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Preliminary communication

ON THE NATURE OF THE "CYCLOHEPTATRIENYL TRIANION": THE DECISIVE IMPORTANCE OF COUNTERION STABILIZATION IN POLYMETALLATED "CARBANION" SYSTEMS

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Summary

Like all other "polycarbanions", the planar (D_{7h}) cycloheptatrienyl "trianion" is much too high in energy to exist as a free entity; instead, stabilization by three lithium counterions results in a non-planar hydrocarbon skeleton and a favorable energy.

A large and increasing number of organic species polymetallated with lithium and other alkali metals are being reported [1]. These are commonly described in oversimplified terms as "dianions", "trianions", etc. [2].

The electrostatic repulsion in polyanions should render almost all of them unstable with respect to loss of one or more electrons in the gas phase. The magnitude of this repulsion (typically 5—10 eV for a dianion) should also make most polyanions unstable in condensed phases in the absence of stabilizing countercations. The coulombic attraction in ion multiplets is, however, stronger than classical covalent bonds, and is therefore likely to be instrumental in determining the behavior of "polyanions" in experimental systems.

When π systems are involved, Hückel and related theories have been used to rationalize the stabilities of various "polyanions" [3,4]. Such treatments assume planarity or near-planarity of the carbanionic moieties. While some insights undoubtedly can be obtained in this manner, we wish to demonstrate that such treatments overemphasize π effects and even may be misleading. Instead, the role of the counterions should be considered specifically as the very strong Coulombic interactions may be behavior-determining. We wish to stress that so-called "polyanions" are better regarded as ion multiplets or as polar organometallic derivatives [5].

