Substituent Effects by Deuterium and Alkyl Groups and ^{13}C Hyperfine Coupling Constants of Cyclopentadienyl Radicals as Studied by Electron Spin Resonance[1]

Mitsuo Kira, Mieko Watanabe, and Hideki Sakurai*

Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan. *Received December 4, 1979*

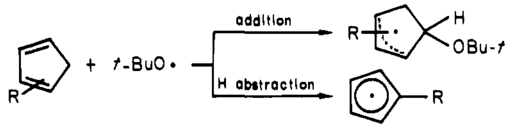
Abstract: ESR spectra of the parent and six substituted cyclopentadienyl radicals ($RC_5H_4\cdot$; R = H, D, Me, Et, *i*-Pr, *t*-Bu, Me_3SiCH_2), generated from the corresponding $RC_5H_4SnMe_3$ by an S_H2 attack on Sn with the photochemically generated *tert*-butoxy radical, have been recorded over the temperature range −95 to +24 °C. Judging from the proton coupling constants, the electron-releasing perturbation of alkyl groups is in the order $(CH_3)_3SiCH_2 > CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C$. Preferred conformations of these alkyl groups are discussed from the temperature effects on the spectra. Notably, the methyl group rotates freely, while the $(CH_3)_3SiCH_2$ group has a fixed conformation in which the $(CH_3)_3Si$ group eclipses the p orbital on the C_1 atom of the cyclopentadienyl. The resonance-integral perturbation effect is more important than the Coulomb-integral perturbation in the deuterium substitution. Finally the coupling constants of ^{13}C for C_nH_n (n = 5–8) radical species are discussed.

Although a number of monosubstituted cyclic π hydrocarbon radicals have been investigated by ESR spectroscopy,[2] there has been no such study on the substituted cyclopentadienyl radical until our report on several silyl-substituted cyclopentadienyl radicals appeared.[3] This work revealed a unique role of the cyclopentadienyl radical as a tool for elucidating substituent effects because the unpaired electron of the cyclopentadienyl radical resides in a bonding π orbital, while in other familiar π radicals such as benzene anion and cycloheptatrienyl radicals, the unpaired electron occupies an antibonding orbital.

We now report results of an ESR study involving deuterio- and alkyl-substituent effects as well as the ^{13}C hyperfine coupling constant of the cyclopentadienyl radical. The required substituted cyclopentadienyl radicals were generated by a novel method in which a mixture of a substituted (cyclopentadienyl)trimethylstannane and di-*tert*-butyl peroxide is photolyzed at low temperature. We discuss particularly the Baker–Nathan effects and the preferred conformations of alkyl groups, enhanced σ(C–Si)–π conjugation of the (trimethylsilyl)methyl group, the significant role of the out-of-plane vibration on deuterium isotope effects, and a rationalization of the ^{13}C coupling constants of a series of C_nH_n (n = 5–8).

Results and Discussion

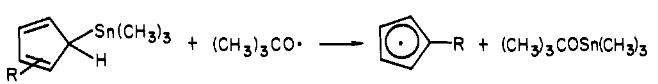
Generation and ESR Spectra of Substituted Cyclopentadienyl Radicals. The parent cyclopentadienyl radical was generated for the ESR study by several routes such as γ irradiation on both crystalline[4,5] and liquid cyclopentadiene,[6] pyrolysis of a molecular beam of ferrocene and azobenzene,[7] and hydrogen abstraction of cyclopentadiene with the *tert*-butoxy radical in solution.[8] The last method appeared to afford a general method of generating the substituted cyclopentadienyl radicals such as alkyl-substituted ones in solution. However, generation of substituted cyclopentadienyl radicals by this method is not always easy except for silyl- and germyl-substituted ones.[3,10] Additional signals due to an allylic radical result from addition of the *tert*-butoxy radical to the parent and alkyl-substituted cyclopentadienes.[8,9] Moreover, steady-state concentrations of these cyclopentadienyl radicals are intrinsically low. Therefore, detailed investigations of ESR spectra of these radicals under these conditions are very difficult (eq 1).



(1)

We have found that photolysis of a mixture of an alkyl-substituted (cyclopentadienyl)trimethylstannane and di-*tert*-butyl peroxide at low temperature allows highly selective production of the corresponding cyclopentadienyl radical in high steady-state concentration through an S_H2 attack of the *tert*-butoxy radical at Sn.[1] The parent cyclopentadienyl radical including $C_5H_4D\cdot$ can also be generated in sufficiently high concentration to allow detailed analysis of the spectra (vide infra). We have thus generated parent (**2a**) and six substituted cyclopentadienyl radicals (**2b–g**) by this novel method (eq 2). Photochemically excited

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO\cdot \qquad (2)$$



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2a, R = H
b, R = D
c, R = CH_3
d, R = C_2H_5
e, R = $(CH_3)_2CH$
f, R = $(CH_3)_3C$
g, R = $(CH_3)_3SiCH_2$

acetone can also be used for the production of these radicals but without any improvement of the signal intensity.

Very recently, Davies and his co-workers have generated the cyclopentadienyl radical by direct photolysis of η^1-$C_nH_nSn^{IV}$ and related organometallic species.[11a] In our hands, photolysis of

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[1] Chemistry of Organosilicon Compounds. 131. For a preliminary communication, see: Kira, M.; Watanabe, M.; Sakurai, H. *Chem. Lett.* **1979**, 973.

[2] (a) Bowers, K. W. "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Wiley: New York, 1968; p 211. (b) Gerson, F.; Hammons, J. H. "Nonbenzenoid Aromatics II"; Snyder, J. P., Ed.; Academic Press: New York, 1971; p 81.

[3] Kira, M.; Watanabe, M.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 7780.

[4] Ohnishi, S.; Nitta, I. *J. Chem. Phys.* **1963**, *39*, 2848.

[5] Liebling, G. R.; McConnell, H. M. *J. Chem Phys.* **1965**, *42*, 3931.

