The Electronic Structures of the Protonated Benzoic Acid and the Related Ions

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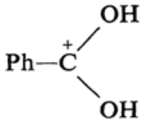
There are two possible positions of the protonation of the carboxyl group: one of them, the oxygen atom of the carbonyl group, and the other, the oxygen atom of the hydroxyl group. In a previous paper[1] we studied the structures of protonated benzoic acid and mesitoic acid by the aid of various spectroscopic methods, such as ultraviolet, infrared and Raman spectra. Consequently, we succeeded in obtaining direct evidence that, in strongly acidic media, a proton attacks the carbonyl oxygen atom of benzoic acid, giving the (ion benzoic acidium ion) :



(I)

Stewart and Yates[2] indirectly induced the

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[1] H. Hosoya and S. Nagakura, *Spectrochim. Acta*, **17**, 324 (1961).

[2] R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960).

same conclusion from ultraviolet absorption measurements showing that the relative magnitudes of the basicities of the benzoic acid derivatives are well correlated with those of the corresponding benzaldehyde and acetophenone derivatives.

Furthermore, it was shown in the previous paper that the ultraviolet absorption spectrum of benzoic acid changes considerably upon the protonation. This reveals that the distribution and energy of the π-electrons of benzoic acid are greatly affected by the protonation. In order to obtain deeper knowledge on this point, we have undertaken to calculate the electronic structures of the benzoic acidium ion (I) and of such related ions as α-hydroxylbenzyl cations.

Method of Calculation

Only π-electrons were explicitly taken into account in the present calculations. Furthermore, the ion was considered to be composed of an electron donor and an acceptor: for example, the benzoic acidium ion (I) was considered to be composed of the two hydroxyl groups serving as an electron donor and the benzyl cation, as an electron acceptor. The ground and the lower excited states of I can be expressed as a linear combination of the ground, locally excited and charge-transfer configurations.[3] The locally excited configurations can be caused by the local excitation within the benzyl cation, and the charge-transfer configurations, by the electron transfer from the hydroxyl groups to the benzyl cation. Calculations of this kind have already been shown to give reliable results for the interpretation of electronic spectra of various unsaturated compounds.[4]

Component MO's. — Roothaan's LCAO-SCF molecular orbitals (φ_1, φ_2,……, φ_7) of the benzyl cation were calculated by Hanazaki et al.[5] on the assumptions that all the C–C bond lengths are 1.39 Å and that all the bond angles are 120°. These MO's are expressed as linear combinations of the Slater-type atomic orbitals with different effective nuclear charges (Z's), the magnitudes of which are, considering the assumed relation between Z's and the net charge densities, q's, self-consistent with the calculated q's on the respective carbon atoms. Symmetric (φ_s) and antisymmetric (φ_a) group orbitals were constructed from the two $2p\pi$ atomic orbitals, ($\chi^1{}_{OH}$ and $\chi^2{}_{OH}$) of the hydroxyl oxygen atoms. The nine above-mentioned component molecular orbitals are given in Table I.

The Configurations and Their Energies. — In addition to the ground configuration, singlet and singly excited configurations with energies lower than 7 eV. were taken. In Table II they are grouped into symmetric (S) and antisymmetric (A) configurations with respect to the σ_V plane shown in Fig. 1. ψ_P and ψ_Q are, respectively, symmetric and antisymmetric charge-transfer configurations, in which an electron migrates from the oxygen atoms to the benzyl cation. ψ_β, ψ_γ and ψ_δ, and ψ_α, ψ_ε and ψ_ζ are symmetric and antimagnetric locally excited configurations respectively. The energies of ψ_α (2.75 eV.) and ψ_β (3.74 eV.) were taken to be equal to the lowest two transition energies of the benzyl cation observed by Hanazaki et al.[5]

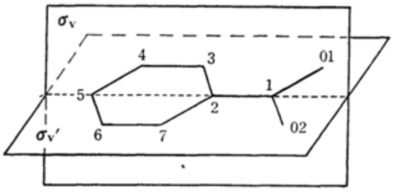

Fig. 1. Geometry and numbering of the atoms of the benzoic acidium ion I.

