A Theoretical Assignment of the ESR Spectra of Cyclohexadienyl and Phenyl Radicals

By Keiji MOROKUMA, Shun-ichi OHNISHI, Takao MASUDA and Kenichi FUKUI

(Received January 23, 1963)

The assignment of observed unknown ESR spectra to a certain radical is often liable to involve some ambiguities; for example, the radicals from benzene and substituted benzenes cause trouble.

Fischer[1] irradiated benzene, toluene, ethylbenzene, cumene, fluorobenzene and chlorobenzene with an electron beam at 77°K and in all of the compounds studied observed the same spectrum, which consisted of a main triplet of the splitting of 50±2 gauss, each component of which separated into four triplets with the splittings 10.6±0.5 gauss (quartet) and 2.6± 0.2 gauss (triplet). He ascribed the spectrum to the cyclohexadienyl radical, $C_6H_7\cdot$, with the largest splitting (50 gauss) said to be that of the two methylene protons, with the splitting (10.6 gauss), that of the two ortho and the one para protons, and with the smallest splitting (2.6 gauss), that of the two meta protons.

Ohnishi et al.[2] studied ESR spectra of

1) H. Fischer, *Kolloid Z.*, **180**, 64 (1962).

2) S. Ohnishi, T. Tanei and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962).

radicals produced by the electron beam irradiation at 77°K of benzene, toluene, chlorobenzene, phenylcyclohexane, benzoic acid and xylenes. For benzene at observation temperatures lower than −50°C, they obtained a triplet spectrum with a quartet structure, each component having a finer triplet structure with splittings of 47.5 gauss (triplet), 10.4 gauss (quartet) and 2.5 gauss (triplet). At the higher temperature this spectrum disappeared, while there remained another singlet spectrum with the width of 25 gauss. They attributed the former complex spectrum, which is very close to that observed by Fischer, to the cyclohexadienyl radical, as did Fischer, while the latter singlet spectrum was ascribed to the phenyl radical, $C_6H_5\cdot$. Kuwata[3] observed a broad spectrum from UV-irradiated halogenobenzenes which was considered to originate from the phenyl radical.

On the other hand, Chkheidze et al.[4] irradiated benzene with an electron beam and observed a triplet spectrum with the intensity ratio of 1 : 2 : 1 and with the splitting of 45.0±1.5 gauss; each component of this spectrum separated into a quartet with the splitting of 10.2±0.5 gauss. Though the spectrum seems to resemble very closely those found by Fischer and by Ohnishi et al., Chkheidze et al. assigned the spectrum to the phenyl radical, where the largest triplet was assigned to the two ortho protons and the quartet, to the two meta and one para protons.

As we have explained here, the assignment of the two kinds of observed spectra, the triplet with quartet structures and the broad singlet, is a matter still to be settled. Judging from the historical evidence that theoretical calculations and discussions have offered a great foundation for the interpretation of ESR spectra, it seems to be worthwhile to make a calculation on cyclohexadienyl and phenyl radicals and to compute the spin densities or the coupling constants of protons. Recently Fischer[5] presented a molecular orbital calculation on the spin density of the cyclohexadienyl radical to support his assignment. In the present paper the authors will make a valence bond calculation on both radicals, will compare the results with the two observed spectra, and will give the theoretical choice between the two assignments of the spectra.

The Valence Bond Calculation of Proton-coupling Constants in the Cyclohexadienyl Radical

The Model of the $C_6H_7\cdot$ Radical. — The cyclohexadienyl radical is treated as a system

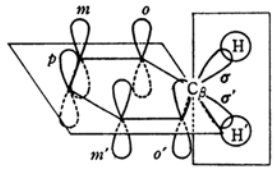

Fig. 1. Model of C_6H_7 radical.

consisting of 9 electrons on the following 9 atomic orbitals (Fig. 1):

