An Electron Spin Resonance Study of the Methylcyclopentadienyl Radicals, $Me_nH_{5-n}C_5\cdot$ (n = 1—5)

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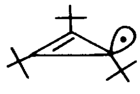
The radicals $Me_nC_5H_{5-n}\cdot$ have been generated by photolysis of the corresponding hydrocarbons (n = 3—5) or mercury derivatives (n = 0—5) and their e.s.r. spectra have been recorded. The spectra are interpreted in terms of thermal population of the ψ_A and ψ_S molecular orbitals, for which the predicted hyperfine coupling constants are calculated by the McLachlan equation, taking λ 0.75 and $Q(C_5H_5\cdot)$ −30 and $Q(Me_5C_5\cdot)$ 31.85 G. The energy separations between the ψ_A and ψ_S MOs can be rationalised on the assumption that a methyl substituent on a carbon atom of the cyclopentadienyl carrying a unit π-electron has a destablising interaction, within a factor of two, of 10 kJ mol^{-1}.

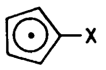
THE even annulenes (I; n even), particularly cyclobutadiene, benzene, and cyclo-octatetraene, have been the subject of many experimental and theoretical studies, which have contributed a great deal to our understanding of π-electron systems. The odd annulenes (I; n odd) have received much less attention because they are free radicals, which, in liquid solution, will normally undergo self-reaction at a diffusion-controlled rate, and which are therefore difficult to prepare in steady-state concentrations greater than *ca.* 10^{-7}M. On the other hand, the fact that they are free radicals makes it possible to examine them by e.s.r. spectroscopy, even at these low concentrations. This is potentially a very powerful technique in that it can be used to determine the electronic configurations of the odd annulenes, but few studies of these compounds by this method have been reported.

$[CH]_n$

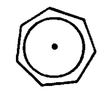
(I)



(II)



(III)



(IV)

The large ^{13}C hyperfine coupling constant of the tri-t-butylcyclopropenyl radical (II) shows that this is a localised σ-radical which cannot be treated by π-electron theory.[1] A number of alkyl-substituted cycloheptatrienyl radicals (IV) have been prepared; these are π-delocalised radicals,[2] and their spectra have been interpreted in terms of the perturbation of the degenerate π-electron molecular orbitals of the parent radical.[3]

Relatively little work has been carried out on the [5]annulene (cyclopentadienyl) radicals (III). The ^{13}C hyperfine coupling constants show that these, like the [7]annulenes (IV), but unlike the [3]annulenes (II), are π-delocalised radicals,[4,5] and they are therefore the simplest neutral odd annulenes to which π-electron theory can be applied. Sakurai reported the e.s.r. spectra of a series of organosilyl-substituted cyclopentadienyl radicals [III; X = R_3Si or $R_3Si(R_2Si)_n$, n = 1 or 2] [6] and we both prepared the radicals (III) where X = D, Me, Et, Pr^i, and Bu^t, with concordant results.[4,5] The spectra were analysed in terms of the splitting of the degeneracy of the ψ_A and ψ_S molecular orbitals by the interaction of the substituent X with the electron system.

In this paper we report the e.s.r. spectra of all the possible methylated cyclopentadienyl radicals, namely $MeC_5H_4\cdot$, 1,2-$Me_2C_5H_3\cdot$, 1,3-$Me_2C_5H_3\cdot$, 1,2,3-$Me_3C_5H_2\cdot$, 1,3,4-$Me_3C_5H_2\cdot$, 1,2,3,4-$Me_4C_5H\cdot$, and $Me_5C_5\cdot$. The simple Hückel model which was used previously is tested against the observed spectra, and is refined to accommodate some of the data.

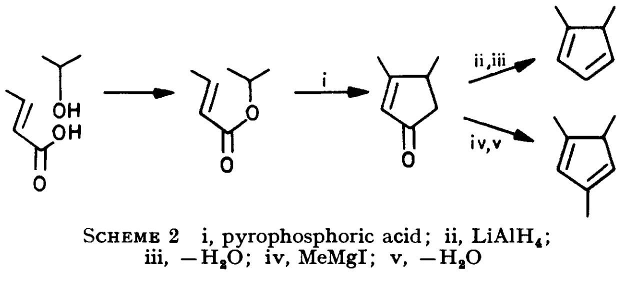
The following two papers then use this improved model to interpret the e.s.r. spectra of cyclopentadienyl radicals carrying various Group IV substituents, $X_3MC_5H_4\cdot$ (M = C, Si, Ge, or Sn),[7] and of penta-alkylated cyclopentadienyl radicals 1-R-2,3,4,5-$Me_4C_5\cdot$ (R = Et, Pr, or Bu) and 1,3,4-Me_3-2,5-$R_2C_5\cdot$ (R = Et).[8]

RESULTS

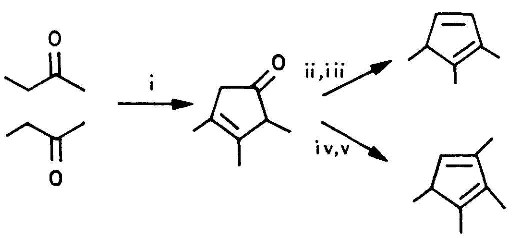
Methylcyclopentadiene was prepared by thermal cracking of the dimer. The other methylcyclopentadienes were prepared as shown in Schemes 1—3. The products usually consisted of mixtures of isomers, and the positions of the double bonds which are shown are arbitrary; all the isomers however gave the same radical on photolysis.

