The Structures of the Stereoisomeric 'Dilithium Semibullvalenides'†

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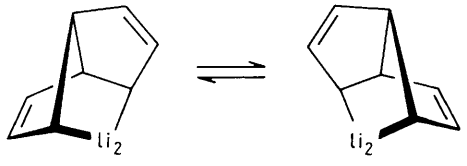
The two previously undefined 'dilithium semibullvalenides' are identified as the C_{2h} and D_2 diastereoisomers of bis-(bicyclo[3.3.0]octa-3,7-diene-2,6-diyl)tetralithium, the first structurally characterized pair of diastereoisomeric organolithium compounds.

We previously reported that lithium reduces dimethyl ether or tetrahydrofuran solutions of semibullvalene to 'dilithium semibullvalenide,' a mixture of two isomeric organolithium clusters, each isomer possessing (**1**) as a common structural element.[1]§ We also noted that reversible isomeric interconversion maximizes the mole fraction of the minor isomer at the lowest temperature (0.33 at −140 °C); this isomer becomes undetectable above −74 °C. The rate of interconversion is uniformly slow on the ^{13}C n.m.r. time-scale. A more rapid intra-isomer process was also characterized, and is reproduced in Scheme 1.



(**1**)

Scheme 1

Unexplained at the time was the observation of four ^6Li n.m.r. signals: δ (−140 °C; C_2D_6O) 1.139 (**a**) and 0.801 (**b**) for the major isomer and 0.605 (**a′**) and 0.332 p.p.m. (**b′**) for the minor one (1.144, 0.813, 0.614, and 0.337 p.p.m. at −154 °C; all ^6Li resonances downfield from 1 M aqueous LiCl at 27 °C). These, we now show, reveal yet a third equilibration process. More important, they contribute the fourth of five essential sets of structural data. Together, these five serve to define the structure of the isomers, the first structurally characterized pair of diastereoisomeric organolithium compounds that we know.[2]

The first three data sets had earlier demonstrated that the two clusters are isomeric, that they have identical bicyclo-[3.3.0]octadienediyl ligands, and that each possesses four chemically distinct and equally populated CH sites.[1] A molecular weight determination (Figure 1) provides the final data, and defines the composition to be dimeric, $Li_4(C_8H_8)_2$, up to the solubility limit (*ca.* 0.2 *F*).

The four CH sites of each isomer now demand that the two C_8H_8 ligands share a common C_2 axis. They also require a second two-fold symmetry operation, one that permutes the

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† Taken in part from the Ph.D. thesis of T.T.W., Cornell University, 1984.

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§ The deliberately ambiguous 'li' serves to indicate carbon–lithium covalency without specifying the full connectivity of the lithium atom or the size of the cluster.

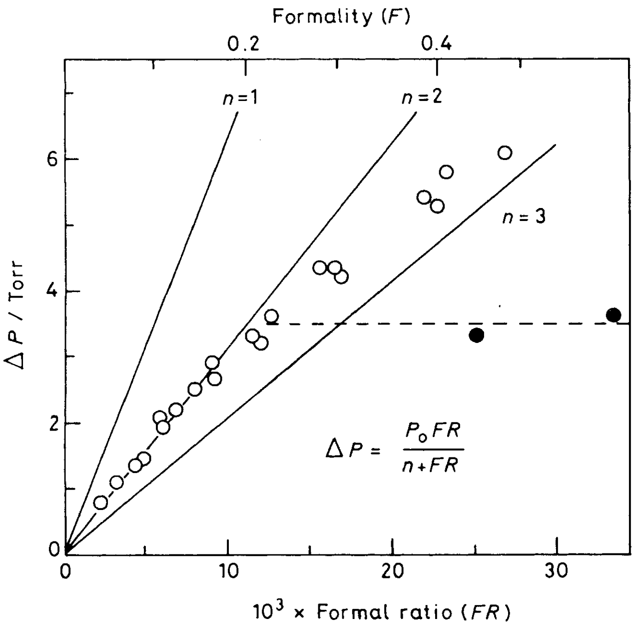
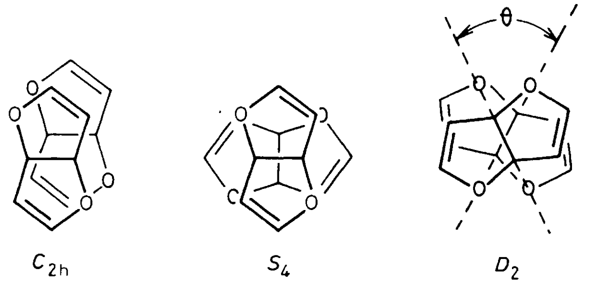


Figure 1. Dimethyl ether vapour pressure determination of dilithium semibullvalenide cluster size [n; P_0 (−29 °C) = 618 Torr[5]]. The formal ratio (FR) is the titrimetrically determined number of equivalents per mole of solvent; ○: vapour pressures of increasingly concentrated, ultimately supersaturated, homogeneous solutions;[6] ● vapour pressures of saturated solutions in equilibrium with freshly precipitated solute.

