BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3443—3449 (1970)

Electronic Structures of Aromatic Ketyl Radicals and Related Hydrocarbon Radicals

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(Received July 7, 1970)

The π-electron structures of neutral aromatic ketyl radicals and their related hydrocarbon radicals were studied theoretically by combining the open-shell SCF MO method with the configuration-interaction calculation. The observed absorption bands of these radicals were well explained by the present theoretical study. From a comparison of the calculated transition energies and intensities with the observed values, it was concluded that the longest and second longest wavelength bands of the benzyl radical and the second longest wavelength band of the diphenylmethyl radical shift to shorter wavelengths upon hydroxy substitution. This may be regarded as characteristic of the substituent effect upon the absorption bands of aromatic radicals. The calculated spin densities were found to be consistent with the reactivity of the ketyl radicals in the formation of pinacols.

Neutral aromatic ketyl radicals and related hydrocarbon radicals are known to be prepared by the photo-reduction of the parent aromatic carbonyl compounds[1-4] and by the photo-decomosition of the parent hydrocarbons,[5,6] respectively. Their electronic spectra have been studied experimentally by several authors and the absorption bands pertinent to each radical have been observed. However, there have been rather few theoretical studies of the electronic structures of the ketyl radicals.

We are interested in the correlation in electronic absorption bands between hydrocarbon radicals and the corresponding ketyl radicals. This is because the latter can be regarded as the hydroxy derivatives of the former and therefore the comparison of their absorption bands may give some information on the substituent effect upon the electronic absorption spectra of radicals. On this line, we have undertaken to study theoretically the electronic absorption spectra of some ketyl radicals and the corresponding hydrocarbon radicals.

Theoretical

The π-electron structures of aromatic ketyl radicals and related hydrocarbon radicals were studied by the method combining the open-shell SCF MO procedure of Longuet-Higgins and

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1) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

2) A. Beckett, A. D. Osborne and G. Porter, *ibid.*, **60**, 873 (1964).

3) N. Kanamura and S. Nagakura, *J. Amer. Chem. Soc.*, **90**, 6905 (1968).

4) W. A. Bryce and C. H. J. Wells, *Can. J. Chem.*, **41**, 2723 (1963).

5) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

6) I. Norman and G. Porter, *Proc. Roy. Soc.*, **A230**, 399 (1955).

Pople[7] with the configuration-interaction (abbreviated hereafter to CI) calculation. The CI calculation was made by taking at most 50 configurations of lower energies constructed by putting $2m+1$ π electrons into the lower molecular orbitals represented by the linear combination of atomic orbitals. They include the ground configuration and also the singly and doubly-excited configurations.

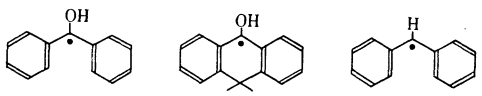
The Coulomb repulsion integrals of the type of (pp|qq) were calculated according to the Pariser-Parr approximation,[8] the radii of the electron clouds being evaluated with the aid of the effective nuclear charge determined by the Slater rule, and the ionization potentials (I) and electron affinities (A) of the appropriate valence states being taken from Pilcher and Skinner's Table.[9] The I_C, A_C, I_{O^+} and A_{O^+} values are 11.22 eV, 0.62 eV, 34.43 eV and 14.97 eV, respectively. The core Coulomb integral, α_p, was evaluated as the sum of the ionization potential of the π electron on the p-th atom and the Coulomb attraction terms due to the other atomic cores. The penetration integrals were disregarded.

