Electronic Structure of Benzyl Radical[1]

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The electronic spectrum of benzyl radical[2,3] has been investigated theoretically by the methods of MO[4-6] and VB[6]. However, there is no theoretical interpretation of the correlation between the electronic structures of benzyl radical and of benzene. The purpose of the present paper is to show the electronic structure of benzyl radical in correlation with that of benzene.

The singlet states of benzene correlate with the doublet states of benzyl radical and the triplet states of benzene correlate with the doublet and quartet states of benzyl radical. Therefore, it is expected that the lowest triplet level $^3B_{1u}$ of the benzene ring will be lowered by the interaction between π-electrons of the benzene ring and methylene radical and that this will give rise to the lowest excited state $^2B_2$ of benzyl radical.

In view of this, a simpie calculation is carried out by using an approximation that the wave function of benzyl radical can be expressed in terms of the π-electron wave function of the benzene ring and that of the methylene group (CH_2).

Method of Caluculation

The method of calculation is similar to the method of composite systems presented by London[7], by Longuet-Higgins and Murrell[8] and by the present author[9].

The molecular orbital of the benzene ring is

$$\varphi_l(\nu)=\sqrt{6}^{-1}\sum_{t=1}^{6}\exp[-2\pi il(t-1)/6]\chi_t(\nu)$$

where $l=0, \pm1, \pm2, 3$ and $\chi_t(\nu)$ is the 2Pπ AO of the tth carbon atom in the benzene ring. At the carbon atom 1 the hydrogen atom is substituted by CH_2 and the 2Pπ orbital of CH_2 is represented by $\chi_7(\nu)$.

The wave functions oe the benzene ring are, with an obvious abbreviation,

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[1] Y. Mori, *J. Chem. Phys.*, **24**, 1253 (1956).

[2] H. Schüler, *Z. Naturforsch.*, **A10**, 559 (1955).

[3] G. Porter and J. Norman, *Nature*, **174**, 508 (1954); J. Norman and G. Porter, *Proc. Roy. Soc.*, **A230**, 399 (1955); G. Porter and F. J. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).

[4] H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **A68**, 591 (1955).

[5] C. Komatsu, Y. Mori and I. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 643 (1956).

[6] W. Bingel, *Z. Naturforsch.*, **A10**, 462 (1955).

[7] A. London, *J. Chem. Phys.*, **13**, 396 (1945).

[8] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955).

[9] Y. Mori, This Bulletin, **28**, 291 (1955).

$^1\mathrm{A}_{1g}$;

$\phi_1 = |\varphi_0(1)\overline{\varphi}_0(2)\varphi_{+1}(3)\overline{\varphi}_{+1}(4)\varphi_{-1}(5)\overline{\varphi}_{-1}(6)|$
$= |0\,\bar{0}\;+1\;+\bar{1}\;-1\;-\bar{1}|$

$^1\mathrm{B}_{1u}$;

$\phi_2 = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;+\bar{2}|$
$-|0\,\bar{0}\;+1\;+\bar{1}\;-\bar{1}\;+2| + |0\,\bar{0}\;-1\;-\bar{0}\;+1\;-2|$
$-|0\,\bar{0}\;-1\;-\bar{1}\;+\bar{1}\;-2|\}$

$^3\mathrm{B}_{1u}$;

$\phi_3{}^{\mathrm{a}} = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;+\bar{2}|$
$+|0\,\bar{0}\;+1\;+\bar{1}\;-\bar{1}\;+2| + |0\,\bar{0}\;-1\;-\bar{1}\;+1\;-\bar{2}|$
$+|0\,0\;-1\;-\bar{1}\;+\bar{1}\;-2|\}$

$\phi_3{}^{\mathrm{b}} = 1/\sqrt{2}\,\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;+2|$
$+|0\,\bar{0}\;-1\;-\bar{1}\;+1\;-2|\}$

$^1\mathrm{E}_{1u}$;

$\phi_4 = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;-\bar{2}|$
$-|0\,\bar{0}\;+1\;+\bar{1}\;-\bar{1}\;-2| + |0\,\bar{0}\;-1\;-\bar{1}\;+1\;+\bar{2}|$
$-|0\,\bar{0}\;-1\;-\bar{1}\;+\bar{1}\;+2|\}$

$\phi_8 = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;-\bar{2}|$
$-|0\,\bar{0}\;+1\;+\bar{1}\;-\bar{1}\;-2| - |0\,\bar{0}\;-1\;-\bar{1}\;+1\;+2|$
$+|0\,\bar{0}\;-1\;-\bar{1}\;+\bar{1}\;+2|\}$

