Electronic Structures of Benzyl Cation and Related Compounds

By Yuji MORI

(Received February 21, 1961)

In previous papers[1,2], the author has shown a theoretical interpretation of the electronic structure of the benzyl radical, with relation to the electronic structure of a separate fragment (benzene). The calculations suggested that the lowest excited state of the benzyl radical, $^2B_2$, can be related to the lowest triplet state of benzene, $^3B_{1u}$.

Longuet-Higgins and Pople[3] have interpreted the spectra of odd alternant hydrocarbon radicals and corresponding cations on the basis of the molecular orbital theory. They have shown that odd alternant hydrocarbon radicals may have absorption bands with a weak intensity in the vicinity of the absorption bands of corresponding cations. For the benzyl radical and cation, a similar result has been reported by Bingel[4].

It will, therefore, be interesting to investigate the electronic structure of the benzyl cation from the viewpoint of the electronic structures of the separate fragments, as was done in the case of the benzyl radical.

The first problem of the present paper will be to show an interpretation of the electronic structure of the benzyl cation based on those of the composite system. This will be followed by an interpretation of the electronic spectra of diphenyl-methyl and triphenyl-methyl cations from the same standpoint, utilizing a simple treatment.

The Benzyl Cation

In the calculations, it is assumed that the system is composed of the benzene ring and the positively-charged methylene group ($-CH_2^+$). The calculations are based on the method of composite systems[5] and are carried out by taking into account the locally excited configurations in the benzene ring and the electron-transfer configurations in which an electron has been transferred from the benzene ring to $-CH_2^+$.

The LCAO MO's of benzene ring are

$$\varphi_0=1/\sqrt{6}\,(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6)$$

$$\varphi_1=1/\sqrt{12}(2\chi_1+\chi_2-\chi_3-2\chi_4-\chi_5+\chi_6)$$

---

[1] Y. Mori, This Bulletin, 34, 1031 (1961).

[2] Y. Mori, ibid., 34, 1035 (1961).

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

[4] W. Bingle, *Z. Naturforschg.*, A10, 462 (1955).

[5] A. London, *J. Chem. Phys.*, 13, 396 (1945); H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, A68, 601 (1955); Y. Mori, This Bulletin, 28, 291 (1955). A similar treatment is described by Nagakura and Tanaka; S. Nagakura and J. Tanaka, *J. Chem. Phys.*, 22, 236 (1954); S. Nagakura, ibid., 23, 1441 (1955); J. Tanaka and S. Nagakura, ibid., 24, 1274 (1956).

$$\varphi_2=1/2(\chi_2+\chi_3-\chi_5-\chi_6)$$
$$\varphi_3=1/\sqrt{12}(2\chi_1-\chi_2-\chi_3+2\chi_4-\chi_5-\chi_6)$$
$$\varphi_4=1/2(\chi_2-\chi_3+\chi_5-\chi_6)$$
$$\varphi_5=1/\sqrt{6}(\chi_1-\chi_2+\chi_3-\chi_4+\chi_5-\chi_6)$$

where χ_r is the 2pπ AO of the r-th carbon atom in the benzene ring.

The bond is formed between the methylene group ($-CH_2^+$) and the carbon atom 1 of the benzene ring. The 2pπ AO of $-CH_2^+$ is expressed by χ_7.

The electronic configurations are shown in Fig. 1, while the wave functions corresponding to these configurations are given in Table I.

TABLE I. THE WAVE FUNCTIONS OF THE BENZYL CATION

$$^1A_1 \begin{cases} \Psi_1=(001122)=\phi_1 \\ \Psi_2=\phi_2(1\rightarrow\chi_7) \\ \Psi_3=\phi_3(0\rightarrow\chi_7) \end{cases}$$
$$^1B_1 \quad \Psi_4=\phi_4(2\rightarrow\chi_7)$$
$$^1A_1 \begin{cases} \Psi_5=1/\sqrt{2}\{\phi_5(1\rightarrow3)+\phi_6(2\rightarrow4)\} \\ \Psi_6=1/\sqrt{2}\{\phi_5(1\rightarrow3)-\phi_6(2\rightarrow4)\} \end{cases}$$
$$^1B_1 \begin{cases} \Psi_7=1/\sqrt{2}\{\phi_7(1\rightarrow4)+\phi_8(2\rightarrow3)\} \\ \Psi_8=1/\sqrt{2}\{\phi_7(1\rightarrow4)-\phi_8(2\rightarrow3)\} \end{cases}$$

