1,3-Dilithio-5,7-dimethyl-2,4,6,8-tetrathia-adamantane: Simultaneous Stabilization of Two Pyramidal Carbanionic Centres by a Single 3*d*-Orbital

By K. C. BANK and D. L. COFFEN*

(*Department of Chemistry, University of Colorado, Boulder, Colorado* 80302)

DESPITE the diffuseness and relatively high energy[1] of the 3*d*-orbitals of sulphur they stabilize carbanions generated by reaction of thioacetals[2] and orthothioformates[3] with strong bases. Studies with bridgehead systems[3,4] have demonstrated that trigonal hybridization of carbon is not a criterion for stabilization of these anions by the sulphur orbitals: moreover the π-overlap integral of a *d*-orbital with a pyramidal carbanion may be as high as $(\frac{2}{3})^{\frac{1}{2}}$ the d_{π}–p_{π} overlap integral.[5]

The π-molecular orbitals involved in thioacetal carbanions extend over the three-atom chain S–C–S, and if the longer chain S–C–S–C–S could be constructed in such a way that each atom could contribute one atomic orbital, it should be possible to form more extensive π-molecular orbitals of this type (see Figure 1).

Such a chain is embodied in the dimethyltetrathia-adamantane (I) synthesized by treating acetylacetaldehyde dimethyl acetal with hydrogen sulphide and hydrogen chloride in ethanol.[6] Treatment of this compound in tetrahydrofuran solution with a mixture of butyl-lithium and *NNN'N'*-tetramethylethylene diamine,[7] leads to a quantitative acid–base reaction to produce the doubly lithiated species (II); this was characterized in the following

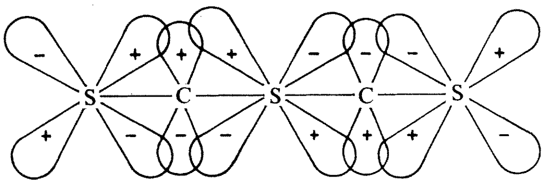
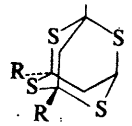


FIGURE 1.

way. Quenching with deuterium oxide gave compound (III), which was shown by mass and n.m.r. spectroscopy to be doubly deuteriated. The triplet at 4·66 p.p.m. arising from the bridgehead protons of compound (I) was absent completely in the n.m.r. spectrum of (III). Alkylation of the dilithio-derivative with methyl iodide gave tetramethyltetrathia-adamantane (IV), which was identical with an authentic sample.[6]

While its stability suggests that some measure of planairty is achieved in the bridgehead carbonium ion of adamantane,[8] it is highly unlikely that two bridgehead carbon atoms could simultaneously approach planarity in this ring system. Consequently, C-1 and C-3 in species (II) are pyramidal. The central sulphur atom is co-planar with the two (formal) carbon–lithium bonds, and thus only one of its *d*-orbitals, the one in this plane, can be involved in π-bonding. The manner in which this can occur is illustrated in Figure 2, in which the lithium atoms and *d*-orbitals of the two other participating sulphur atoms are omitted. The importance of *d*-orbital bonding in stabilizing species (II) is, of course, inversely dependent on the degree of covalency of the carbon–lithium bonds. While we have no information on this latter point, the possibility that the observed lithiation is a manifestation of some anique property of the adamantane bridgeheads can be excluded by the fact that adamantane is recovered free of deuterium after exposure to the conditions used to prepare compound (III).



(I) R = H

(II) R = Li 

(III) R = D

(IV) R = Me

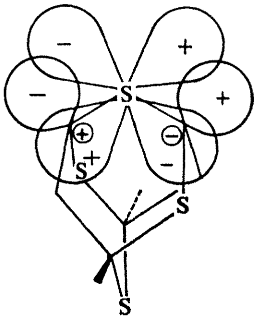


FIGURE 2.

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