A planar structure was assumed for the radicals under consideration, all the C–C bond lengths and all the bond angles being taken to be equal to 1.39 Å and 120°, respectively. The C–O bond length was taken to be equal to that of 1,4-dimethoxybenzene, 1.36 Å.[10] The core resonance integral, β_{CC}, for the neighbouring carbon atoms was taken to be -2.39 eV, the value for benzene. The core resonance integral, β_{CO}, for the neighbouring carbon and oxygen atoms was taken to be -3.42 eV on the basis of its proportionality to the overlap integrals taken from the table of Mulliken *et al.*[11]

The actual calculation was carried out by an electronic computer HITAC 5020E located at the Computer Centre, The University of Tokyo.*2 The energies and wave functions of the ground and excited states, the spin densities in the ground state, and also the transition moments (in Å) were evaluated for the benzyl, diphenylmethyl and ketyl radicals.

Results and Discussion

Concerning the π-electron structures, the benzophenone (a) and anthrone (b) ketyl radicals may be regarded as equal to each other and as the hydroxy derivative of the diphenyl-methyl radical (c). The situation is same for the benzaldehyde and acetophenone ketyl radicals, the hyperconjugation effect of the methyl group being disregarded.



(a) (b) (c)

Hydrocarbon Radicals. The energies of the ground and lower excited states are shown in Table 1. This table also shows the percentages of the configurations mainly contributing to each state. The effect of CI upon the energy levels is shown in Fig. 1. An inspection of Table 1 and Fig. 1 shows that the CI procedure has a great effect upon the energy values and wave functions and is indispensable for this kind of calculation. The excitation energies, the oscillator strengths, and the directions of the transition moments obtained theoretically for the benzyl and diphenylmethyl radicals are shown in Table 2, together with the observed excitation energies and molar extinction coefficients.

From the consideration of the transition energies and oscillator strengths given in Table 2a), the 453 mμ and 318 mμ bands observed for the benzyl radical[5] are assigned to the $E_1^B \leftarrow G^B$ and $E_3^B \leftarrow G^B$ transitions, respectively. The band corresponding to the $E_2^B \leftarrow G^B$ transition may be too weak to be observed and may be covered by the $E_1^B \leftarrow G^B$ transition band.

Longuet-Higgins and Pople[7] made a calculation on the benzyl radical, taking only the first-order CI among five configurations. According to their result, the lower excited states corresponding to E_1^B and E_3^B in our calculation can be represented as follows:

	State function	Excitation energy (eV)
$E_1^{B'}$	$\frac{1}{2}(\psi_{3-4}+\psi_{4-5})$	3.46
$E_3^{B'}$	$\frac{1}{2}(\psi_{3-4}-\psi_{4-5})$	4.18

The present calculation greatly improves the agreement between the observed and theoretical transition energies compared with the Longuet-Higgins and Pople calculation.

A similar consideration was made of the diphenylmetyl radical, with the results given in Table

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11) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

*2 A program written by Dr. Suehiro Iwata, The Institute of Physical and Chemical, Research, was used for the calculation. The authors' thanks are due to his kind help in the calculation.

TABLE 1. THEORETICAL RESULTS OF THE GROUND AND THE LOWER EXCITED STATES OF THE HYDROCARBON RADICALS

a) Benzyl

State*	Energy**	Configurations mainly contributed to each state***
$G^{B}(a)$	−0.612	g (94)
$E_1{}^{B}(b)$	2.333	4—5(42), 3—4(44)
$E_2{}^{B}(a)$	2.401	4—6(42), 2—4(43), 4—7(5)
$E_3{}^{B}(b)$	3.442	4—5(45), 3—4(43), $(2—5)_{\alpha}(5)$
$E_4{}^{B}(a)$	4.075	$(3—5)_{\alpha}(53)$, $(3—5)_{\beta}(18)$, 1—4(9), 4—7(9)
$E_5{}^{B}(a)$	4.304	4—6(37), 2—4(38), $(3—5)_{\beta}(12)$