$^3\mathrm{E}_{1u}$;

$\phi_5{}^{\mathrm{a}} = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;-2|$
$+|0\,0\;+1\;+\bar{1}\;-\bar{1}\;-2| + |0\,\bar{0}\;-1\;-\bar{1}\;+1\;+\bar{2}|$
$+|0\,\bar{0}\;-1\;-\bar{1}\;+\bar{1}\;+2|\}$

$\phi_5{}^{\mathrm{b}} = 1/\sqrt{2}\,\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;-2|$
$+|0\,0\;-1\;-\bar{1}\;+1\;+2|\}$

$\phi_9{}^{\mathrm{a}} = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;-\bar{2}|$
$+|0\,0\;+1\;+\bar{1}\;-\bar{1}\;-2| - |0\,\bar{0}\;-1\;-\bar{1}\;+1\;+\bar{2}|$
$-|0\,\bar{0}\;-1\;-\bar{1}\;+\bar{1}\;+2|\}$

$\phi_9{}^{\mathrm{b}} = 1/\sqrt{2}\,\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;-2|$
$-|0\,\bar{0}\;-1\;-\bar{1}\;+1\;+2|\}$

$^1\mathrm{B}_{2u}$;

$\phi_6 = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;+\bar{2}|$
$-|0\,\bar{0}\;+1\;+\bar{1}\;-\bar{1}\;+2| - |0\,\bar{0}\;-1\;-\bar{0}\;+1\;-\bar{2}|$
$+|0\,\bar{0}\;-1\;-\bar{1}\;+1\;-2|\}$

$^3\mathrm{B}_{2u}$;

$\phi_7{}^{\mathrm{a}} = 1/2\{|0\,\bar{0}\;+1\;+\bar{1}\;-1\;+\bar{2}|$
$+|0\,\bar{0}\;+1\;+\bar{1}\;-\bar{1}\;+2| - |0\,\bar{0}\;-1\;-\bar{1}\;+1\;-\bar{2}|$
$-|0\,\bar{0}\;-1\;-\bar{1}\;+\bar{1}\;-2|\}$

$\phi_7{}^{\mathrm{b}} = 1/\sqrt{2}\,\{|0\,0\;+1\;+\bar{1}\;-1\;+2|$
$-|0\,\bar{0}\;-1\;-\bar{1}\;+1\;-2|\}$

The unperturbed wave functions of benzyl radical are given in Table I, where those are the eigenfunctions of the operators of spin component S_z and total spin S^2.

TABLE I. THE UNPERTURBED WAVE FUNCTIONS OF BENZYL RADICAL

a) Doublet configurations ($M_S = +1/2$)

$^2\mathrm{B}_2$;

$\Psi_1 = |\phi_1 \cdot \chi_7|$
$\Psi_2 = |\phi_2 \cdot \chi_7|$
$\Psi_3 = \sqrt{3}^{\,-1}\,[|\phi_3{}^{\mathrm{a}} \cdot \chi_7| - \sqrt{2}\,|\phi_3{}^{\mathrm{b}} \cdot \overline{\chi}_7|]$
$\Psi_4 = |\phi_4 \cdot \chi_7|$
$\Psi_5 = \sqrt{3}^{\,-1}\,[|\phi_5{}^{\mathrm{a}} \cdot \chi_7| - \sqrt{2}\,|\phi_5{}^{\mathrm{b}} \cdot \overline{\chi}_7|]$

$^2\mathrm{A}_2$;

$\Psi_6 = |\phi_6 \cdot \chi_7|$
$\Psi_7 = \sqrt{3}^{\,-1}\,[|\phi_7{}^{\mathrm{a}} \cdot \chi_7| - \sqrt{2}\,|\phi_7{}^{\mathrm{b}} \cdot \overline{\chi}_7|]$
$\Psi_8 = |\phi_6 \cdot \chi_7|$
$\Psi_9 = \sqrt{3}^{\,-1}\,[|\phi_9{}^{\mathrm{a}} \cdot \chi_7| - \sqrt{2}\,|\phi_9{}^{\mathrm{b}} \cdot \overline{\chi}_7|]$

b) Quartet configurations ($M_S = +3/2$)

$^4\mathrm{B}_2$;

$\Psi_{10} = |\phi_3{}^{\mathrm{b}} \cdot \chi_7|$
$\Psi_{11} = |\phi_5{}^{\mathrm{b}} \cdot \chi_7|$

$^4\mathrm{A}_2$;

$\Psi_{12} = |\phi_7{}^{\mathrm{b}} \cdot \chi_7|$
$\Psi_{13} = |\phi_9{}^{\mathrm{b}} \cdot \chi_7|$

* χ_7 is the $2\mathrm{P}\pi$ orbital of CH_2.