The example chosen here for illustration is $C_7H_7Li_3$, an intriguing "black

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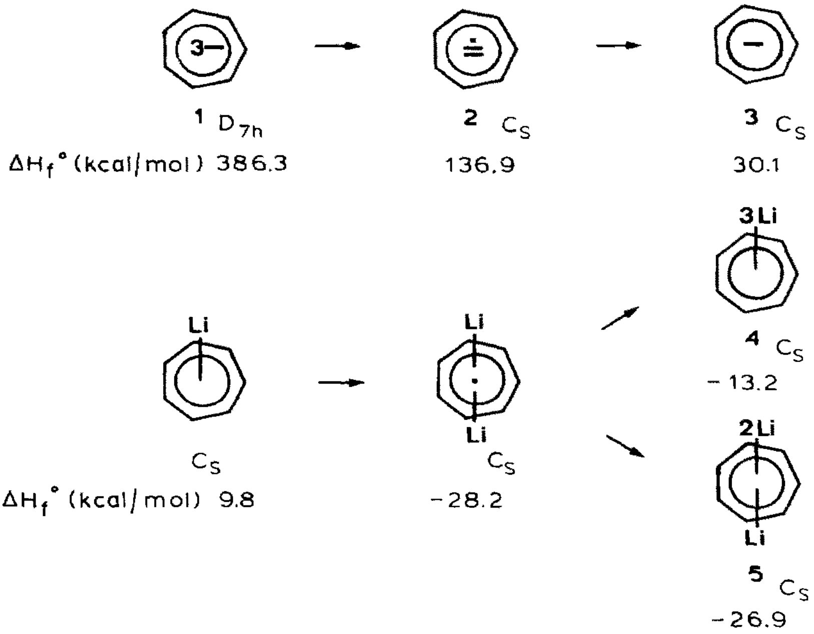
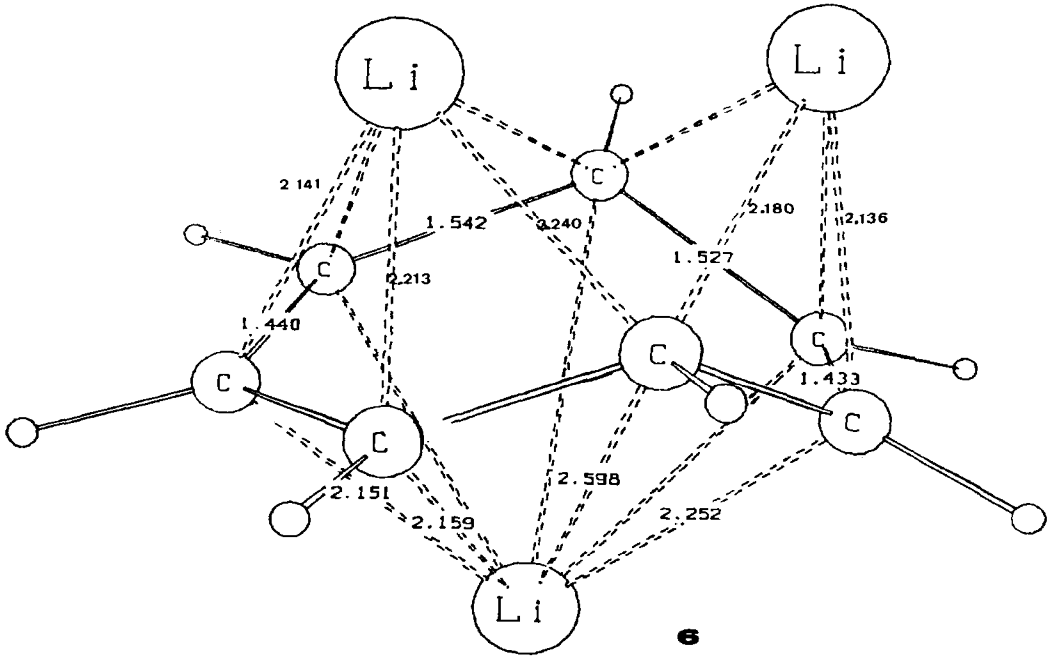
precipitate" discovered by Bates et al. [6]. His group was able to prepare a species, formulated as the "cycloheptatrienyl trianion" (1) from cyclic and from acyclic precursors. Both ^1H and ^{13}C NMR (one line each) and quench reactions (trideutero and triethyl products) were used to characterize 1. The related dianion radical (2) gave an ESR spectrum; other groups [7], including our own [8], have made similar observations.



Bates et al. [6] termed 1 to be "the third member in the series of 10 π aromatic anions that begins with cyclononatetraenyl anion and cyclooctatetraene dianion . . .". Hückel MO theory (modified to consider the resonance energy per atom) has been used to rationalize the preparation of this species [3]. While this treatment may help to organize a number of observations, we feel that the simplifications are too drastic to provide any realistic description of multiply charged species.

In the first place, formal fulfilment of Hückel's $4n+2$ rule does not ensure a relatively low energy: the value of n is critical. Thus, the last four electrons in 1 occupy degenerate antibonding molecular orbitals. That this is a very unhappy arrangement, is shown by the results of MNDO calculations on the ficticious π trianion, 1. The least unfavorable geometry is found to have planar, D_{7h} symmetry in agreement with qualitative expectations. However, the C—C bond length, 1.475 Å, too long for an "aromatic" system, indicates considerable antibonding character. Indeed, ten (all five π and five σ) of the 19 MOs have positive eigenvalues and are unbound! The large positive MNDO heat of formation of 1, ΔH_f° 386.3 kcal mol^{-1} is further dramatic evidence demonstrating how unlikely such multiply negatively charged species really are. The MNDO heat of formation of the cycloheptatrienyl anion (3, C_{2v}) is only 30.1 kcal mol^{-1} [10]. Thus, the loss of two electrons from $C_7H_7^{3-}$ should be exothermic by hundreds of kcal mol^{-1} ! Such ionizations of isolated species are expected to be very fast.