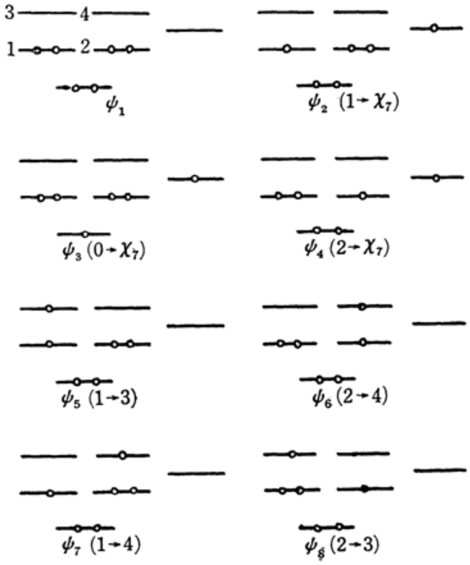

Fig. 1. The electron configurations of the benzyl cation.

In the table, Ψ_5, Ψ_6, Ψ_7 and Ψ_8, which represent the locally excited states of the benzene ring, are introduced for the purpose of considering the effect of the polarization in the benzene ring induced by $-CH_2^+$. The wave functions, Ψ_2, Ψ_3 and Ψ_4, correspond to the electron-transfer configurations, in which one electron has been transferred from the benzene ring to the 2pπ AO of $-CH_2^+$.

A standard bond length, 1.39 Å, is assumed for all C–C bonds throughout the present work. The values for the molecular integrals are taken from the work of Pariser[6], and the penetration integrals from neutral carban atoms are disregarded.

The matrix elements are given in Table II, and the calculared energy levels of the benzyl cation are shown in Table III. The energy of the ground state is -61 kcal., relative to the energy of Ψ_1.

TABLE II. THE MATRIX ELEMENTS OF THE BENZYL CATION (eV.)

	1	2	3	5	6
1	0				
2	−1.9359	−0.0865			
3	−1.3689	0	+3.0295		
5	−1.9290	−0.9680	0	+6.7595	
6	+0.0350	−0.9680	0	0	+5.9595

	4	7	8
4	−0.0865		
7	−0.9680	+4.7095	
8	+0.9680	+0.3303	+6.7595

TABLE III. THE ENERGY LEVELS OF THE BENZYL CATION

Symmetry	Energy, eV.	Polarization*
$^1A_1$	0	
$^1B_1$	2.23	⊥
$^1A_1$	3.91	∥
$^1A_1$	6.24	∥
$^1B_1$	7.54	⊥

* ⊥ and ∥ mean perpendicular and parallel polarization with respect to the long axis in the benzyl cation.

The wave functions of the ground state and of the two excited states are as follows:

($^1A_1$; 0)

$$\Phi_1=0.7118\cdot\Psi_1+0.6435\cdot\Psi_2+0.1715\cdot\Psi_3+0.2121\cdot\Psi_5+0.0694\cdot\Psi_6$$

($^1A_1$; 3.91 eV.)

$$\Phi_2=0.5396\cdot\Psi_1-0.7124\cdot\Psi_2+0.4178\cdot\Psi_3+0.0639\cdot\Psi_5-0.1508\cdot\Psi_6$$

($^1B_1$; 2.23 eV.)

$$\Phi_4=0.9735\cdot\Psi_4+0.1928\cdot\Psi_7-0.1232\cdot\Psi_8$$

The calculated charge distributions of the ground state are shown in Fig. 2. In the calculation of the electron densities, it is necessary to take into account the interconfigurational electron densities. The interconfigurational electron density can be defined by the following expression for a small change in the Coulomb

---

[6] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

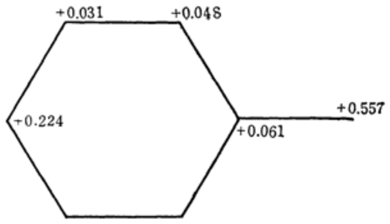

Fig. 2. The charge distribution of the benzyl cation.

