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AB INITIO STRUCTURES OF ALLYLLITHIUM

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Summary

Complete optimization of classical and nonclassical allyllithium structures at the RHF/STO-3G level with subsequent RHF/4-31G and RHF/6-31G* calculations confirms the C_s bridged species to have the lowest energy. The allyl fragment of this structure is significantly distorted from a planar arrangement in order to enhance bonding between the allyl anion HOMO (on C(1), C(3)) and the lithium *p*-orbital with axis parallel to C(1)—C(3).

The structure of allyllithium has been the subject of considerable experimental [1,2] and theoretical [3—5] work. An earlier ab initio investigation involved only a partial geometry search [5][***]; we have not carried out complete optimization of bridged allyllithium, I (C_s), and the *syn* and *anti* classical C_s forms, II and III, at the minimal basis RHF/STO-3G [6a,b] level. Although not an energy minimum, an unsymmetrically bridged C_1 structure, 2—3 kcal mol^{-1} higher in energy than I was also investigated[†]. The STO-3G optimum geometries of I—III, shown in Table 1, were then used for single point RHF/4-31G [8] and RHF/6-31G* [9] calculations. Total and relative energies are listed in Table 2. The

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[***] The lowest RHF/STO-3G energy of allyllithium reported was −122.3741 a.u. for a structure with C_s symmetry. The RHF/4-31G total energy for the reported $C_3H_5^-$ geometry is −116.22639 a.u.

[†] An unsymmetrically bridged structure, IV, was obtained when complete optimization of a classical allyllithium (Li initially perpendicular to the CCC plane) was carried out by cyclic variation of all parameters one at a time [5a]. Our interest in this problem arose when we found IV to have a lower energy than that reported for I by the earlier workers. Although IV met our criteria for an energy minimum (total energy change was less than 10^{-5} a.u. (6×10^{-3} kcal mol^{-1}) per complete cycle), (multiplayer search) Fletcher et al. [7] showed this conclusion to be incorrect as it led to I.

TABLE 1

CALCULATED (RHF/STO-3G) GEOMETRIES

Parameter	I	II	III
Bond lengths			
C(1) C(2)	1.401	1.315	1.312
C(2) C(3)	1.401	1.522	1.535
C(2)Li	2.006	2.527	3.046
C(3)Li	2.039	1.961	2.025
C(1) H(1)	1.084	1.098	1.081
C(1) H(2)	1.075	1.080	1.081
C(2) H(3)	1.090	1.094	1.084
C(3) H(4)	1.084	1.085	1.087
C(3) H(5)	1.075	1.085	1.087
Bond angles			
C(1) C(2) C(3)	123.0	126.0	123.5
C(2) C(3)Li	82.6	92.2	117.0
C(2) C(1) H(1)	116.1	123.4	122.0
C(2) C(1) H(2)	118.6	124.0	122.5
C(1) C(2) H(3)	107.6	116.5	117.6
C(2) C(3) H(4)	116.1	107.5	107.3
C(2) C(3) H(5)	118.6	107.5	107.3
Out-of-plane angles [a]			
C(2)Li	46.9	0.0	0.0
C(1) H(1)	—31.1	0.0	0.0
C(1) H(2)	—3.0	0.0	0.0
C(2) H(3)	11.1	0.0	0.0
C(3) H(4)	—31.1	56.4	55.5
C(3) H(5)	—3.0	—56.4	—55.5

[a] Out-of-plane angles are positive when the given bond is above the C(1) C(2) C(3) plane and negative below the plane.

bridged C_s structure, I, proved to be most stable at all levels. This is consistent with previous work [5]. The *anti* classical species proved to be the least stable in all the calculations. The relative energies of I, II and III are close: 0, 16 and 18 kcal mol^{-1}, respectively, at both RHF/4-31G and RHF/6-31G* (Table 2).