[6] Fessenden, R. W.; Ogawa, S. *J. Am. Chem. Soc.* **1964**, *86*, 3591.

[7] Zandstra, P. J. *J. Chem. Phys.* **1964**, *40*, 612.

[8] (a) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1968**, 90, 7155. (b) Kawamura, T.; Kochi, J. K. *J. Organomet. Chem.* **1973**, *47*, 79.

[9] Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1977**, *67*, 1413.

[10] (a) ESR spectra of (trimethylgermyl)cyclopentadienyl and other related radicals will be published in a forthcoming paper. (b) Cl_3Si group, one of the most electron-accepting silyl group, gave the a_1* of −0.56 G at −105 °C.

[11] (a) Davies, A. G.; Tse, M. W. *J. Chem. Soc., Chem. Commun.* **1978**, 353. (b) Barker, P. J.; Davies, A. G.; Fisher, J. D. *Ibid.* **1979**, 587. (c) Professor Davies has informed us that they have investigated independently the ESR spectra of deuterio- and several alkylcyclopentadienyl radicals generated by their method. (d) Barker, P. J.; Davies, A. G.; Tse, M.-W. *J. Chem. Soc., Perkin Trans.* 2, to be submitted for publication.

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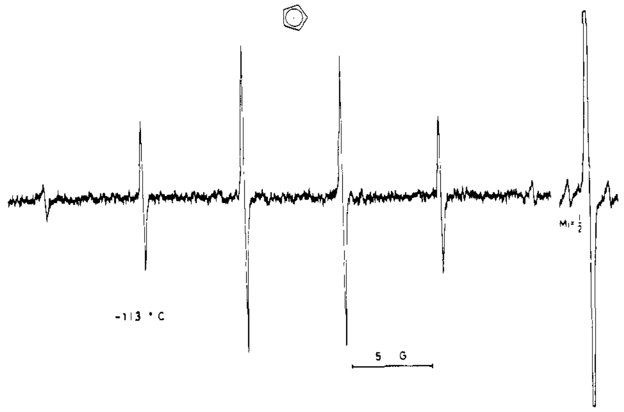


Figure 1. ESR spectrum of the cyclopentadienyl radical (**2a**) at -113 °C.

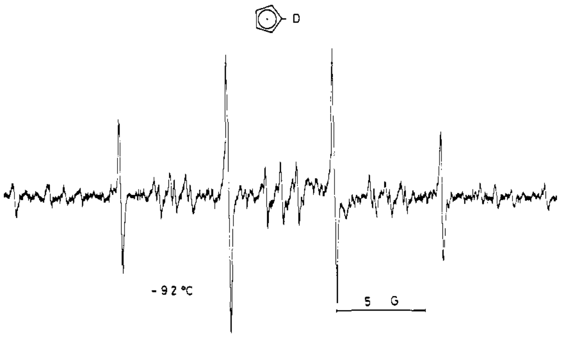
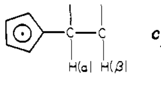


Figure 2. ESR spectrum of the monodeuteriocyclopentadienyl radical (**2b**) superimposed with **2a** at -92 °C.

Table I. ESR Parameters of Substituted Cyclopentadienyl Radicals

radical	temp, °C	hfcc/G $a_1{}^{*a}$	$a_{2,5}$	$a_{3,4}$	$a_\alpha{}^b$	other	R^c
2b	−92	5.86	6.19	5.99		$a_D = 0.90$	
2c	−95	13.04	0.76	7.82	15.29		1.17
	−50	12.98	0.82	7.79	15.14		1.17
	24	12.72	1.00	7.73	14.80		1.17
2d	−95	12.74	0.94	7.79	15.99		1.26
	−50	12.80	1.00	7.70	15.33		1.20
	24	12.28	1.24	7.72	14.50		1.18
2e	−95	12.54	1.12	7.71	12.56	$a_\beta = 0.41^b$	1.00
	−50	12.66	1.15	7.62	12.28	0.42	0.97
	24	12.24	1.30	7.68	11.78	0.41	0.96
2f	−50	12.38	1.30	7.61		$a_\beta = 0.67$	
	24	12.20	1.48	7.52		0.63	
2g	−95	14.04	0.50	7.58	10.40		0.74
	−50	14.00	0.48	7.62	10.49		0.75
	24	14.06	0.56	7.51	10.57		0.75

[a] $a_1{}^* = Q_H - \Sigma_{i=2}{}^5 a_i$ (Q_H = 30.20 G; see this text).

[b] 

[c] $R = a_\alpha / a_1{}^*$.

trimethyltin species in the presence of di-*tert*-butyl peroxide gave stronger ESR signals. The ESR spectrum of **2a**, as shown in Figure 1, was dramatically improved over that obtained by the previous route (eq 1).[8] Highly selective production of **2a** with no additional paramagnetic species such as a *tert*-butoxy adduct radical allowed the first observation of the satellite spectrum due to cyclopentadienyl-^{13}C radical in natural abundance. Since **2b** was produced from the mixture of (deuteriocyclopentadienyl)trimethylstannane and (cyclopentadienyl)trimethylstannane (ca. 1:1), the ESR spectrum was superimposed with that of **2a** as shown in Figure 2. The latter served as an internal standard for precise determination of the hyperfine coupling constants (hfcc). The ESR spectra of five alkylcyclopentadienyl radicals (**2c–g**) are shown in Figures 3–7.

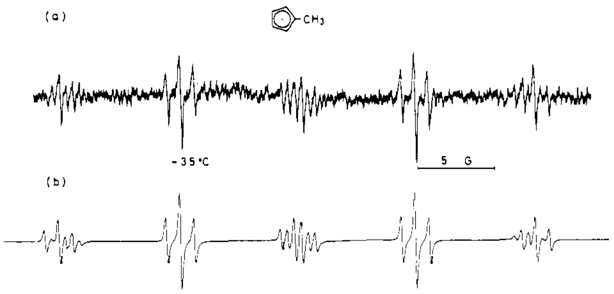


Figure 3. ESR spectra of methylcyclopentadienyl radical (**2c**) at -35 °C: (a) experimental; (b) computer simulated.

