The Structure of an Aromatic 10π Electron 'Dianion': Dilithium Pentalenide

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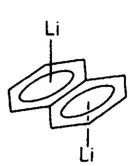
In agreement with the predictions of MNDO calculations, a crystal structure determination shows that the metal atoms in a dilithium pentalenide–dimethoxyethane complex bridge opposite faces of the 10π aromatic system; this arrangement (**5**) is favoured because each carbon atom in the delocalized dianion moiety has a lithium neighbour, the lithium cations 'communicate' electrostatically, and dipolar repulsion does not occur.

Hückel theory predicts that the pentalene dianion should be aromatic, like its 10π electron counterparts, naphthalene and the indenyl anion. This analogy led Katz and Rosenberger[1] to synthesize dilithium pentalenide by the direct dilithiation of dihydropentalene. We now report the structure of the dimethoxyethane (DME) complex of this compound, which can be prepared by a convenient procedure.[2]

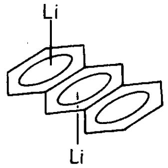
Experimental precedents do not allow a decision to be made about the expected structure. In dilithium naphthalenide (**1**)[3] and dilithium anthracenide (**2**)[4] the metal atoms are on different rings at opposite sides, but in dilithium acenaphthalenide (**3**)[5] both metal atoms are associated with the five membered ring. Although only in association with metal–metal bonding, a number of transition complexes of pentalene are known with both metals on the same side of the ligand *i.e.* (**4**).[6]

Part of our work on the principles which determine lithium structures are computations at appropriate theoretical levels.[7] In the present instance, MNDO calculations are quite suitable;[8] five structures (**5**)—(**9**) were examined. The first three of these (**5**)—(**7**) involve η^5 lithium bridging, and are more favourable than the edge-lithiated alternatives, (**8**) and (**9**). The lowest energy arrangement (**5**) has both lithium atoms bridging different rings on opposite faces; π-allyl nickel complexes of pentalene also prefer this arrangement.[6] The *syn* alternative (**7**), with lithium bridging different rings but on the same side of the molecule, is much less satisfactory electrostatically since the lithium-based dipoles are orientated in the same direction. The possibility (**6**) also has a favourable opposite-side lithium orientation, but is somewhat less stable than (**5**). All the carbon atoms in (**6**) share the π-delocalized negative charges, but do not have a lithium cation neighbour. In (**5**), the lithium ions 'communicate' by interacting electrostatically *via* the partially negatively charged central ring atoms.[7,9,10] The MNDO structure of (**5**) has been published;[2] this communication confirms those predictions experimentally.

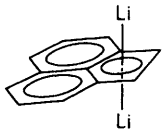
Dilithium pentalenide · 2-tetramethylethylenediamine,[2] could not be obtained in crystalline form suitable for *X*-ray analysis. Instead, dimetallation in DME at −30 °C gave white needles. *Crystal data:* Monoclinic, space group $P2_1/c$, $a = 8.447(3)$, $b = 14.537(8)$, $c = 7.883(4)$ Å, $\beta = 121.630°$, at *ca.* 120 K $Z = 2$. Intensities were collected from the cooled crystal to a resolution of $2\theta_{max.} = 60°$ (monochromatized Mo radiation.) The initial model was obtained with SHELXS-84,[11] developed by difference Fourier techniques and refined by least square methods;[12] 1572 reflections contributed to the refinement of 152 variables to give *R* 0.041.†



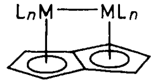
(**1**)



(**2**)



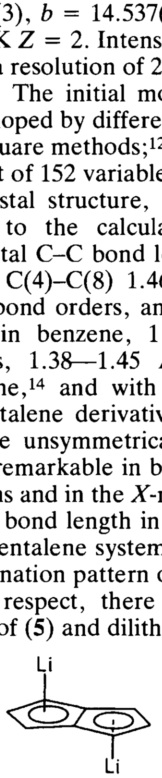
(**3**)



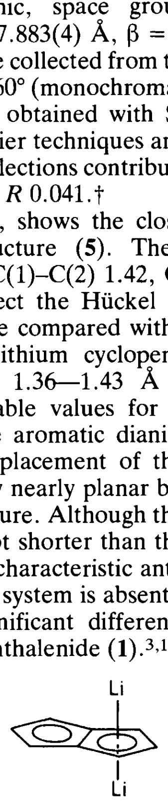
(**4**)