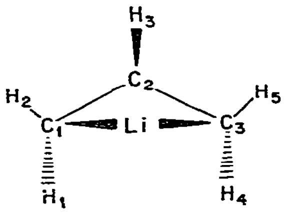
It should be emphasized that II and III were optimized within the constraints of C_s symmetry, i.e., all non-hydrogen atoms were held in a plane. Were this restriction to be removed, both II and III would probably collapse to I, without

TABLE 2

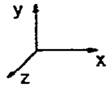
TOTAL AND RELATIVE ENERGIES OF ALLYLLITHIUM SPECIES I—III AT THE RHF/STO-3G OPTIMIZED GEOMETRIES

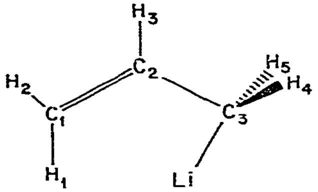
Structure	Total energies (a.u.)			Relative energies (kcal mol^{-1})		
	STO-3G	4-31G	6-31G*	STO-3G	4-31G	6-31G*
I, bridged	—122.39929	—123.74560	—123.91360	0.0	0.0	0.0
II, *syn*	—122.35659	—123.72025	—123.88862	26.8	15.9	15.7
III, *anti*	—122.34928	—123.71733	—123.88419	31.4	17.7	18.5

encountering a significant energy barrier. Thus, I not only is the most stable form, but also may be the sole minimum on the C_3H_5Li potential energy surface. Unsuccessful searches were made for other minima, but these were not exhaustive.

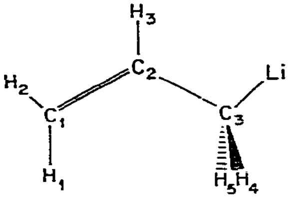


I





II



III

The structure of the *anti* classical species, III, gave no unexpected geometrical features upon optimization. However, the *syn* classical isomer collapsed to a "semi-bridged" form (II) with a CCLi angle of 92.2°. In the bridged C_s isomer, I, the geometry of the C_3H_5 moiety closely approaches that of the allyl anion (C_{2v}) [5], but the CCC angle diminishes from 132.7° to 123.3°, presumably because of improved C(1)Li and C(3)Li overlap. The methylene CH bonds are all somewhat bent down below the CCC plane (Li being above). The central CH bond (C(2)H(3)) bends towards lithium so that H(3) lies above the CCC plane.

The energy of the isodesmic exchange reaction 1 provides estimates of the relative stability of allyl- and ethyl-lithium structures. These are given in Table 3 *.

$$C_2H_5Li + CH_3CH{=}CH_2 \rightarrow C_3H_5Li + C_2H_6 \qquad (1)$$

At the RHF/6-31G* level, the energies are negative for all three species. For the *anti* classical isomer III, the value is very small, indicating no significant double bond inductive effect relative to ethyllithium. However, there is a somewhat larger stabilization (3.2 kcal mol^{-1}) with the *syn* classical form II. This arises partly by donation from the double bond πz orbital to the empty $p\pi z$ orbital on lithium, an interaction which also leads to the closing of the CCLi angle.

The high additional stabilization in the bridged form I of 18.9 kcal mol^{-1} (RHF/6-31G*) can be attributed to several stabilizing features of this structure. An important effect, which has been discussed previously [3–5], is the bonding overlap between the highest occupied molecular orbital (HOMO) of an allyl

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* RHF/STO-3G, RHF/4-31G and RHF/6-31G* total energies for ethyllithium are −84.99605, −85.92765 and −86.04106 a.u., respectively, at the STO-3G optimum geometry [10].

