The Ultraviolet Transitions of Benzoic Acid. 2. Hydrogen Bonding in the Ground and Excited States

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Abstract: The spectral shifts that occur when benzoic acid is involved in hydrogen bonding are explained in detail. INDO molecular orbital calculations show that benzoic acid undergoes the following ground-state changes in its electronic distribution upon hydrogen bonding: as a proton donor, the hydroxyl oxygen gains σ density, and loses π density to the carbonyl oxygen; as a proton acceptor, the carbonyl oxygen loses σ density, and gains π density from the ring and the hydroxyl oxygen. The effects of hydrogen bonding in the excited states of benzoic acid are simulated using Pariser-Parr-Pople molecular orbital theory, and the computed spectroscopic changes agree very closely with the experimental data. Excitation of the hydrogen-bonded complexes of benzoic acid produces a predicted increase in electron density on both oxygens of the carboxyl group. These calculations are confirmed by the observed changes in the enthalpies of hydrogen bonding and proton transfer that take place upon excitation.

I. Introduction

In general, hydrogen bonding has been expected to cause a red shift of $\pi\pi^*$ electronic states and a blue shift of $n\pi^*$ states.[1] However, Ito et al.[2] recognized that the spectral shift of the lowest $^1\pi\pi^*$ transition of benzoic acid (280 nm) depends on the ability of benzoic acid to behave as a proton acceptor (C=O group), a proton donor (O-H group), or both simultaneously. These authors determined that when benzoic acid is the proton acceptor (e.g., methyl benzoate-trichloroacetic acid) there is a red shift, but when benzoic acid is the proton donor (e.g., addition of ether) there is a blue shift. In those cases where benzoic acid acts simultaneously as a proton donor and acceptor either red shifts (e.g., dimerization of benzoic acid) or blue shifts (e.g., addition of ethanol) can occur.

We discussed the assignment of the ultraviolet bands of benzoic acid in the first paper of this series.[3] In the present study we have carried out INDO and Pariser-Parr-Pople molecular orbital calculations for the monomer and hydrogen-bonded complexes of benzoic acid. With experimental results, these calculations form the basis for a detailed interpretation of the effects of hydrogen bonding on the ground and excited states of benzoic acid. In a paper to follow,[4] the influences of hydrogen bonding on the emission properties of benzoic acid are examined.

II. Results

Hydrogen Bonding in the Ground State. To investigate the changes in the electron distribution of benzoic acid in its ground state when it is involved in hydrogen bonding, we chose the INDO molecular orbital method.[5] Formic acid was selected as the hydrogen-bonding partner. (See Appendix for the input geometries.) The heats of formation predicted by INDO for the monomer and hydrogen-bonded complexes of benzoic acid give the correct order of stability: benzoic acid (proton donor + acceptor) > benzoic acid (donor) > benzoic acid (monomer). This is exactly the order expected because formic acid is a stronger acid (i.e., a better proton donor) than benzoic acid. If the calculated stabilities *per hydrogen bond* are compared, then the (donor + acceptor) stabilization energy is between the (acceptor) and the (donor) energies in agreement with the acceptor-donor role benzoic acid plays in the doubly hydrogen-bonded complex. Finally, the sum of the (acceptor) and (donor) hydrogen-bond stabilities is less than the (donor + acceptor) stability indicating a (small) cooperative stabilization in the latter case. The correspondence of these trends with experiment gives us confidence that the detailed information about the electron distributions in the monomer and complexes of benzoic acid provided by INDO is meaningful.

The INDO charge densities on benzoic acid (monomer) in its ground state are compared with those on formic acid in Figure 1. The values for formic acid agree qualitatively with the published CNDO/2 results,[6,7] although our INDO charge densities are somewhat higher. They also agree in sign and approximate magnitude with the Mulliken charge densities of formic acid obtained by Snyder and Basch in double-ζ calculations.[8] The main differences are that the charge is more unevenly distributed in the OH group in the latter calculations than in the INDO ones, and the H atom on the carbon is slightly positive, while in INDO it is nearly neutral. The distribution between π and σ orbitals given by the double-ζ calculation is also qualitatively reproduced by the INDO calculation. The comparison is given in Table I. This comparison of the two calculations for formic acid gave us some confidence in the results of the more approximate INDO calculation applied to benzoic acid.

The charge distributions on the atoms of the carboxyl group are quite similar for the aromatic and aliphatic acids. As expected, the electronegative oxygens attract the largest electron density—mostly at the expense of the carboxyl carbon and hydrogen. The transfer of electron density from the aromatic ring, primarily the ortho and para carbons, to the substituent is 0.045 electron.

