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Preliminary communication

DOUBLE LITHIUM BRIDGING: THE STRUCTURE OF 1,4-DILITHIO-1,4-DIPHENYL-*cis*-2-BUTENE

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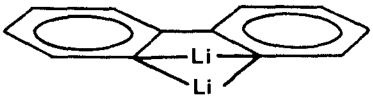
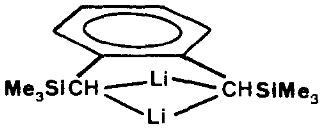
Summary

The title compound is shown by both X-ray analysis (Fig. 2) and MNDO calculations (4) to prefer a doubly lithium bridged *cis* structure (C_2 rather than C_{2v}) in contrast to the *trans* geometry expected for the isolated 1,4-diphenylbutadiene dianion.

Organic "polyanions", often useful synthetic intermediates [1] are only likely to exist when stabilized by metallic counterions [2]. These species are better regarded as ion clusters held together strongly by a combination of electrostatic and multicentre covalent bonding [2,3]. In particular, the energetic advantages of doubly bridged geometries, which have lithium or other alkali metal cations on opposite faces of a "carbodianion" framework, have been demonstrated by theoretical and reactivity studies [2—6]. X-ray structures, e.g. on *o,o'*-dilithiobiphenyl (1) [7], have confirmed calculational predictions [4]. An α,α'-dilithio-*o*-xylene derivative (2)* is also known exper-



(1), C_{2v}



(2), C_{2v}

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*The X-ray structure of a relative of 2 (with phenyl in place of $SiMe_3$ groups) is unsymmetrical (G. Boche et al., ref. 17).

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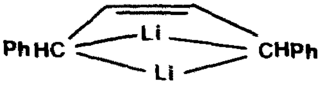
imentally to have a symmetrical doubly bridged structure [8]. We now show that a substituted "butadiene dianion" [9,10], 1,4-dilithio-1,4-diphenyl-*cis*-2-butene (**3**) is similar, but has interesting, new geometrical features.



(**3**), C_2

Metallation of a mixture of *cis*- and *trans*-1,4-diphenylbut-2-ene with two equivalents of n-butyllithium/TMEDA in hexane at room temperature yields dark green crystals of a single compound in 90% yield. Quench reactions show this to be a salt of the 1,4-diphenylbutadiene dianion. The corresponding radical anion has been assumed to prefer the *trans* structure [11], but the dianion geometry has not been established before. Our MNDO [12] calculations on the dianion indicate the *trans* geometry to be 3.1 kcal mol^{-1} more stable than the *cis*. As found before [13], the charges derived experimentally from ^{13}C chemical shifts of the dilithium compound are in good agreement with those computed from the MNDO π electron populations for the *cis* and *trans* dianions (the calculated charges as well as the C—C bond lengths are practically identical). The MNDO C—C bond lengths alternate more strongly in the dianions than in the dilithium compounds but in all cases the central bond in the butadiene dianion moiety is shortest. This is expected from simple MO considerations and from our ab initio calculations on the parent systems [10].

However, the stereochemical preference of the dilithium compound is the reverse of that found for the dianion. The MNDO structures of the more stable *cis*-**4** as well as the *trans*-**5** forms are shown in Fig. 1. The *trans* structure (**5**) is analogous to that of benzyllithium [4] with no interaction between the two lithium atoms. The *cis* isomer (**4**) has the now familiar [2—8] doubly bridged structure, but the lithiums are less symmetrically situated than in **1** or **2** (local C_2 instead of C_{2v})*. *Cis*-**4** is calculated (MNDO) to be 8.2 kcal mol^{-1} more stable than *trans*-**5**, a change of 11.3 kcal mol^{-1} in relative stabilities on going from the dianions to the dilithium compounds.

The X-ray crystal structure** of the bis(tetramethylethylenediamine) (TMEDA) complex (Fig. 2) is fully in accord. The central *cis*-butene moiety is disordered, half of the molecules being in the orientation shown in Fig. 2 and the other half having the two central carbons on the opposite side (a

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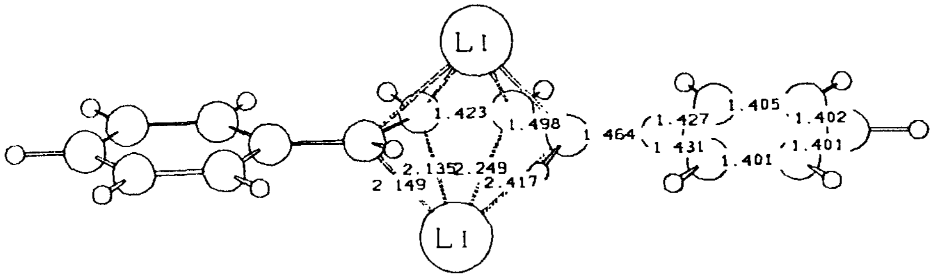
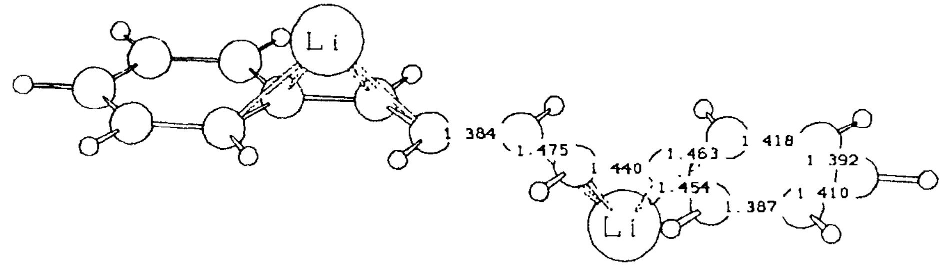
*If C_{2v} symmetry is imposed, the resulting *cis* structure is only 0.9 kcal mol^{-1} less stable than **4**.