In order to simplify the procedure of calculation, the following assumption will be used. Namely, all of the interactions between the benzene ring and the CH_2 group are ignored except only that by exchange of π-electrons.

Though this is very crude and theoretically insufficient, this will not be unacceptable because the perturbation by the odd electron in the π-orbital of the CH_2 group is not so large that this assumption causes serious error in the results.

Neglecting non-neighbors, the interaction by electron exchange can be written

$$\begin{aligned}&\iint \varphi_l(\nu)\chi_7(\mu)H\chi_7(\nu)\varphi_m(\mu)\,\mathrm{d}\tau_\nu \mathrm{d}\tau_\mu \\ &= [l\theta H\theta m] \\ &= 1/6 \iint \chi_1(\nu)\chi_7(\mu)H\chi_7(\nu)\chi_1(\mu)\,\mathrm{d}\tau_\nu \mathrm{d}\tau_\mu \\ &= \alpha/6 \qquad (1)\end{aligned}$$

where α is the exchange energy in the VB theory and H is the complete electronic Hamiltonian. The value of the interaction integral is evaluated to be -0.32 eV. taking the value of α as -1.92 eV. as suggested by Sklar[10] and Craig[11].

Results

The numerical values of the matrix elements are shown in Table II. In evaluating the diagonal matrix elements the energy levels of

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[10] A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937).

[11] D. P. Craig, *Proc. Roy. Soc.*, **A200**, 399 (1950).

benzene which were given by Pariser[12] have been used. In Table III the calculated energy levels of the benzyl radical are shown as the roots of the secular determinants, relative to the energy of the ground state.

TABLE II. THE VALUES OF H_{jk} (eV.)

$H_{22}=H_{11}-5.9595$
$H_{33}=H_{11}-2.9495$
$H_{44}=H_{11}-6.7595$
$H_{55}=H_{11}-3.5095$

$H_{66}=H_{11}+4.7095$
$H_{77}=H_{11}+4.0695$
$H_{88}=H_{11}+6.7595$
$H_{99}=H_{11}-3.5095$

$H_{10,10}=H_{11}+3.9095$
$H_{11,11}=H_{11}+4.4695$

$H_{12,12}=H_{11}+5.0295$
$H_{13,13}=H_{11}+4.4695$

$H_{12}=\ 0.32$
$H_{13}=-0.5543$
$H_{14}=\ 0.32$
$H_{15}=-0.5543$
$H_{23}=H_{45}=0$
$H_{24}=0$
$H_{25}=H_{34}=0$
$H_{35}=-0.64$

$H_{67}=H_{89}=0$
$H_{68}=\ 0.32$
$H_{69}=-0.5543$
$H_{78}=-0.5543$
$H_{79}=\ 0.32$

$H_{10,11}=0.32$
$H_{12,13}=0.32$

The calculated wave functions of the ground and lower excited states, $^2B_2$ (ground state), $^2B_2$ (2.99 eV.) and $^2A_2$ (3.42 eV.) are;

$$\left.\begin{aligned}
&\text{ground state } (^2B_2)\\
&\quad \Phi_1=0.9612\Psi_1-0.0495\Psi_2+0.2018\Psi_3\\
&\qquad -0.0439\Psi_4+0.1761\Psi_5\\
&\text{excited states}\\
&\quad (^2B_2;\ 2.99\text{ eV.})\\
&\quad \Phi_2=0.2625\Psi_1+0.0261\Psi_2-0.8259\Psi_3\\
&\qquad +0.0209\Psi_4-0.4978\Psi_5\\
&\quad (^2A_2;\ 3.42\text{ eV.})\\
&\quad \Phi_6=0.3297\Psi_6-0.3599\Psi_7-0.0849\Psi_8\\
&\qquad +0.8686\Psi_9
\end{aligned}\right\}\tag{2}$$

Since all of the dipole matrix elements

$$eq_{jk}=e\int\Psi_j^*\sum_\nu q(\nu)\Psi_k\mathrm{d}V$$

are zero except for eq_{14} and eq_{18}[13], the moments of the transitions from the ground state to Φ_2 and Φ_6 are

$$\left.\begin{aligned}
eQ_{12}&=e\int\Phi_1^*\sum_\nu q(\nu)\Phi_2\mathrm{d}V\\
&=0.00856eq_{14}\\
eQ_{16}&=e\int\Phi_1^*\sum_\nu q(\nu)\Phi_6\mathrm{d}V\\
&=0.0816eq_{18}
\end{aligned}\right\}\tag{3}$$

