The Electron Spin Resonance Spectrum of the Fulvalene Radical Anion

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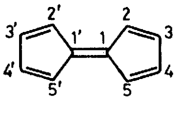
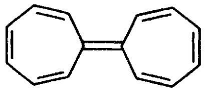
The fulvalene radical anion has been prepared by the oxidation of cyclopentadienyl-lithium or dilithium fulvalenediide with oxygen, and by the reduction of fulvalene with sodium, or electrolytically. The e.s.r. spectrum shows a(H-2,-2',-5,-5') 1.55, a(H-3,-3',-4,-4') 3.70, a(^{13}C-1,-1') 2.90, a(^{13}C-2,-2',-5,-5') 1.40, and a(^{13}C-3,-3',-4,-4') 2.15 G. The assignments for a(H) are based on the HMO model, and those for a(^{13}C) on the Yonezawa–Kawamura–Kato relationship.

THE fulvalene molecule (I) is interesting as an example of a conjugated hydrocarbon for which only dipolar resonance structures can be written, apart from the basic neutral structure, and it has been the subject of a number of theoretical calculations.[1]



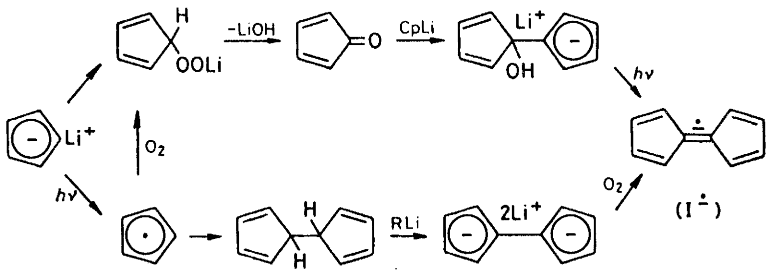
(I)



(II)

The compound has been prepared in dilute solution, and characterized by its reactions and its u.v. spectrum but it has never been isolated because it polymerises when the solutions are concentrated above 0.001M.[2] The e.s.r. spectrum of the radical anion or cation of (I) would establish the electron distribution in the corresponding singly occupied molecular orbitals, but neither (I$^{+\cdot}$) nor (I$^{-\cdot}$) has been prepared, though they have been studied theoretically.

Nakajima applied to (I$^{+\cdot}$) and (I$^{-\cdot}$) the open-shell SCF formalism of the Pariser–Parr–Pople method in conjunction with the variable bond-length technique.[3] This showed that (I$^{+\cdot}$) should have C_{2v} rather than D_{2h} symmetry with the unpaired electron confined to one ring, whereas in (I$^{-\cdot}$) there should be moderate double bond fixation in both of the rings, with the unpaired electron delocalised over the entire molecule. The derived hyperfine coupling constants are referred to later. Similar calculations on the radical anion and cation of heptafulvalene (II) gave hyperfine coupling constants in reasonable agreement with experimental data, and, in particular, were successful in predicting that the radical anion (II$^{-\cdot}$) should have C_{2v} symmetry with the unpaired electron localized in one ring,[3] as is observed.[4]



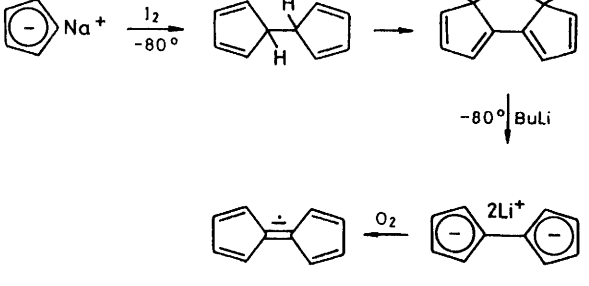
(1)

We report here four different routes by which the radical anion (I$^{-\cdot}$) can be prepared, and the e.s.r. spectrum can be recorded.

The Preparation of the Fulvalene Radical Anion.—Photolysis of a solution of cyclopentadienyl-lithium in tetrahydrofuran under strictly anaerobic conditions shows the characteristic sextet spectrum of the cyclopentadienyl radical.[5] If air is admitted to the sample, that spectrum is replaced by one consisting of a quintet of quintets, which we assign, on the basis of the further experiments described below, to the radical anion (I$^{-\cdot}$). Two reasonable routes by which the reaction might occur are illustrated in equation (1), where the two rings become linked either by the condensation of cyclopentadienyl-lithium with cyclopentadienone resulting from the autoxidation of cyclopentadienyl-lithium, or by the coupling of two cyclopentadienyl radicals.