integral $\varDelta\alpha_r$ at the r-th atom:

$$q_r(ij)=\frac{\partial}{\partial(\varDelta\alpha_r)}\varDelta W_r(ij)$$

where

$$\varDelta W_r(ij)=\int\Psi_i\varDelta\alpha_r\Psi_j\mathrm{d}\tau$$

Also, $q_r(ii)$ can be defined by the expression:

$$q_r(ii)=\frac{\partial}{\partial(\varDelta\alpha_r)}\cdot\varDelta W_r(ii)$$

Then the electron density at the carbon atom r may be written as follows:

$$\begin{aligned}q_r&=\frac{\partial}{\partial(\varDelta\alpha_r)}\cdot\int\Phi_1\varDelta\alpha_r\Phi_1\mathrm{d}\tau\\&=\sum_i\sum_j C_iC_j\cdot q_r(ij)\end{aligned}$$

where $\Phi_1=\sum_i C_i\cdot\Psi_i$

From the wave functions and wave numbers obtained in this section, the oscillator strengths⁷⁾ may be given as follows:

$$f_{12}=0.34$$

$$f_{14}=0.11$$

It seems that there has been no reliable experimental observation of the electronic absorption spectrum of the benzyl cation. The calculations, however, may be compared with the absorption spectrum of the carbonium ion in a sulfuric acid solution of benzyl alcohol. Grace and Symons[8] have observed that the solution shows an absorption band at 4700 Å (2.6 eV.) and so have assigned it to the benzyl cation.

The calculations show a qualitative agreement with those by Bingel[4] and by Longuet-Higgins and Pople[3]. The energy and charge distribution of the ground state are similar to the results of the calculations by Brickstock and Pople[9].

The transition moment of the $\Phi_1-\Phi_4$ transition arises from the local transition in the benzene ring, and the direction of this is orthogonal to the long axis of the system, i. e., the direction of the electron transfer. The transition moment from Φ_1 to Φ_2 is due to the electron transfer and is parallel to the direction of the electron transfer.

The charge density on $-\mathrm{CH}_2{}^+$ is $+0.05$ in the lowest excited state, ${}^1\mathrm{B}_1$, according to the wave function obtained in the present paper. Therefore, the lowest excited state, ${}^1\mathrm{B}_1$, can be represented approximately by the single configuration, Ψ_4, the electron-transfer configuration from φ_2 to χ_7. In a similar way, the approximate wave function of the ground state of the benzyl cation can be represented by the linear combination of Ψ_1 and Ψ_2, Ψ_2 being the electron-transfer configuration from φ_1 to χ_7. According to the above simple approximation, the longest absorption band of the benzyl cation may be interpreted as the band arising from the transition from the ground state to the excited state which is represented by Ψ_4. This relation is shown in Fig. 3. This simple treatment will be applied in the calculations of diphenyl-methyl and triphenyl-methyl cations in the next section.

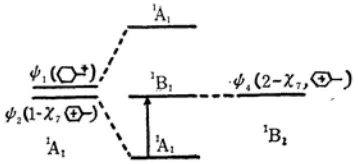

Fig. 3. Effect of electron transfer interaction in the benzyl cation.

Diphenyl-methyl and Triphenyl-methyl Cations. —In the preceding section, it was shown that the role of the electron-transfer configurations is important for the ground and the lowest excited states of the benzyl cation, and that the role of the locally excited configurations is minor. In this section, therefore, calculations will be carried out taking into account only the interactions arising from electron-transfer configurations of low energies.

The LCAOMO's of the benzene rings in the diphenyl-methyl cation are similar to those in the case of the benzyl cation. The MO which belongs to a benzene ring A or B is denoted by a subscript a or b, and the $2\mathrm{p}\pi$ AO of $-\mathrm{CH}^+-$ in the diphenyl-methyl cation is represented by χ_7.

The electronic wave functions of the diphenyl-methyl cation are shown in Table IV. In the table, Ψ_1 represents the state in which the positive charge is localized on $-\mathrm{CH}^+-$, while Ψ_2, Ψ_3, Ψ_4 and Ψ_5 are the electron transfer states.

---

7) R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.*, **8**, 231 (1941).

8) J. A. Grace and M. C. R. Symons, *J. Chem. Soc.*, **1959**, 958.

9) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

TABLE IV. THE WAVE FUNCTIONS OF THE DIPHENYL-METHYL RADICAL CATION

$$^1A_1 \begin{cases} \Psi_1=(0_a0_a1_a1_a2_a2_a)(0_b0_b1_b1_b2_b2_b) \\ \Psi_2=1/\sqrt{2}\{\phi(1_a\rightarrow\chi_7)+\phi(1_b\rightarrow\chi_7)\} \end{cases}$$

$$^1B_1 \begin{cases} \Psi_3=1/\sqrt{2}\{\phi(1_a\rightarrow\chi_7)-\phi(1_b\rightarrow\chi_7)\} \\ \Psi_4=1/\sqrt{2}\{\phi(2_a\rightarrow\chi_7)+\phi(2_b\rightarrow\chi_7)\} \end{cases}$$

$$^1A_1 \quad \Psi_5=1/\sqrt{2}\{\phi(1_a\rightarrow\chi_7)-\phi(2_b\rightarrow\chi_7)\}$$

A planar configuration of the diphenyl-methyl cation is assumed in the calculation, although the system may not be planar. The possible effect of nonplanarity on the energy levels will be discussed in a later section. The matrix elements are shown in Table V. The calculated energy levels are given in Table VI.

