

Preliminary communication

THE DOUBLY BRIDGED STRUCTURE OF 1,4-DILITHIO-*cis*-2-BUTENE. A THEORETICAL DEMONSTRATION OF THE IMPORTANCE OF COUNTER-ION EFFECTS AND OF LITHIUM MULTICENTER BONDING

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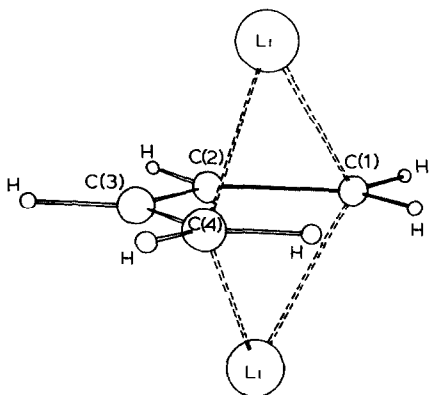
Summary

Due to electrostatic interactions and a contribution of multicenter bonding involving lithium 2*s* and 2*p* valence orbital contributions to cyclic 6*π* delocalization, the doubly bridged *cis* structure 1 for the title compound is more stable than other alternatives.

“Dilithiobutadiene” (1,4-dilithio-2-butene) is the simplest linearly π conjugated “dianion” system which has been reported experimentally [1]. Since neither the structure nor even the preferred configuration is known, we have investigated this species computationally [2]. We wished to ascertain the relative stabilities of *cis* and *trans* isomers, both of the free dianion and of the dilithium derivatives, and the reasons for such preferences. Precedents for both configurations are known. The X-ray structure of 1,6-dilithio-2,4-hexadiene, the next higher polyene homolog, shows an *s-trans* arrangement at the central bond [3]. On the other hand, the double lithium bridging [2] exemplified in the structure of an α,α' -dilithio-*o*-xylene derivative [4a] might favor a *cis* orientation [4b].

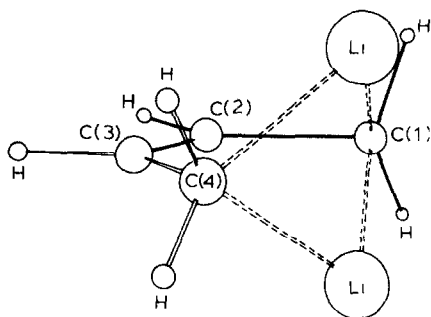
A MNDO [5] search of many structural possibilities for 1,4-dilithio-2-butene located three favorable local minima (1–3). These were reoptimized at the ab initio split valence 3–21 G basis set level [6]; key geometrical parameters are shown. While 1 and 2 are more competitive in energy, the best *trans* arrangement (3) is significantly less stable (Table 1).

Conjugation, the feature favoring 1, is shown by the rather similar C(2)C(3) and C(1)C(2) (and C(3)C(4)) bond lengths (1.388 and 1.450 Å, respectively). Three occupied MO's (Fig. 1), reminiscent of those in 5-membered aromatic systems [7], are utilized by the 6 π electrons. Lithium 2*s* and 2*p* orbitals help



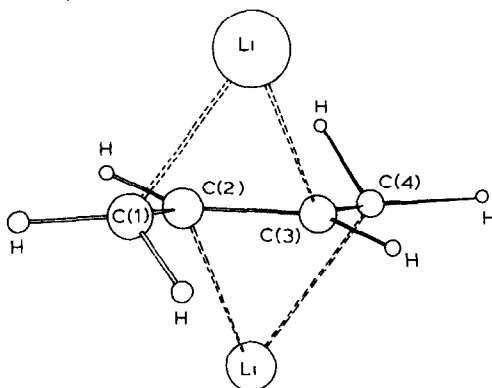
$$\begin{aligned} \text{C}(1)\text{C}(2) &= 1.450 \text{ \AA} \\ \text{C}(2)\text{C}(3) &= 1.388 \text{ \AA} \\ \text{C}(1)\text{Li} &= 2.245 \text{ \AA} \\ \text{LiLi} &= 3.391 \text{ \AA} \\ \angle \text{C}(1)\text{C}(2)\text{C}(3) &= 121.8^\circ \end{aligned}$$