The same spectrum is obtained by the autoxidation of the dilithium salt of dihydrofulvalene (III) prepared by Doering and Matzner's method [equation (2)];[2] the pink colour of the suspension of the dianion (III) in tetrahydrofuran changes first to deep green then to violet when the e.s.r. spectrum of the radical anion becomes apparent.

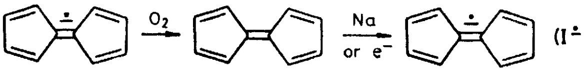
Further autoxidation gives the characteristic orange



(2)

(III)

colour of fulvalene,[2] and reaction of this with a sodium mirror and subsequent photolysis restores the colour and the e.s.r. spectrum of the radical anion. Similarly, electrolytic reduction of the fulvalene shows the same 25-line spectrum [equation (3)].



(3)

The E.s.r. Spectrum of the Fulvalene Radical Anion.—The e.s.r. spectrum of the radical anion ($I^{-\cdot}$) is shown in Figure 1, together with an expansion at higher gain of the two lines at highest field to illustrate the ^{13}C coupling. The spectrum was unchanged from −135 to +60 °C, using tetrahydrofuran as solvent, and no evidence could be found for the localization of the unpaired electron in one ring, as is observed with the heptafulvalene radical anion.[4] When ($I^{-\cdot}$) was generated in tetrahydrofuran at −80 °C over a sodium mirror, a small hyperfine coupling of *ca.* 0.15 G with the sodium counterion could be detected.

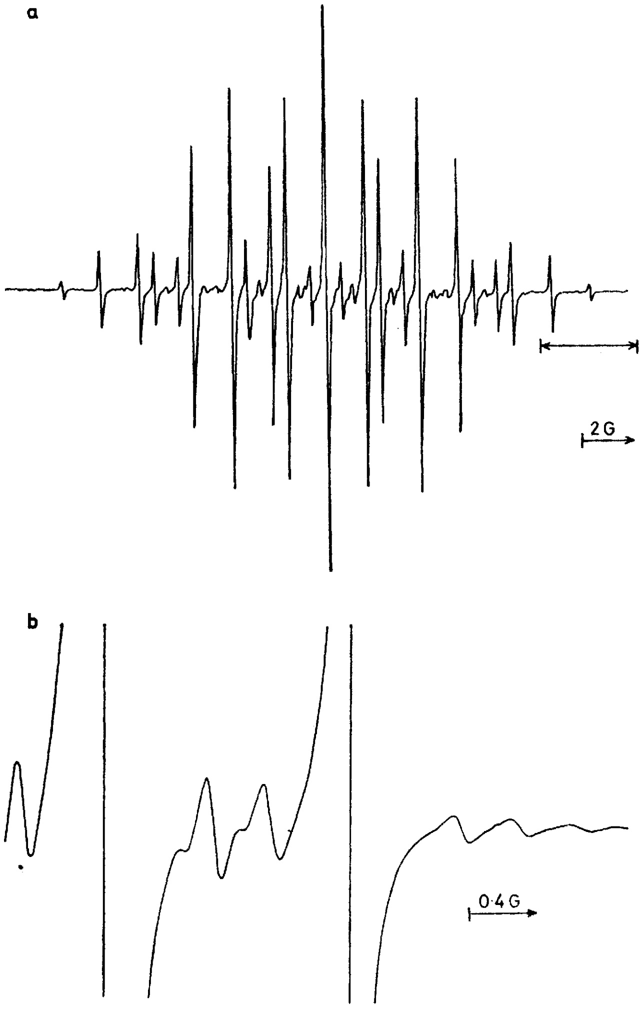


Figure 1 a, E.s.r. spectrum of the fulvalene radical anion in tetrahydrofuran at −20 °C. The region which is expanded in Figure 1b is indicated. b, Expansion of the two lines at highest field, showing the ^{13}C satellites

Values for the ^1H and ^{13}C hyperfine coupling constants are given in the Table, and the assignments are discussed in the following section.