- o: 2pπ orbital on one of the ortho carbons
- o': 2pπ orbital on the other ortho carbon
- m: 2pπ orbital on one of the meta carbons
- m': 2pπ orbital on the other meta carbon
- p: 2pπ orbital on the para carbon
- σ: Hybridized orbital on the carbon β directed to the AO H
- σ': Hybridized orbital on the carbon β directed to the AO H'
- H: Hydrogen 1s orbital on the hydrogen bonding with σ
- H': Hydrogen 1s orbital on the other hydrogen bonding with σ'

The plane on which the σ H and the σ' H' bonds are located is always assumed to be perpendicular to the molecular plane. As the hybridization of the methylene carbon, C_β in Fig. 1, and the bond length of the C_β–C_{ortho} bond do not seem to have been determined experimentally, we employed the following four different sets of configurational parameters in order to see the variation of the calculated results arising from these configurational differences.

a) The hybridization of the carbon β in the C_β–C_{ortho} bonds is assumed to be sp^2, which implies that the C–C bonds in benzene are not affected by a hydrogen addition; therefore, the hybridization of the σ and σ' orbitals is sp^5 (s nature 1/6 and p nature 5/6). The C_β–C_{ortho} bond length (r) is assumed to be 1.39Å, the C–C bond length in benzene.

b) The same hybridization as in a). The C_β–C_{ortho} bond length is 1.54Å, the bond length of a normal C–C single bond.

c) The carbon β is assumed to have the tetrahedral configuration: that is, all the valence orbitals of the carbon β are sp^3 hybridized. The C_β–C_{ortho} bond length is 1.39Å.

d) The same hybridization as in c). The bond length is 1.54Å.

In all of the four sets, the C_o–C_β–$C_{o'}$ angle is assumed to be 120°; this choice of angle affects the calculated value of the spin density scarcely at all.

3) K. Kuwata, private communication.
4) I. I. Chkheidze, Yu. N. Molin and N. Ya. Buben, *Dokl. Akad. Nauk. SSSR*, **130**, 1291 (1960).
5) H. Fischer, *J. Chem. Phys.*, **37**, 1094 (1962).

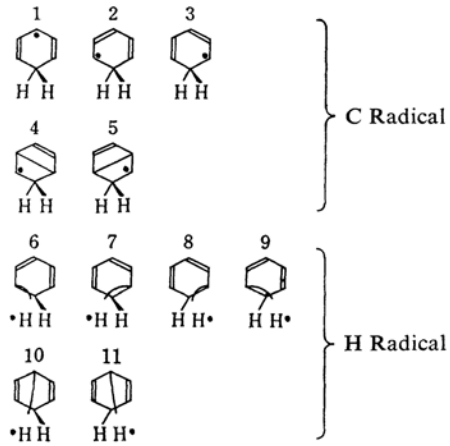

Fig. 2. Canonical structures taken into calculation of C_6H_7.

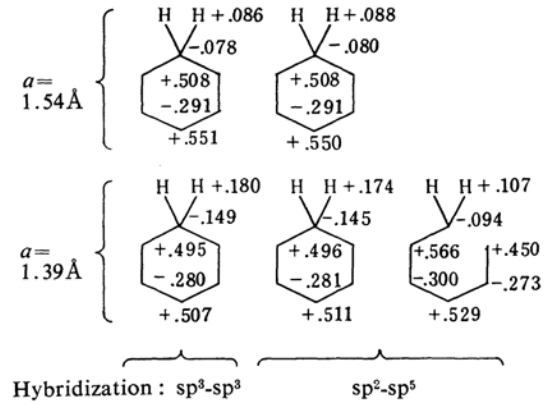

Fig. 3. Calculated spin density of C_6H_7 radical.

Canonical Structures. — Of all the possible canonical structures that have maximum bondings, 11 structures of lower energies corresponding to Kekulé and Dewar structures are taken into account on calculation. They are illustrated in Fig. 2.

