Electron Spin Resonance Spectra and the Structures of Substituted Cyclopentadienyl Radicals

By Philip J. Barker, Alwyn G. Davies,* and Jonathan D. Fisher

(Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ)

Summary The e.s.r. spectra of substituted cyclopentadienyl radicals are in agreement with the predictions of Hückel molecular orbital theory.

The cyclopentadienyl radicals $XC_5H_4\cdot$ constitute an important group of small annulene radicals, but little work has been reported on their e.s.r. spectra because no general preparative methods have been available.† Attention has instead been concentrated more on the next higher members of the series, the benzene radical ions, the e.s.r. spectra of which have provided an important test of M.O. theory.

We have found that the cyclopentadienyl derivatives of tin[1] and mercury[2] can be photolysed to yield the corresponding cyclopentadienyl radicals, which makes it possible to study for the first time the spectra of many of these species. We discuss here the e.s.r. spectra and structures of the radicals $XC_5H_4\cdot$, where X = H, D, H_3C, Me_3C, and Me_3Si. The sources of the radicals, and the e.s.r. spectra which were observed, are listed in the Table.

The spectra of the substituted cyclopentadienyl radicals can be interpreted in terms of the perturbation of the ψ_A and ψ_S molecular orbitals (see Figure),[3] following the treatment which was first applied to the benzene radical ions.[4] An electron-releasing substituent will not affect the energy of the antisymmetric orbital ψ_A which has a node at C^1, but it will destabilise ψ_S, and the radical will prefer the configuration $\psi_A{}^2\ \psi_S{}^1$. Conversely an electron-attracting substituent will stabilise ψ_S, and the radical will prefer the configuration $\psi_S{}^2\ \psi_A{}^1$. Some mixing between the two configurations may occur if their separation is small.

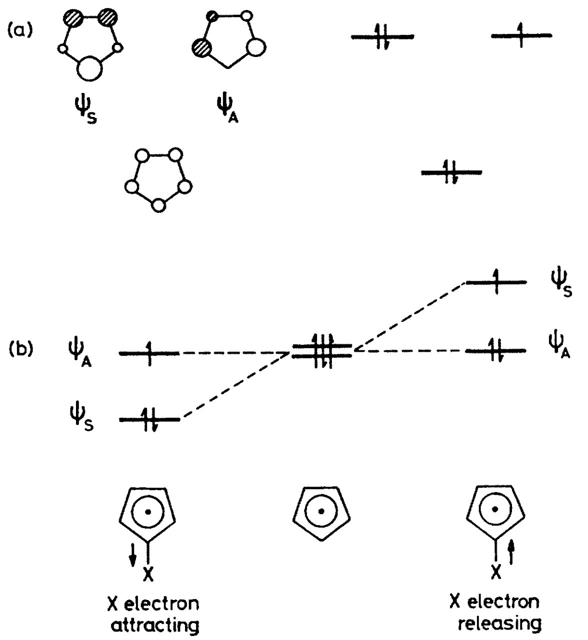

Figure. (a) Hückel molecular orbital diagram for the cyclopentadienyl radical. (b) Splitting of degenerate ψ_S and ψ_A energy levels by electron-attracting and electron-releasing substituents.

The spin density at a particular carbon centre should be proportional to the square of the coefficient of the atomic orbital at that centre, where $\psi_S = 0{\cdot}632\phi_1 + 0{\cdot}195(\phi_2 + \phi_5) - 0{\cdot}512\ (\phi_3 + \phi_4)$, and $\psi_A = 0{\cdot}602(\phi_2 - \phi_5) + 0{\cdot}372(\phi_3 - \phi_4)$.