The crystal structure, Figure 1, shows the close overall similarity to the calculated structure (**5**). The average experimental C–C bond lengths, C(1)–C(2) 1.42, C(1)–C(4) 1.44, and C(4)–C(8) 1.46 Å reflect the Hückel molecular orbital π bond orders, and may be compared with the C–C distances in benzene, 1.40 Å, lithium cyclopentadienide derivatives, 1.38—1.45 Å,[13] the 1.36—1.43 Å range in naphthalene,[14] and with comparable values for transition metal–pentalene derivatives.[6] The aromatic dianionic ring, despite the unsymmetrical (C_{2h}) placement of the lithium atoms, is remarkable in being very nearly planar both in the calculations and in the *X*-ray structure. Although the average calculated bond length in (**5**) is not shorter than those in 8π electron pentalene systems,[15] the characteristic antiaromatic bond alternation pattern of the 8π system is absent.

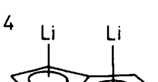
In this respect, there is a significant difference in the geometry of (**5**) and dilithium naphthalenide (**1**).[3,16] While in



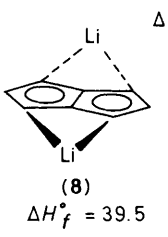
(**5**)
$\Delta H^\circ_f = 9.4$



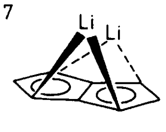
(**6**)
$\Delta H^\circ_f = 14.4$



(**7**)
$\Delta H^\circ_f = 30.7$



(**8**)
$\Delta H^\circ_f = 39.5$



(**9**)
$\Delta H^\circ_f = 43.5$

ΔH°_f values in kcal mol^{-1} are those predicted from MNDO calculations. 1 kcal = 4.184 kJ.

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† The atomic co-ordinates 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.

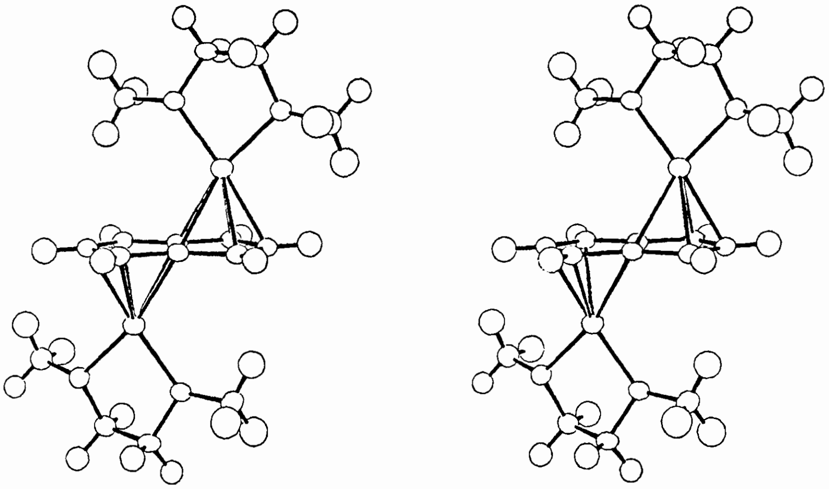

Figure 1. Stereoview of dilithium pentalenide–2(1,2-DME). The lithium atoms are slightly closer to C(1)—C(3) (average 2.22 Å) than to the bridge head carbons [C(4)–Li 2.31 Å]. The Li–O distances average 2.01 Å.

(**1**) the lithium atoms still favour similar different-ring, opposite-face placements, the naphthalene dianion system is 'warped' out of plane. This deformation can be convincingly attributed to unfavourable interactions in this 12π electron anti-aromatic system.[3,16] The repulsions of out-of-phase adjacent p-orbitals in 'antiaromatic' systems can be alleviated by bending; the strongly non-planar cyclopropenyl anion affords a good example.[17]

The *X*-ray structures of (**2**) and (**3**) can also be understood on the basis of the principles established in this paper. The lithium atoms in (**2**) are not symmetrically placed, *i.e.*, both are not on the end rings. Instead, one lithium is above the central ring and the second below an end ring. This permits favourable electrostatic 'communication' which is an extension of the ion multiplet arguments espoused by Streitwieser[9] and demonstrated by us in a number of symmetrically-bridged dilithium structures.[7,10,18] In (**3**), both lithium atoms are associated with the same cyclopentadienide ring because of its relatively large negative charge density.

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