

## Fulvene Radical Cations

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The radical cation of 6,6-dimethylfulvene has been observed in a  $\text{CFCl}_3$  matrix at low temperatures by e.s.r. spectroscopy; this is discussed in the light of a recent CIDNP study of the radical cations of some fulvene derivatives.

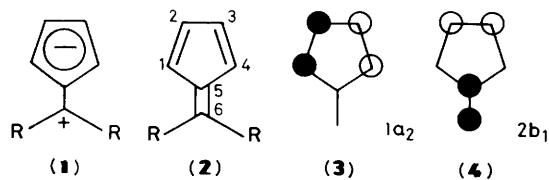
Fulvenes have long been of interest as hydrocarbons with some unique properties. Their structures and electron distributions have been investigated theoretically<sup>1,2</sup> in the context of their orbital energies and reactivities. A detailed n.m.r. study of fulvenes substituted at the 6-position has been published<sup>3</sup> which demonstrates the importance of the charge-separated form (1), which is stabilised by electron-releasing groups at C-6; this is reflected by changes in the ring proton coupling constants and chemical shifts. The relatively large dipole moments of fulvenes<sup>4</sup> are also in accord with a significant contribution from structure (1).

A report has appeared of a CIDNP study of a photochemical reaction of a number of substituted fulvenes, which is believed to involve the fulvene radical cations as intermediates.<sup>5</sup> The nature of the CIDNP effects observed indicates that the spin density in the radical cation of a fulvene is greatest on C(1) and C(4), [see (2)], rather less on C(2) and C(3), and extremely low on C(5) and C(6). This is qualitatively in accord with the distribution expected for the fulvene HOMO (3), with the node passing through C(5) and C(6). However, Abelt and Roth<sup>5</sup> favour a relaxed cation in which the HOMO is more extended, placing significant positive charge on C(6). The idea of a relaxed cation structure is supported by photoelectron spectra of fulvenes<sup>6</sup> in which the ionisation potentials of both orbitals  $\pi_2$  (4) and  $\pi_3$  (3) are lowered to a similar extent by alkyl substitution at C(6). If the

HOMO were simply as in the  $\pi_3$  orbital (3), then because of the node passing through C(6), no change in the ionisation potential of this orbital would be caused by the alkyl substitution; however, the observed effects may be explained in terms of electronic relaxation in the cation, which allows a drift of electron density from the exocyclic double bond unit, placing positive charge density on C(6).

In the light of these observations, it seemed worthwhile to study the e.s.r. spectrum of the radical cation of 6,6-dimethylfulvene, since this would provide direct evidence of the unpaired electron distribution. We are not aware of any previous e.s.r. study of fulvene radical cations. The spectrum (Figure 1) consists essentially of a triplet (16.8 G), each line of which appears to be further split into a smaller triplet (4.5 G) (the resolution is greatest on the low-field line). We assign the larger coupling to the C(1)/C(4) protons and the smaller coupling to the C(2)/C(3) protons: the ratio of the couplings ( $16.8/4.5 = 3.7$ ) is very similar to the ratios of the CIDNP enhancements of the C(1) and C(4) to the C(2) and C(3) resonances in the fulvene derivatives, which are in the range 3–4. The radical cation structure therefore clearly approximates to that expected from ionisation of  $\pi_3$  (3) rather than  $\pi_2$  (4), despite the possibility of hyperconjugative stabilisation of the  $\pi_2$  state: apparent switching of a radical cation structure to a formally excited state, but one which can be stabilised by hyperconjugation with alkyl substituents, has been observed in other cases.<sup>7</sup>

Our results are therefore in accord with the CIDNP work, and nicely demonstrate the complementary nature of the photo-CIDNP technique and matrix isolation e.s.r. spectroscopy for determining the spin density distributions in radical cations. Interestingly, Abelt and Roth<sup>5</sup> noted much weaker polarisations of nuclei associated with C(6), which we feel might be interpreted as arising from a small negative spin density at this position. However, the e.s.r. spectrum of the



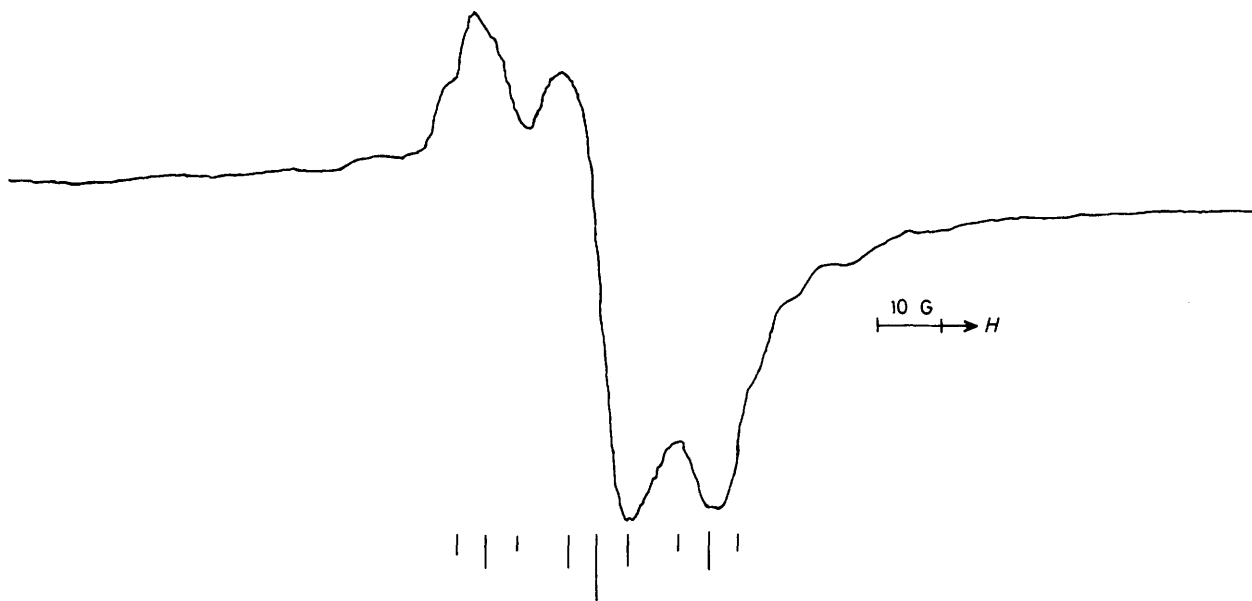


Figure 1. E.s.r. spectrum of 6,6-dimethylfulvene radical cations in a  $\text{CFCl}_3$  matrix at 77 K.

6,6-dimethyl derivative shows no evidence of coupling to the methyl protons, but, from the magnitude of the polarisations observed, we would expect couplings of probably  $<1$  G which would not be resolved in a solid-state spectrum. The couplings of 16.8 G are very large and reminiscent of the values (*ca.* 16 G) observed for the radical cations of pyrrole derivatives:<sup>8</sup> this has been explained in terms of a positive charge effect, such as is observed in benzene radical cations.<sup>9</sup> If there is a real negative spin density in the nodal region of the fulvene radical cation, then a small enhancement might be accounted for by an increase in the positive spin density on C(1) and C(4).

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