SCHEME 1 i, MeMgI; ii, $-H_2O$

Irradiation of the tetramethylcyclopentadiene, and of both the trimethylcyclopentadienes, in toluene solution in the e.s.r. cavity with u.v. light from a high pressure mercury arc, showed the spectra of the corresponding polyalkylcyclopentadienyl radicals. The spectra were weaker than that which is observed with pentamethylcyclopentadiene under the same conditions,[9] but the reactions probably



SCHEME 2 i, pyrophosphoric acid; ii, $LiAlH_4$; iii, $-H_2O$; iv, MeMgI; v, $-H_2O$



SCHEME 3 i, PbO_2; ii, $LiAlH_4$; iii, $-H_2O$; iv, MeMgI; v, $-H_2O$

follow the same mechanism which we believe to involve unimolecular homolysis of the C–H bond [equation (1)].

$$Me_nC_5H_{6-n} \xrightarrow{h\nu} Me_nC_5H_{5-n}\cdot + H\cdot \quad (n = 3—5) \qquad (1)$$

The mercury derivatives of all the cyclopentadienes in diethyl ether solution underwent photolysis by equation (2) to show good spectra of the corresponding methylcyclopentadienyl radicals over the range −120 to +20 °C: this reaction has been established previously when n = 0, 1,[4] or 5.[9]

$$(Me_nC_5H_{5-n})_2Hg \xrightarrow{h\nu} 2Me_nC_5H_{5-n}\cdot + Hg^0 \qquad (2)$$

Examples of the spectra, and their computer simulations, for the radicals $Me_nC_5H_{5-n}\cdot$ (n = 2—4) are shown in Figures 1—5. Spectra for the radicals when n = 0, 1,[4] and 5[9] have been published previously. Values of the hyperfine coupling constants as determined by computer simulation of the observed spectra are given in Table 1.

DISCUSSION

Application of the Hückel–McLachlan Model.—The form of the ψ_A and ψ_S molecular orbitals for the cyclopentadienyl system and their Hückel coefficients, are shown in equations (3) and (4).[10]

$$\psi_A = 0.602(\phi_2 - \phi_5) + 0.372(\phi_3 - \phi_4) \qquad (3)$$

$$\psi_S = 0.632\phi_1 + 0.195(\phi_2 + \phi_5) - 0.512(\phi_3 + \phi_4) \qquad (4)$$

We previously assumed that the electron densities, q_i, as given by equation (5) were equal to the spin densities, ρ_i, (Table 2) and we derived the predicted values of the hyperfine coupling constants, a_i, for the $C_5H_5\cdot$ radical in the pure ψ_A and ψ_S configurations from the McConnell equation (6) (Table 3) where the value of

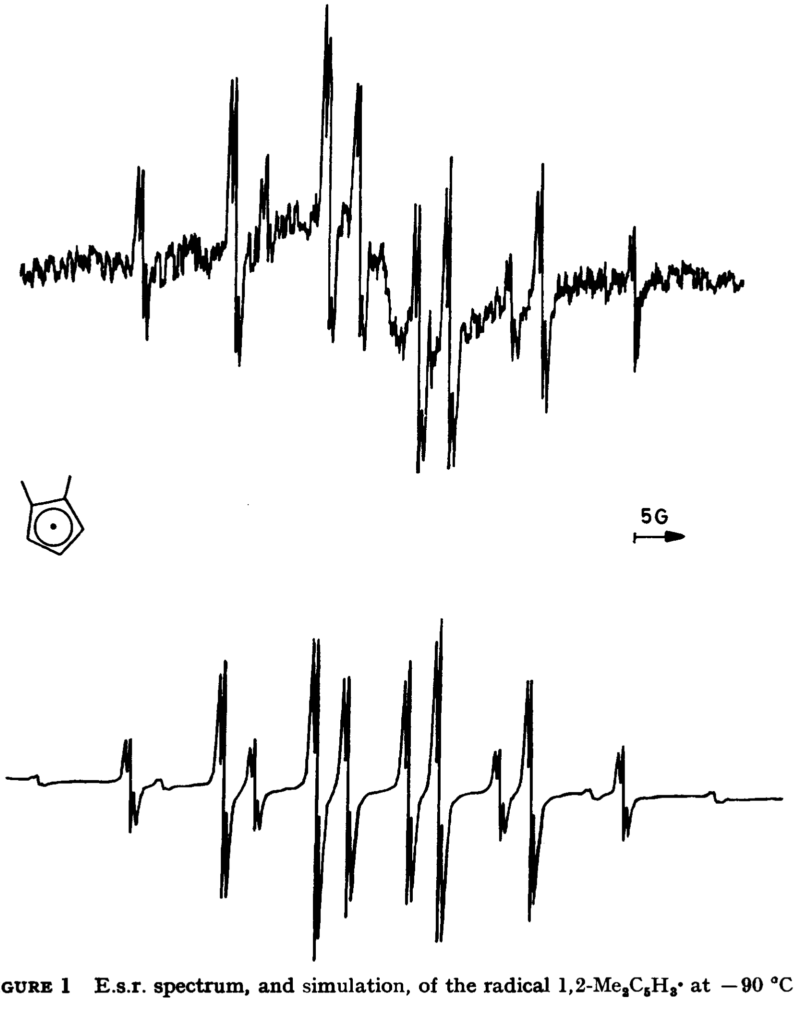


FIGURE 1 E.s.r. spectrum, and simulation, of the radical 1,2-$Me_2C_5H_3\cdot$ at −90 °C