Atomic Integrals.—The method of the evaluation of the necessary atomic integrals is the same as in the previous paper,[6] mainly the method of van Vleck[7] and of Karplus et al.[8], except for Altman's[9] exchange integrals between pπ orbitals. The values of the pπ-pπ exchange integrals employed are $N_{\pi\pi\pi\pi}$ (1.39Å) $=-2.27$ eV. and $N_{\pi\pi\pi\pi}$ (1.54Å) $=-1.24$ eV. Exchange integrals between non-neighboring atomic orbitals are completely neglected.

Calculation Results.—The calculated coefficients of all the canonical structures in the ground state wave function are collected in Table I, from which the spin densities are derived in Fig. 3.

Figure 3 also gives the result of a comparative calculation on an imaginary compound in which the interaction of one of the ortho carbons with the methylene group is omitted. One can clearly see that the ring formation very markedly increases the spin density on the methylene proton; the calculated spin density on the methylene protons in a ring compound is almost twice as large as in an open-chain compound.

In Fig. 3 it is also obvious that the change of the hybridization of the carbon β have little effect on the spin distribution. Thus, the observed coupling constants seem to offer no information on the hybridization.

On the other hand, the change in the C_β–C_{ortho} distance, that is, the change in the exchange integral between C_β and C_{ortho}, exerts a great influence on the spin density in the methylene group. Elongation of the C_β–C_{ortho} bond length from 1.39Å to 1.54Å reduces the methylene proton spin density by half.

From these calculated values of spin density are derived the proton coupling constants in Table II, constants which are independent of the hybridization of C_β. The coupling constants of " σ " protons, that is, of ortho, meta and para protons, are calculated by the following popular relationship between the spin density on the adjacent carbon pπ orbital, ρ_C, and the proton isotropic constants, a_H:

$$a_H = Q_{HC}\rho_C \qquad (1)$$

where Q_{HC} is taken to be, as usual, -22.5

TABLE I. COEFFICIENTS OF CANONICAL STRUCTURES IN THE GROUND STATE WAVE FUNCTION OF C_6H_7

Hybridization of carbon C_1	C_1–C_{ortho} distance, Å	Coefficient				
		C_1	C_2, C_3	C_4, C_5	C_6, C_7, C_8, C_9	C_{10}, C_{11}
sp^3-sp^3	1.54	+0.3955	−0.3118	+0.0986	+0.0572	+0.0055
sp^2-sp^5	1.54	+0.3951	−0.3100	+0.0993	+0.0584	+0.0053
sp^3-sp^3	1.39	+0.3737	−0.2499	+0.1058	+0.1152	+0.0093
sp^2-sp^5	1.39	+0.3752	−0.2537	+0.1051	+0.1118	+0.0086

6) K. Morokuma and K. Fukui, This Bulletin, 36, 534 (1963).
7) J. H. van Vleck, *J. Chem. Phys.*, 1, 219 (1933); 2, 20 (1934).
8) M. Karplus and D. H. Anderson, ibid., 30, 6 (1959); M. Karplus, ibid., 30, 11 (1959).
9) S. L. Altman, *Proc. Roy. Soc.*, A210, 327, 343 (1951-2).

TABLE II. CALCULATED AND OBSERVED PROTON-COUPLING CONSTANTS OF C_6H_7 RADICAL

Proton	Isotropic coupling constant (in gauss)			
	Calculated[b]		Observed	
	$r=1.54$Å	$r=1.39$Å	Ohnishi[2] and Fischer[1]	Chkheidze[4]
Ortho	−11.4	−11.1∼11.2	10.4∼10.6	10.2 (meta)[a]
Para	−12.4	−11.4∼11.5	10.4∼10.6	10.2 (para)[a]
Meta	+ 6.5	+ 6.3	2.5∼ 2.6	—
Methylene	+36∼37	+73∼76	47.5∼50.0	45.2 (ortho)[a]
Spectrum (lines)	3×4×3	3×4×3	3×4×3	3×4 (Assigned to C_6H_5·)

a) Assignment by Chkheidze.[4] Assigned to C_6H_5· radical.
b) No matter what the hybridization of C_β is.

gauss.[10] The isotropic coupling constants of methylene protons are related to spin densities on them by the equation:

$$a_H = Q_H \rho_H \qquad (2)$$

Though a_H is theoretically given as +507 gauss, a smaller value, +420 gauss, which has been previously used by the authors in a similar valence bond calculation on a deformed methylene group,[6] would be more appropriate. This is mainly due to our disregard of any contribution of ionic structures. The coupling constants in Table II are calculated with the latter Q_H value.