TABLE I. COMPONENT MOLECULAR ORBITALS

$$\psi_k=\sum_p C_{kp}\chi_p \qquad k,p=1,2,\ \cdots\cdots,7^{a)} \qquad \varphi_{s,a}=1/\sqrt{2}\,(\chi_{01}\pm\chi_{02})$$

$k \diagdown p$	1	2	3	4	5	6	7
1	0.3413	0.5360	0.3940	0.3116	0.3027	0.3116	0.3940
2	0.4481	0.4463	0.0163	−0.3777	−0.5600	−0.3777	0.0163
3	0	0	0.5279	0.4705	0	−0.4705	−0.5279
4	0.6987	−0.1120	−0.4041	0.0235	0.4142	0.0235	−0.4041
5	0	0	0.4705	−0.5279	0	0.5279	−0.4705
6	0.4073	−0.5785	0.1859	0.2888	−0.5134	0.2888	0.1859
7	0.1694	−0.4078	0.3829	−0.4199	0.3989	−0.4199	0.3829

a) The numbering of the carbon atomic orbitals is given in Fig. 1.

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[3] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **A68**, 969 (1955).

[4] S. Nagakura, *Mol. Phys.*, **3**, 105 (1960); H. Hosoya, J. Tanaka and S. Nagakura, This Bulletin, **33**, 850 (1960); *Tetrahedron*, **18**, 859 (1962), etc.

[5] I. Hanazaki and S. Nagakura, unpublished.

TABLE II. CONFIGURATIONS AND THEIR ENERGIES

Configuration	Character	Energy, eV.
(Symmetric)		
$\psi_G=\lvert 1\bar{1}2\bar{2}3\bar{3}s\bar{s}a\bar{a}\rvert$ [a]	Ground	0
$\psi_P=1/\sqrt{2}\{\lvert 1\bar{1}2\bar{2}3\bar{3}s4a\bar{a}\rvert+\lvert 1\bar{1}2\bar{2}3\bar{3}4sa\bar{a}\rvert\}$	CT [b]	3.12 [d]
$\psi_\beta=1/\sqrt{2}\{\lvert 1\bar{1}2\bar{4}3\bar{3}s\bar{s}a\bar{a}\rvert+\lvert 1\bar{1}4\bar{2}3\bar{3}s\bar{s}a\bar{a}\rvert\}$	LE [c]	3.74 [e]
$\psi_\gamma=1/\sqrt{2}\{\lvert 1\bar{4}2\bar{2}33s\bar{s}a\bar{a}\rvert+\lvert 4\bar{1}2\bar{2}3\bar{3}s\bar{s}4\bar{a}\rvert\}$	LE	5.97 [d]
$\psi_\delta=1/\sqrt{2}\{\lvert 1\bar{1}2\bar{2}3\bar{5}s\bar{s}a\bar{a}\rvert+\lvert 1\bar{1}2\bar{2}5\bar{3}s\bar{s}a\bar{a}\rvert\}$	LE	6.39 [d]
(Antisymmetric)		
$\psi_\alpha=1/\sqrt{2}\{\lvert 1\bar{1}2\bar{2}3\bar{4}s\bar{s}a\bar{a}\rvert+\lvert 1\bar{1}2\bar{2}4\bar{3}s\bar{s}a\bar{a}\rvert\}$	LE	2.75 [e]
$\psi_Q=1/\sqrt{2}\{\lvert 1\bar{1}2\bar{2}3\bar{3}s\bar{s}a\bar{4}\rvert+\lvert 1\bar{1}2\bar{2}3\bar{3}s\bar{s}4\bar{a}\rvert\}$	CT	3.12 [d]
$\psi_\varepsilon=1/\sqrt{2}\{\lvert 1\bar{1}2\bar{2}36s\bar{s}a\bar{a}\rvert+\lvert 1\bar{1}2\bar{2}6\bar{3}s\bar{s}a\bar{a}\rvert\}$	LE	6.52 [d]
$\psi_\zeta=1/\sqrt{2}\{\lvert 1\bar{1}2\bar{5}3\bar{3}s\bar{s}a\bar{a}\rvert+\lvert 1\bar{1}5\bar{2}3\bar{3}s\bar{s}a\bar{a}\rvert\}$	LE	6.90 [d]