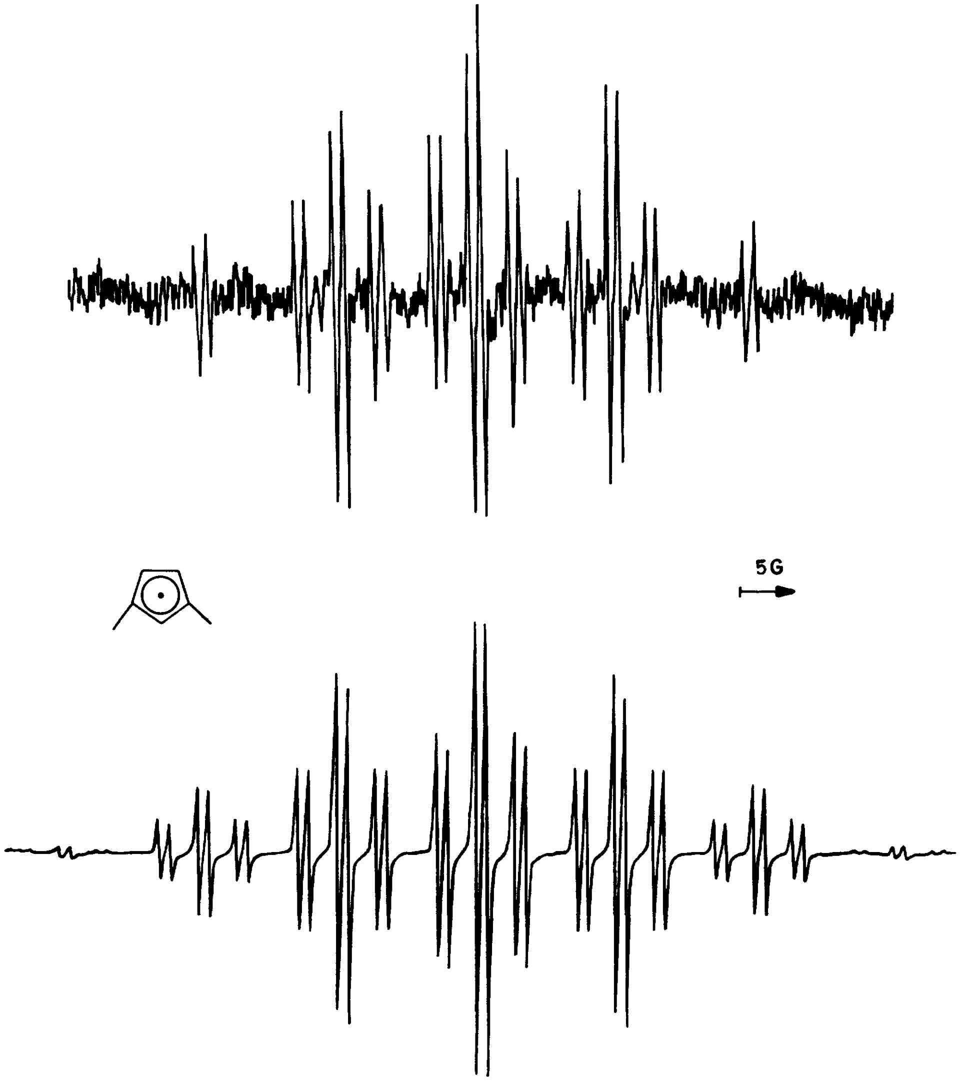


FIGURE 2 E.s.r. spectrum, and simulation, of the radical 1,3-$Me_2C_5H_3\cdot$ at −90 °C

the constant Q was equated to the observed spectral width of the unsubstituted $C_5H_5\cdot$ radical (30.00 G).[4]

$$q_i = c_i^2 \qquad (5)$$

$$a_i = Qq_i \qquad (6)$$

Similarly the values of the hyperfine coupling constants for the pentamethylcyclopentadienyl radical in the ψ_A and ψ_S configurations were calculated (Table 4) from the observed spectral width of the $Me_5C_5\cdot$ radical (31.85 G).[9]

It will be seen that a number of the coupling constants observed for the methylated cyclopentadienyl radical (Table 1) lie outside the limits imposed by this simple Hückel model (Tables 3 and 4), and a more refined model must be used if a semi-quantitative interpretation of the spectra is to be attempted. To this end, we have used the McLachlan modification [11] of the Hückel model [equation (7)] to take into account the polarisation of spins of the spin-paired π-electrons by the spin of the unpaired electron.[11,12]

$$\rho_i = c_i^2 + \lambda \sum_{r=1}^{5} \pi_{ir} c_r^2 \qquad (7)$$

$$a_i = Q\rho_i \qquad (8)$$

The value of the McConnell constant Q to be used for calculating the predicted hyperfine coupling constants by equation (8) first needs to be justified.

