

The Azulene Dianion: a Stable Paratropic Species

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An n.m.r. study of the reaction between azulene and lithium metal shows the initial formation of a doubly-charged dimer and then its gradual transformation into the antiaromatic azulene dianion.

In order to increase our understanding of ion-pairing and counter-ion effects in multi-charged systems we have made a reinvestigation of the reaction between azulene (**1**) and lithium metal in [²H₈]tetrahydrofuran. The main reason for this n.m.r. study is the discrepancy noticed when one compares earlier results from proton and lithium-7 n.m.r. studies.¹ A proton n.m.r. spectrum assigned to the formation of a dilithium compound has been reported but, contrary to the expectations of a $4n\pi$ -electron system, the proton signals were reported to be only slightly shifted upfield relative to the signals of azulene.^{1a} These shift changes are of a magnitude that could be predicted from charge considerations alone, and the observed shifts are characteristic for a diatropic anion system.² However, since then the lithium-7 shift of the two-electron reduction product was reported and the chemical shift [$\delta +2.05$ p.p.m., tetrahydrofuran (THF)] is quite similar to those observed for other paratropic anions in this medium.^{1b}

By using multinuclei n.m.r. facilities we were able to follow the reaction between azulene and lithium metal in [²H₈]THF in a tube sealed after three freeze-pump-thaw cycles. Azulene rapidly converts into a diamagnetic species; this reaction is accompanied by a decolourization of the blue solution. The

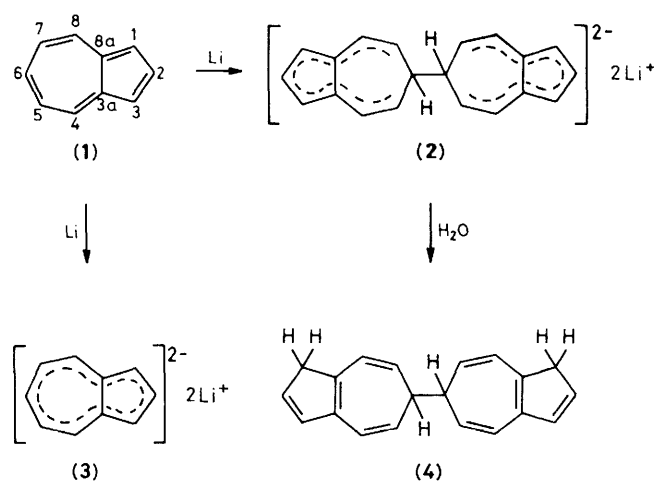
product formed probably has the same structure as that reported in the earlier proton n.m.r. investigation.^{1a} Hence, we could identify the same proton signals, except the one from the 6-H proton which did not appear at δ 5.8 but at δ 2.5. The assignment was confirmed by integration and by the coupling pattern. The corresponding ¹³C spectrum showed signals at frequencies that could be expected for a monoanion except for the C-6 carbon signal which was detected at extremely high field.

This high-field position of C-6, combined with a one-bond ¹³C-¹H coupling of 123 Hz, is only compatible with an sp³ carbon atom. Further information could be obtained by comparing this carbon spectrum with a spectrum using sodium as counter-ion. The data clearly reveal a redistribution of charge towards the seven-membered ring when using a larger, less π -charge-polarizing cation (such an observation had earlier been made for indenyl and fluorenyl anions³). However, no chemical shift change is observed for the C-6 carbon atom, a fact that supports the assumption that this carbon atom is not part of the delocalized system. The immediate appearance of a well resolved spectrum also indicates that the electron exchange is slow between the radical anion and this

Table 1. Proton and carbon-13 chemical shifts for compounds (1), (2), and (3).^a Coupling constants (J/Hz) are given in parentheses.