Experimental and calculated hyperfine coupling constants (G) for the fulvalene radical anion [a]

1	2	3	4	5	6	7
	Exp. [b]	HMO [c]	INDO	SCF/ PPP [d]	KF [e]	YKK
H(2,2′,5,5′,)	1.55	−1.85	−1.30	−1.69		
H(3,3′,4,4′)	3.70	−3.31	−2.60	−2.52		
C(1,1′)	2.90		4.58		0.88	2.27
C(2,2′,5,5′)	1.40		0.32		−1.51	−1.81
C(3,3′,4,4′)	2.15		3.37		1.53	2.04

[a] $g = 2.0025$. [b] $|a|$. [c] Taking $Q = -30$ G. [d] Taking $Q = -26$ G; [3] if $Q = -30$ G, as it is in the cyclopentadienyl radical,[5] the calculated values are −1.95 and −2.91 G. [e] Karplus and Fraenkel method,[8] using the Hückel coefficients of equation (5), whence $a(^{13}C1) = (-12.7 + 3 \times 14.4)\,0.156 - 13.9\,(0.156 + 2 \times 0.0615)$ G, $a(^{13}C2) = (-12.7 + 2 \times 14.4 + 19.5)\,0.0615 - 13.9\,(0.156 + 0.110)$ G, and $a\,(^{13}C3) = (-12.7 + 2 \times 14.4 + 19.5)\,0.110 - 13.9\,(0.0615 + 0.110)$ G. [f] Yonezawa–Kawamura–Kato method,[10] using the Hückel coefficients of equation (5), whence $a(^{13}C1) = 46.0\,(0.156) - 17.3\,(0.0615 + 0.0615 + 0.156) - 1.95\,(0.0980 + 0.0980 - 0.156)$ G, $a(^{13}C2) = 46.0\,(0.0615) - 17.3\,(0.1102 + 0.156) - 1.95\,(-0.0823 + 0.0980)$ G, and $a(^{13}C3) = 46.0\,(0.1102) - 17.3\,(0.1102 + 0.0615) - 1.95\,(0.1102 - 0.0823)$ G.

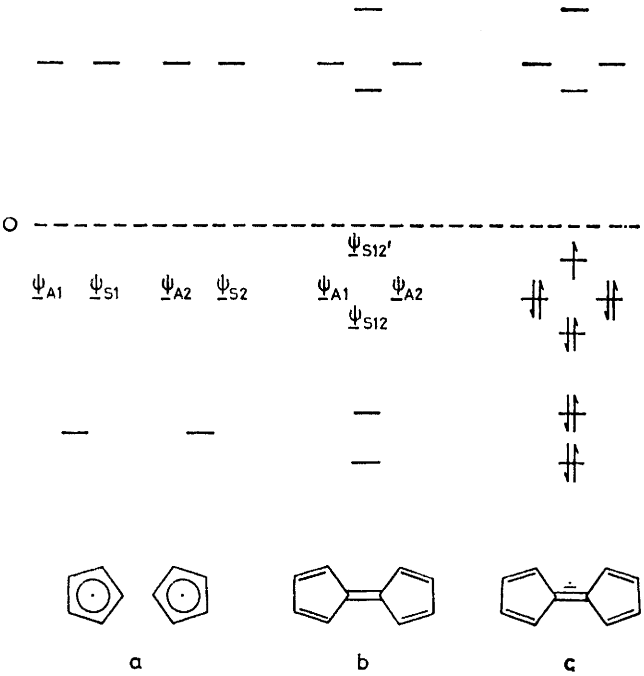


Figure 2 HMO energy levels: a, two non-interacting cyclopentadienyl halves; b, the fulvalene molecule; c, electronic configuration of the fulvalene radical anion

The HMO model in which fulvalene is regarded as consisting of two weakly interacting cyclopentadienyl halves is shown in Figure 2. The antisymmetric MOs ψ_{A1} and ψ_{A2} of the cyclopentadienyl radicals have zero coefficients at the points where the rings are linked (C-1 and -1′) and are unperturbed, but the symmetric MOs

ψ_{S1} and ψ_{S2} with non-zero coefficients at these positions have their degeneracies lifted yielding the new MOs ψ_{S12} and $\psi_{S12'}$ as illustrated.

The unpaired electron in the radical cation ($I^{+\cdot}$) would occupy either of the two degenerate MOs ψ_{A1} or ψ_{A2}, with the coefficients c_i given by equation (4), and in the radical

$$\psi_{A1} = \psi_{A2} = 0(\phi_1 + \phi_{1'}) + 0.425(\phi_2 - \phi_5 + \phi_{2'} - \phi_{5'}) + 0.263(\phi_3 - \phi_4 + \phi_{3'} - \phi_{4'}) \quad (4)$$

anion ($I^{-\cdot}$) it would occupy a unique bonding MO, $\psi_{S12'}$, with the coefficients given by equation (5).[6]

$$\psi_{S12'} = 0.395(\phi_1 - \phi_{1'}) + 0.248(\phi_2 + \phi_5 - \phi_{2'} - \phi_{5'}) + 0.332(-\phi_3 - \phi_4 + \phi_{3'} + \phi_{4'}) \quad (5)$$

If the Q value for ($I^{-\cdot}$) is taken to be -30 G as it is in the cyclopentadienyl radical,[5] the proton hyperfine coupling constants calculated by the McConnell equation (6) are given in the third column of the Table. The

$$a(H_i) = c_i^2 Q \quad (6)$$

experimental values of a(H) are assigned as indicated on the basis of their reasonable correlation with these calculated values.

