolvated lithiums; however, because of high ionic character of bonds to lithium the barrier should be lower for solvated lithium cations. Indeed, this result is in qualitative agreement with a recent low-temperature ^{7}Li and ^{6}Li NMR study of the tetraphenyl derivative.[5b]

The planar tetracoordinate carbon structure is about 13 kcal mol^{-1} above the local minimum corresponding to "tetrahedral carbon" and about 19 kcal mol^{-1} above the global minimum structure of 2-lithioallyllithium.

Acknowledgment. This research was supported in part by National Science Foundation grants. A.R. thanks Dr. Steven Bachrach for help with the preliminary calculations.

---

(17) Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 1397.

(18) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 1919.

(19) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(20) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778; McDowell, R. S.; Grier, D. L.; Streitwieser, A., Jr. *Comp. Chem.* **1985**, *9*, 165.

(21) Williams, J. E., Jr.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 2634.