For equilibrating radicals with population P_A in the ψ_A MO and P_S in the ψ_S MO, the resultant values of a_i will be given by equation (9). For the equilibrating

$$a_i = P_A a_{iA} + P_S a_{iS} \qquad (9)$$

$C_5H_5\cdot$ radicals with degenerate ψ_A and ψ_S orbitals, $P_A = P_S = 0.5$, and equations (10)—(13) apply.

$$\bar{a}_1 = \bar{a}_{2,5} = \bar{a}_{3,4} = 6.00 \text{ G} \qquad (10)$$

$$\bar{a}_1 = 0.5(Q_S\rho_{1S} + Q_A\rho_{1A}) \qquad (11)$$

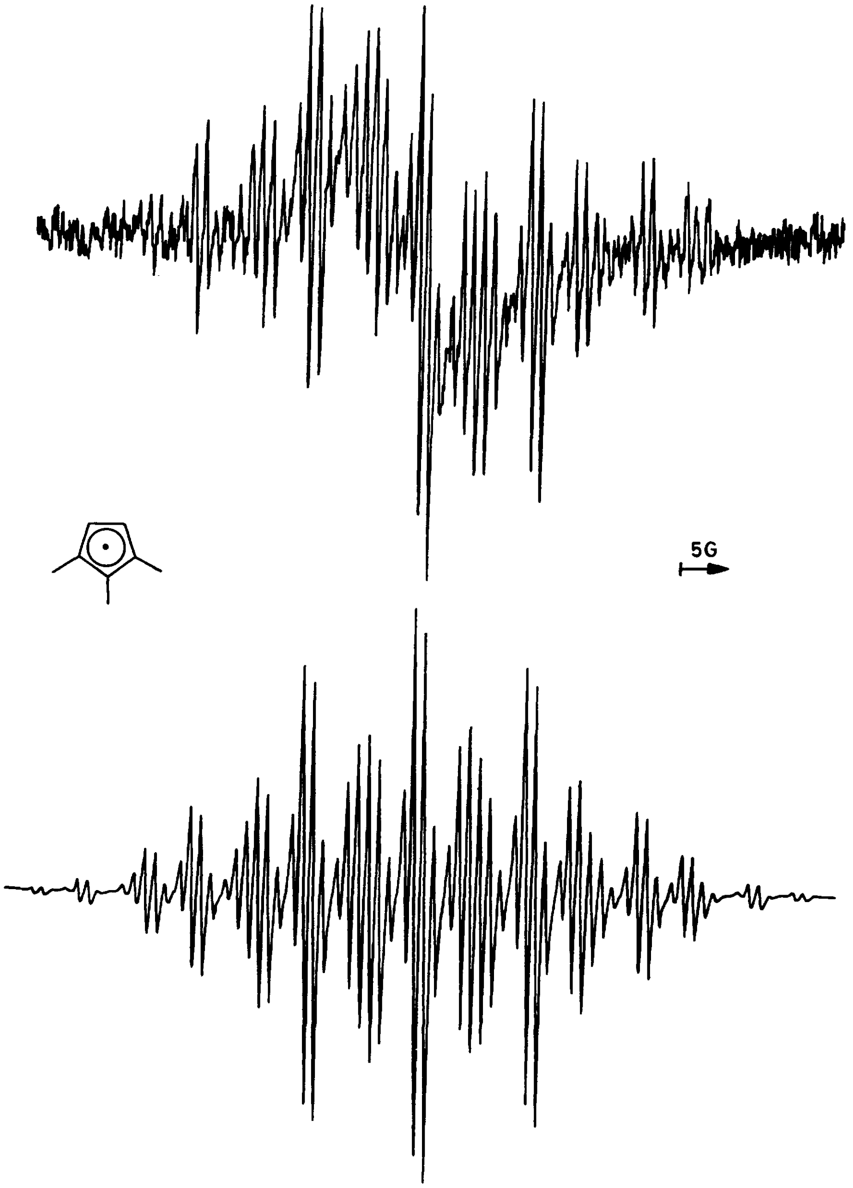


FIGURE 3 E.s.r. spectrum, and simulation, of the radical 1,2,3-$Me_3C_5H_2\cdot$ at 0 °C

$$\bar{a}_{2,5}\ 0.5(Q_S\rho_{2,5S} + Q_A\rho_{2,5A}) \qquad (12)$$

$$\bar{a}_{3,4} = 0.5(Q_S\rho_{3,4S} + Q_A\rho_{3,4A}) \qquad (13)$$

Whatever value of λ is taken in equation (7), solving any pair of these equations gives, for $C_5H_5\cdot$, $Q_A = Q_S = -30.00$ G. Similarly, for $Me_5C_5\cdot$, $Q_A = Q_S = +31.85$ G: * for both systems we conclude that the McConnell Q values are the same for the ψ_A and ψ_S configurations, and equal to the observed spectral width of the equilibrating configurations.

The value of λ is then chosen to give the best fit with the observed values of a_i. To accommodate the radicals in Table 1, a value of λ of not less than 0.7 is needed, and it is possible that even here the limit has not been reached, that is, that the electron configuration of these radicals still cannot be described in terms of purely the ψ_A and ψ_S orbitals.

We have therefore adopted a value of λ of 0.75. Sakurai[6] similarly selected a value of 0.75 because it gave the best fit to the observed e.s.r. spectrum of the indenyl radical, but Möbius *et al.* used a value of 1.15 in interpreting the spectra of the methylated pentaphenylcyclopentadienyl radicals.[13]

Spin densities calculated for the cyclopentadienyl system by the McLachlan equation (7; λ = 0.75), are compared in Table 2 with the electron densities calculated on the Hückel model, and in Tables 3 and 4, comparisons are drawn between the hyperfine coupling constants

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* The signs of Q are not directly measured, but are inferred on the basis of the coupling mechanism, *i.e.* spin polarisation acting through the C–H σ-bond for $C_5H_5\cdot$, and hyperconjugation for $Me_5C_5\cdot$.