***Crystal data for* **4**: $C_{28}H_{46}N_4Li_2$, $M = 452.582$, monoclinic, space group $P2_1/n$, a 8.255(3), b 8.889(3), c 19.004(6) Å, β 96.26(3)°, V 1365 Å^3, $Z = 2$ (one half molecule at a crystallographic inversion centre), D_c 1.084 g/cm^3 (113 K). Graphite monochromated Mo-K_α radiation, λ 0.71069 Å. The specimen was mounted in a capillary under argon. The 12874 reflection profiles which had been measured in the range $2° < \theta < 25°$ at 113 K were averaged to a unique set of 2398 structure factors. The structure was solved by direct methods (MULTAN 76) [15] and refined by least squares methods (X-RAY 76) [16] with weights $1/\sigma^2(F_o^2)$ and anisotropic thermal parameters for all atoms including the hydrogen atoms. R values, based on 2465 reflections with $|F_o|^2 > 2\sigma(F_o^2)$: $R(F^2) = 0.076$, $R_w(F^2) = 0.066$.
The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



(4), C_2



(5), C_2

Fig. 1. MNDO structures for *cis*-4 and *trans*-5 1,4-dilithio-1,4-diphenyl-2-butene. Note the agreement of 4, including the off-center locations of the lithium atoms, with the X-ray structure (Fig. 2).

pseudo 6-ring). The lithium atoms occupy the same "twisted" doubly bridging positions indicated by the calculations (4). Each lithium prefers to interact with only three of the four carbon atoms of the butadiene anion moiety. There is thus remarkably good agreement between the MNDO geometry and the structure found in the crystal. Only the C(1)—C(2) bond lengths in the butadiene fragment differ significantly from those calculated, but the asymmetry found experimentally is probably an artifact caused by averaging over the static disorder in the benzyl groups with respect to the pseudosymmetry of the crystal packing. The experimental C—Li bond lengths are all longer than calculated, but this is due to a systematic error in the MNDO parametrization (C—Li bond lengths are too short). The calculations also did not include the ligands.

Only one of the TMEDA moieties can adopt the ideal orientation [15] in each of the disordered isomers. Thus, in Fig. 2 the lower TMEDA is optimally oriented, but the upper one is oriented to suit the other disordered form. This arises because the ligands associated with the disordered dianion are themselves not disordered.

The above results and those of the accompaning paper [10] confirm the importance of the doubly bridged dilithium unit in "dianion" chemistry and reaffirm the ability of metal counterions to control the stereochemistry of intermediates.

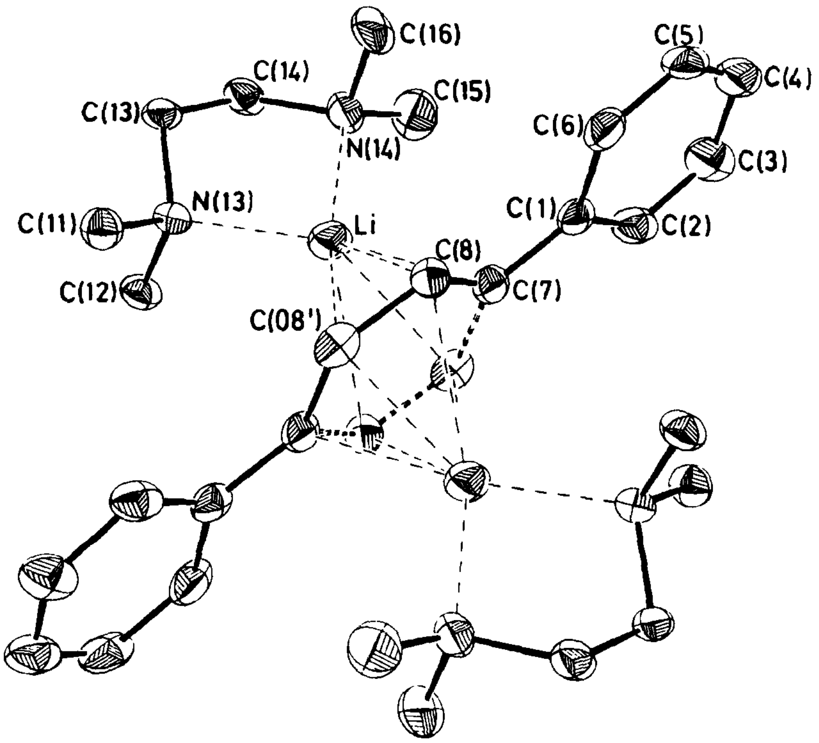


Fig. 2. The X-ray structure of 1,4-dilithio-1,4-diphenyl-*cis*-2-butene (2 TMEDA). The disorder in the CH=CH unit is shown.

The lithium placements in **3** deviate from the idealized C_{2v} symmetry exhibited by **1** and **2**, but only slightly. The benzo derivative of **3** appears to be closely related, but the structure is quite different [17]. A comprehensive discussion of the geometries of this dilithium derivative as well as **1**—**3** is given elsewhere [18].

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