a) $$\psi_G=1/\sqrt{10}\,!\sum_p(-1)^p P\begin{Bmatrix}\varphi_1(1) & \varphi_1(2) & \varphi_2(3) & \varphi_2(4) & \varphi_3(5) & \varphi_3(6) & \varphi_s(7) & \varphi_s(8) & \varphi_a(9) & \varphi_a(10)\\ \alpha(1) & \beta(2) & \alpha(3) & \beta(4) & \alpha(5) & \beta(6) & \alpha(7) & \beta(8) & \alpha(9) & \beta(10)\end{Bmatrix}$$
$$=\lvert\varphi_1(1)\ \varphi_1(\bar{2})\ \varphi_2(3)\ \varphi_2(\bar{4})\ \varphi_3(5)\ \varphi_3(\bar{6})\ \varphi_s(7)\ \varphi_s(\bar{8})\ \varphi_a(9)\ \varphi_a(\overline{10})$$

b) Charge-transfer

c) Local excitation

d) Calculated values (Ref. 5)

e) Observed values (Ref. 5)

The energies of the other locally excited configurations were those calculated by them. The energies of the two charge-transfer configurations were estimated to be the difference between the ionization potentials of methanol (10.85 eV., observed[6]) and the benzyl radical (7.73., calculated[7]).[8]

Configuration Interaction. — The above-mentioned configurations interact with one another through the core and electronic repulsion parts in the total electronic Hamiltonian H:

$$H=\sum_i H^{\text{core}}(i)+\sum_{i>j} e^2/r_{ij}$$

$$H^{\text{core}}(i)=H^{\text{core}}_{\text{benzyl}}(i)+H^{\text{core}}_{\text{OH}}(i)$$

The antisymmetrized product wave functions, $\lvert k\bar{l}m\bar{n}\cdots\cdots\rvert$ and $\lvert k'\bar{l}'m'\bar{n}'\cdots\cdots\rvert$, interact with each other through the above Hamiltonian. The interaction energies can be degraded under the zero-differential overlap approximation[9,10] into the atomic integrals as follows:

(i) $\langle\varphi^*_k(i)\vert H^{\text{core}}(i)\vert\varphi_{k'}(i)\rangle=H^{\text{core}}_{kk'}$

if $k\neq k'$, $l=l'$, $m=m'$, $n=n'$, $\cdots\cdots$,

where

$H^{\text{core}}_{kk'}=0$, if k and k' are pertinent to the same composite,

$H^{\text{core}}_{kk'}=C_{kp}C_{k'q}\beta_{pq}$, if k and k' are pertinent to the two different composites which are jointed together through the bond between the p and q atoms,

C_{kp}: the LCAO coefficient for the p-th atom in the k-th MO, and

β_{pq}: the core resonance integral for the $p—q$ bond.

(ii) $$\langle\varphi^*_k(i)\varphi^*_l(j)\vert e^2/r_{ij}\vert\varphi_{k'}(i)\varphi_{l'}(j)\rangle$$
$$=(kk'\vert ll')_{\text{MO}}$$
$$=\sum_{p,q}C^*_{kp}C_{k'p}C^*_{lq}C_{l'o}(pp\vert qq)_{\text{AO}}$$

if $k\neq k'$, $l\neq l'$, $m=m'$, $n=n'$, $\cdots\cdots$

(iii) $$\langle\varphi^*_k(i)\varphi^*_m(j)\vert e^2/r_{ij}\vert\varphi_{k'}(i)\varphi_{m'}(j)\rangle$$
$$=(kk'\vert mm')_{\text{MO}}-(km'\vert mk')_{\text{MO}}$$
$$=\sum_{p,q}(C^*_{kp}C_{k'p}C^*_{mq}C_{m'q}$$
$$-C^*_{kp}C_{m'p}C^*_{mq}C_{k'q})(pp\vert qq)_{\text{AO}}$$

if $k\neq k'$, $l=l'$, $m\neq m'$, $n=n'$, $\cdots\cdots$

(iv) 0 otherwise.

