The Pentalene Radical Anion

Dieter Wilhelm,[a] John L. Courtneidge,[b] Timothy Clark,[a] and Alwyn G. Davies[b]

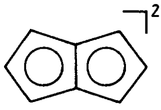
[a] *Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany*

[b] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.*

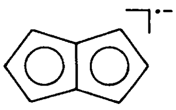
The title radical anion has been prepared for the first time by photolysis of a pentalene dianion dilithium salt.

The sensitivity and selectivity of the e.s.r. technique makes it possible to observe the spectra of radical ions of hydrocarbons which cannot themselves be isolated. In a number of cases in which the neutral hydrocarbon is not stable, however, the dianions are readily accessible.[1—3] The corresponding radical anions may then be observed by chemical oxidation of the dianion[4,5] or even in thermal equilibria.[6,7] We now report the photochemical oxidation of the pentalene dianion[3] to give the hitherto unknown unsubstituted pentalene radical anion.[8,9]

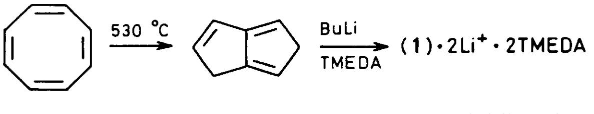
The pentalene dianion (**1**) can be prepared conveniently as the 2,5-diaza-2,5-dimethylhexane (TMEDA) complex of its dilithium salt by direct metallation of the mixture obtained by pyrolysis of cyclo-octatetraene at 530 °C[10] with a 1 : 1 mixture of Bu^{n}Li–TMEDA. The TMEDA complex of the dilithium salt of (**1**) is the only hexane-insoluble product, and can be isolated by filtration [equation (1)].



(1)



(2)



(1)

When (**1**)·2Li$^+$·2TMEDA is dissolved in dry tetrahydrofuran (THF) and photolysed at −48 °C in the e.s.r. cavity the spectrum shown in Figure 1(a) is observed. Addition of dry 12-crown-4 removes the lithium coupling, yielding the spectrum shown in Figure 1(b). Both spectra disappear on shuttering the light. The observed coupling constants [7.8 G (4H)† and 0.9 G (2H)] are in agreement with those [−7.37 G (4H) and +1.74 G (2H)] calculated[8] for (**2**) using the McLachlan equation. The lithium coupling increases, as

---

† 1 G = 10^{-4} T.

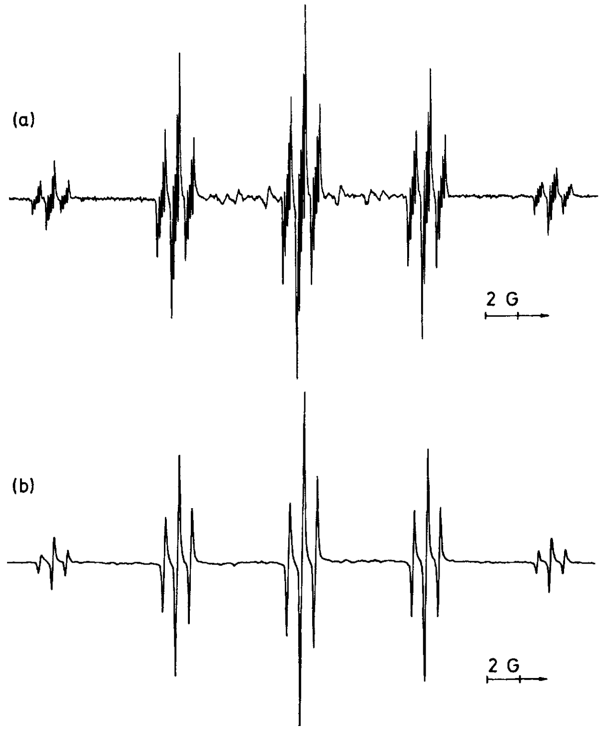
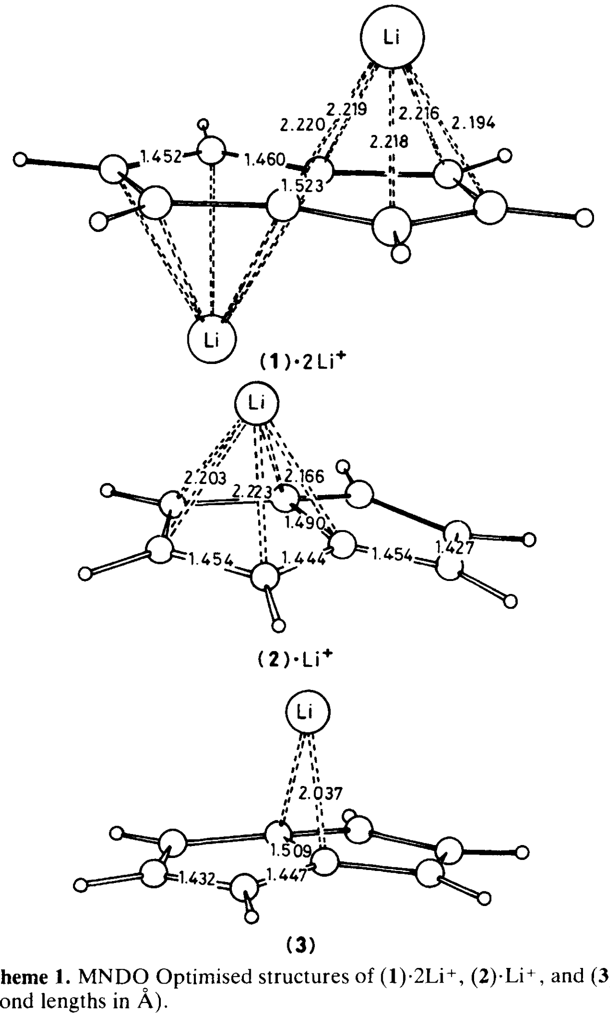