In a $C_5H_5\cdot$ radical of D_{5h} symmetry the spin density, ρ_{C_α}, on any one carbon centre is 1/5, identifying the value of Q in the McConnell equation $a(H\alpha) = Q\rho_{C_\alpha}$ as (−)29·8 G, whence the values of a(H) in the substituted cyclopentadienyl radicals in the two limiting electronic configurations are calculated to be as follows: ψ_S: $a(H^2, H^5) = 0{\cdot}195^2Q = 1{\cdot}1$ G, $a(H^3, H^4) = 0{\cdot}512^2Q = 7{\cdot}8$ G; and ψ_A: $a(H^2, H^5) = 0{\cdot}602^2Q = 10{\cdot}8$ G, $a(H^3, H^4) = 0{\cdot}372^2Q = 4{\cdot}1$ G.

The observed hyperfine couplings in the radical $H_3CC_5H_4\cdot$ (see Table),‡ and their temperature independence, are in good agreement with those calculated for an electron wholly in the ψ_S orbital, confirming that the methyl group releases electrons strongly into the π-system of the ring, as it does in the benzene radical anions[4] and cations,[5] and, less effectively, in the cycloheptatrienyl radicals.[6]

Table. E.s.r. spectra of cyclopentadienyl radicals.

Radical	Source	Hyperfine coupling constants/G[a]	T/°C
$C_5H_5\cdot$	$C_5H_5SnCl_3$[b]	5·97 (5H), 2·66 (^{13}C)	−98
$DC_5H_4\cdot$	$DC_5H_4SnBu_3$[c]	6·09 (4H), 0·89 (D)	−47
$H_3CC_5H_4\cdot$	$(H_3CC_5H_4)_2Hg$[c]	0·90 (H^2, H^5), 7·65 (H^3, H^4), 15·30 (3H)	−73
$Me_3CC_5H_4\cdot$	$(Me_3CC_5H_4)_2Hg$[c]	1·20 (H^2, H^5), 7·40 (H^3, H^4), 0·65 (9H)	−45
$Me_3SiC_5H_4\cdot$	$(Me_3SiC_5H_4)_2Hg$[c]	7·78 (H^2, H^5), 5·29 (H^3, H^4)	−57

[a] For assignments, see text. [b] In ethylene. [c] In toluene. [d] Sakurai (ref. 3) reports *a ca.* 7·70 (2H) and 5·25 (2H) G at −60 °C.

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† Photolysis of di-t-butyl peroxide in the presence of cyclopentadienes gives principally the radical resulting from the addition of the t-butoxyl radical to the unsaturated system. The only substituted cyclopentadienyl radicals which have been generated by this (or indeed any other) method, as far as we are aware, are the silyl-substituted cyclopentadienyls described by Sakurai (ref. 3).

‡ From the expression, $a(H\beta) = \rho_{C\alpha}(A + B\cos^2\theta)$, where A = 1 G and B = 58 G, the value of $a(CH_3)$ is calculated to be *ca.* 12 G.

In $Me_3CC_5H_4\cdot$, the perturbing effect of the t-butyl group appears to be less. Again, this is parallel to the effect in $Me_3CC_6H_5^{\cdot -}$.[7]

In contrast, as Sakurai has shown,[3] the Me_3Si group in $Me_3SiC_5H_4\cdot$ is rather weakly electron attracting probably by interaction between the aromatic ψ_A orbital and the vacant Si 3*d* orbital. Appreciable mixing of the two configurations occurs, and, for example at −57 °C, the population distribution is *ca.* 30% ψ_S and 70% ψ_A. Again, the situation in $Me_3SiC_6H_5^{\cdot -}$ is similar.[8]

It is interesting that the four hydrogen atoms in $DC_5H_4\cdot$ are equivalent,§ and deuterium therefore, exerts no detectable perturbation on the molecular orbitals of the cyclopentadiene ring. The $DC_7H_6\cdot$ radical similarly shows no inequivalence of the hydrogen atoms,[9] but $DC_6H_5^{\cdot -}$ [10] does, the unpaired electron occupying predominantly the antisymmetric antibonding orbital.

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§ *Added in proof*: We have since been able to resolve the coupling of $H^{2,5}$ and $H^{3,4}$ in $C_5H_4D\cdot$. This work will be reported shortly.

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