		Solvent	1,3	2	Position 3a,8a	4,8	5,7	6	δ_{av}^{\dagger}	ref.
¹ H	(1)	cyclohexane	7.3	7.9		8.2	7.0	7.4	7.5	1a
	(2)	[² H ₈]THF	5.78	5.78		6.58	5.03	2.54	5.4	
	(3)	[² H ₈]THF	4.27 d (2)	4.84 t (2)		2.66 d (10)	3.47 q (8, 10) (7)	0.77 (152)	3.3	
¹³ C	(1)	CDCl ₃	118.1 (168) ^b	136.9 (163)	140.2	136.4 (152)	122.6 (156)	136.9 (152)	130.8	7a 7b
	(2)	THF	104.6 (159)	105.3 (157)	121.4	127.8 (146)	117.6 (154)	43.8 (123)		
	(2) (Na ⁺)	THF	105.0	106.9	122.2	128.1	114.8	44.0		
	(3)	THF	110.6 (155)	100.5 (162)	123.5	99.2 (155)	133.7 (140)	67.9 (151)	110.2	
	q_{π}^c		1.10 (1)	0.98 (3)	1.01 (2)	0.88 (1.30)	1.05 (1.01)	0.95 (1.39)		8 1a

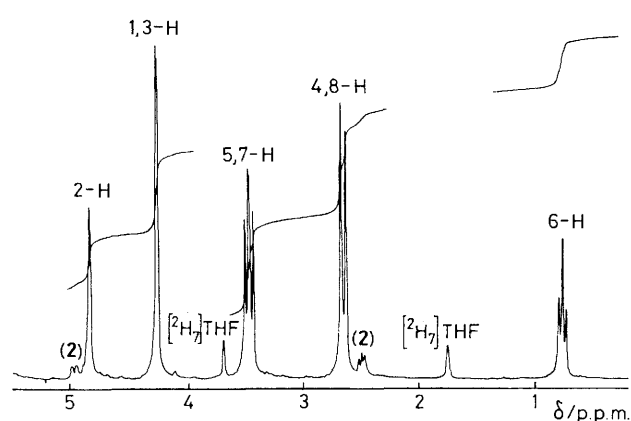
^a The n.m.r. spectra were obtained by using a Bruker WM-250 multinuclei Fourier transform spectrometer. Typical anion solutions were approximately 0.2 M, and the probe temperature was 25 °C. The chemical shifts are with reference to tetramethylsilane. For the carbon-13 measurements a small amount of cyclohexane was added to the carbanion solution as an internal reference using $\delta(\text{SiMe}_4) = \delta(\text{cyclohexane}) + 27.7$ p.p.m. ^b One bond ¹³C-¹H coupling constants. ^c Hückel π -charges.

**Scheme 1**

species.⁴ A significant change in molecular structure relative to that of the radical anion is thus likely.

Further structural information was obtained by quenching the THF solution with water. A single product was afforded, (4), the 1,1'-dihydro-derivative of (2), whose ¹H n.m.r. spectrum consisted of two singlets [δ 2.06 and 3.33 (H-6, H-1)], two doublets [δ 5.16 and 5.27 (J 9 Hz, H-2, H-3)], and one multiplet [δ 6.54 (H-4, H-5, H-7, H-8)].[†] Furthermore, titration resulted in a species having only one single charge per azulene unit, thus supporting the dianion dimer structure (2) (Scheme 1). The lithium-7 signal of this species appeared at $\delta -6.25$ p.p.m. which is similar to that found for cyclopentadienyl-lithium and indenyl-lithium under similar conditions.^{5‡}

Prolonged metal contact in an ultrasonic bath resulted in the appearance of a new set of peaks in the ¹H and ¹³C n.m.r.

**Figure 1.** 250.13 MHz ¹H N.m.r. spectrum of the lithium dianion of azulene (3) in [²H₈]tetrahydrofuran. Residual signals are due to the doubly charged dimer (2).

spectra. All protons absorb substantially upfield from the frequencies expected on the basis of charge effects alone. A chemical shift:charge ratio of 21 p.p.m. per e⁻ is almost twice that empirically found in planar conjugated systems.² In the ¹³C spectrum the most noticeable change relative to the spectrum of (2) is the shift of the C-6 resonance to lower field. The indicated change in the composition of the anions was accompanied in the ⁷Li n.m.r. spectrum by a continuous shift change to lower field reaching $\delta +2.59$ p.p.m. at the end of the reduction.[‡] Only one lithium signal was observed at any composition of the anion mixture. This indicates a fast Li exchange within and between the species. These observations, combined with the result from a titration after quenching with water, confirmed the doubly charged species (3). All shift data and the coupling constants are given in Table 1 and a representative ¹H n.m.r. spectrum of (3) is shown in Figure 1.

