Symmetrical Double Bridging in Dilithiated Propene, $CH_2CHCHLi_2$

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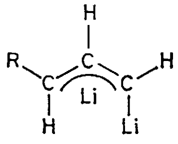
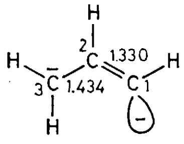
Two symmetrically doubly lithium-bridged structures for dilithiated propene, $CH_2CHCHLi_2$ (**3**) and (**4**), are indicated to be comparably stable by *ab initio* (3-21G//3-21G) calculations.

Klein and Medlik-Balan discovered that the reaction both of propene and of allylbenzene with butyl-lithium in the presence of tetramethylethylenediamine (TMEDA) proceeded in two stages: a fast conversion to the corresponding allyl-lithium followed by a slower dimetallation to $CH_2CHCHLi_2$ and $PhCHCHCHLi_2$.[1] Formulation (**1**), favoured by Klein and Medlik-Balan, implies that the two lithium atoms are in different environments. Based on the hypothetical dianion (**2**), (bond lengths are given in Å), one lithium atom would be



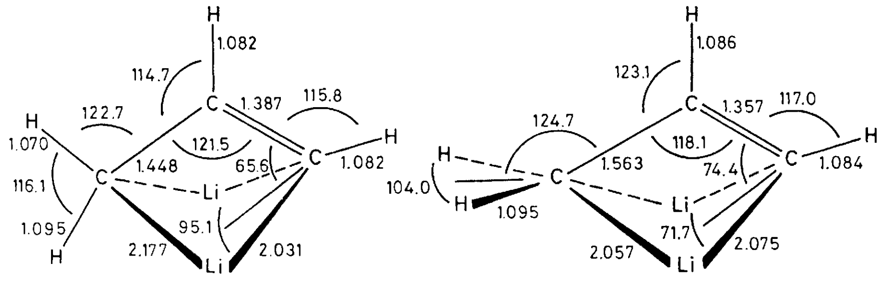
(1)

R = H or Ph



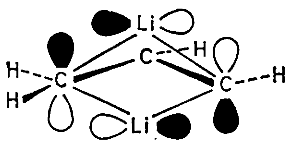
(2)

$\Delta H_f°$ (MNDO) 229.9 kcal mol^{-1}

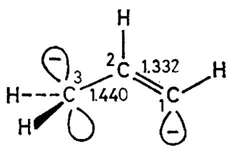


(3) (4)

Figure 1. *Ab initio* (3-21G//3-21G) geometries of $CH_2CHCHLi_2$ isomers. Bond lengths are in Å, angles in degrees.

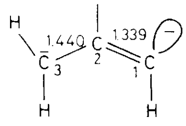


(5)

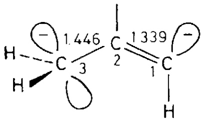


(6)

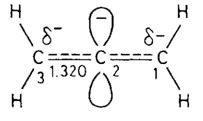
$\Delta H_f°$(MNDO) 233.6 kcal mol^{-1}



(7)



(8)



(9)

$\Delta H_f°$(MNDO) 229.3 kcal mol^{-1} 232.6 211.3

associated with the allyl anion-like π system[2] and the second with the terminal vinyl anion.[3]

Assuming such dilithiated species to be monomeric,[4] their structures can easily be examined by calculation. Our detailed studies of allyl-lithium,[2] vinyl-lithium,[3] as well as the lithiated products of allene or propyne, C_3H_3Li, $C_3H_2Li_2$, C_3HLi_3, and C_3Li_4,[5] serve as models for the present investigation. The results reveal unexpected features and illustrate bonding principles which we believe to be general for polylithium compounds.

Structure (**1**) was not a minimum on either the MNDO[6] or the *ab initio* (3-21G basis set)[7] potential energy surfaces. Instead, when starting geometries corresponding to (**1**) were employed, full optimization (carried out automatically by the analytic gradient routines built into the computer programs)[6,8] gave the symmetrically doubly bridged (C_s) structure (**3**). The *ab initio* geometry (designated 3-21G//3-21G) is given in Figure 1. Structure (**3**) is easy to understand. Each lithium atom is associated simultaneously with both the anionic systems of (**2**), one lithium atom above the allyl anion plane[2] and the other arranged symmetrically below. We consider (**3**) to be a 4π aromatic system.[9] The HOMO is shown in (**5**). Similar double 1,3-bridging is indicated in the most favourable geometries of LiCHCCHLi, C_3HLi_3, and C_3Li_4.[5] We have also reported instances of 1,2-[3,10] and 1,4-[9] double lithium bridging.