1



$$\begin{aligned} \text{C}(1)\text{C}(2) &= 1.545 \text{ \AA} \\ \text{C}(2)\text{C}(3) &= 1.343 \text{ \AA} \\ \text{C}(1)\text{Li} &= 2.084 \text{ \AA} \\ \text{LiLi} &= 2.313 \text{ \AA} \\ \angle \text{C}(1)\text{C}(2)\text{C}(3) &= 124.4^\circ \end{aligned}$$

2

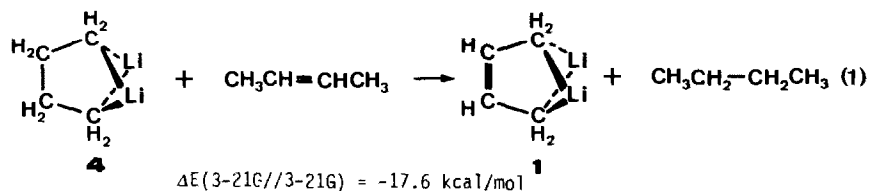


$$\begin{aligned} \text{C}(1)\text{C}(2) &= 1.485 \text{ \AA} \\ \text{C}(2)\text{C}(3) &= 1.372 \text{ \AA} \\ \text{C}(1)\text{Li} &= 2.009 \text{ \AA} \\ \text{C}(3)\text{Li} &= 2.149 \text{ \AA} \\ \angle \text{C}(1)\text{C}(2)\text{C}(3) &= 126.7^\circ \end{aligned}$$

3

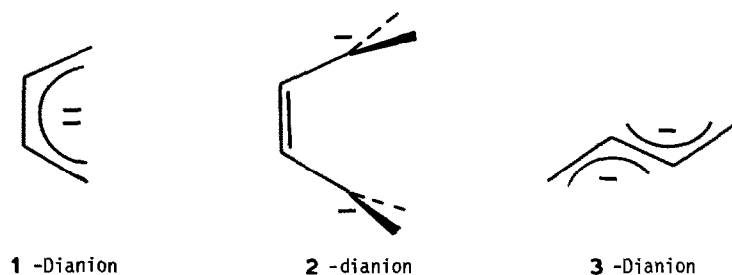
to complete the cyclic delocalization [8]. The C(1)Li bond length (2.245 Å) agrees with values typically found experimentally in lithium-bridged structures [2,4,9,10]. Equation 1 shows that 1 enjoys considerable extra stabilization relative to a doubly bridged saturated model, 1,4-dilithiobutane (4), in its most stable conformation [11].

Isomer 2 is only 6.7 kcal/mol less stable than 1, despite the perpendicular conformation of the terminal methylene groups which preclude π conjugation. The C(2)C(3) double bond (1.343 Å) and the C(1)C(2) (and C(3)C(4)) single



bonds (1.546 Å) are now normal in length. However, due to the orientation of the terminal CH_2 groups which point their sp^3 -hybridized lone pair lobes more directly at the lithium atoms, **2** benefits even more than **1** from double lithium bridging. This is reflected in the shorter CLi distances, 2.084 Å, in **2**. Methylene conformations in which the hybridized lone pairs point towards the Li atoms (as in **2**) are indicated to be more favorable in α,ω -dilithioalkanes (e.g., **4**) where no conjugation is present [11]. Lone pair orientation also competes effectively with π conjugation in dilithiopropene [12].