TABLE 3

CALCULATED ENERGIES FOR EQUATION 1

C_3H_5Li structure	ΔE (kcal/mole) [a]		
	RHF/STO-3G	RHF/4-31G	RHF/6-31G*
I, bridged	−30.8	−18.3	−18.9
II, *syn*	−4.0	−2.4	−3.2
III, *anti*	+0.6	−0.6	−0.4

[a] All calculations at the STO-3G optimized geometries given in Table 1; other data used are taken from refs. 10—12.

anion moiety and the vacant Li^+ *px*-type orbital (with axis parallel to C(1)C(3)). This type of bonding was first suggested by X-ray crystal structures of benzyl and related lithium compounds [13]. As lithium is the acceptor in such an interaction, the effect is to reduce the overall charge transfer from lithium to allyl. The interaction is enhanced by inclination of the lobes of the C(1), C(3) $p\pi$ orbitals towards lithium. The bending down of the methylene hydrogen accentuates such inclination. Indeed, this bending results in a destabilization of the C(1)C(2)C(3) π bonding orbital by 0.0103 a.u. but a stabilization of the HOMO by 0.0294 a.u. relative to the structure with C_3H_5 planar. Similarly, the C(2)H(3) bond bends up to further increase HOMO bonding between *px* on lithium and the twisted *p*-orbitals of C(1) and C(3). This type of interaction is further demonstrated by the Mulliken population analysis for I, shown in Table 4. Lithium is clearly bonded to C(1) and C(3), although C(2) is the closest carbon. At RHF/STO-3G, C(2) and Li are actually antibonding.

The recently reported enthalpies of reaction of allyllithium and ethyllithium with ethanol in ether [14] afford a means of evaluating the energy of reaction 1 experimentally; a value of -13.7 ± 2.6 kcal mol^{-1} is obtained. The agreement with the calculated values (Table 3) is fortuitous, since the experimental measurements are complicated by different degrees of association of ethyllithium and of allyllithium and by possible differences in solvation energies. The calculations, of course, refer to isolated species at 0 K.

The proton NMR spectrum of allyllithium [15] shows an ABB′CC′ pattern

TABLE 4

MULLIKEN POPULATION ANALYSIS FOR C_s ALLYLLITHIUM, I

		RHF/STO-3G	RHF/4-31G
Net atomic charges	C(1)	−0.197	−0.548
	C(2)	0.013	0.146
	Li	0.110	0.439
Total overlap populations	C(1) C(2)	0.983	0.801
	C(1)Li	0.310	0.300
	C(2)Li	−0.066	0.030
	C(2)Li(p_π) [a]	0.227	0.212
Dipole moment (*D*)		0.922	2.820 [b]

[a] The π component of the total overlap. [b] Value 2.868 debyes at RHF/6-31G* level.

at −87°C but coalesces to AB_4 at higher temperatures. This behavior has been attributed to exchange of H(1) (H(4)) and H(2) (H(5)) due to rotation about the C(1)C(2) (C(2)C(3)) bond. The experimental activation energy for this process is 10.5 ± 2 kcal mol^{-1} in tetrahydofuran [15]. Since organolithium compounds are known to be strongly solvated and/or associated, our calculations on isolated monomers can only be expected to approximate this value. Nevertheless, it is revealing to consider the mechanism of HH exchange. If the metal and allyl fragment are bound to the same degree in ground and transition states, as would be the case in a dissociated species, the barrier should be independent of the metal and should be approximated by that of the allyl anion itself (29 kcal mol^{-1} at 4-31G) [16]. If the metal is bound to a greater extent in the rotational transition state than in the ground state, a reduced barrier and a dependency on the metal would result. Both are found experimentally; the rates of *cis—trans* stereomutation of crotyl(1-methylallyllithium, -sodium, -potassium, and -cesium increase markedly in that order [2].

Our calculated barrier for allyllithium, approximated by the 6-31G* energy difference between I and II (III is higher in energy), is 16 or 13 kcal mol^{-1} lower than that calculated for the allyl anion at the same level [16]. Preliminary calculations on allylsodium indicate the barrier to be higher than that for allyllithium.