An extensive MNDO examination of all 1,1-, 1,2-, and 1,3-dilithiated propene and cyclopropane possibilities indicated a second, unexpected $CH_2CHCHLi_2$ isomer (**4**) (Figure 1) to be the global $C_3H_4Li_2$ MNDO minimum. At the 3-21G//3-21G *ab initio* level, the energy of (**4**), −130.02718 a.u.,† is slightly higher (0.7 kcal mol^{-1}) than that of (**3**), −130.02831 a.u. At first, the stability of (**4**) seems surprising. Isomer (**4**) is based on the hypothetical dianion (**6**); the 90° rotation of the CH_2 group 'turns off' the allylic resonance. In the allyl anion, similar rotation of a terminal CH_2 group is calculated to require 22 kcal mol^{-1}.[11] However, in (**2**) π-delocalization to C-1 is decidedly unfavourable electrostatically, and the π negative charge resides largely at C-3. In (**6**), the negative charges are localized, but this structure is only 3.7 kcal mol^{-1} (MNDO) less stable than (**2**). A similar small difference of 3.3 kcal mol^{-1} is found for the *trans*-dianions, (**7**) *vs.* (**8**). The calculated (MNDO) C–C distances in all four of these dianions are nearly the same: the C_1–C_2 lengths correspond to double bonds and the C_2–C_3 bonds are longer.

The hypothetical dianions do not model the energies of the corresponding dilithium derivatives accurately. As indicated by qualitative considerations and MNDO calculations (heats of formation given under the formulae), the most stable $C_3H_4^{2-}$ isomer clearly should be the allene dianion[12] (**9**), a linear, planar D_{2h} species with rather short C–C bonds. Allylic resonance in (**9**) distributes the π negative charge to C-1 and C-3, the most favourable arrangement possible with respect to the anion at C-2. However, dilithium structures, CH_2CLiCH_2Li,[12] based on the dianion (**9**) are *not* as stable (MNDO) as (**3**) or (**4**). This is consistent with the experimental observation that CH_2CLiCH_2Li species are not formed by further lithiation of allyl-lithium. Moreover, both *trans*-dianions, (**7**) and (**8**), are slightly more stable (MNDO) than the corresponding *cis*-isomers, (**2**) and (**6**), respectively, but the energies of the *cis* doubly bridged dilithium derivatives, (**3**) and (**4**), are much lower than the isomeric structures based on (**7**) or (**8**). 'Dianion' is a misleading designation for such a dilithium species. While kinetic factors also may be involved, the dilithiation products appear to be determined by the stabilities of the dilithiated compounds rather than the dianions.

In solution, lithium compounds generally are associated and solvated.[4] Nevertheless, energies from theoretical calculations (which pertain to isolated species) often mirror solution thermochemistry and chemical behaviour.[2,3,13] The lithiation of propene can be modelled by equations (1), first step, and (2), second step.[2,3,14] The 3-21G//3-21G heats of reaction[15] show, in general agreement with the experimental observations,[1] the first step to be somewhat more exothermic than the second. If equations (1) and (2) are recalculated for the corresponding anions, the first is still exothermic (−17.6 kcal mol^{-1}, MNDO) since the allyl anion is more stable than

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† 1 a.u. = 2625.42 J; 1 cal = 4.184 J.

the methyl anion, but equation (2) for the anions is strongly endothermic (+135.2 kcal mol^{-1}).

$$\underset{}{CH_2{=}CHCH_3} + CH_3Li \rightarrow \underset{\text{allyl-lithium}^{15}}{CH_2CHCH_2Li} \quad -18.0\text{ kcal mol}^{-1} \quad (1)$$

$$\underset{\text{allyl-lithium}^{15}}{CH_2CHCH_2Li} + CH_3Li \rightarrow \underset{(3)}{CH_2CHCHLi_2} \quad -15.4\text{ kcal mol}^{-1} \quad (2)$$

Symmetrical double bridging of lithium should also be important in synthetically useful polylithium reagents involving heteroatoms.[16]

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Added in proof: An independent study of dilithiated propene at the 3-21G//3-21G level has also concluded (3) to be the global minimum. (J. Klein, D. Kost, W. G. Schriver, and A. Streitwieser, Jr., *Proc. Natl. Acad. Sci. USA*, in the press).

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