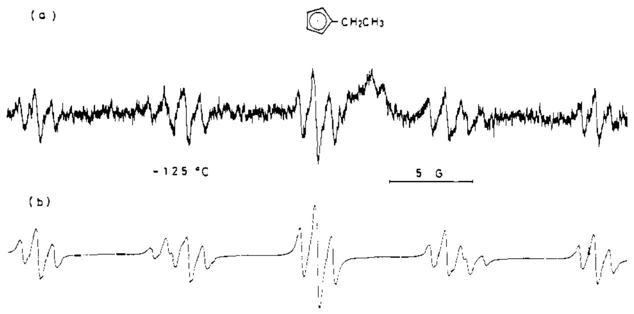


Figure 4. ESR spectra of ethylcyclopentadienyl radical (**2d**) at −125 °C: (a) experimental; (b) computer simulated.

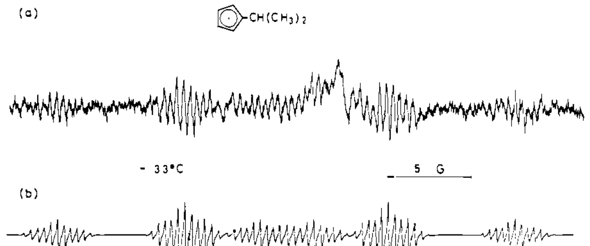


Figure 5. ESR spectra of isopropylcyclopentadienyl radical (**2e**) at −33 °C: (a) experimental; (b) computer simulated.

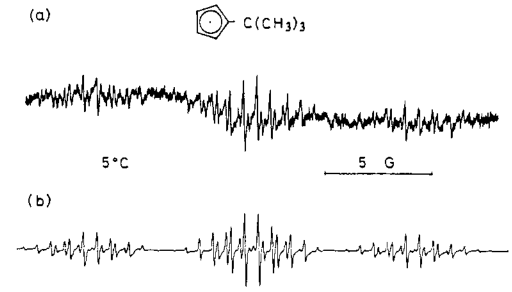


Figure 6. ESR spectra of *tert*-butylcyclopentadienyl radical (**2f**) at 5 °C: (a) experimental; (b) computer simulated.

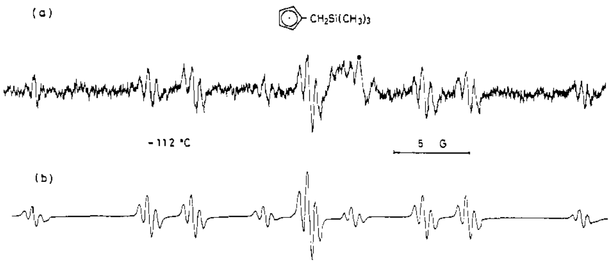


Figure 7. ESR spectra of [(trimethylsilyl)methyl]cyclopentadienyl radical (**2g**) at −112 °C: (a) experimental; (b) computer simulated.

All the ESR spectra of these radicals were analyzed with the aid of computer simulations. Table I lists the hfcc's and other ESR parameters of these radicals. Ring proton hfcc's were as-

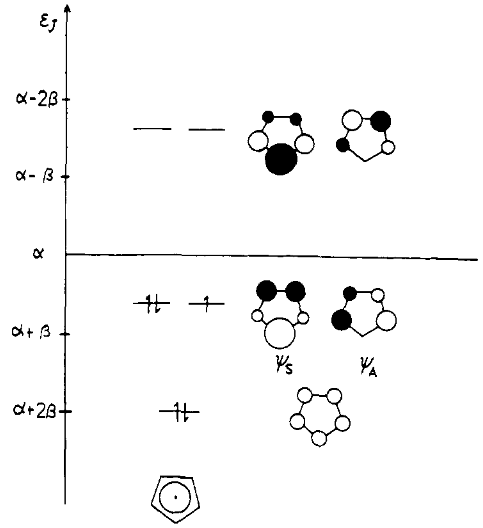


Figure 8. HMO energy diagram for cyclopentadienyl radical.

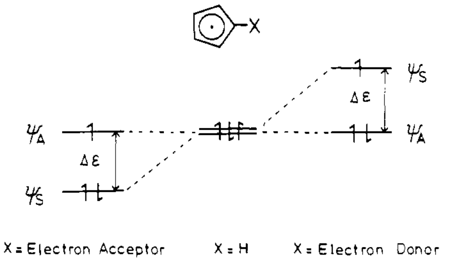


Figure 9. Splitting of degeneracy of the highest occupied molecular orbitals in the monosubstituted cyclopentadienyl radical.

signed on the basis of the prediction of the HMO theory.

Following the previous publication,[3] we discuss the substituent effects by the Hückel molecular orbital model without taking into consideration the effects of extensive configuration interaction and vibronic coupling. The Jahn–Teller effects for cyclopentadienyl radical are concluded to be rather weak by the investigation of the photoelectron spectra of $C_5H_5^-$.[9] This simple treatment is useful enough to draw a qualitative picture of the character of the substituent, especially for a series of closely related cyclopentadienyl radicals.

The HMO Model for Substituted Cyclopentadienyl Radicals. Since the perturbation treatment of the substituent effects on the D_{5h} cyclopentadienyl radical was already been described in detail in the previous publication within the framework of Hückel molecular orbital theory,[3] only the essential points necessary for the subsequent discussion are repeated.