b) Diphenylmethyl

State*	Energy**	Configurations mainly contributed to each state***
$G^{D}(a)$	−0.275	g (96)
$E_1{}^{D}(b)$	2.447	7—8(45), 6—7(43)
$E_2{}^{D}(b)$	2.803	7—9(41), 5—7(40), $(4—8)_{\alpha}(6)$
$E_3{}^{D}(a)$	2.899	4—7(41), 7—10(42), $(6—9)_{\beta}(5)$, $(5—8)_{\alpha}(7)$
$E_4{}^{D}(a)$	3.358	7—11(37), 3—7(38), $(6—8)_{\beta}(5)$, $(6—8)_{\alpha}(14)$
$E_5{}^{D}(b)$	3.562	7—8(5), 6—7(5), 7—9(37), 5—7(38)
$E_6{}^{D}(a)$	3.671	4—7(41), 7—10(40), $(6—9)_{\alpha}(6)$
$E_7{}^{D}(b)$	3.793	7—8(38), 6—7(40), 7—9(5), 5—7(5)

c) Acetophenone (benzaldehyde) ketyl

State	Energy**	Configurations mainly contributed to each state***
G^{Ak}	−0.444	g (94)
$E_1{}^{Ak}$	2.391	5—6(76), 4—5(11)
$E_2{}^{Ak}$	2.544	5—7(61), 3—5(26)
$E_3{}^{Ak}$	3.869	5—6(12), 4—5(71)
$E_4{}^{Ak}$	4.273	$(4—6)_{\alpha}(51)$, $(4—6)_{\beta}(15)$, 5—8(18), 2—5(7)
$E_5{}^{Ak}$	4.456	5—7(21), 3—5(51), $(4—6)_{\alpha}(7)$, $(4—6)_{\beta}(8)$, $(3—7)_{\alpha}(6)$

d) Benzophenone (anthrone) ketyl

State*	Energy**	Configurations mainly contributed to each state***
$G^{Bk}(a)$	−0.260	g (96)
$E_1{}^{Bk}(b)$	2.320	8—9(72), 7—8(15)
$E_2{}^{Bk}(a)$	2.692	8—10(73), 5—8(11)
$E_3{}^{Bk}(b)$	2.699	8—11(73), 6—8(10), $(7—10)_{\beta}(5)$
$E_4{}^{Bk}(a)$	3.242	8—12(45), 4—8(31), $(7—9)_{\alpha}(12)$
$E_5{}^{Bk}(b)$	3.788	8—11(11), 7—8(18), 6—8(49), $(5—9)_{\alpha}(10)$
$E_6{}^{Bk}(a)$	3.861	8—10(13), 5—8(63), $(7—10)_{\alpha}(13)$
$E_7{}^{Bk}(b)$	3.932	8—9(16), 7—8(47), 6—8(16), $(4—9)_{\alpha}(6)$

* The signs a and b represent the symmetry of each state.

** The energy values are indicated in the unit of eV, the ground configuration being taken as the standard.

*** In this column, the notations g and $n—m$ are used for representing the ground configuration and the excited configuration caused by the electron excitation from ϕ_n to ϕ_m, respectively. Here ϕ_n and ϕ_m represent the nth and mth SCF MO's of each radical. The number in parenthesis represents the contribution (in %) of a corresponding configuration to each state. Furthermore, suffixes α and β represent the spin state for each doublet configuration.

