

E.s.r. Study of Non-alternant Radical Ions

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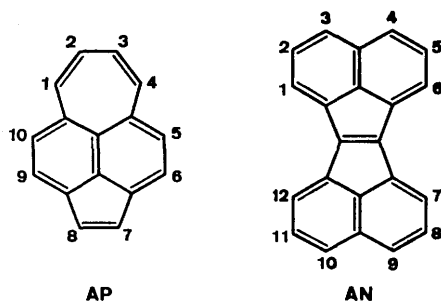
As a consequence of the well-known pairing properties of the orbitals,¹ Hückel and SCF-MO theories predict that the radical anion and the radical cation derived from the same alternant hydrocarbon should have identical spin populations² and therefore should give rise to similar e.s.r. spectra. This prediction has been abundantly confirmed.³ Since the pairing properties break

down in a non-alternant system, the radical anion and the radical cation produced from such a hydrocarbon should have different spin populations and should result in dissimilar e.s.r. spectra.

We have now examined the spectra of the radical ions of two non-alternant hydrocarbons, acepleiadylene^{4,5} (AP) and acenaphth[1,2-*a*]acenaphthylene⁶ (AN).

Large differences have been found between the spectra of the corresponding ions AP⁻, AP⁺ and AN⁻, AN⁺, and are reasonably accounted for by simple MO theory. This is shown by comparison of the total widths of the spectra with the sums $\sum_{\mu} c_{a\mu}^2$ or $\sum_{\mu} c_{b\mu}^2$ of the squares of Hückel coefficients for the lowest antibonding and the highest bonding orbitals of AP and AN respectively (μ refers only to proton-bearing centres).

Analysis of the hyperfine structures yields five coupling constants for the five pairs of equivalent protons in AP⁻ or AP⁺ and three coupling constants



¹ C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, **A**, 192, 16.

² A. D. McLachlan, *Mol. Phys.*, 1959, **2**, 271; 1961, **4**, 49.

³ S. I. Weissman, E. de Boer, and J. J. Conradi, *J. Chem. Phys.*, 1957, **26**, 963; A. Carrington, F. Drawnieks, and M.C.R. Symons, *J. Chem. Soc.*, 1959, 947.

⁴ V. Boekelheide and G. K. Wick, *J. Amer. Chem. Soc.*, 1956, **78**, 653.

⁵ The e.s.r. spectra of the radical ions of acepleiadylene have been previously observed by S. I. Weissman and E. de Boer (*J. Amer. Chem. Soc.*, 1958, **80**, 4549), who gave only a rough estimate of the total widths.

⁶ R. L. Letsinger and J. A. Gilpin, *J. Amer. Chem. Soc.*, 1964, **86**, 243.

for the three sets of four equivalent protons in AN⁻ or AN⁺. These constants (a_μ in gauss) are listed below, together with the corresponding

squares $c_{a\mu}^2$ or $c_{b\mu}^2$. The assignment made is that suggested by theory.

| Radical anion | Width (gauss) | $\sum_\mu c_{a\mu}^2$ | Radical cation | Width (gauss) | $\sum_\mu c_{b\mu}^2$ |
|-----------------|---------------|-----------------------|-----------------|---------------|-----------------------|
| AP ⁻ | 20.49 | 0.674 | AP ⁺ | 32.04 | 0.756 |
| AN ⁻ | 29.44 | 0.784 | AN ⁺ | 12.00 | 0.268 |

Radical ions of acepleiadylene (AP)

| μ | $c_{a\mu}^2$ | $a_\mu(AP^-)$ | $c_{b\mu}^2$ | $a_\mu(AP^+)$ |
|-------|--------------|---------------|--------------|---------------|
| 1,4 | 0.027 | } or 0.80 | 0.116 | 4.53 |
| 5,10 | 0.000 | | 0.143 | 5.88 |
| 2,3 | 0.087 | } or 2.76 | 0.056 | 2.70 |
| 7,8 | 0.087 | | 0.056 | 2.13 |
| 6,9 | 0.136 | 4.04 | 0.007 | 0.78 |

Radical ions of acenaphth[1,2-a]acenaphthylene (AN)

| μ | $c_{a\mu}^2$ | $a_\mu(AN^-)$ | $c_{b\mu}^2$ | $a_\mu(AN^+)$ |
|-----------|--------------|---------------|--------------|---------------|
| 1,6, 7,12 | 0.093 | } or 3.30 | 0.030 | 1.00 |
| 3,4, 9,10 | 0.100 | | 3.35 | 0.036 |
| 2,5, 8,11 | 0.003 | 0.71 | 0.001 | 0.24 |

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