The Valence Bond Calculation of Proton-coupling Constants in the Phenyl Radical

The Model of the C_6H_5· Radical. — In the phenyl radical, the migration of the odd electron may be achieved in several ways. One example is such a mechanism as the σ-π interaction between the non-bonding σ orbital and the pπ orbital, both on the carbon, C_1 (see Fig. 4), followed by the π-π migration to the pπ orbital on the ortho carbon and then by σ-π interaction between the ortho pπ orbital and the ortho C–H bond. However, this mechanism seems less significant because of the double σ-π interaction, which would bring about a spin density on the ortho proton of the order of 1/500.

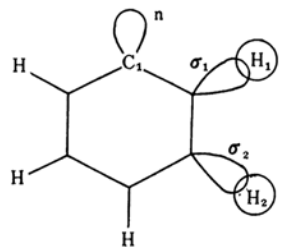

Fig. 4. Model of C_6H_5 radical.

A more probable mechanism would be direct interaction between the non-bonding σ orbital and the ortho C–H bond in the molecular plane. Therefore, in the present section we adopted the model in Fig. 4, consisting of 5 electrons on the following 5 atomic orbitals:

n: sp^2 hybridized non-bonding orbital on the carbon C_1
σ_1: sp^2 hybridized orbital on the ortho carbon, making a C–H bond with H_1
H_1: hydrogen 1s orbital on the hydrogen H_1
σ_2: sp^2 hybridized orbital on the meta carbon, making a C–H bond with H_2
H_2: hydrogen 1s orbital on the hydrogen H_2

For the sake of simplicity, the C–H bonds on only one side of the n orbital are considered. The inclusion of the other side would not affect the result seriously. Moreover, the para C–H bond is not taken into account, for the spin density of the para proton derived by the direct and in-plane interaction is relatively small and its order of magnitude can be estimated by the above calculation.

The change of the hybridization of the carbon, C_1, is not taken into consideration, for the change of the hybridization does not seem to affect the results. The C_1–C_{ortho} bond length is fixed as 1.39Å and the C_o–C_1–$C_{o'}$ angle, 120°. As the elongation of the C_1–C_{ortho} bond would reduce the coupling, as we saw in the previous section, the results of this calculation give the maximum value of the coupling constant.

Canonical Structures and Integrals. — All of the independent canonical structures that have the maximum bonding number, five structures in all, are taken as bases of the calculations, they are shown in Fig. 5. Ionic structures are not included in the present calculation at all. Integrals are evaluated by the same methods as in the preceding section.

Calculation Result.—The normalized ground state wave function is obtained as follows:

10) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

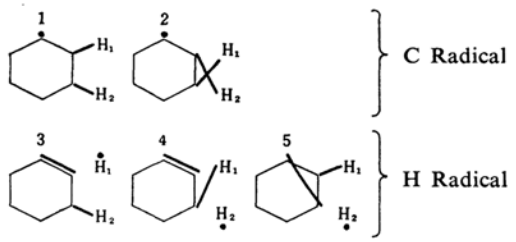

Fig. 5. Canonical structures taken into calculation of C_6H_5.