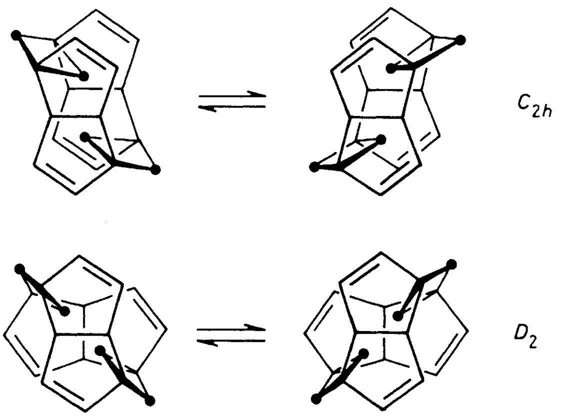


Scheme 2

two ligands and describes their mutual orientation.[3] The planar projection in Scheme 2 illustrates the three possibilities: C_{2h} or S_4 if the ligands are of opposite chirality, and D_2 if not. The open circles represent potential sites for C–Li bonding, as yet further undefined; the angle θ is also undefined.

We next assume that steric, if not also electronic, factors restrict C–Li bonding to the *endo* faces of the bicyclo[3.3.0]-octadienediyl ligands. The observation of two ^{6}Li n.m.r. signals for each of the isomers then requires either two or four lithium atoms to lie on a common symmetry element. More precisely, the S_4 hypothesis demands that all four lithium atoms be colinear with the S_4 axis. Such bonding is not easily compatible with the orbitals available either to Li^+ or to $C_8H_8^{2-}$, nor has it yet been encountered in any organolithium *X*-ray crystallographic analysis that we know. We therefore reject the S_4 hypothesis.

The four lithium atoms must then intersect the symmetry plane of the C_{2h} diastereoisomer and the equatorial C_2 axes of the D_2. These atoms are illustrated by closed circles in the representations in Scheme 3. The resulting 1,3-dilithiacyclobutane subunits are a common feature of organolithium cluster structures.[4]



Scheme 3

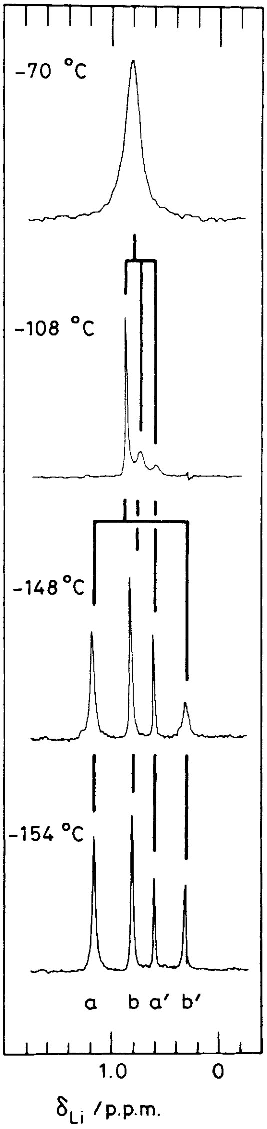


Figure 2. 44.17 MHz ^{6}Li n.m.r. spectra of the dilithium semibullvalenides in di[$^2H_3$]methyl ether at four temperatures.

A newly discovered equilibration process appears in the selective Li line broadening at −148 °C (Figure 2); only the **a** peak of the major diastereoisomer and the **b′** peak of the minor one participate. This process, necessarily an *inter*molecular one, retains the structural distinction between the C_{2h} and D_2 diastereoisomers. It also retains the distinction between internal and external lithium atoms within each of the diastereoisomers. The two *intra*molecular processes of Scheme 3, automerization of the achiral, *meso* C_{2h} diastereoisomer and racemization of the chiral, $(\pm)$-D_2, are probably more rapid than this intermolecular one.¶ If so, they too must conserve the same distinctions: the external lithium atoms must remain external, and the internal ones remain internal.

The higher temperature ^{6}Li spectra reveal a second intermolecular process: diastereoisomeric equilibration, one that is uniformly too slow to have been detected by line-broadening in ^{13}C n.m.r. spectra.[1] Other evidence[1,7] suggests that the free ligand, the bicyclo[3.3.0]octadienyl dianion, is again not an intermediate, but further mechanistic speculation would be premature.

More noteworthy is the persistence of the diastereoisomeric distinction, over a wide temperature range and despite the incursion of both intramolecular and intermolecular processes which might have destroyed it. This conclusion remains unaffected by the obvious limitations of our structural proposals; the major and minor diastereoisomers have not been identified nor have tightly held dimethyl ether ligands been located. The absence of the minor isomer at higher temperatures requires diastereoisomeric equilibration to be entropy-controlled, and it is difficult to imagine any source of entropy apart from the dimethyl ether solvent; the higher symmetry of the D_2 diastereoisomer is exactly cancelled by its enantiomeric entropy of mixing. It will be interesting to learn how these solution structures are altered, if at all, in the crystalline solid state.

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¶ This is certainly so for the minor isomer. Similar line broadening is observed in both the ^{6}Li and ^{13}C n.m.r. spectra at similar concentrations and temperatures. Differences in chemical shifts and resonant frequencies then require the intramolecular process (^{13}C line broadening) to proceed 10.1 times more rapidly than the intermolecular one (^{6}Li line broadening).

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