Consequently, the non-zero off-diagonal matrix elements were obtained as follows:

$$H_{GP}=\sqrt{2}\langle\varphi_4 H\varphi_s\rangle=2C_{41}\beta_{CO}=1.3974\beta_{CO}$$

$$H_{\beta P}=-\langle\varphi_2 H\varphi_s\rangle=-\sqrt{2}C_{21}\beta_{CO}=-0.6337\beta_{CO}$$

$$H_{\beta\delta}=2(24\vert 35)_{\text{MO}}-(23\vert 45)_{\text{MO}}$$
$$=2\times 0.4438-0.1736=0.7140\text{ eV.}$$

$$H_{p\gamma}=-\langle\varphi_1 H\varphi_s\rangle=-\sqrt{2}C_{11}\beta_{CO}=-0.4827\beta_{CO}$$

$$H_{\gamma\delta}=2(14\vert 35)_{\text{MO}}-(13\vert 45)_{\text{MO}}$$
$$=-2\times 0.3134+0.6004=-0.0264\text{ eV.}$$

$$H_{\alpha\zeta}=2(25\vert 34)_{\text{MO}}-(23\vert 45)_{\text{MO}}$$
$$=-2\times 0.3954-0.1674=-0.9582\text{ eV.}$$

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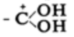
[6] K. Watanabe, *J. Chem. phys.*, **26**, 542 (1957).

[7] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

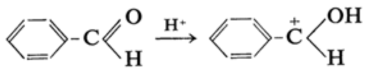
[8] In this calculation, the interaction between the two lone-pair π-electrons on the different oxygen atoms of the  $-\overset{+}{C}\lessdot\begin{matrix}OH\\OH\end{matrix}$ group is not taken into account. Furthermore, the difference in the electrostatic interaction energies before and after the electron transfer was estimated to be small and was, therefore, disregarded.

[9] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

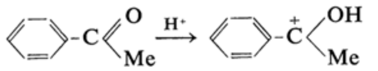
[10] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); *Proc. Phys. Soc.*, **A68**, 81 (1955).

The LCAO MO coefficients C's and the Coulomb repulsion integrals of the type $(pp|qq)_{AO}$ were calculated by Hanazaki et al.⁵⁾ using Pariser and Parr's approximation.⁹⁾

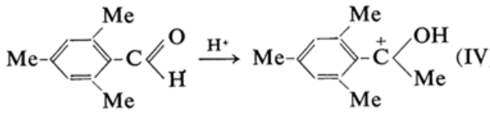
Matrix Elements for the Related Ions.—Similar calculations were performed for the benzaldehydium ion (II), the acetophenonium ion (III) and the 2, 4, 6-trimethylbenzaldehydium ion (IV), which are, respectively, the monohydroxyl derivatives of the benzyl, α-methylbenzyl and 2, 4, 6-trimethylbenzyl cations. These ions are known to be produced, presumably from benzaldehyde, acetophenone and mesitaldehyde respectively, in strongly acidic media.



(II)



(III)



(IV)

Each of these ions is separated into an electron donor (the hydroxyl group) and an electron accepter (the benzyl, α-methylbenzyl and 2, 4, 6-trimethylbenzyl cations for II, III and IV respectively). The interaction between the components is taken into account by means of the configurational interaction among the ground, locally excited and charge-transfer configurations. These three cations have only one hydroxyl group and, accordingly, one charge-transfer configuration,

$$\psi_O = 1/\sqrt{2}\{|1\bar{1}2\bar{2}3\bar{3}0\bar{4}| + |1\bar{1}2\bar{2}3\bar{3}4\bar{0}|\}$$