Figure 1. E.s.r. spectra of (**2**)·Li$^+$: (a) in THF at −48 °C; (b) on addition of 12-crown-4.



Scheme 1. MNDO Optimised structures of (**1**)·2Li$^+$, (**2**)·Li$^+$, and (**3**) (bond lengths in Å).

Table 1. E.s.r. spectral data for (**2**) (coupling constants in G).

Solvent	Temp. (°C)	*a*(4H)	*a*(2H)	*a*(Li)	*g*-Value
THF	25	7.76	0.95	0.27	2.00267
THF	−48	7.80	0.90	0.17	2.00267
THF–TMEDA	17	7.90	0.85	0.50	
THF–12-crown-4	22	7.73	0.83		2.00268
THF–12-crown-4	−47	7.73	0.83		2.00269

expected,[11] on warming but also on addition of excess of TMEDA (see Table 1).

The oxidation of (**1**)·2Li$^+$·2TMEDA, which could not be achieved electrochemically,[8] is similar to the photochemical generation of the cyclopentadienyl radical from cyclopentadienyl-lithium[12] and of the fulvalene radical anion from the sodium salt of the dianion.[4] This behaviour may be related to a common structural feature. MNDO Calculations[13] indeed suggest that (**1**)·2Li$^+$ has a doubly pentahapto structure, analogous to that of cyclopentadienyl-lithium (Scheme 1).[14] The calculated structure for (**2**)·Li$^+$ is that obtained by removal of one lithium atom from (**1**)·2Li$^+$. The observed equivalence of the hydrogen atoms can be brought about by a fast isomerisation *via* the C_{2v} structure (**3**), which is calculated to be 37.2 kJ mol^{-1} higher in energy than (**2**)·Li$^+$. This barrier will be substantially reduced by solvation.

We thank Dipl. Chem. I. Löffler for assistance with the pyrolysis experiments and Professor P. v. R. Schleyer for his interest. This work was supported by the Deutsche Forschungsgemeinschaft, the S.E.R.C., and by the award of a N.A.T.O. travel grant.

Received, 2nd April 1984; Com. 464

References

1 T. Clark and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1976, 798.

2 C. LeVanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela, and R. L. Collins, *J. Am. Chem. Soc.*, 1976, **98**, 3181.

3 T. J. Katz, *J. Am. Chem. Soc.*, 1960, **82**, 3784, 3785; T. J. Katz and M. Rosenberger, *ibid.*, 1962, **84**, 867.

4 A. G. Davies, J. R. M. Giles, and J. Lusztyk, *J. Chem. Soc., Perkin Trans. 2*, 1981, 747.

5 D. Wilhelm, T. Clark, P. v. R. Schleyer, and A. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1984, 558.

6 D. Wilhelm, T. Clark, J. L. Courtneidge, and A. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1983, 213.

7 D. Wilhelm, T. Clark, P. v. R. Schleyer, J. L. Courtneidge, and A G. Davies, *J. Am. Chem. Soc.*, 1984, **106**, 271.

8 R. W. Johnson, *J. Am. Chem. Soc.*, 1977, **99**, 1461; P. Fürderer, F. Gerson, and K. Hafner, *Helv. Chim. Acta*, 1978, **61**, 2974.

9 P. Fürderer, F. Gerson, M. Rabinovitz, and I. Willner, *Helv. Chim. Acta*, 1978, **61**, 2981.

10 M. Jones, Jr., and L. O. Schwab, *J. Am. Chem. Soc.*, 1968, **90**, 6549.

11 J. H. Sharp and M. C. R. Symons, in 'Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Ch. 5, Wiley-Interscience, New York, 1972.

12 P. J. Barker, M.-W. Tse, and A. G. Davies, *J. Chem. Soc., Perkin Trans. 2*, 1980, 946.

13 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899. Li parametrisation: W. Thiel and T. Clark, unpublished work.

14 S. Alexandratos, A. Streitwieser, and H. F. Schefer, *J. Am. Chem. Soc.*, 1976, **98**, 7959; E. D. Jemmis and P. v. R. Schleyer, *ibid.*, 1982, **104**, 4781; P. Jutzi, G. Schlüter, C. Krüger, and S. Pohl, *Angew. Chem.*, 1983, **95**, 1015; M. F. Lappert, A. Singh, L. M. Engelhardt, and A. H. White, *J. Organomet. Chem.*, 1984, **262**, 271.