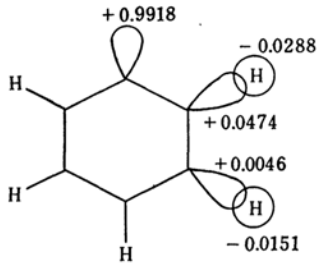

Fig. 6. Calculated spin density of C_6H_5 radical.

$$\Psi = 1.1338\phi_1 + 0.0968\phi_2 + 0.1144\phi_3 + 0.0673\phi_4 + 0.1779\phi_5 \quad (3)$$

where ϕ_i is the i-th canonical structure (for the numbering of them, see Fig. 5). From this function is derived the spin density shown in Fig. 6. The spin density is almost completely localized on the non-bonding hybridized orbital, n, on the carbon C_1; the phenyl radical may be said to be essentially a localized radical. From the spin densities in Fig. 6 the coupling constants of the ortho and meta protons are calculated by means of Eq. 2. The results are shown in Table III.

TABLE III. CALCULATED AND OBSERVED PROTON-COUPLING CONSTANTS OF C_6H_5· RADICAL

Proton	Coupling constants (in gauss)		
	Calculated	Observed	
		Ohnishi[2]	Chkheidze[4]
Ortho	−12.1	—	45.0
Meta	− 6.3	—	10.2
Para	—	—	10.2
Spectrum (lines)	3×3×2	1 ($\Delta H_{msl} \simeq 25$ gauss)	3×4

The Assignment of Observed Spectra and Discussion

After inspection of the calculated proton-coupling constants of the cyclohexadienyl radical C_6H_7·, the complex spectrum, the triplet with finer structures of four triplets, observed by Ohnishi et al. and by Fischer, may safely be assigned to the cyclohexadienyl radical (see Table II). Agreement with the observed and the calculated spectra seems to be very good.* Though the coupling constant of methylene protons depends on the C_β–C_{ortho} bond length, the coincidence with the experimental value of 47.5∼50.0 gauss is accomplished at the bond length between 1.54 Å (C–C single bond) and 1.39 Å (C–C bond in benzene). This would be rational in the cyclohexadienyl radical, for it is produced from the regular hexagonal benzene molecule by hydrogen addition.

On the other hand, according to the theoretical results in Table III, the phenyl radical is considered to give a triplet with finer triplet structures. The singlet spectrum observed by Ohnishi has the width of 25 gauss between the maximum slopes and, depending on conditions, has slight nicks, showing that it might be a triplet. The large width just corresponds to the unresolved hyperfine structures of the theoretically-predicted splittings of 12 gauss. Thus, this broad singlet spectrum may safely be assigned to the phenyl radical. Chkheidze's assignment, in which the largest coupling constants, of 45 gauss, are attributed to ortho positions of the phenyl radical, does not correspond to the theoretical result at all. His spectrum, which is like those of Ohnishi and Fischer, would have to be ascribed to the cyclohexadienyl radical.

By the aid of this valence bond calculation, it seems that a theoretical basis can be given for the assignment of the two kinds of observed ESR spectra from irradiated benzene.

Summary

Two kinds of spectra—a triplet with a finer structure of four triplets, and a singlet—are known to be observed in ESR of irradiated benzene, and two different assignments of these spectra have been proposed—one assigning the triplet to the cyclohexadienyl radical and the singlet to the phenyl radical, and the other assigning the triplet to the phenyl radical. In the present paper, in order to give ground for a theoretical choice between the assignments, a valence bond calculation on the spin distribution of cyclohexadienyl and phenyl radicals has been carried out. On the cyclohexadienyl radical, though the numerical value of the spin density for methylenic protons is dependent on the C–$C_{methylene}$ bond length, the calculated spectrum is in good agreement with the observed triplet with four

* The coupling constant calculated for meta protons is a little too large. This seems to be either a general trend or a defect of the simple valence bond calculation of the conjugated system.

triplets. On the other hand, the phenyl radical has been shown theoretically to be an essentially localized radical and to give a singlet spectrum, which also agrees with that of the observed singlet.

Numerical calculations were carried out on the KDC-I digital computer of Kyoto University.

Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto
(K. M., T. M. & K. F.)

Osaka Laboratories
Japanese Association for
Radiadion Research on Polymers
Mii, Neyagawa, Osaka
(S. O.)