where 0 is the abbreviated representation of the 2pπ atomic orbital, χ_O, of oxygen. The off-diagonal elements, H_{GO}, $H_{\beta O}$ and $H_{O\delta}$, with which the ψ_O configuration is related, are equal to $1/\sqrt{2}H_{GP}$, $1/\sqrt{2}H_{\beta P}$ and $1/\sqrt{2}H_{P\delta}$ respectively. The E_α (the energy of the α-locally excited configuration and E_β (the energy of the β-locally excited configuration) of III and IV were taken from the observed transition energies of the α-methylbenzyl (2.88 and 4.07 eV.) and 2, 4, 6-trimethylbenzyl (2.64 and 3.65 eV.) cations respectively.⁵⁾ The electron affinities of these parent ions were taken to be 7.43 eV. and 6.88 eV. respectively, by referring to the observed ionization potentials of the benzyl radical derivative¹¹⁾ and methylbenzenes.⁶,¹²,¹³⁾

Results and Discussion

Calculated Energy Levels and Wave Functions.—Calculations were performed, using the core resonance integral β as a parameter for each ion, by the aid of an electronic computer FACOM-202 in our institute. The calculated energy levels and wave functions are given in Fig. 2 and Table III, the cation I being taken as an example and the value of β_{CO} being taken to be equal to -2.0 eV., the optimal value for the energy level calculations.

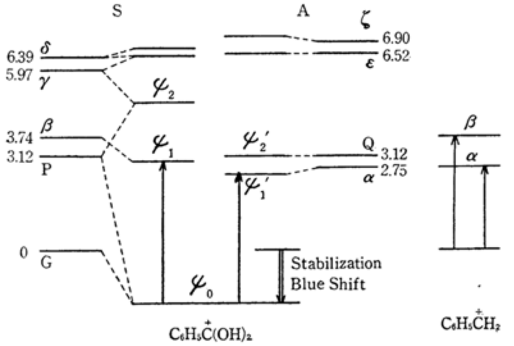


Fig. 2. Energy level diagram showing configuration interaction for the ion I.

In order to obtain accurate experimental results on the absorption intensities, the ultraviolet absorption spectra of the ions I—IV in concentrated sulfuric acid were remeasured by the present authors, since most of the published data¹⁴⁾ for these ions have been concerned only with the location and peak intensity of the second longest wavelength band. Table IV summarizes the calculated and observed transition energies, ΔW, the calculated and observed oscillator strengths, f, the predicted directions of their transition moments, the half-widths of the second longest wavelength bands, $\nu_{1/2}$, the π-electronic stabilization energies due to the configuration interaction, ΔE, and the optimal β_{CO} values. The difficulty of the intensity calculation being kept in mind, it may be said that agreements between the calculated and observed values are good except for the oscillator strength of the $W_0 \rightarrow W_2$ transition of I.

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11) A. G. Harrison, P. Kebarle and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 777 (1961).

12) It was assumed that the ionization potential of the α-methylbenzyl radical is nearly equal to that of the p-methylbenzyl radical (7.46 eV.).¹¹⁾ Also, the difference between the ionization potentials of the 2, 4, 6-trimethylbenzyl radical and the benzyl radical was assumed to be equal to the difference between mesitylene (8.39 eV.)⁶⁾ and benzene (9.24 eV.)⁶⁾. One methyl group substituted at these hydrocarbon species seems to be lower the ionization potential by about 0.3 eV.

13) Although the cations II, III and IV do not possess the C_{2v} symmetry properties, the secular equations for them were factorized into groups in the same manner as for the case of the cation I because of the nil value of the coefficient C_{31}. Therefore, the matrix elements other than the above-mentioned ones are equal to the corresponding elements for the case of I.

14) W. M. Schubert and R. E. Zahler, *J. Am. Chem. Soc.*, **76**, 1 (1954); R. Stewart and K. Yates, ibid., **80**, 6355 (1958); K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959).