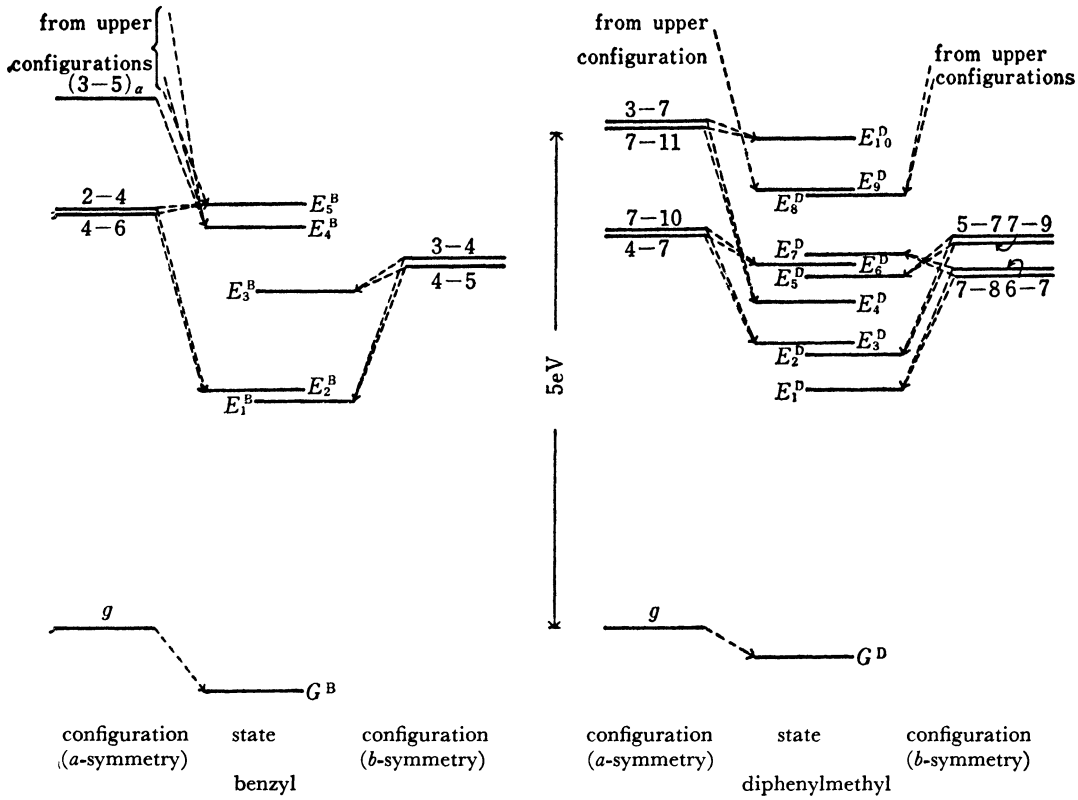

Fig. 1. The CI diagrams of the hydrocarbon radicals. The symbols of the configurations are explained in the footnote of Table 1.

TABLE 2. OBSERVED AND CALCULATED RESULTS FOR THE ABSORPTION SPECTRA OF THE HYDROCARBON RADICALS

a) Benzyl

Transition	Observed[5]		Calculated		
	E (eV)	ε	E (eV)	f	Direction of transition moment*
$E_1^B \leftarrow G^B$	2.74	230	2.945	6.4×10^{-5}	Y
$E_2^B \leftarrow G^B$			3.013	7.0×10^{-7}	X
$E_3^B \leftarrow G^B$	3.90	1100	4.053	5.9×10^{-2}	Y
$E_4^B \leftarrow G^B$			4.687	4.2×10^{-6}	X
$E_5^B \leftarrow G^B$			4.916	2.2×10^{-1}	X

b) Diphenylmethyl

Transition	Observed[6,12]		Calculated		
	E (eV)	ε (ratio)	E (eV)	f	Direction of transition moment*
$E_1^D \leftarrow G^D$	2.70	1	2.722	1.4×10^{-4}	Y
$E_2^D \leftarrow G^D$			3.078	7.5×10^{-6}	Y
$E_3^D \leftarrow G^D$			3.174	1.1×10^{-5}	X
$E_4^D \leftarrow G^D$			3.633	3.0×10^{-6}	X
$E_5^D \leftarrow G^D$			3.837	1.7×10^{-2}	Y
$E_6^D \leftarrow G^D$			3.946	5.7×10^{-2}	X
$E_7^D \leftarrow G^D$	3.70	150	4.068	5.6×10^{-1}	Y

* X is the symmetry axis of the radical.