The major changes in σ and π electron density upon hydrogen bonding are listed in Table II. As a proton donor in hydrogen bonding, benzoic acid loses σ density on the proton involved while the hydroxyl oxygen gains σ density. The increased σ density on the hydroxyl oxygen decreases its π-electron "core potential" and this oxygen loses some π density to the carbonyl oxygen. The carbonyl oxygen gains additional π density from the carboxyl carbon, whose core is made less positive as a result of a slight increase in σ density. The ring carbon at the point of substitution gains σ density and loses π density to the rest of the ring. The electronegative carbonyl oxygen also attracts some of the new σ density in the molecule. The σ density transfer from the proton acceptor, formic acid, is 0.034 electron. Comparison of the bond orders in the proton-donor complex of benzoic acid with those in the monomer of benzoic acid shows the expected[9] strengthening of the C–O bond and weakening of the O-H bond upon hydrogen bonding. The observed[10] weakening of the C=O bond is also predicted.

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Table I. Comparison of INDO and POLYATOM (in Parentheses) Calculations of Mulliken Charge Densities on Formic Acid

	1s	2s	$2p_x + 2p_y$	$2p_z$	total
H1(CH)	1.048 (0.807)				1.048 (0.8071)
H2(OH)	0.798 (0.573)				0.798 (0.5730)
O1(C=O)	2. (1.999)	1.773 (1.814)	3.242 (3.527)	1.328 (1.434)	8.343 (8.3755)
O2(OH)	2. (1.999)	1.724 (1.820)	2.754 (2.858)	1.883 (1.871)	8.310 (8.5473)
C1	2. (1.999)	1.044 (1.105)	1.668 (1.898)	0.789 (.695)	5.502 (5.6970)

Table II. Calculated Changes in Ground-State Electron Density of Benzoic Acid upon Hydrogen Bonding (INDO)

	proton donor		proton acceptor		proton donor and acceptor	
atom	σ	π	σ	π	σ	π
C(OOH)	+0.005	−0.007	+0.005	−0.020	+0.005	−0.029
C(COOH)	+0.007	−0.005	−0.006	+0.008	−0.001	+0.003
=O	+0.005	+0.013	−0.028	+0.032	−0.025	+0.052
O(H)	+0.041	−0.009	0.000	−0.006	+0.060	−0.019
(O)H	−0.032	—	−0.004	—	−0.045	—
change in total density on benzoic acid	+0.034		−0.040		+0.003	

When benzoic acid acts as a proton acceptor, it loses 0.040 σ electron to formic acid, the proton donor. The loss of σ density causes the core potential on the carbonyl oxygen to become more positive and this atom attracts π density—mostly from the carboxyl carbon but also from the ortho and para ring carbons and the hydroxyl oxygen. The C=O bond is weakened by the hydrogen bonding and the C—O bond is strengthened.

Benzoic acid is both a proton donor and acceptor in the complex containing two hydrogen bonds. The effects are therefore a combination of those occurring in the individual donor and acceptor complexes. The hydroxyl oxygen gains σ density and thus loses π density. The carbonyl oxygen loses σ density and gains π density from the hydroxyl oxygen, the carboxyl carbon, and the ortho and para ring carbons. The C=O bond is weakened, the C—O bond is strengthened, and the O—H bond is weakened. These predicted bond energy changes are also observed in the infrared spectra.[9,10]

Hydrogen Bonding in the Excited States. The influence of hydrogen bonding on the excited states was examined by adopting the charge-migration model of Besnainou et al.[11] in the Pariser-Parr-Pople molecular orbital framework.[12] As shown by the INDO calculations, the hydroxyl oxygen gains core electron density when benzoic acid acts as a proton donor and the carbonyl oxygen loses core electron density when benzoic acid acts as a proton acceptor. The charge-migration model assumes that the electron-density increase on the proton donor will be aided by the negative electrostatic charge on the proton acceptor and by the transfer of (negative) charge to the proton donor. For the proton acceptor, the loss of electron density is aided by the positive electrostatic charge on the proton, hindered by the negative electrostatic charge on the proton donor, and aided by the transfer of charge from the proton acceptor. The expressions are

$$\Delta W_{\text{don}} = \frac{-Q_{\dot{\text{O}}}}{R_{\text{O}\cdots\text{O}}} - Q_{\text{CT}}\gamma_{\ddot{\text{O}}\ddot{\text{O}}} \qquad (1)$$

$$\Delta W_{\text{acc}} = \frac{Q_{\text{H}}}{R_{\text{O}\cdots\text{H}}} - \frac{Q_{\ddot{\text{O}}}}{R_{\text{O}\cdots\text{O}}} + Q_{\text{CT}}\gamma_{\dot{\text{O}}\dot{\text{O}}} \qquad (2)$$

where ΔW_{don} and ΔW_{acc} are the change in core potential for the oxygen that is a proton donor or proton acceptor, respectively, and $Q_{\dot{\text{O}}}$ and $Q_{\ddot{\text{O}}}$ are the fractional charges on the acceptor C=O bond and donor O—H bond, respectively. Q_{CT} is the fractional charge transferred with the formation of the hydrogen bond. Numerical evaluation of the above expressions using the benzoic acid dimer hydrogen-bond distances is given in the Appendix.