In a monosubstituted cyclopentadienyl radical with the local symmetry of C_{2v} in which the substituent occupies the position 1, the unpaired electron is unequally distributed between the two orbitals Ψ_S and Ψ_A which are no longer degenerate as they are in the parent radical (eq 3 and 4). These orbitals are depicted

$$\Psi_S = 0.632x_1 + 0.195(x_2 + x_5) - 0.512(x_3 + x_4) \quad (3)$$

$$\Psi_A = 0.602(x_2 - x_5) + 0.372(x_3 - x_4) \quad (4)$$

schematically in Figure 8. An electron-donating substituent raises the Ψ_S level and the electronic configuration $\Psi_A{}^2\Psi_S{}^1$ (S form) is preferred, while an electron-accepting substituent lowers the Ψ_S level and the $\Psi_S{}^2\Psi_A{}^1$ configuration (A form) is preferred. Two types of perturbations on the degenerate highest occupied MO's of $C_5H_5\cdot$ are schematically shown in Figure 9.

When the energy difference (ΔE) between the two configurations is small, appreciable mixing of the two forms occurs (eq 5). The observed spectrum is a result of the rapid exchange

$$\Psi_A{}^2\Psi_S{}^1 \overset{\Delta E}{\rightleftharpoons} \Psi_S{}^2\Psi_A{}^1 \quad (5)$$

between S and A forms. According to this assumption, the spin density ρ_i at position i of a substituted cyclopentadienyl is given by eq 6 and 7, where P_S and P_A are the relative probabilities that

$$\rho_i = P_S\rho_i{}^S + P_A\rho_i{}^A \quad (6)$$

$$P_S + P_A = 1 \quad (7)$$

the radical is in the S and A forms, respectively, at a particular temperature and $\rho_i{}^S$ and $\rho_i{}^A$ are the spin densities at position i in the S and A forms, respectively. According to the McConnell relationship, $a_i = Q_H\rho_i$,[12a] the equivalent relation to eq 6 for the hfcc is deduced as eq 8 where a_i is the proton splitting in the radical

$$a_i = P_Sa_i{}^S + P_Aa_i{}^A \quad (8)$$

at position i and $a_i{}^S$ and $a_i{}^A$ are the proton hfcc's at position i in the S and A forms, respectively. Since the total π-electron spin density must be unity, the spin density at position 1 would give rise to an α-proton splitting $a_1{}^*$ defined by eq 9.

$$a_1{}^* = Q_H - \sum_{i=2}^{5} a_i \quad (9)$$

In addition, one can evaluate P_A and P_S from the measured values of a_i's on the basis of both HMO and McLachlan calculations. Values of ΔE can be calculated from the temperature dependence of P_A/P_S (see eq 10).

$$P_A/P_S = \exp(-\Delta E/kT) \quad (10)$$

On the basis of the observed Q_H value of the cyclopentadienyl radical (Q_H = 30.2 G) and HMO or McLachlan[12b] calculation, the following spectrum of $a_1{}^*$ values is expected by systematically changing the electronic properties of the substituent.

X = a strong donor ←	X = H	→ X = a strong acceptor
pure S form		pure A form
$a_1{}^*$ = 12.1 G		$a_1{}^*$ = 0 G (HMO)
$a_1{}^*$ = 14.5 G	←a_1 = 6.04 G→	$a_1{}^*$ = −2.7 G (McLachlan, λ = 0.75)

We have actually observed $a_1{}^*$ values in the range −0.56 to +10.7 G for substituted silyl groups.[3,10]

Alkyl-Substituent Effects on $C_5H_5\cdot$:[13] Baker–Nathan Effects and Enhanced σ–π Conjugation of (Trimethylsilyl)methyl Group. All the alkyl-substituted cyclopentadienyl radicals (**2c–f**) showed $a_1{}^*$ values larger than 12 G as seen in Table I. Since the $a_1{}^*$ value of the pure S form can be estimated as 12.08 G from the HMO spin density calculation,[3] one might judge that all the alkyl substituents raise the Ψ_S orbital of $C_5H_5\cdot$ to make the energy difference between the ground S form and the excited A form large enough to force the S form population P_S to unity. We have observed, however, small but appreciable temperature dependences of $a_1{}^*$ values for **2c–f** even for the methyl derivative where the substituent has the local symmetry of C_{3v}. On the other hand, the $a_1{}^*$ of **2g** whose substituent is the strongest electron donor due to extensive σ–π conjugation[14] was rather larger than those of **2c–f** and temperature independent. These observations suggest that the limiting value of the $a_1{}^*$ for the pure S form may be a little larger than 12.1 G predicted by the HMO theory, being taken

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(12) (a) McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 764. (b) McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233. λ = 0.75 was used so as to give the best fit between the observed five-membered ring proton hfcc values for the indenyl radical and the calculation.[3]

(13) Substituent effects of methyl group on $C_5H_5\cdot$ were examined by photodetachment investigations of $CH_3C_5H_4^-$: Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Chem. Phys.* **1973**, *59*, 5068.

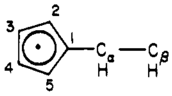
(14) (a) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 649. (b) Symons, M. C. R. *Ibid.* **1972**, *94*, 8589. (c) *Tetrahedron Lett.* **1975**, 793. (d) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6459. (e) *Ibid.* **1974**, *96*, 6715. (f) Sakurai, H.; Uchida, T.; Kira, M. *J. Organomet. Chem.* **1976**, *107*, 15. (g) Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 3892. (h) Bock, H.; Kaim, W. *Tetrahedron Lett.* **1977**, 2343. (i) Bock, H.; Kaim, W.; Rohwer, H. E. *J. Organomet. Chem.* **1977**, *135*, C14. (j) *Chem. Ber.* **1978**, *111*, 3573. (k) Bock, H.; Kaim, W. *Ibid.* **1978**, *111*, 3552, 3585. (l) Bock, H; Kaim, W; Kira, M.; Osawa, H.; Sakurai, H. *J. Organomet. Chem.* **1979**, *164*, 295.

