The Influence of Carbanion Orbital Orientation and Charge Distribution on the Structures of Polylithium Compounds

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Symmetrical (C_{2v}) double bridging, commonly exhibited by 1,4-dilithium compounds *e.g.* in (**1**) and (**2**), is not favoured in (**4**) and (**5**) since charge delocalization in the dianion, hybridization, and orbital orientation effects are more important than quadrupole-like electrostatic interactions (**3**).

Double bridging is predicted to be a common structural feature of polylithium compounds.[1—4] The first *X*-ray crystallographic examples of 1,4-dilithium bridging, (**1**)[5] and (**2**),[6] showed symmetrical (effectively C_{2v}) geometries in accord with simple electrostatic expectations.[2] Ion triplets comprised of dianions associated with two alkali metal cations favour cyclic arrangements (**3**) because of Coulomb attraction.[2] Double bridging can be considered to be the intramolecular equivalent of dimerization.[3,7]

However, two new *X*-ray structures deviate from expectations based on the simple electrostatic model (**3**).[2] The distortion towards C_2 symmetry found in (**4**)[8] is relatively minor, but the unsymmetrical structure found for (**5**)[9] is completely different. The latter finding is especially noteworthy since the dianion moieties of (**1**) and (**5**) are so similar.

Since MNDO calculations on unsolvated and solvated models reproduce the preferred structures of (**2**),[3] (**4**),[10] and (**5**)[9] remarkably well, underlying electronic effects must be responsible for the lower symmetries rather than ligand co-ordination or artifacts associated with the solid state. While these molecules participate to some extent in multicentre covalent bonding involving lithium valence orbitals,[10] an ionic model provides a simple rationalization of the differences in behaviour.

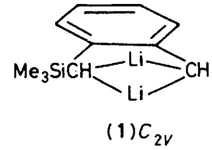
The decisive factors are the degree of localization or delocalization of the negative charges as well as the orientation (and hybridization) of the orbitals interacting with the lithium atoms, but these sometimes work at cross purposes. Which of the arrangements [generalized by (**6**)—(**9**)] is favoured depends upon the intervening group, G, and the substituents attached to the carbanion centres.

Ion triplet interactions (**3**) are best when the carbanions are localized or have a high negative charge density, and when the lone pair lobes have high s-character and are oriented towards the cations as in (**6**). As Streitwieser has pointed out,[2] this extends the effective centres of negative charge away from carbon and better electrostatic interactions result. Our calculations on doubly bridged 1,3-dilithiopropanes[4] illustrate this well. The geometry corresponding to (**6**) (G = CH_2) is about 17 kcal/mol more stable than conformation (**7**) with both carbanions in p-orbitals. The open (+ − + −) arrangement (**8**), which resembles that found in (**5**), is 15 kcal/mol higher in energy than (**6**) but is somewhat better than (**7**).

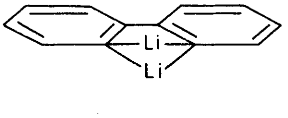
The strong preference of (**2**) for the symmetrical (C_{2v}) structure is due to a combination of factors all favouring this geometry. The localized sp^2 carbanion lobes are oriented, as in (**6**), toward lithium and the Coulombic interactions are particularly strong. The lithium valence orbitals also interact favourably with the aromatic π-system in this geometry.[3] Thus, electrostatic, hybridization, and orbital orientation effects are all favourable in (**2**).

When a conjugated π-system is involved [G in (**6**)—(**9**) is a double bond or an aromatic ring], a conflict with the electrostatic preference for conformation (**6**) develops. However, the dianion HOMO's in (**2**), (**4**), and (**5**) have antibonding π-character, and the conjugation energies favouring planar geometries are much reduced. This is illustrated by the model calculations on 1,4-dilithio-*cis*-but-2-ene;[10] the localized form (**6**, G = CH=CH) with the end CH_2 groups twisted 90° out of conjugation, is only about 7 kcal/mol less stable than (**7**, G = CH=CH) with a planar hydrocarbon moiety and C_{2v} symmetry. We thus expect a flatter potential energy surface for such π-systems.

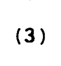
The preferred geometry depends on the degree of charge delocalization in each case. The phenyl substituents in (**4**) reduce the negative charge at the termini (C-1 and C-4) of the central butadiene dianion; the lithium atoms respond by moving in opposite directions so that each is more nearly associated with its own carbanion p-orbital (**9**). This is an example of what we have called 'electrostatic orbital localization',[11] which cannot occur in the symmetrical C_{2v} geometries. Energy lowering can be achieved when orbitals on individual atoms with relatively modest negative charge densities are



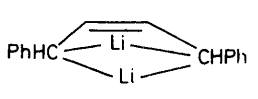
(**1**)C_{2v}



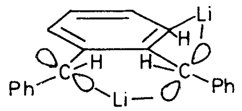
(**2**)C_{2v}



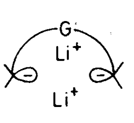
(**3**)



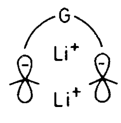
(**4**) C_2



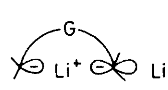
(**5**) C_1



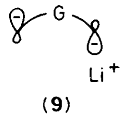
(**6**)



(**7**)



(**8**)



(**9**)

directed towards positively charged counterions. This changes the hybridization (more s character is introduced) and, if the interactions are strong enough, leads to alterations in geometry. The polymeric structure of allyl-lithium shows an arrangement analogous to (**9**).[12]

As the energy difference between the C_2 (**9**) and C_{2v} (**7**) arrangements for (**4**) is quite small (about 1 kcal/mol),[8] no discernible deviation of the dianion moiety from planarity is noted. Twisting or other distortions of the carbon skeleton are to be expected in cases when the energy differences are larger. Indeed, structural alterations in (**5**) are much more pronounced. Both (**5**) and the simplified calculational model, α,α′-dilithio-*o*-xylene, prefer unsymmetrical locations for the lithium atoms.[9] In the *o*-xylene dianion, the charge is delocalized to the aromatic ring,[13] and the two lithium cations are no longer stabilized effectively electrostatically by interacting with the two α-CH_2 groups either in C_{2v} (**7**) or C_2 (**9**) geometries. Specifically, the PhCH carbon atoms in (**5**) bear less charge than those in (**4**). Hence, only one lithium atom in (**5**) remains in a central position; the other prefers a benzyl-lithium-like[14] location since the Hückel π-charges on the ring are largest at the C-3 and C-6 positions.[15] As indicated in (**5**) and the *X*-ray structure,[9] the benzyl groups tilt to orient the 'carbanion' orbitals towards the lithium atoms; this also favours the open (**8**)-like arrangement.

Finally, $SiMe_3$ substituents, as in Lappert's compound (**1**), stabilize carbanions very effectively. Such groups redistribute the electrons in part by polarization.[16] Owing to the presence of a positive charge on the electropositive silicon atom, the adjacent carbanion centre becomes *more negative*. In (**1**), minus charge builds up on the two Me_3SiCH carbon atoms. The ^{13}C chemical shift of the benzylic carbon atoms of (**1**) in [$^2H_8$]tetrahydrofuran is 49.1 p.p.m. as compared to 68.5 p.p.m. in (**5**). Hence, the two lithium cations bridge the benzylic centres in (**1**) symmetrically because of better Coulomb interaction.

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