Charge Densities and Stabilization Energies. —From the wave functions given in Table III, the π-electronic charge densities for the ground and two excited states of I were calculated as shown in Fig. 3, which also shows those of the ground state of the benzyl cation for purposes of comparison. The result on the protonated benzoic acid may be translated roughly into the valence bond method description as follows:

State The degree of contribution of each resonance structure

Ground state (W_0)

Excited state (W_1')

Excited state (W_1)

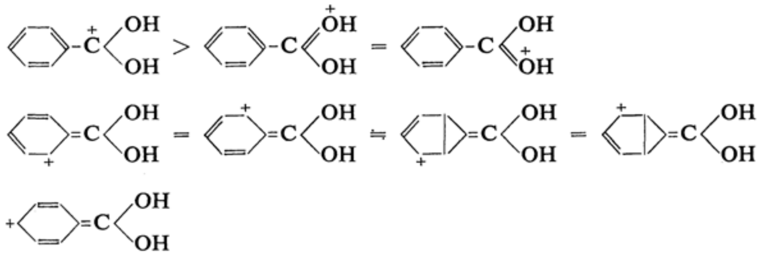

TABLE III. ENERGY LEVELS AND WAVE FUNCTIONS OF THE BENZOIC ACIDIUM ION

Energy, eV.	Wave function
Symmetric	
$W_0=-1.753$	$\Psi_0=0.8389\phi_G-0.1227\phi_\beta+0.5261\phi_P-0.0657\phi_\gamma+0.0106\phi_\delta$
$W_1=2.953$	$\Psi_1=0.3839\phi_G+0.8027\phi_\beta-0.4055\phi_P+0.1282\phi_\gamma-0.1658\phi_\delta$
$W_2=4.898$	$\Psi_2=-0.3279\phi_G+0.4812\phi_\beta+0.5746\phi_P-0.5230\phi_\gamma-0.2394\phi_\delta$
$W_3=6.430$	$\Psi_3=-0.1408\phi_G-0.0079\phi_\beta+0.3240\phi_P+0.7138\phi_\gamma-0.6047\phi_\delta$
$W_4=6.693$	$\Psi_4=-0.1469\phi_G+0.3302\phi_\beta+0.3517\phi_P+0.4430\phi_\gamma+0.7412\phi_\delta$
Antisymmetric	
$W_1'=2.540$	$\Psi_1'=0.9767\phi_\alpha+0.2146\phi_\zeta$
$W_2'=3.120$	$\Psi_2'=\phi_Q$
$W_3'=6.520$	$\Psi_3'=\phi_\varepsilon$
$W_4'=7.110$	$\Psi_4'=0.2146\phi_\alpha-0.9767\phi_\zeta$

TABLE IV. THEORETICAL AND OBSERVED RESULTS ON THE BENZOIC ACIDIUM CATION AND ITS RELATED CATIONS

		ΔW, eV.		f[a]		b)	$\nu_{1/2}$ cm^{-1}	ΔE eV.	β_{CO} eV.
		Calcd.	Obs.[c]	Calcd.	Obs.[c]				
I	$Ph\overset{+}{C}(OH)_2$	4.29	4.16	0.067	0.032	⊥	3900	1.75	−2.0
		4.71	4.73	0.693	0.297	∥			
		4.87		0.171		⊥			
		6.65	6.20	0.058	0.4	∥			
II	$Ph\overset{+}{C}H(OH)$	3.72	3.64	0.065	0.028	∼⊥	3300	1.00	−2.2
		4.15	4.20	0.702	0.308	∼∥			
		5.77	5.99	0.079	0.2	∼∥			
III	$Ph\overset{+}{C}CH_3(OH)$	3.61	3.70	0.065	0.024	∼⊥	3000	0.94	−2.0
		4.19	4.22	0.720	0.268	∼∥			
		5.66	6.14	0.053	0.15	∼∥			
IV	$Mes\overset{+}{C}H(OH)$	3.29	3.21	0.065	0.037	∼⊥	2900	0.71	−2.0
		3.95	3.91	0.660	0.276	∼∥			
		5.72	5.6	0.099	0.1	∼∥			

a) The oscillator strengths were calculated by the following equations:

$$f_{\text{calcd}}=4.704\times10^{-7}\tilde{\nu}Q^2 \qquad (\tilde{\nu}\text{ in cm}^{-1},\ Q\text{ in Debye})$$

$$f_{\text{obs}}=4.32\times10^{-9}\int\varepsilon d\tilde{\nu} \qquad (\tilde{\nu}\text{ in cm}^{-1},\ \varepsilon\text{ in l.}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1})$$

b) Directions of the calculated transition moments (with respect to the long axis of the molecule).

c) All the observed values were obtained by the present authors.