TABLE III. THE ENERGY LEVELS OF BENZYL RADICAL

State	Energy, eV.	
	Calculated	Observed
$^2B_2$	—	—
$^2B_2$	2.99	2.8
$^2A_2$	3.42	
$^4B_2$	4.01	
$^2B_2$	4.18	4.0
$^2A_2$	4.33	
$^4A_2$	4.57	
$^4B_2$	4.86	
$^2A_2$	5.13	
$^4A_2$	5.42	
$^2B_2$	6.23	
$^2B_2$	7.02	
$^2A_2$	7.17	

By using the calculated wavelengths for these transitions, the oscillator strength are given

$$\left.\begin{aligned}
f_{12}&=3.7\times10^{-5}\\
f_{16}&=3.8\times10^{-3}
\end{aligned}\right\}\tag{4}$$

Discussion

The emission spectrum of benzyl radical has a band which was observed by Schüler[2] at about 4500 Å. This will arise from the transition between the ground state and the lowest excited state $^2B_2$(2.99 eV.). However, no absorption band which corresponds to this transition has been observed. The result that the bands arising from the lower excited states of benzyl radical will have very weak intensities will serve as an interpretation for this experimental result. By a similar consideration it will be explained that the band arising from the transition to $^2A_2$(3.42 eV.) has not been observed.

It is seen that the lower excited states of benzyl radical, $^2B_2$(2.99 eV.) and $^2A_2$(3.42 eV.), have the character of the triplet states of benzene. Then the oscillator strengths are due to the degrees of contributions from Ψ_4 or Ψ_8 which have the components of $^1E_{1u}$ of benzene. Therefore the transitions from the ground state to these excited states are almost forbidden though these are allowed by selection rule.

The small oscillator strengths to the lower excited levels were suggested by Longuet-Higgins[4] and Bingel[6] in terms of molecular orbital theory. The results of the present paper, however, differ from those by molecular orbital calculations in the order of the positions of energy levels. In the present paper, the lowest excited state is $^2B_2$(2.99 eV.). This is inconsistent with the prediction by the other calculations[4,6] that the lowest excited state of benzyl radical will be $^2A_2$. This discrepancy arises,

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12) R. Pariser. *J. Chem. Phys.*, **24**, 250 (1956).

13) eq_{14} and eq_{18} are those of the transitions $^1A_{1g}$-$^1E_{1u}$ of benzene,

$$|q_{14}|=|q_{18}|=R=1.39\text{Å},$$

where R is the C-C bond-length in benzene ring.

TABLE IV. THE ESTIMATED LOWEST EXCITED STATES OF RADICALS

Radical	$\Delta E(T-N)$, eV.	$\|C_{mr}\|^2=\|C_{m'r}\|^2$	$-2\|C_{mr}\|^2\cdot\alpha$, eV.	Excitation energy, eV.
Allyl	5.78[a]	0.5	1.92	3.86
Pentadienyl	3.92[b]	0.3618[c]	1.39	2.53
Benzyl	3.59	0.1667	0.64	2.95
Triphenylmethyl	3.59	0.1667[d]	0.64[d]	2.95[d]
α-Naphthylmethyl	2.16[e]	0.1809[e]	0.69	1.47
β-Naphthylmethyl	2.16	0.0691[e]	0.27	1.89

a R. G. Parr and R. Pariser, *J. Chem. Phys.*, **23**, 711 (1955).
b R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
c Calculated by the simple LCAO-MO method.
d See Appendix.
e R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

in some degree, from the difference of configuration interactions included in the calculations. In the present treatment the first order configuration interaction is that between the locally excited configurations in the benzene ring. The first order configuration interaction in molecular orbital treatment has the character of interaction between the electron transfer configurations between the benzene ring and the methylene group.

The assignment of the excited state which will give rise to the absorption band³⁾ at 3100 Å is uncertain, since there are two excited levels in the vicinity of 4 eV., $^2B_2$(4.18 eV.) and $^2A_2$(4.33 eV.).

The intensities of the bands arising from the higher excited states will be more intense than those of the lower ones, because larger contributions from the configurations Ψ_4 and Ψ_8 are expected.