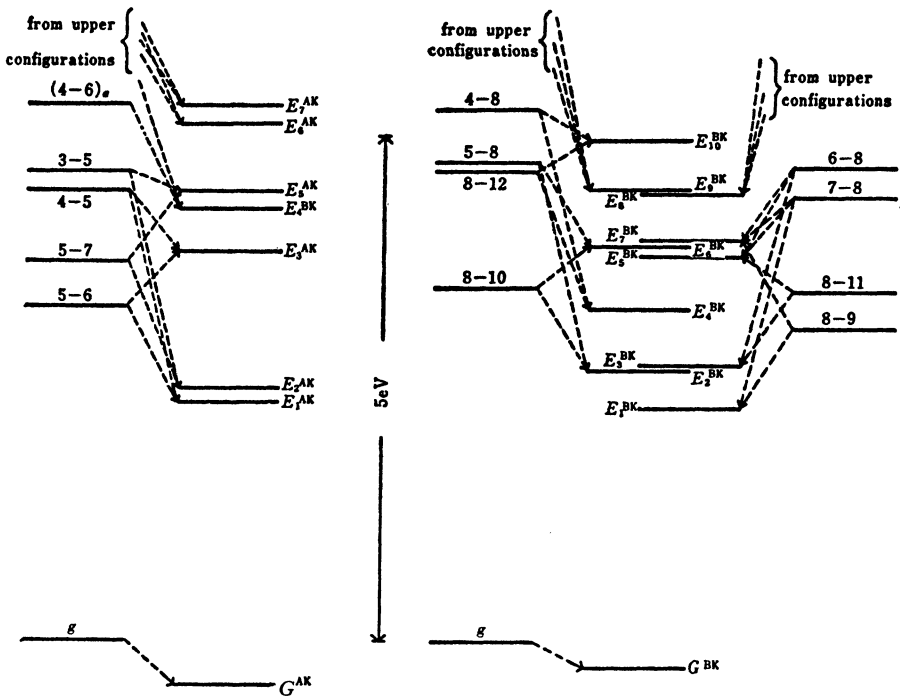

Fig. 2. The CI diagrams of the ketyl radicals. The symbols of the configurations are explained in the footnote of Table 1.

TABLE 3. OBSERVED AND CALCULATED RESULTS FOR THE ABSORPTION SPECTRA OF THE KETYL RADICALS

a) Acetophenone (benzaldehyde) ketyl

Transition	Observed[2]		Calculated	
	E (eV)*	ε (ratio)	E (eV)	f
$E_1^{Ak} \leftarrow G^{Ak}$			2.835	5.3×10^{-3}
$E_2^{Ak} \leftarrow G^{Ak}$	2.99(2.99)	0.05	2.988	2.2×10^{-2}
$E_3^{Ak} \leftarrow G^{Ak}$			4.313	3.8×10^{-2}
$E_4^{Ak} \leftarrow G^{Ak}$			4.717	2.0×10^{-2}
$E_5^{Ak} \leftarrow G^{Ak}$	4.48(4.59)	0.5	4.900	2.2×10^{-1}

b) Benzophenone (anthrone) ketyl

Transition	Observed[1,3]		Calculated		
	E (eV)*	f	E (eV)	f	Direction of transition moment**
$E_1^{Bk} \leftarrow G^{Bk}$	2.28(2.25)	0.065	2.580	8.0×10^{-2}	Y
$E_2^{Bk} \leftarrow G^{Bk}$			2.952	5.3×10^{-3}	X
$E_3^{Bk} \leftarrow G^{Bk}$			2.959	2.1×10^{-3}	Y
$E_4^{Bk} \leftarrow G^{Bk}$			3.502	5.9×10^{-4}	X
$E_5^{Bk} \leftarrow G^{Bk}$			4.048	2.2×10^{-2}	Y
$E_6^{Bk} \leftarrow G^{Bk}$			4.121	4.0×10^{-2}	X
$E_7^{Bk} \leftarrow G^{Bk}$	3.76(3.65)	0.32	4.192	4.2×10^{-1}	X

* The values in the parentheses are concerned with the benzaldehyde or anthrone ketyl radical.
** X is the symmetry axis of the benzophenone (anthrone) ketyl radical.