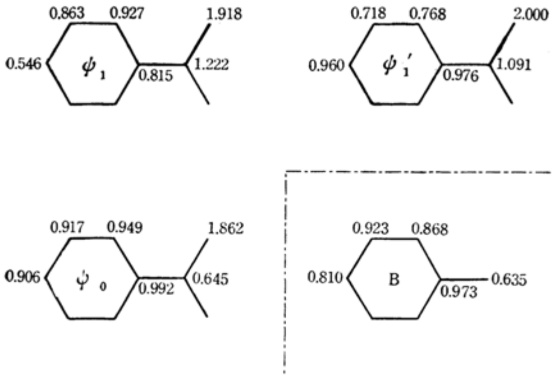

Fig. 3. π-Electronic charge-densities of the various states of the benzoic acidium ion (ψ_0, ψ_1', ψ_1) and of the ground state of the benzyl cation (B).

The π-electronic densities of the ground and excited states of the other ions are not very different from the corresponding values of I.

The stabilization energy, ΔE, due to delocalization of π-electrons amounts to 1.75 eV. for I, as is shown in Table IV. Most of this stabilization energy is brought about by the contribution of the charge-transfer configuration, ψ_P. Of the four ions concerned here, I is the most stable. According to our experiments, the ultraviolet absorption spectrum of benzoic acid in concentrated sulfuric acid does not change appreciably for more than ten days, while a gradual change is observed for the other ions. It may be expected that the hydroxyl groups stabilize the benzyl cation to some extent by their conjugation and steric hindrance effects. A similar stabilization effect is also found with the methyl group; the benzyl cation can not be stably produced under the usual conditions, while α- and/or ortho-methyl-substituted benzyl cations are stable enough for spectroscopic detection[15] because of the hyperconjugative and steric potencies of the methyl group.

The Shift of Bands of the Benzyl Cation by the Substitution.—The benzyl cation is characterized by its reddish color, while II is yellow and I is colorless, and their stabilities increase in just this order. These inclinations through less prominent, are also found for the α-methylated benzyl cations, which may be regarded as one of the most typical examples predictable of the unequivocal effect of hyperconjugation in ionic species.[5,15] The energy level diagram in Fig. 2 shows that the substitution of an electron donating group at the α-carbon atom of the benzyl cation, through the charge-transfer configuration, ψ_P, not only stabilizes the ion but also shifts the β-band ($\psi_G \rightarrow \psi_\beta$ transition) of the benzyl cation to blue. This is because the mixing of the charge-transfer configuration with the ground configuration, ψ_G, considerably lowers its energy, while the energy of the lowest excited configuration, ψ_β or ψ_P which had the same symmetry property as ψ_G, is little affected. Furthermore, because of the nil value of the coefficient C_{31}, α-substitution has no effect on the ψ_α configuration but makes the α-band ($\psi_G \rightarrow \psi_\alpha$ transition band) of the benzyl cation also shift to blue. On the other hand, as may be seen from the results of II and IV, the substitution of an electron-donating group at the benzene ring carbon atom (especially at the *o*- or *p*-position) is found to shift these characteristic bands to red. This phenomenon can be explained as resulting from the lowering of the ψ_α and ψ_β levels by the charge delocalization.

For the other ions the substitution effects on the absorption spectra are almost the same as those for I except for the second longest wavelength band. Because they have only one hydroxyl group, those ions have no ψ_Q configuration; therefore, unlike I, their second longest wavelength bands are not doubly degenerated. The observed half-widths of the second lowest bands seem to support this interpretation (see Table IV).

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[15] M. C. R. Symons, *J. Chem. Soc.*, 1959, 958.