Indeed, no polycarbanion has ever been observed in the gas phase [9,11]. The electrostatic repulsion of two negative charges is simply too great; as in the above case, the second extra electron is not bound and will dissociate. Since most monocarbanions have relatively modest electron affinities [9] the binding of a second electron is out of the question. To put the matter bluntly, "dicarbanions" or higher multiply charged species are not likely to exist as



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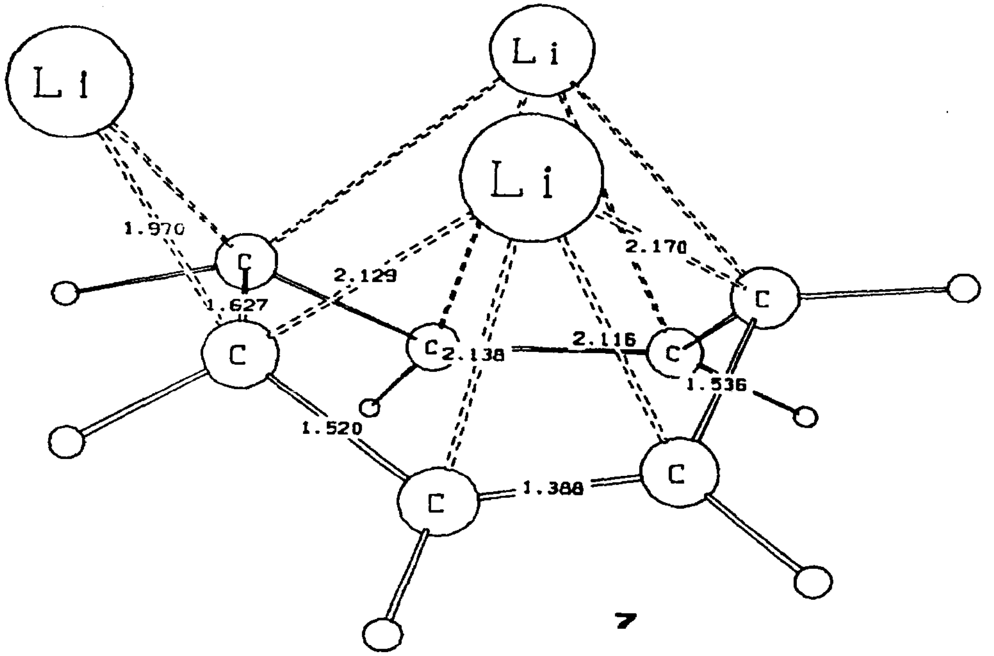

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Fig. 1. MNDO optimized structures of $C_7H_7Li_3$.

isolated entities. Carbanions, in general, are not effectively solvated by ethers or by similar solvents. They derive their stability predominantly from interactions with the counterions. These interactions are decisive, and should not be overlooked in considering the nature of such species.

Thus, MNDO calculations on $C_7H_7Li_3$ reveal a very different situation than do those on 1. We have considered the two most reasonable placements of the metallic counterions, all three above the ring (4) and two lithiums above and one below (5). In contrast to 1, both 4 and 5 exhibit markedly non-planar structures and all occupied MOs are bound.

The C—C bond lengths are quite different, and correspond to the formulations 6 and 7, respectively (see Fig. 1). The bond distances as well as the molecular orbitals indicate that 5 can be considered to be a derivative of the more or less localized trianion, 7, while 6 can be represented as a juxtaposition of allyl anion and butadiene "dianion" moieties. Both 4 and 5, in dramatic contrast to 1 have negative heats of formation —13.2 (4) and —26.9 kcal mol^{-1} (5). Thus, when the counterions are present, the energies are quite reasonable thermodynamically. Since 5 is considerably more stable than 4, we propose the former to be the structure of Bates' "cycloheptatrienyl trianion". Although we have not calculated the barrier, 5 is likely to be fluxional. Modest activation energy should result in equivalence of all the carbon and all the hydrogen atoms.

Treatments of "polyanions" have fundamental flaws: such species are inherently unlikely. It is better to consider the metallated species specifically.

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