The ⁷Li n.m.r. shift and the extreme high-field ¹H shifts support the existence of an induced paramagnetic ring current in (3). Any estimation of the relative magnitudes of the paramagnetic ring currents at individual positions seems rather meaningless, since C-H bond polarization due to variable cationic fields will partly mask these contributions.^{3b,c} The carbon shift:charge ratio of 103 p.p.m. per e⁻ is somewhat low compared with the most commonly quoted value,

[†] The ¹³C chemical shifts (δ , CDCl₃) of the quenching product (4) are 42.2 (d), 43.9 (t), 120.1 (d), 122.2 (d), 123.6 (d), 124.7 (d), 132.0 (d), 134.8 (d), 144.0 (s), and 144.4 p.p.m. (s).

[‡] The ⁷Li resonances are with reference to external aqueous 1.0 M LiCl, where a positive sign denotes a downfield shift. The earlier reported ⁷Li chemical shift for (3) ($\delta +2.05$ p.p.m.)^{1b} is comparable with the present shift ($\delta +2.59$ p.p.m.) after magnetic susceptibility corrections.

160 p.p.m. per e^- , but deviations are frequently reported, especially for paratropic systems.⁶ Deviations from planarity relative to the parent hydrocarbon could be one explanation of this inconsistency. From Table 1 it can also be seen that an overall correlation exists with the Hückel charge densities. The most charged positions are (in order) C-6, C-4, C-2, and C-1. The stability of the dianion (**3**) is remarkable for a charged paratropic species. The solution can be kept for weeks without change in a sealed n.m.r. tube. The experiment could be conducted in dimethoxyethane but the solubility of (**3**) is limited in this solvent. Reoxidation by dry oxygen at any stage of the reduction affords azulene (**1**) as the sole product.

The initial reduction process is quite similar to that suggested for the reduction of 1,1-diphenylethylene.⁹ The radical anions which are formed combine reversibly to yield initially the dimeric dianion. In our case, the reduction proceeds further, most likely by disproportionation, to yield the stable paratropic azulene dianion.

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References

- 1 (a) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 1963, **41**, 966; (b) R. H. Cox, H. W. Terry, Jr., and L. W. Harrison, *Tetrahedron Lett.*, 1971, **50**, 4815.
- 2 D. H. O'Brien, in 'Comprehensive Carbanion Chemistry,' eds. E. Buncl and T. Durst, Elsevier, New York, 1980, p. 271.
- 3 (a) D. H. O'Brien, C. R. Russel, and A. J. Hart, *J. Am. Chem. Soc.*, 1979, **101**, 633; (b) C. Gooijer and N. H. Velthorst, *Org. Magn. Reson.*, 1979, **12**, 684; (c) U. Edlund, *Org. Magn. Reson.*, 1979, **12**, 661; (d) H. W. Vos, C. MacLean, and N. H. Velthorst, *J. Chem. Soc., Faraday Trans. 2*, 1976, 63; (e) J. Van der Giessen, C. Gooijer, C. MacLean, and N. H. Velthorst, *Chem. Phys. Lett.*, 1978, **55**, 33.
- 4 J. F. M. Oth, K. Müllen, H. Königshofen, J. Wassen, and E. Vogel, *Helv. Chim. Acta*, 1974, **57**, 2387.
- 5 R. H. Cox, H. W. Terry, Jr., and L. W. Harrison, *J. Am. Chem. Soc.*, 1971, **93**, 3297.
- 6 K. Müllen, *Helv. Chim. Acta*, 1978, **61**, 1296; H. Baumann and H. Olsen, *ibid.*, 1980, **63**, 2202.
- 7 (a) S. Braun and J. Kinkeldei, *Tetrahedron*, 1977, **33**, 1827; (b) S. Braun, J. Kinkeldei, and L. Walther, *Org. Magn. Reson.*, 1980, **14**, 466.
- 8 R. Pariser, *J. Chem. Phys.*, 1949, **25**, 1112.
- 9 J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168.