2b). A weak band was observed by Shida[12] at 460 mμ in addition to the strong band at 335 mμ. The absorbance ratio of the former to the latter is about 1:150. From the comparison of the calculated transition energies and intensities with those obtained experimentally, the observed bands at 460 mμ and at 335 mμ can be assigned to the $E_1^{D}\leftarrow G^{D}$ and $E_7^{D}\leftarrow G^{D}$ transitions, respectively. The $E_5^{D}\leftarrow G^{D}$ and $E_6^{D}\leftarrow G^{D}$ transitions also contribute to the 335 mμ band. The weak bands due to the $E_2^{D}\leftarrow G^{D}$, $E_3^{D}\leftarrow G^{D}$ and $E_4^{D}\leftarrow G^{D}$ transitions may be covered by the two bands.

Ketyl Radicals. The energies of the ground and lower excited states calculated for the ketyl radicals are shown in Table 1. This table also gives the percentages of the configurations mainly contributing to each state. The effects of CI upon the energy levels are shown in Fig. 2. The calculated transition energies and oscillator strengths are given in Table 3, together with the observed values.

From the comparison of the observed and calculated transition energies given in Table 3a), the 415 and 277 mμ bands of the acetophenone ketyl radical may be assigned to the $E_2^{Ak}\leftarrow G^{Ak}$ transition overlapped by the weak $E_1^{Ak}\leftarrow G^{Ak}$ transition and to the $E_5^{Ak}\leftarrow G^{Ak}$ transition overlapped by the $E_3^{Ak}\leftarrow G^{Ak}$ and $E_4^{Ak}\leftarrow G^{Ak}$ transitions, respectively.

An inspection of Table 3b) shows that the longer and shorter wavelength bands of the benzophenone ketyl radical can be ascribed to the $E_1^{Bk}\leftarrow G^{Bk}$ and $E_7^{Bk}\leftarrow G^{Bk}$ transitions, respectively. The latter band may be overlapped by the $E_6^{Bk}\leftarrow G^{Bk}$ and $E_5^{Bk}\leftarrow G^{Bk}$ transition bands, and the weak bands corresponding to the $E_2^{Bk}\leftarrow G^{Bk}$, $E_3^{Bk}\leftarrow G^{Bk}$ and $E_4^{Bk}\leftarrow G^{Bk}$ transitions may be covered by the two bands.

Substituent Effects upon the Absorption Bands of Hydrocarbon Radicals. First let us compare the absorption bands of the benzophenone ketyl radical with those of the diphenylmethyl radical. The observed longer wavelength band of the former shifts to longer wavelengths upon hydroxy substitution, as is usually observed with substituted aromatic hydrocarbons. On the other hand, the shorter wavelength band shows the reverse tendency. That is to say, the band corresponding to the 335 mμ band of the diphenylmethyl radical appears at 330 mμ for the benzophenone ketyl radical. The calculated transition energies given in Tables 2b) and 3b) can well explain the above-mentioned substituent effect on the two bands.

Concerning the benzyl and acetophenone radicals, either the longer or the shorter wavelength band was observed to shift to shorter wavelengths upon hydroxy substitution. This tendency is the opposite of the ordinary substituent effect observed for absorption bands of aromatic molecules like benzene and its derivatives; it may be regarded as characteristic of the aromatic radicals. According to the present calculation, the energies for the $E_5^{Ak}\leftarrow G^{Ak}$ and $E_2^{Ak}\leftarrow G^{Ak}$ transitions corresponding to the 277 mμ and 415 mμ bands of the acetophenone ketyl radical are greater than those