TABLE V. THE MATRIX ELEMENTS OF THE DIPHENYL-METHYL RADICAL CATION

Values are given in eV.

$$\begin{array}{c|ccc} & 1 & 2 & 5 \\ \hline 1 & 0 & & \\ 2 & -2.738 & -0.086 & \\ 5 & 0 & 0 & -0.086 \end{array}$$

$$\begin{array}{c|cc} & 3 & 4 \\ \hline 3 & -0.086 & \\ 4 & 0 & -0.086 \end{array}$$

TABLE VI. THE ENERGY LEVELS OF DIPHENYL-METHYL RADICAL CATION

Symmetry	Energy, eV.
$^1A_1$	0
$^1A_1$	2.69
$^1B_1$	2.69
$^1B_1$	2.69
$^1A_1$	5.48

The calculations may be compared with the absorption spectrum of the solution of diphenylmethanol in the mixture of trichloroacetic acid and benzene, which has been observed by Grace and Symons[8]. They assign the absorption band at 4420 Å (2.81 eV.) to the diphenylmethyl cation. In spite of their very simple calculations, the results seems satisfactory as an explanation of the characteristic features of the absorption band of the diphenyl-methyl cation. Also, the calculations will serve for the qualitative interpretation of the absorption band of the protonated compound of anthracene at 4100 Å[10], since this compound may have a structure similar to that of the diphenyl-methyl cation.

In the case of the triphenyl-methyl cation, a similar calculation has been carried out for the energy levels. The wave functions are shown in Table VII. The subscripts a, b and c denote the benzene rings A, B and C respectively, while χ_7 represents the $2p\pi$ AO of the carbon atom at the center of the system. The matrix elements are shown in Table VIII.

TABLE VII. THE WAVE FUNCTIONS OF THE TRIPHENYL-METHYL RADICAL CATION

$$^1A'_1 \begin{cases} \Psi_1=(0_a0_a1_a1_a2_a2_a)(0_b0_b1_b1_b2_b2_b)(0_c0_c1_c1_c2_c2_c) \\ \Psi_2=1/\sqrt{3}\{\phi(1_a\rightarrow\chi_7)+\phi(1_b\rightarrow\chi_7)+\phi(1_c\rightarrow\chi_7)\} \end{cases}$$

$$^1A'_2 \quad \Psi_3=1/\sqrt{3}\{\phi(2_a\rightarrow\chi_7)+\phi(2_b\rightarrow\chi_7)+\phi(2_c\rightarrow\chi_7)\}$$

$$^1E' \begin{cases} \Psi_4=1/\sqrt{3}\{\phi(1_a\rightarrow\chi_7)+\exp(\pm 2\pi i/3)\phi(1_b\rightarrow\chi_7) \\ \qquad +\exp(\pm 4\pi i/3)\phi(1_c\rightarrow\chi_7)\} \\ \Psi_5=1/\sqrt{3}\{\phi(2_a\rightarrow\chi_7)+\exp(\pm 2\pi i/3)\phi(2_b\rightarrow\chi_7) \\ \qquad +\exp(\pm 4\pi i/3)\phi(2_c\rightarrow\chi_7)\} \end{cases}$$

TABLE VIII. THE MATRIX ELEMENTS OF THE TRIPHENYL-METHYL RADICAL CATION

Values are given in eV.

$$\begin{array}{c|cc} & 1 & 2 \\ \hline 1 & 0 & \\ 2 & -3.353 & -0.086 \end{array}$$

$H_{33}=-0.086$

$$\begin{array}{c|cc} & 4 & 5 \\ \hline 4 & -0.086 & \\ 5 & 0 & -0.086 \end{array}$$

TABLE IX. THE ENERGY LEVELS OF THE TRIPHENYL-METHYL RADICAL CATION

Symmetry	Energy, eV.
$^1A'_1$	0
$^1A'_2$	3.27
$^1E'$	3.27
$^1E'$	3.27
$^1A'_1$	6.71

The energy levels given in Table IX are relative to the energy of the ground state. The system may not be planar, but the calculations may be compared with the absorption spectrum of the triphenyl-methyl cation, which has its first absorption band at about 4300 Å[11] (2.88 eV.). The calculated value is too high compared with the observed value. However, in view of the simple calculation and the assumed planar structure, it would be reasonable to say that this absorption band arises from the electron-transfer configuration.