The correlation is less satisfactory with values calculated by the INDO method (column 4) using the bond lengths for the radical anion calculated by Nakajima[3] and the arbitrary bond angle of $\angle C(2)C(1)C(5) = 110°$.* Nakajima's calculated values of the proton hyperfine coupling constants are given in column 5.[3]

The relative intensities of the ^{13}C satellites (see Figure 1b) show that the largest hyperfine coupling constant of $a(^{13}C) = 2.90$ G is to be assigned to C-1 and -1'.

The assignment of the other values of $a(^{13}C)$ has to be based on the semi-empirical relationships which have been developed for π-systems to take account of the spin polarisation of the σ-bonds by the π-electron densities, ρ, on the carbon centre, C, in question and on the neighbouring atoms X_i ($i = 1$, 2, or 3).

The Karplus–Fraenkel relationship[8] takes the form shown in equation (7), where $S_C = -12.7$ G, $Q_{CC_i} = 14.4$, $Q_{CH} = 19.5$, $Q_{C_iC} = 13.9$ G, $\rho_C = c_C^2$, and $\rho_{X_i} = c_{X_i}^2$, where c is the Hückel coefficient.

$$a(^{13}C) = (S_C + \sum_{i=1}^{3} Q_{CX_i})\rho_C + \sum_{i=1}^{3} Q_{X_iC}\rho_{X_i} \quad (7)$$

This correlation breaks down when bond angles deviate from 120°, as in $C_5H_5\cdot$,[8,9] or when bond lengths vary; both distortions occur in the fulvalene radical anion, and, as expected, calculations based on this equation (Table, column 6) are of no interpretive value.

For such molecules, including the cyclopentadienyl radical,[9] the alternative Yonezawa–Kawamura–Kato model[10] gives better results. This can be expressed in the form shown in equation (8), where $Q_C = 46.0$, $Q_{C_i} = -17.3$ G, $R_{CC_i} = -1.95$ G, and $\rho_{CX_i} = c_C c_{X_i}$.

$$a(^{13}C) = Q_C\rho_C + \sum_{i=1}^{3} Q_{X_i}\rho_{X_i} + \sum_{i=1}^{3} R_{CX_i}\rho_{CX_i} \quad (8)$$

The results of calculations by this method are shown in column 7 of the Table, and are seen to correlate reasonably well with the observed values of $a(^{13}C)$ if it is accepted that a(C-2, -2' -5, -5') is negative, and these values are therefore assigned as shown. The correlation between the experimental values and those from the INDO calculation (column 4) is less satisfactory.

Our attempts to observe the e.s.r. spectrum of the fulvalene radical cation ($I^{+\cdot}$) by treating fulvalene with aluminium chloride or antimony trichloride in butyronitrile, or with concentrated sulphuric acid, or by electrolytic oxidation in butyronitrile, were unsuccessful. This would be an interesting radical to prepare in order to investigate Nakajima's suggestion that the unpaired electron should be confined to one ring.

EXPERIMENTAL

Cyclopentadienyl-lithium was prepared in tetrahydrofuran by treating cyclopentadiene with butyl-lithium (1.6M in hexane), and fulvalene and the fulvalene dianion were obtained by Doering and Matzner's method.[2] The solution of fulvalene in a mixture of pentane and tetrahydrofuran was used for further studies. The dianion was oxidised to the radical anion by treating a stirred suspension of the dilithium derivative with air.

The electrolytic reduction of fulvalene was carried out in the cavity of the e.s.r. spectrometer at -30 to -80 °C, using the standard variable temperature insert.[11] A platinum cathode was used with n-butyronitrile as solvent, and tetra-n-butylammonium tetrafluoroborate (0.1M) as carrier electrolyte.

E.s.r. spectra were recorded on a Varian E4 instrument. INDO Calculations were performed using a program modified from the standard CNINDO (obtainable from QCPE). We are grateful to Dr. A. R. Gregory for making this program available to us.

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* Professor P. K. Bischof[7] has used the MINDO/3-UHF and MNDO-UHF methods for deriving the optimized geometries of the radical anion, and then taken them as input geometries for INDO calculations of spin densities and hyperfine coupling constants, but the values obtained are not substantially different from those in column 4.

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