more properly as 14.5 G based on the McLachlan calculations ($\lambda = 0.75$).[12b] The observed small differences among $a_1{}^*$ values of **2c–f** at a definite temperature can be taken as the reflection of the difference of the electronic effects of alkyls. The order of electron-donating ability of the alkyl groups estimated by this method is as follows: Me > Et > *i*-Pr > *t*-Bu, being apparently in accord with the order of the Baker–Nathan effect.[15]

Recently, Baker–Nathan effects have often been explained by some nonvertical effect such as steric hindrance to solvation,[16–19] since ionization potentials,[16b,20] and charge-transfer spectra[19] of alkylbenzenes give the reverse order of the Baker–Nathan effects. However, it should be noted that the substituent effects on some cyclic π radicals such as benzene anion[21] and cycloheptatrienyl radicals[22] have also revealed stronger apparent electron-donating ability of the methyl group than the *tert*-butyl group as observed in the cyclopentadienyl system. Baker–Nathan effects may be caused in a certain situation by some vertical electronic interaction. The difference of electron-donating ability between methyl and *tert*-butyl groups can possibly arise from the more effective negative hyperconjugation[21c,23a,b] of the latter than the former, since the σ–σ^* splitting is probably smaller for a C–C than a C–H bond.[23c]

As indicated by the $a_1{}^*$ value of 14.0 G and the temperature independence, the [(trimethylsilyl)methyl]cyclopentadienyl radical is considered to be in the pure S form in the experimental temperature range due to the extensive electron donation by σ(C–Si)–π conjugation.[14] The significantly larger $a_1{}^*$ of **2g** than that of **2c** is incompatible with the idea of homo (p–d) conjugation.[14a,d,e]

Conformational Preference of Alkyl Substituents on Cyclopentadienyl Radicals. From the molecular orbital consideration for cyclopentadienyl radicals one can expect that the electron-donating alkyl substituents make the Ψ_S orbital the singly occupied molecular orbital (SOMO). The alkyl proton hfcc values on C_α, defined as a_α here, can be induced mainly by a hyperconjugation mechanism from the rather high spin density on the C_1 pπ orbital, while a_α values of cycloheptatrienyl and benzene anion radicals are fairly small since one of the nodal planes of the SOMO passes through the substituted C_1 atom. Relatively large a_α values allow one to investigate the conformational preference of alkyl groups in XC_5H_4 radicals.



The magnitude of a_α should be dependent on both the spin density at C_1 and the time-averaged dihedral angle between the α-CH bond and the C_1 pπ orbital, as represented by the following equation[24] ($A \simeq 0$):

$$a_\alpha = \rho_1(A + B\langle\cos^2\theta\rangle) \simeq \rho_1 B\langle\cos^2\theta\rangle \qquad (11)$$

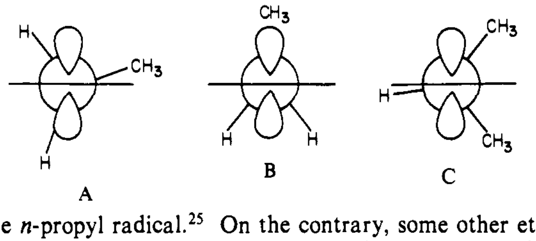
Combining the above equation with the McConnell relationship, we introduce R values as defined by eq 12. The R values are

$$R \equiv a_\alpha/a_1{}^* \simeq (B/Q_H)\langle\cos^2\theta\rangle \qquad (12)$$

also listed in Table I. Since the values of Q_H and B should be independent of the alkyl substitutent, the observed R values depend only on $\langle\cos^2\theta\rangle$. In other words, we can take the R value as an indication of the time-averaged conformation of the alkyl group.

The methyl group in **2c** gives a value for R (=1.17) which is constant over the entire temperature range. Hence, we conclude that the methyl group is freely rotating ($\langle\cos^2\theta\rangle = {}^1/_2$) and $B/Q_H = 2.34$, in reasonable agreement with values for other radicals.[25]

A slightly but appreciably larger R value for **2d** (R = Et) than for **2c** as well as the negative temperature coefficient dR/dT of the former radical suggests that **2d** is more stable in conformation A than in B. A similar conformational preference is observed for the *n*-propyl radical.[25] On the contrary, some other ethyl-substituted cyclic π radicals such as ethylcyclooctatetraene anion,[26] *p*-ethylnitrobenzene anion,[27a] *p,p'*-diethylbiphenyl anion,[27b] and *p*-ethylphenyl alkoxy nitroxide radicals[14f] are known to prefer another conformation B. Such a remarkable difference in the preferred conformations may be rationalized in terms of the smaller interior angle of the regular pentagon than those of the hexagon and the octagon. The steric hindrance between the ortho hydrogens and the methyl group in conformation A, as suggested by Carrington and Todd,[26] may be reduced. As a consequence, conformation A is preferred by **2d**. Here one may call to mind the delicate balance between C–H and C–C hyperconjugations.



The preferred conformation of **2e** (R = *i*-Pr) is rather complicated to decide since the temperature dependence of the R value was not monotonous as seen in Table I, although the smaller R value than that of **2c** can be taken as the indication of the preferred conformation C for **2e**, in accord with those for other isopropyl-substituted aromatic anion radicals.[21c,28]

A small and constant R value for **2g** is another indication of the extensive σ(C–Si)–π conjugation. R (for **2g**)/R (for **2c**), which means $2\langle\cos^2\theta\rangle$ for **2g**, is 0.64 and can be compared with the values for (trimethysilyl)ethyl (0.66)[14a] and some other related radicals.[29]

Removal of Degeneracy by Deuterium Substitution. Verification of the Resonance-Integral Perturbation Model. Until now, there have been many investigations of deuterium isotope effects on cylic π radicals, but the splitting of the two degenerate electronic configurations has been observed, only for the benzene-*d* anion radical.[30] The substitution of benzene cation,[31a] cycloheptatrienyl,[31b] and cyclooctatetraene anion radical[32] with deuterium showed no appreciable effect on the residual proton couplings.