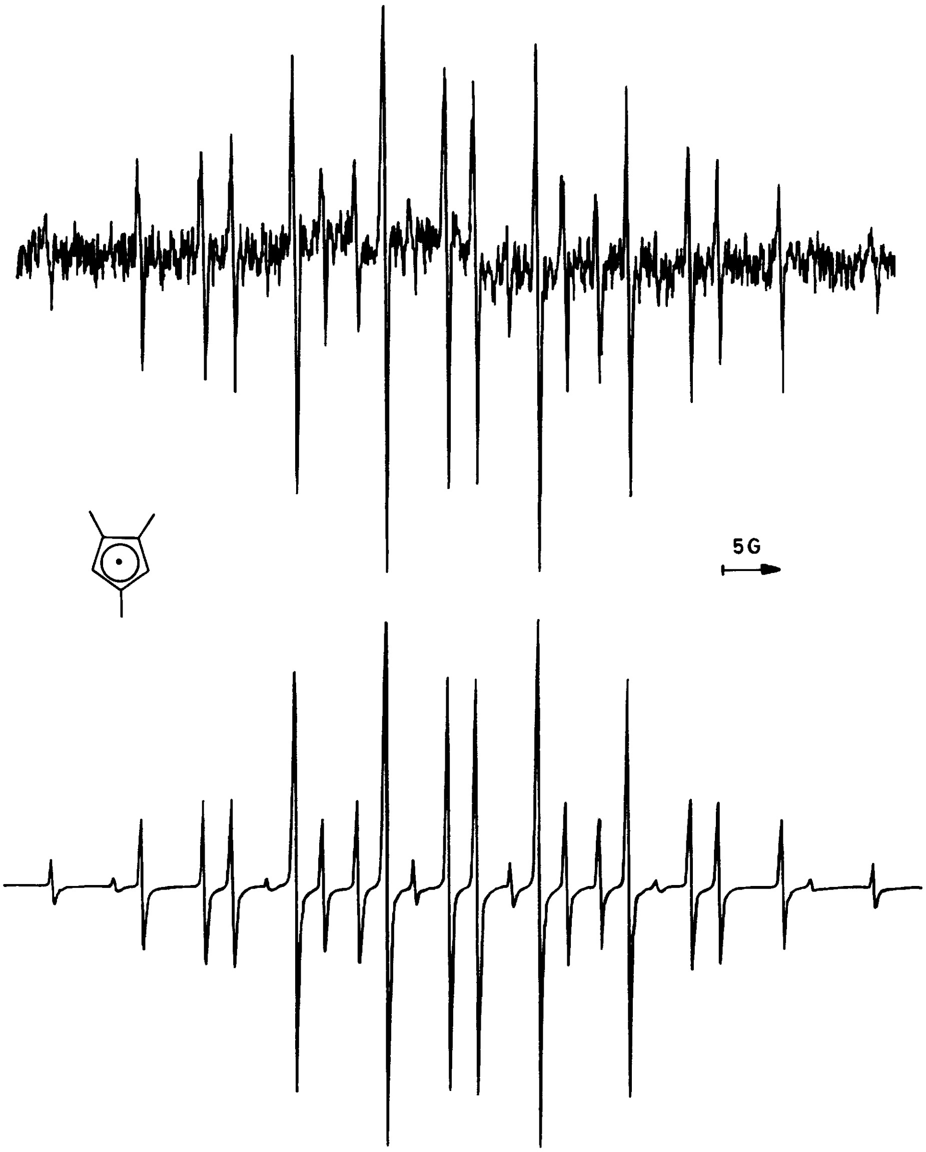

FIGURE 4 E.s.r. spectrum, and simulation, of the radical $1,3,4\text{-}Me_3C_5H_2$ at −90 °C

predicted by the two models for the $C_5H_5\cdot$ radicals and the $Me_5C_5\cdot$ radicals respectively.

The calculated width of the spectra of the $C_5H_5\cdot$ radicals in the ψ_A and ψ_S configuration can then be derived from equation (14) to be 35.49 and 33.91 G, respectively, both larger than the value (30.00 G) for the equilibrating degenerate pair of radicals. Similarly, for the $Me_5C_5\cdot$ radicals, the calculated spectral widths are 37.47 and 35.99 G, both again larger than the time-averaged value of 31.85 G.

$$W = Q\sum_i|\rho_i| = \sum_i |a_i| \qquad (14)$$

This is supported by the observed spectral width of some radicals carrying mixed methyl and hydrogen substituents, which confer on them almost pure ψ_A or ψ_S character. For example, the spectrum of $1,3,4\text{-}Me_3C_5H_2\cdot$ (ψ_S) at −120 °C shows a width of 32.90 G against a calculated value of 31.11 G ($2 \times 30/5 + 3 \times 31.85/5$), and, for $1,3\text{-}Me_2C_5H_3\cdot$ (ψ_A) at −120 °C, 35.62 G against a calculated value of 30.74 G ($3 \times 30/5 + 2 \times 31.85/5$).