Discussion

The charge distribution of the benzyl cation calculated in the present paper is similar to that calculated by Brickstock and Pople[9]. According to the prediction by the simple

---

[10] G. Dallinga, E. L. Makor and A. A. V. Stuart, *Mol. Phys.*, **1**, 123 (1958).

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

MO theory, the positive charge densities are identical at the para- and ortho-positions, and there is no apparent charge at the meta-position. This charge distribution differs from that of the present calculations shown in Fig. 2. This difference may be due to the effect of polarization.

The stabilization energy, 61 kcal., of the ground state, that is, the resonance energy of the benzyl cation relative to that of benzene, is large compared to that of the benzyl radical[9,12]. Brickstock and Pople[9] have obtained a value of 21.9 kcal. for the benzyl radical. This is due to the facts that the electron affinity of $-CH_2^+$ (benzyl cation) is much larger than that of $-CH_2$ (benzyl radical), and that the largest contribution to this energy comes from the electron-transfer interaction.

The transition moment from Φ_1 to Φ_4, which is orthogonal to the direction of the electron transfer, is due to the (interconfigurational) dipole matrix elements between Ψ_3 and Ψ_4 and between Ψ_1 and Ψ_8. The dipole matrix element

$$q_{34}=e\int\Psi_3\sum_{\nu}q(\nu)\Psi_4\mathrm{d}V$$

corresponds to that of the one-electron transition between φ_0 and φ_2 in the positively-charged benzene ring, while q_{18} corresponds to that of the transition ($^1A_{1g}-{}^1E_{1u}$) of benzene.

A simple treatment, which deals with only the three electron-configurations, Ψ_1, Ψ_2 and Ψ_4, can interpret the characteristic features of the absorption band of the benzyl cation. However, there are some difficulties in explaining the charge distribution of the ground state and the intensity of the absorption band. The charge distribution which will be given by this simple treatment will show the same positive charge densities on the carbon atoms 1 and 4, and also on the carbon atoms 2 and 3. The transition moment from the ground state to the lowest excited state, $^1B_1$, will be zero, since no contributions from the non-vanishing dipole matrix elements, q_{34} and q_{18}, can be expected.

For the diphenyl-methyl and triphenyl-methyl cations, the planar configuration has been assumed, although the benzene rings in these systems may not be coplanar. The matrix element H_{12} (Tables V and VIII), the interconfigurational interaction between Ψ_1 and Ψ_2 (Tables IV and VII), can be expressed by the resonance integral between the benzene ring and the carbon atom at the center of the system. If the bond is twisted by an angle θ, the resonance integral $\beta(\theta)$ is given by the relation

$$\beta(\theta)=\beta(0)\cos\theta$$

Therefore, the excitation energies from the ground states to the lowest excited states of these systems will decrease with the increase in the angle of twist. However, it is difficult to determine the angle of twist for these cations from the results of the present calculations, because the calculations are so very simple that there must be some errors in them which would affect the results.

Any transition from the ground state to the excited state ($^1A_2$) of the triphenyl-methyl cation is forbidden in the planar configuration. This transition is allowed in the twisted configuration, which has a transition moment perpendicular to the σ-bonds of the central atom of the system. (This transition corresponds to that from Φ_1 to Φ_4 in the case of the benzyl cation.)

The three excited levels of the diphenyl-methyl cation have the same energy, and for the triphenyl-methyl cation a similar degeneracy of the energy levels has been found. This may be due to disregarding the configurations in which more than one electron has been transferred and the locally excited configurations in the benzene rings.

Summary

The electronic structure of the benzyl cation has been calculated on the basis of an approximation of the composite systems in order to explain the electronic spectrum of the benzyl cation from the point of view of electron-transfer interaction between the fragments. The calculations show a satisfactory agreement with the experimental observations.

For the electronic spectra of some other cations, simple calculations have been carried out as an application of the treatment for the benzyl cation. The results for the diphenyl- and triphenyl-methyl cations show qualitative agreement with the experimental results.

The author is greatly indebted to Professor Ikuzo Tanaka for his continuous encouragement.

Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

---

[12] A value of 17 kcal. has been elsewhere calculated by the present author (cf. footnote 2).