Two types of perturbing effects for deuterium substitution on a cyclic π radical, i.e., Coulomb-integral and resonance-integral perturbation, have been suggested previously.[30,33] The former

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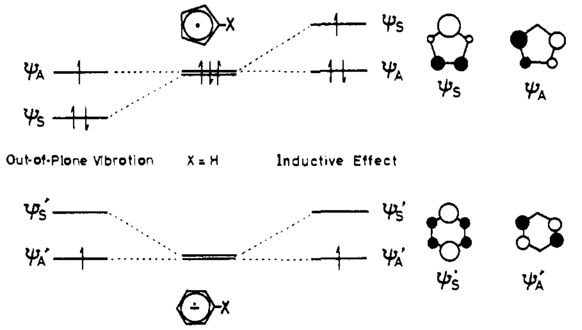

Figure 10. Splitting of degeneracy of the highest occupied molecular orbitals in the deuterium-substituted cyclopentadienyl radical and benzene radical anion.

takes account of the fact that deuterium releases electrons more strongly than hydrogen which will perturb the Coulomb integral (α). The perturbation energy depends on the atomic coefficient at the substitution position (c_r) and can be described by the following equation:

$$\Delta\epsilon(\alpha) = c_r^2 \delta_r^\alpha \beta_0 \tag{13}$$

where $\delta_r^\alpha\beta_0$ is the Coulomb-integral change by deuterium substitution and should be positive. The resonance-integral (β) model considers the out-of-plane vibration of hydrogen or deuterium, which determines the average angle between the pπ orbital on the C_1 atom and the pπ orbitals on the two adjacent carbon atoms. The β should decrease with increasing angle. The perturbation energy can be expressed as follows:

$$\Delta\epsilon(\beta) = 2(c_r c_{r+1} \delta_{r,r+1}^\beta + c_r c_{r-1} \delta_{r,r-1}^\beta)\beta_0 \tag{14}$$

where $\delta_{r,r\pm1}^\beta\beta_0$ is the resonance-integral change between the two adjacent carbon atoms produced by deuterium substitution and should be taken as negative owing to the reduced amplitude of the vibration.

As shown schematically in Figure 10, the HMO perturbation theory predicts that for the benzene anion radical both perturbations destabilize the symmetric orbital Ψ_S', while the antisymmetric orbital Ψ_A' is unchanged; one can expect the $\Psi_A'^1$ configuration should be more important for the benzene-*d* anion radical than the $\Psi_S'^1$ configuration, although the latter contributes considerably, owing to thermal excitation and vibronic coupling. Experimental results[30] are reasonably explained by both perturbation models. On the other hand, for the cylcopentadienyl radical two models give rise to different situations. According to eq 13 and 14, the symmetric orbital Ψ_S should be stabilized and destabilized by the resonance-integral and the Coulomb-integral perturbation, respectively; the former makes the $\Psi_S^2\Psi_A^1$ configuration more important than the $\Psi_A^2\Psi_S^1$, while the situation is inversed for the latter. Although considerable contribution from the excited electronic configuration is expected because of thermal mixing and vibronic coupling, $\gamma = a_1^*/a_H$, where a_1^* is a proton splitting at the deuterium-substituted position of **2b**, and should be the proper criterion of the predominant perturbation. Thus it should be expected that resonance-integral perturbation is more effective if γ is less than unity, while Coulomb-integral perturbation should be the major factor if γ is greater than unity.

The spectrum of **2b** shows that the twofold degeneracy of the ground-state electronic configuration of the cyclopentadienyl radical is lifted by deuterium substitution. Thus, two sets of triplets (intensity ratio 1:2:1) of 6.19 ± 0.02 G and 5.99 ± 0.02 G, which are further split into a triplet (1:1:1) of 0.90 ± 0.01 G, are observed. The ratio, r, is 0.969 ± 0.008 from 12 measurements, which indicates that the resonance-integral perturbation is more important than Coulomb-integral perturbation.

While the apparent ratio of magnetic moments of hydrogen to deuterium, a_i^H/a_i^D, in the benzene anion has been shown to differ significantly from g_H/g_D (=6.514),[29c] a_1^*/a_1^D in **2b** was found to be 6.48 ± 0.08, bordering on 6.514 within the experimental error. We cannot account for such a difference between $C_6H_5D^-\cdot$ and $C_5H_4D\cdot$ since the exact source of the anomalous deuterium hyperfine coupling has not been known up to date.[34]

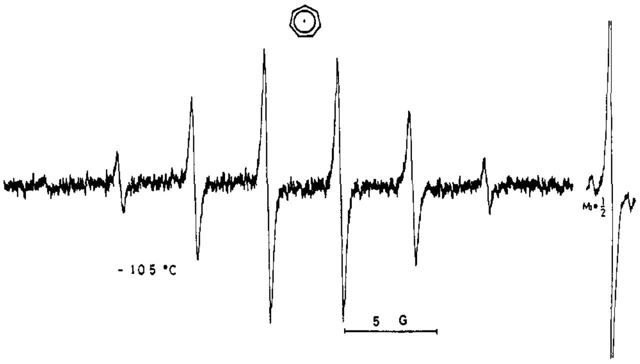

Figure 11. ESR spectrum of the cycloheptatrienyl radical at −105 °C.