Treatment of the Data.—In Figure 6, the intersecting unbroken lines represent the calculated values of a_i(Me) for methylated cyclopentadienyl radicals, calculated according to equation (9) using the McLachlan values of a_{iA}(Me) and a_{iS}(Me) from Table 4. Similarly the broken lines represent the calculated values of a_i(H) for equilibrating cyclopentadienyl radicals, the McLachlan values of a_{iA}(H) and a_{iS}(H) being taken from Table 3.* At the centre of the plot, ($P_A = P_S = 0.5$), the lines intersect at the values of a(Me) (6.37 G) and a(H) (6.00 G)

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* More correctly, values of $-a_i$(H) have been used, so that hyperfine coupling constants to H and to Me can appear together in the same quadrant.

for the $Me_5C_5\cdot$ and $C_5H_5\cdot$ radicals respectively. At the extremes (P_A 1.0 and P_S 1.0) the y axis is intersected at the values of a_{iA}(H) and a_{iA}(Me) or a_{iS}(H) and a_{iS}(Me) calculated for the radicals $Me_5C_5\cdot$ and $C_5H_5\cdot$ in the pure ψ_A or ψ_S configurations, respectively. Points lying to the left of the centre of the plot represent an excess population of the ψ_A MO, and points to the right represent over-population of ψ_S.

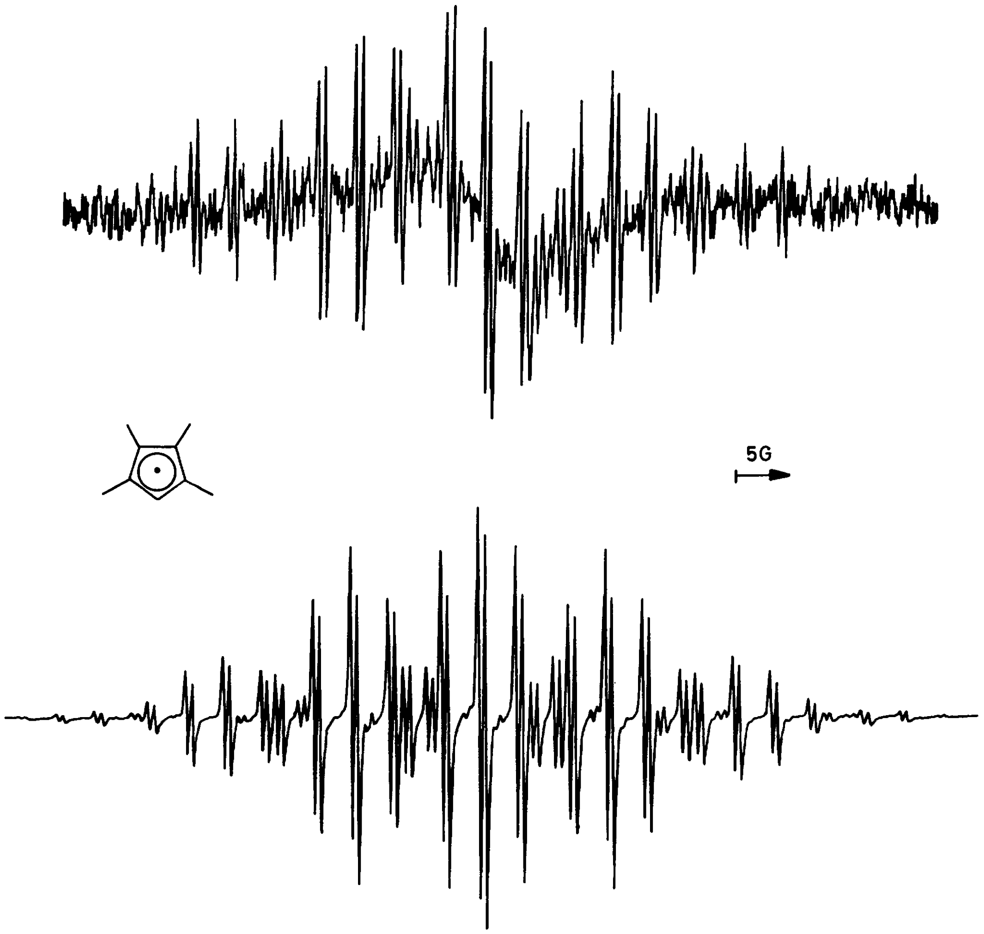

FIGURE 5 E.s.r. spectrum, and simulation, of the radical 1,2,3,4-$Me_4C_5H\cdot$ at −60 °C

Experimental values of a_i(Me) and a_i(H) from Table 1 for the radicals $Me_nC_5H_{5-n}\cdot$ (n = 0—5) at −120 °C have been added to the graph to give the best fit with these theoretical lines: this involves making the assumption that some of the small hyperfine coupling constants involve an inversion of sign (see Table 1).

The reasonable fit between the positions of the experimental points and the theoretically calculated lines supports the validity of the model on which the interpretation is based.

The direction of the change in the coupling constants towards the values for $C_5H_5\cdot$ and $Me_5C_5\cdot$ as the temperature increases also accords with the predictions of the model. In particular, the *decrease* in the absolute value of a_1(H) for the radical $Me_4C_5H\cdot$ as the temperature is increased, which is well outside experimental error, confirms the existence of negative spin densities, and the need to use the McLachlan equation to take these into account.*

The temperature dependencies of the hyperfine coupling constants are too small to permit the energy separations, ΔE, between the ψ_A and ψ_S MOS to be obtained from Boltzmann plots, but a rough estimate of ΔE (see Table 5) can be obtained from the Boltzmann equation (15) using values of P_A and P_S taken from the x-axis of Figure 6. If this perturbation ΔE arises from the

$$P_A/P_S = \exp \Delta E/RT \qquad (15)$$

differential electronic interaction of the hydrogen and methyl substituents with the π-electron system, it might be expected to be proportional by a constant, which we designate as κ_H^{Me}, to the difference between the sums of the electron densities at the substituted positions, j, in the ψ_A and ψ_S configurations of the radical [equation (16)].