Though the present treatment showed satisfactory results, it is difficult to undertake a more precise quantitative discussion concerning the energy levels and the intensities of the bands, because of the assumption that the effect of interaction by electron transfer is completely neglected. Therefore, the treatment in this paper may be useful for the qualitative discussion of the correlation between the electronic structures of the radical and the parent molecule, for instance, between the benzene and benzyl radicals.

As the application of this treatment, simplified consideration can be made on the lowest excited levels of some conjugated free radicals, like benzyl radical. It will be possible that the lowest excited state of a radical can be approximated by the single configuration. The component is the lowest triplet state of the parent molecule.

By this approximation, the excitation energy from the ground state to the lowest excited state of the radical will be given

$$\Delta E=\Delta E(T-N)+3/2\,[m\theta H\theta m]$$
$$+1/2\,[m'\theta H\theta m']$$

In the above, $\Delta E(T-N)$ is the excitation energy from the ground state to the lowest triplet state of the parent molecule in which one electron is excited to a vacant MO $\varphi_{m'}$ from an occupied MO φ_m, and $[m\theta H\theta m]$ is the integral of interaction by the exchange of π-electron in φ_m and the methylene group.

By using the nearest neighbor approximation, the excitation energy of the radical can be written

$$\Delta E=\Delta E(T-N)+\{3/2\,|C_{mr}|^2+1/2\,|C_{m'r}|^2\}\alpha \tag{5}$$

where C_{mr} is the coefficient of φ_m at carbon atom r, where the hydrogen atom is substituted by a methylene radical. In Table IV, the lowest excitation energies of the conjugated free radicals calculated by Eq. 5 are shown.

It is interesting that the excitation energy of the lowest excited state of α-naphthylmethyl radical is lower than that of β-naphthylmethyl radical and the lowest excited states of benzyl radical and triphenylmethyl radical have the same excitation energy. Although triphenylmethyl radical is not planar, the result of this paper shows qualitative agreement with the experimental result that this radical has the first absorption band at about 5000 Å¹⁴⁾ with weak intensity. The lowest excitation energy of allyl radical in Table IV may be compared with those by Moffit¹⁵⁾, by Higuchi¹⁶⁾ and by Longuet-Higgins and Pople⁴⁾.

By this treatment it can be said that the lowest excited levels of each free radical in Table IV will be lower than the lowest triplet levels of the parent molecule and will give rise to a weak absorption band.

Summary

The electronic structure of benzyl radical was shown by the approximation of the composite system in which all of the interactions

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14) T. L. Chu and S. I. Weissman, *J. Chem. Phys.*, **22**, 21 (1954).

15) W. Moffit, *Proc. Roy. Soc.*, **A218**, 486 (1953).

16) J. Higuchi, *J. Chem. Phys.*, **26**, 151 (1957).

are ignored except only the interaction by exchange between π-electrons of the benzene ring and the methylene group (CH_2). The results are qualitively in agreement with the experimental observations[2,3] and the results of the other calculations[4,6]. The discrepancy between the results of the present paper and the other calculations are discussed.

The lowest excited states of some conjugated free radicals are also discussed.

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Appendix

The wave function of the ground state of triphenylmethyl radical is

$$\Psi_1=\phi_1\phi_1'\phi_1''\theta$$

where ϕ_1, ϕ_1' and ϕ_1'' are the wave functions of the ground states of the benzene rings I, II and III respectively, and θ is the $2P\pi$ orbital of carbon atom at the center of the molecule.

For the excited states, the wave functions are

$$\begin{aligned}\Psi_2^{\pm}=\sqrt{3}^{-1/2}[&(\phi_3\cdot\theta)\phi_1'\phi_1''\\ &+\exp(\pm 2\pi i/3)\phi_1(\phi_3'\cdot\theta)\phi_1''\\ &+\exp(\pm 4\pi i/3)\phi_1\phi_1'(\phi_3''\cdot\theta)]\end{aligned}$$

$$\begin{aligned}\Psi_3=\sqrt{3}^{-1/2}[&(\phi_3\cdot\theta)\phi_1'\phi_1''+\phi_1(\phi_3'\cdot\theta)\phi_1''\\ &+\phi_1\phi_1'(\phi_3''\cdot\theta)]\end{aligned}$$

where $(\phi_3\cdot\theta)$, $(\phi_3'\cdot\theta)$ and $(\phi_3''\cdot\theta)$ are similar to Ψ_3 in the case of benzyl radical.

Therefore, neglecting non-neighbors, the lowest excitation energy is given as

$$\begin{aligned}H_{22}-H_{11}&=H_{33}-H_{11}\\ &=2.95\,\text{eV}.\end{aligned}$$