Table II. Experimental and Calculated ^{13}C hfcc Values for Cyclic π Radicals (G)

		calcd			
radical	exptl (temp/°C)	K-F[37]	Y-K-K[38]	INDO[41]	ref
$C_5H_5\cdot$	2.66 ± 0.02 (−105)	1.56	2.04	4.1	this work
$C_6H_6^-\cdot$	2.8 ± 0.1 (−100)	1.30	2.23	4.0	42
$C_7H_7\cdot$	1.98 ± 0.02 (−105)	1.11	1.76	3.5	this work
$C_8H_8^-\cdot$	1.28 ± 0.05	0.98	1.43	3.0	43

Although vibronic coupling should be taken into account for the quantitative estimation of the deuterium isotope effect,[35] one may obtain the qualitative feature by the rough calculation without inclusion of the vibronic coupling. According to the method of Volland and Vincow,[31b] the energy splitting (ΔE) between the two nearly degenerate states of $C_5H_4D\cdot$ can be calculated as follows:

$$\Delta E = E_S - E_A = 2RT\Delta a_{23}/(\Delta a_{23} + Q_H(\rho_3^S - \rho_2^S)) \tag{15}$$

where Δa_{23} is the hfcc difference between a_2 and a_3 observed for $C_5H_4D\cdot$ and ρ_i^S is the spin density at position i calculated for the S form. The value of ΔE for $C_5H_4D\cdot$ is 22 cal/mol which can be compared with 57 cal/mol for $C_6H_5D^-\cdot$ and 25 cal/mol for $C_7H_6D\cdot$.[31b] On the other hand, one can expect the ratio of $\Delta\epsilon(\beta)$ (for $C_6H_5D^-\cdot$)/$\Delta\epsilon(\beta)$ (for $C_5H_4D\cdot$) to be 1.4 from eq 14 under the assumption of the same $\delta^\beta\beta_0$ for both radicals. Therefore, the relatively small ΔE for $C_5H_4D\cdot$ may be attributed to the partial cancellation by Coulomb-integral perturbation.

^{13}C Hyperfine Coupling Constant of $\cdot C_5H_5$–^{13}C. The carbon-13 hfcc, $a(^{13}C)$, of $C_5H_5\cdot$ was measured from the satellite lines in the spectrum of **2a** (see Figure 1) as 2.66 ± 0.02 G at −105 °C. To compare the $a(^{13}C)$ values of a series of cyclic π radicals at a low temperature, we have investigated the ESR spectrum of $C_7H_7\cdot$[36,8a] by generating the radical with the photolysis of the mixture of cycloheptatriene and di-*tert*-butyl peroxide at −105 °C. The ESR spectrum is shown in Figure 11. The estimated $a(^{13}C)$ for $C_7H_7\cdot$ is 1.98 ± 0.02 G, which may be compared with the value of 1.86 G extrapolated from the temperature dependence of the values determined at around 165 °C.[36] Table II lists the $a(^{13}C)$ values of pertinent cyclic π radicals together with the theoretical ones calculated by three different methods.

The well-known Karplus–Fraenkel equation[37] for $a(^{13}C)$ is generally expressed as follows:

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[33] The absence of a significant deuterium isotope effect in $C_8H_7D^-\cdot$ is explained by an alternative consideration. See ref 32.

[34] Jones, M. T.; Cairncross, A.; Wiley, D. W. *J. Chem. Phys.* **1965**, *43*, 3403.

[35] Purins, D.; Karplus, M. *J. Chem. Phys.* **1975**, *62*, 2 have calculated the deuterium isotope effects on the benzene anion radical, by taking account of the vibronic coupling to suggest the importance of the out-of-plane vibration for the vibronic energy.

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$$a(^{13}\mathrm{C}) = (S_\mathrm{C} + \sum_{i=1}^{3} Q_{\mathrm{CX}_i})\rho_\mathrm{C} + \sum_{i=1}^{3} Q_{\mathrm{X}_i\mathrm{C}}\rho_{\mathrm{X}_i} \qquad (16)$$

where $S_\mathrm{C} = -12.7$ G, $Q_{\mathrm{CC}_i} = 14.4$ G, $Q_\mathrm{CH} = 19.5$ G, and $Q_{\mathrm{C}_i\mathrm{C}} = 13.9$ G are taken according to the original proposal by the authors. For simple cyclic π radicals, this equation can be put in the following form:

$$a(^{13}\mathrm{C}) = (S_\mathrm{C} + Q_\mathrm{CH} + 2Q_{\mathrm{CC}_i} + 2Q_{\mathrm{C}_i\mathrm{C}})\rho_\mathrm{C} \qquad (17)$$

Theory predicts that $a(^{13}\mathrm{C})$ should increase with decreasing ring size as shown in the third column of Table II.

The Yonezawa–Kawamura–Kato treatment,[38] an alternative method for estimating $a(^{13}\mathrm{C})$ from the π AO spin density matrix, is described by the following equation:

$$a(^{13}\mathrm{C}) = Q_\mathrm{C}\rho_\mathrm{CC} + \sum_{i=1}^{3} Q_{\mathrm{X}_i}\rho_{ii} + \sum_{i=1}^{3} R_{\mathrm{CX}_i}\rho_{\mathrm{C}_i} \qquad (18)$$

where $Q_\mathrm{C} = 46.0$ G, $Q_{\mathrm{C}_i} = -17.3$ G, and $R_{\mathrm{CC}_i} = -1.95$ G. For a simple cyclic π radical

$$a(^{13}\mathrm{C}) = (Q_\mathrm{C} + 2Q_{\mathrm{X}_i})\rho_{ii} + 2\mathrm{R}_{\mathrm{CC}_i}\rho_{\mathrm{C}i} \qquad (19)$$

The theory emphasizes the importance of off-diagonal elements of the π AO spin density matrix (ρ_C), predicting smaller ^{13}C hfcc of $C_5H_5\cdot$ than that of $C_6H_6^{-}\cdot$ due to the positive $\rho_{\mathrm{C}i}$ value for SOMO of the former, as shown in the fourth column of Table II. This treatment gives rather good agreement with experiments, especially for the drop of the ^{13}C hfcc from $C_6H_6^{-}\cdot$ to $C_5H_5\cdot$.