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* The spectrum was also obtained by the photolysis of the hydrocarbon in dibutyl ether at +145 °C, in an attempt to observe the inversion of the sign of $a(H_1)$; the line-width increased to *ca.* 0.5 G, perhaps indicating the incursion of an unresolved coupling, but no further splitting could be observed.

$$\Delta E = \kappa_{\mathrm{H}}^{\mathrm{Me}}(\sum_{j} q_{j\mathrm{A}} - \sum_{j} q_{j\mathrm{S}}) \quad (16)$$

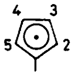
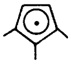
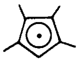
$$= \kappa_{\mathrm{H}}^{\mathrm{Me}}\delta q \quad (17)$$

Values of δq and of the derived values of $\kappa_{\mathrm{H}}^{\mathrm{Me}}$ are given in Table 5. The positive sign of all the κ terms, according to the convention given in a footnote to Table 5 is consistent with the model on which a methyl group releases electrons more strongly than a hydrogen atom, and thereby has a destabilising effect on attached carbon atoms carrying non-zero π-electron density.

If these substituent effects are additive around the

TABLE 1

Hyperfine coupling constants observed for methylated cyclopentadienyl radicals in diethyl ether[a]

Radical	T/°C	a_1/G	$a_{2,5}$/G	$a_{3,5}$/G
		Me	2 H[b]	2 H
	0	14.88	1.00	7.73
	−60	15.10	0.85	7.80
	−90	15.30	0.80	7.85
	−120	15.35	0.75	7.88
		H	2 H	2Me
	0	11.55	0.95	8.90
	−60	12.00	0.64	9.02
	−90	12.25	0.43	9.15
	−120	12.50	0.25[e]	9.30
		H[b]	2Me	2 H
	0	1.03	13.20	3.85
	−60	1.07	13.40	3.78
	−90	1.08	13.45	3.75
	−120	1.10	13.55	3.71
		Me	2Me	2 H
	0	1.00	11.05	4.47
	−60	0.60	11.40	4.38
	−90	0.36	11.57	4.34
	−120	0.20[c]	11.70	4.30
		Me	2 H	2Me
	0	14.55	<0.15	8.80
	−60	14.80	<0.15	8.85
	−90	15.00	<0.15	8.88
	−120	15.10	<0.15	8.90
		H[b]	2Me	2Me
	+145[d]	$\nless$0.3[c]	11.49	4.14
	+20	0.20[e]	12.30	3.96
	0	0.41	12.45	3.92
	−60	0.66	12.75	3.75
	−90	0.74	12.98	3.70
	−120	0.82	13.15	3.67

[a] Spectra were analysed by computer simulation, using a line width of 0.2—0.3 G depending on the modulation amplitude at which the experimental spectra were recorded. [b] Assumed to be of opposite (positive) sign to those of the other (negative) values of $a(\mathrm{H}_\alpha)$. [c] Unresolved coupling, estimated from simulation of the line width. [d] From the hydrocarbon in dibutyl ether.

TABLE 2

Electron densities and spin densities for the ψ_{A} and ψ_{S} configurations of the cyclopentadienyl system, calculated by equations (5) and (7) (λ 0.75), respectively

	Hückel		McLachlan	
i	$q_{i\mathrm{A}}$	$q_{i\mathrm{S}}$	$\rho_{i\mathrm{A}}$	$\rho_{i\mathrm{S}}$
1	0.0000	0.4000	−0.0869	0.4869
2,5	0.3618	0.0382	0.4330	−0.0322
3,4	0.1382	0.2618	0.1116	0.2892

TABLE 3

Hyperfine coupling constants (G) for the ψ_{A} and ψ_{S} configurations of the C_5H_5• radical, calculated by equations (6) and (8) (Q −30.00 G)

	Hückel		McLachlan	
i	$a_{i\mathrm{A}}$	$a_{i\mathrm{S}}$	$a_{i\mathrm{A}}$	$a_{i\mathrm{S}}$
1	0.00	−12.00	2.61	−14.61
2,5	−10.85	−1.15	−12.99	0.97
3,4	−4.15	−7.85	−3.45	−8.68

TABLE 4

Hyperfine coupling constants (G), for the ψ_{A} and ψ_{S} configurations of the Me_5C_5• radical, calculated by equations (6) and (8) (Q 31.85 G)

	Hückel		McLachlan	
i	$a_{i\mathrm{A}}$	$a_{i\mathrm{S}}$	$a_{i\mathrm{A}}$	$a_{i\mathrm{S}}$
1	0.00	12.74	−2.79	15.51
2,5	11.52	1.22	13.79	−1.03
3,4	4.40	8.34	3.56	9.21