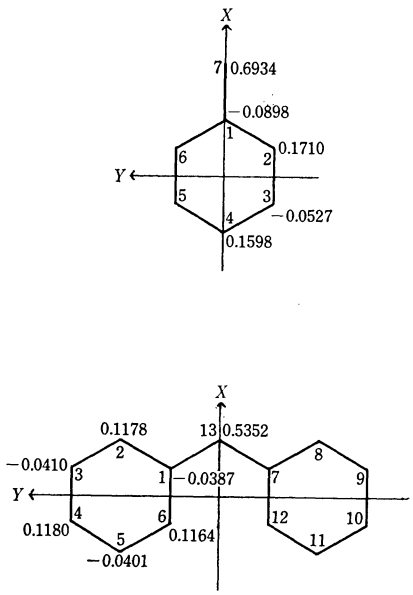

Fig. 3. Spin densities calculated for the benzyl and diphenylmethyl radicals.

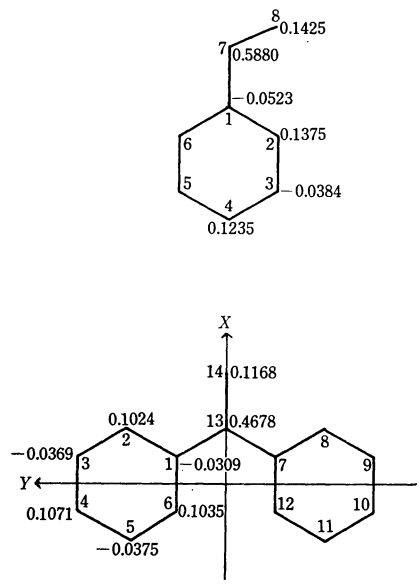

Fig. 4. Spin densities calculated for the acetophenone (benzaldehyde) and benzophenone (anthrone) ketyl radicals.

12) Private communication from Dr. Tadamasa Shida, The Institute of Physical and Chemical Research.

for the $E_3^B \leftarrow G^B$ and $E_1^B \leftarrow G^B$ transitions corresponding to the 318 mμ and 453 mμ bands of the benzyl radical, respectively. Therefore, the substituent effect upon the longest and second longest wavelength bands of the benzyl radical can be explained by the present theory.

Since the characters of the wave functions of the E_1^B and E_2^{Ak} states are similar to each other, the 415 mμ band of the acetophenone ketyl radical may be regarded as a shifted band of the 453 mμ band of the benzyl radical. This is the real blue shift phenomenon due to the hydroxy substitution. On the other hand, the E_3^B state does not correspond to the E_5^{Ak} state, but to the E_3^{Ak} state. Therefore, the 277 mμ band of the acetophenone ketyl radical can not be regarded as a shifted band of the 318 mμ band of the benzyl radical. In this sense, this band may be interpreted as apparently exhibiting the blue shift.*3

Spin Densities. The electron spin densities of the radicals under consideration were calculated with the results shown in Figs. 3 and 4. According to the results, the electron spin densities of the acetophenone and benzophenone ketyl radicals are greatest at the 7 th and 13 th positions, respectively. This is consistent with the fact that the formation of pinacol occurs at the above positions. A similar tendency holds for the hydrocarbon radicals.

The authors are greatly indebted to Dr. Tadamasa Shida, The Institute of Physical and Chemical Research, for his kindness in informing them of his unpublished results on the absorption spectrum of the diphenylmethyl radical.

*3 According to the present calculation, the transition energy for the $E_3^{Ak} \leftarrow G^{Ak}$ is greater than for the $E_3^B \leftarrow G^B$. This means that the 318 mμ band of the benzyl radical shows the real blue shift upon the substitution of the hydroxy group. In view of this, it may be interesting to carry out detailed experimental studies of the 277 mμ band of the acetophenone ketyl radical, if possible, and to separate it into the three components due to the $E_3^{Ak} \leftarrow G^{Ak}$, $E_4^{Ak} \leftarrow G^{Ak}$ and $E_5^{Ak} \leftarrow G^{Ak}$ transitions.