Differences of the bond angle[39] as well as the difference of excess charge[40] between $C_5H_5\cdot$ and $C_6H_6^{-}\cdot$ are not included in the above discussion. However, the influence of the bond angle may be small because $a(^{13}\mathrm{C})$, calculated by INDO,[41] which may be regarded as a Karplus–Fraenkel type calculation including the bond angle effects, give the same order as the Karplus–Fraenkel theory in the series of cyclic π radicals, as seen in Table II. When Bolton's theory[40] of excess charge effects for the proton coupling constants is applied to the ^{13}C coupling constant, $a(^{13}\mathrm{C})$ for the benzene anion radical is modified to even a smaller value than that evaluated by eq 17; thus the excess charge effect cannot account for the difference of $a(^{13}\mathrm{C})$ between $C_5H_5\cdot$ and $C_6H_6^{-}\cdot$.

Experimental Section

Materials. Cyclopentadiene and methylcyclopentadiene were obtained by thermal depolymerization of the corresponding dimers. Cyclopentadiene-*d* was prepared with a D content of over 95% (analyzed by mass spectroscopy) by the treatment of C_5H_5MgBr with D_2O in di-*n*-butyl ether according to the procedure of Mironov et al.[44] Ethyl- and isopropylcyclopentadiene were obtained from C_5H_6 and the appropriate alkyl bromide by using phase-transfer reagents.[45] *tert*-Butylcyclopentadiene was prepared by the procedure described in the literature.[46] [(Trimethylsilyl)methyl]cyclopentadiene[47] was prepared from the reaction of sodium cyclopentadienide with (iodomethyl)trimethylsilane in THF in 41.9% yield; bp 39–40 °C (3–4 mmHg).

(*tert*-Butylcyclopentadienyl)trimethylstannane (**1f**) was prepared by the reaction of t-BuC_5H_4Li with Me_3SnCl according to the method of Davison and Rakita[48] in 13% yield: bp 56–60 °C (2 mmHg); NMR (60 MHz, CCl_4) δ 0.082 (s, 9 H, $J_{^{117}\mathrm{Sn-CH_3}} = 51.0$ Hz, $J_{^{119}\mathrm{Sn-CH_3}} = 54.0$ Hz), 1.27 (s, 9 H), 5.13 (m, 2 H), 6.30 (m, 2 H). Deuterio-, methyl-, ethyl-, isopropyl-, and ([(trimethylsilyl)methyl]cyclopentadienyl)trimethylstannane were prepared according to the general method[49] in which Me_3SnNMe_2[50] was reacted with the corresponding RC_5H_5. $C_5H_4DSnMe_3$ (**1b**) (76% yield; ca. 1:1 mixture of $C_5H_5SnMe_3$ (**1a**) and $C_5H_4DSnMe_3$ (**1b**)): bp 33 °C (1.5 mmHg); MS *m/e* 231 (M^+), 165 (100%, Me_3Sn^+); NMR (60 MHz, CCl_4) δ 0.06 (s, 9 H, $J_{^{117}\mathrm{Sn-CH_3}} = 51.0$ Hz, $J_{^{119}\mathrm{Sn-CH_3}} = 53.3$ Hz), 5.94 (s, 4.5 H, $J_\mathrm{Sn-H} = 22.5$ Hz). $CH_3C_5H_4SnMe_3$[48] (**1c**) (40.6% yield): bp 83 °C (15 mmHg). $CH_3CH_2C_5H_4SnMe_3$ (**1d**) (43% yield): bp 100 °C (25 mmHg); MS *m/e* 258 (M^+), 165 (100%, Me_3Sn^+); NMR (60 MHz in CCl_4) δ 0.01 (s, 9 H, $J_{^{117}\mathrm{Sn-CH_3}} = 51.2$ Hz, $J_{^{119}\mathrm{Sn-CH_3}} = 53.4$ Hz), 1.15 (t, 3 H, $J = 7.5$ Hz), 2.52 (q, 2 H, $J = 7.5$ Hz), 5.80 (m, 2 H), 5.40 (m, 2 H). Anal. Calcd for $C_{10}H_{18}Sn$: C, 46.75; H, 7.06. Found: C, 46.99; H, 6.81. $(CH_3)_2CHC_5H_4SnMe_3$ (**1e**) (40% yield): bp 95 °C (15 mmHg); MS *m/e* 272 (M^+), 165 (100%, Me_3Sn^+); NMR (60 MHz, CCl_4) δ 0.07 (s, 9 H, $J_{^{117}\mathrm{Sn-CH_3}} = 50.4$ Hz, $J_{^{119}\mathrm{Sn-CH_3}} = 52.6$ Hz), 1.20 (d, 6 H, $J = 6.9$ Hz), 2.72 (sept, 1 H, $J = 6.9$ Hz), 6.05 (m, 2 H), 5.31 (m, 2 H, $J_\mathrm{Sn-C-C-H} = 19.5$ Hz). Anal. Calcd for $C_{11}H_{28}Sn$: C, 48.76; H, 7.44. Found: C, 49.05; H, 7.14. $(CH_3)_3SiCH_2C_5H_4SnMe_3$ (**1g**) (26% yield): bp 72 °C (0.2 mmHg); MS *m/e* 316 (M^+), 73 (100%, Me_3Si^+); NMR (60 MHz, CCl_4) δ −0.08 (s, 9 H, $J_{^{117}\mathrm{Sn-CH_3}} = 52.0$ Hz, $J_{^{119}\mathrm{Sn-CH_3}} = 54.4$ Hz), −0.12 (s, 9 H), 3.38 (s, 2 H), 5.37 (m, 2 H), 5.67 (m, 2 H).

ESR Spectroscopy. A degassed solution of di-*tert*-butyl peroxide, an appropriate (cyclopentadienyl)trimethylstannane, and cyclopropane (ca. 1:1:1) in a sealed quartz tube was photolyzed in a cavity of a Varian E-12 ESR spectrometer with a 500-W Ushio super-high-pressure mercury lamp. Further details of the measurements have been described in a previous paper.[3] Computer simulations were carried out by using a Varian Data Machine's ADAPTS.

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