Calculations on the dianions themselves emphasize the importance of counter-ion effects. As anticipated by Hoffmann and Olofson [13], the *cis* dianion corresponding to **1** again is the most stable isomer (3-21 G basis set), but the *trans*-**3**-like planar (C_{2h}) dianion is only 3.8 kcal/mol higher in energy. The **1**–**3** difference, 23.8 kcal/mol (Table 1), is much greater. The *cis* perpendicular dianion corresponding to **2** (or its *trans* counterpart) is 19 kcal/mol less favorable than the **1**-dianion (MNDO), whereas the **1**–**2** energy difference when the lithiums are present is less than 7 kcal/mol. This emphasizes the essential role of the counterions which should not be omitted in discussions of “polyanion” chemistry



In **3**, the least stable dilithium isomer considered here, both lithiums bridge different sets of atoms in allyl-like fashion [14] on opposite faces. This results in better charge distribution since each carbon has the opportunity of a lithium contact. Besides dilithiohexadiene [**3**] this feature has precedents in several X-ray structures, e.g., dilithionaphthalene [15] and dilithiobutatriene [16].

The energy difference of 23.8 kcal/mol between **1** and **3** indicates the electrostatic advantages of symmetrical double lithium bridging. This arrangement is the intramolecular equivalent of the dimerization of two LiX molecules to give a cyclic array of alternating positive and negative charges [2,8,9, 11,17,18]. However, this simple ionic description does not account for all the bonding characteristics of lithium compounds. Multicenter bonding involving lithium valence orbitals also contributes significantly [2,12,16]. This

TABLE 1

RELATIVE ENERGIES (kcal/mol) OF 1,4-DILITHIO-2-BUTENES, AND THE INFLUENCE OF THE LITHIUM VALENCE ORBITALS

	Rel. Energy		
	3-21G// ^a 3-21G	3-21+G/3-21G(-Li _{2p})// 3-21G	3-21+G/3-21G(-Li _{2sp})// 3-21G
1, C _{2v}	0.0	0.0	0.8
2, C _{2v}	6.7	1.0	0.0
3, C ₂	23.8	19.8	19.1

^a Total energies (a.u.): 1 -168.86550; 2 -168.85479; 3 -168.82760.

was demonstrated by repeating the calculations with added diffuse functions on carbon [19] (to avoid basis set superposition error) [20] but with truncated Li basis sets. When all the Li_{2p} orbitals were omitted, the stability of 1 and 2 became nearly equal (Table 1). With an ionic Li⁺ model, achieved by leaving out all the Li_{2sp} valence functions, 2 was favored even more. The molecular orbitals shown in Fig. 1 indicate how the lithium 2s and 2p orbitals act to complete the cyclic conjugation [8].

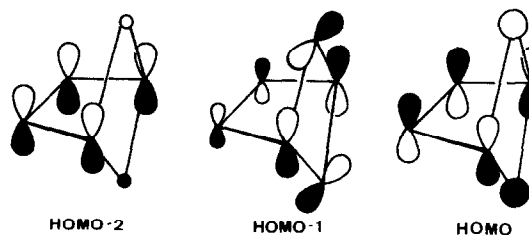
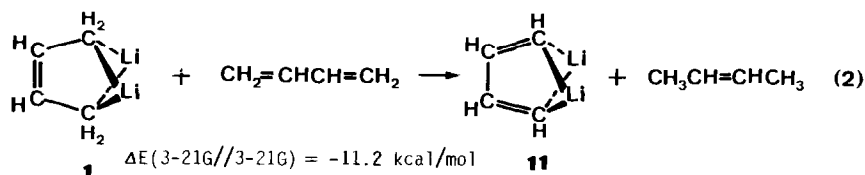


Fig. 1. The three occupied π MO's of 1,4-dilithio-*cis*-2-butene (1).

The 4 π doubly Li bridged butadiene derivative 11, which we have termed "Möbius-Hückel" [8], is shown by eq. 2 to be even more stable than the 6 π (6). The sp^2 hybridization and the more favorable lone pair orientation of the terminal carbon centers in 11 are responsible.



Experimental support for structure 1 is reported in the following paper [21]; the X-ray structure of 1,4-dilithio-1,4-diphenyl-2-*cis*-butene shows a very similar doubly bridged geometry.

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