A reasonable interpretation of these observations focuses on the degree of covalent character in the metal to carbon bonding. The larger and more electropositive alkali metals are not expected to stabilize the more localized transition state (e.g., II) as well as the delocalized ground state (e.g. I). Lithium—carbon bonding, because of partial covalent character in II, reduces the rotational barriers appreciably. However, when it is recalled that the methyl rotation barrier in propene is only 2 kcal mol^{-1} (the barriers in the usual methyl-substituted propenes are not much larger), the large degree of ionic character of allyllithium is apparent.

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References

1 For a recent review see L.D. McKeever in M. Szwarc (Ed.), Ions and Ion Pairs in Organic Reactions, Vol. 1, John Wiley Inc., New York, 1972, see also T.E. Hogen-Esch, Advan. Phys. Org. Chem., 15 (1977) 153.
2 M. Schlosser and J. Hartmann, J. Amer. Chem. Soc., 98 (1976) 4674, and ref. therein.
3 E.R. Tidwell and B.R. Russell, J. Organometal. Chem., 80 (1974) 175.
4 J.F. Sebastian, J.R. Grunwell and B. Hsu, J. Organometal. Chem., 78 (1974) C1.
5 A. Bongini, G. Cainelli, G. Cardillo, P. Palmieri and A. Umani-Ronchi, J. Organometal. Chem., 110 (1976) 1.
6 (a) The Gaussian 70 series of programs was employed: W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton and J.A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana; (b) W.J. Hehre, R.F. Stewart and J.A. Pople, J. Chem. Phys., 51 (1969) 2657; (c) W.J. Hehre, R. Ditchfield, R.F. Stewart and J.A. Pople, J. Chem. Phys., 52 (1970) 2769.
7 R. Fletcher and M.J.D. Powell, Comp. J., 6 (1963) 163; J.B. Collins, P. v. R. Schleyer, J.S. Binkley and J.A. Pople, J. Chem. Phys. 64 (1976) 5142.

8 (a) R. Ditchfield, W.J. Hehre and J.A. Pople, J. Chem. Phys., 54 (1971) 724, (b) W.J. Hehre and J.A. Pople, ibid., 56 (1972) 4233; (c) J.D. Dill and J.A. Pople, ibid., 62 (1975) 2921.

9 P.C. Hariharan and Y.A. Pople, Theor. Chim. Acta, 28 (1973) 213.

10 T. Clark, P. v. R. Schleyer, J.S. Binkley and J.A. Pople, unpublished calculations. T. Clark, P. v. R. Schleyer and J.A. Pople, Chem. Commun., (1978) 137, cf. Y. Apeloig, P. v. R. Schleyer and J.A. Pople, J. Amer. Chem. Soc., 99 (1977) 5901.

11 L. Radom, W.A. Lathan, W.J. Hehre and J.A. Pople, J. Amer. Chem. Soc., 93 (1971) 5339; W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle and J.A. Pople, Progr. Phys. Org. Chem., 11 (1974) 175.

12 P.C. Hariharan and J.A. Pople, Chem. Phys. Lett., 16 (1972) 217.

13 (a) S.P. Patterman, I.L. Karle, and G.D. Stucky, J. Amer. Chem. Soc., 92 (1970) 1150; (b) J.J. Brooks, W. Rhine and G.D. Stucky, ibid., 97 (1975) 737; (c) S.K. Arora, R.B. Bates, W.A. Beavers and R.S. Cutler, ibid., 97 (1975) 6271.

14 G.R. Brubaker and P. Beak, J. Organometal. Chem., 136 (1977) 147.

15 P. West, J.I. Purmont and S.V. McKinley, J. Amer. Chem. Soc., 90 (1968) 797.

16 J.E. Bartmess, W.J. Hehre, R.T. McIver, Jr. and L.E. Overman, J. Amer. Chem. Soc., 99 (1977) 1976; W.J. Hehre, personal communication.

17 See, e.g., W.J. Hehre and J.A. Pople, J. Amer. Chem. Soc., 97 (1975) 6941.