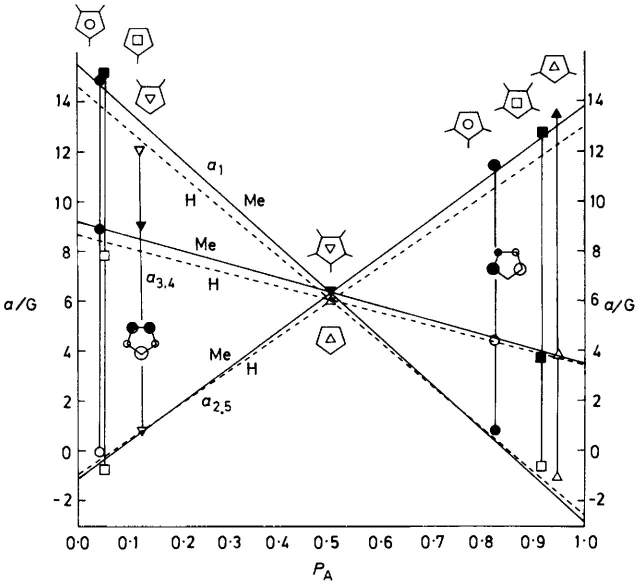


FIGURE 6 Correlation between observed hyperfine coupling constants for the methylcyclopentadienyl radicals at −60 °C and the values calculated for different populations of the ψ_{A} and ψ_{S} orbitals (see text). The key to the symbols are given in the centres of the formulae. The solid symbols refer to values of a(Me) and correlate with the full lines. The open symbols refer to values of a(H) and correlate with the broken lines

TABLE 5

Orbital populations, energy separations, and interaction factors for methylcyclopentadienyl radicals at −60 °C

	$P_{\mathrm{A}} : P_{\mathrm{S}}$	ΔE/ kJ mol^{-1} [a]	δq [b]	$\kappa_{\mathrm{H}}^{\mathrm{Me}}$/ kJ mol^{-1}
MeC_5H_4•	5 : 95	−5.21	+0.400	−13.0
1,2-$Me_2C_5H_3$•	12 : 88	−3.53	+0.247	−14.3
1,3-$Me_2C_5H_3$•	95 : 5	+5.21	−0.647	−8.1
1,2,3-$Me_3C_5H_2$•	82 : 18	+2.68	−0.247	−10.9
1,3,4-$Me_3C_5H_2$•	4 : 96	−5.62	+0.647	−8.7
1,2,3,4-Me_4C_5H•	92 : 8	+4.32	−0.400	−10.8

[a] Defined as $\Delta E = E(\psi_{\mathrm{A}}) - E(\psi_{\mathrm{S}})$, increasing stability being denoted by a larger negative value of E. [b] In units of the charge on the electron.

ring, the values of $\kappa_{\mathrm{H}}^{\mathrm{Me}}$ should be constant, representing the difference in the energy of interaction of a methyl group and a hydrogen atom, with unit π-electron density on the carbon atom to which it is attached.

The variation in the values of κ which are observed is within the accuracy of the experiment and encourages us in the belief that the model which we have followed is useful. If substituents could be chosen so that ΔE was smaller, and the temperature dependence of the hyperfine coupling constants could be determined more accurately, more reliable estimates of κ could be obtained.

Conclusions.—The model which we have followed was initially proposed by Bolton and Carrington to account for the e.s.r. spectra of the radical anions of toluene, *p*-xylene, and *m*-xylene,[14] and later, of *o*-xylene,[15] and has subsequently been widely used for rationalising the e.s.r. spectra of substituted arene anions and cations.[16] For these radical ions in ethereal solution, the methyl groups behave as electron-releasing substituents, as we observe, but it has recently been shown by electron transmission spectroscopy [17] and by calculation,[18] that, in the gas phase, the methyl substituent *attracts* electrons, rendering the ψ_{S} MO of the toluene radical anion *more* stable than ψ_{A}. The inversion of this order in solution has been suggested to be the result of solvation.

It seems most unlikely that a similar effect could be significant in our system. Solvation of the neutral hydrocarbon cyclopentadienyl radicals by a hydrocarbon solvent would be negligible, and there is no counterion to be considered, and indeed we observe identical e.s.r. spectra whether the solvent is an ether or a hydrocarbon. Our results encourage us to believe that the e.s.r. spectra of the cyclopentadienyl system will prove to be useful for investigating short- and long-range substituent effects in solution.

This is not to say that it might not be possible to interpret the data in other terms. Clark and Chandrasekhar have developed an alternative model for $\mathrm{MeC_5H_4}\cdot$ based on an equilibrium between two pseudo-Jahn–Teller isomers.[19] This approach shows promise, but the calculations would as yet be prohibitively expensive for the rest of the radicals we have considered here.

EXPERIMENTAL

Preparation of Materials.—3-Methylcyclopent-2-enone used in the preparation of 1,3-dimethylcyclopentadiene was a commercial product (Aldrich). 3,4-Dimethylcyclopent-2-enone was prepared by Conia's method,[20] and 2,3,4-trimethylcyclopent-2-enone by the method described by Feitler and Whitesides [21] for the synthesis of 3-ethyl-2,4,5-trimethylcyclopent-2-enone from pentan-3-one.

Reduction and methylation of the ketones was carried out following the procedure described by Mironov *et al.*,[22] and the resulting alcohols were dehydrated thermally by distillation. The cyclopentadienes were dried and distilled and analysed by g.l.c.–m.s.

Bis(cyclopentadienyl)mercury compounds were obtained by lithiation of the appropriate cyclopentadiene in diethyl ether with butyl-lithium in hexane, then mercury(II) chloride was added. The resulting mixture was filtered, and the solution was used for e.s.r. experiments without further purification.

E.s.r. Experiments.—Solutions of the cyclopentadienes in toluene, or of the mercury derivatives in diethyl ether, were sealed under nitrogen in Suprasil silica tubes, and photolysed in the cavity of a Varian E109 e.s.r. spectrometer with light from a 500 W high pressure mercury arc.

Calculations.—McLachlan spin densities were calculated according to equation (7), using the atom–atom polarisabilities quoted for the cyclopentadienyl anion.[10]

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