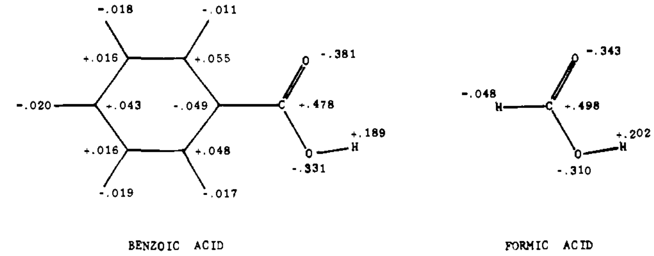

Figure 1. INDO ground-state charge densities.

The spectroscopic changes of benzoic acid with hydrogen bonding computed using the charge-migration model are compared with the experimental data in Table III. The experimental values for the monomer and dimer of benzoic acid were measured in dilute (10^{-5} M) and concentrated (10^{-2} M) hydrocarbon solutions, respectively.[13] It is difficult to decide on experimental numbers for the proton-donor and proton-acceptor species because they are determined by the specific hydrogen bonding partner. We chose the donor values measured for a dilute solution of benzoic acid in ethyl ether.[13] The proton-acceptor data are those reported[2] for a complex formed between methyl benzoate and trichloroacetic acid in hydrocarbon solvent. In all cases account was taken of the solvent shift caused by non-hydrogen-bonding forces and the wavelengths were corrected to the vapor[14] for better comparison with the calculated results. The observed red shifts and blue shifts, which depend on the site of the hydrogen bonding, are both correctly predicted for the absorption bands. The magnitudes of these shifts and the intensity variations are also well reproduced.

III. Discussion

The electronic excitation energy and intensity of a molecule in solution are different from their values in the vapor because of the interactions of solvent with molecule and of solvent with radiation. For a relatively inert solvent such as a hydrocarbon, the red shift in the spectrum of benzoic acid going from vapor to solution is about 400 cm^{-1}. The additional effects of other solvents can be related to hydrogen bonding or ionization. That solvent polarity is not an important factor is shown by the small

Table III. Spectroscopic Changes of Benzoic Acid with Hydrogen Bonding

state	monomer		proton donor		proton acceptor		proton donor + acceptor (dimer)	
	calcd	exptl[a]	calcd	exptl[a]	calcd	exptl[a]	calcd	exptl[a]
^1L_b								
λ, nm	265	278	263	276	270	285	267	281
$\Delta\nu^b$	0	0	+170	+270	−716	−900	−350	−310
f^c	0.011	0.014	0.011	0.013	0.030		0.028	0.016
^1L_a								
λ, nm	227	230	224	225	237		233	234
$\Delta\nu^b$	0	0	+598	+970	−1855		−1070	−750
f^c	0.21	0.22	0.18	0.21	0.24		0.24	0.32

[a] See text. [b] Change in frequency (cm^{-1}) relative to monomer; experimental error ±50 cm^{-1}. [c] Oscillator strength.

Table IV. Calculated Changes in Electron Density upon Excitation of Benzoic Acid

atom	monomer		proton donor		proton acceptor		proton donor and acceptor	
	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a
C(OOH)	+0.151	+0.194	+0.120	+0.148	+0.259	+0.333	+0.208	+0.274
=O	+0.042	+0.055	+0.023	+0.034	+0.047	+0.062	+0.039	+0.049
O(H)	+0.007	+0.009	+0.016	+0.013	+0.013	+0.018	+0.021	+0.025

Table V. Change in Hydrogen Bond Strengths upon ^1L_b Excitation of Benzoic Acid

benzoic acid	$\Delta\nu$,[a] cm^{-1} ± 50	$\Delta\Delta H$,[b] kcal/mol ± 0.1
monomer	0	
H donor (complex with ethyl ether)	+270	+0.8
H acceptor (methyl benzoate-trichloroacetic acid)	−900	−2.6
H donor + H acceptor (dimer)	−310	−0.9
H donor + H acceptor (complex with ethanol)	+255	+0.7

[a] Frequency shift relative to monomer (from Table II). [b] Change in H-bond enthalpy upon excitation.

(35 cm^{-1}) blue shift of the methyl benzoate bands in going from hydrocarbon to acetonitrile.

There is an interdependence between the electron distribution and the hydrogen bonding of benzoic acid. The success of the charge-migration model shows that it is the increase in σ density on the hydroxyl oxygen of benzoic acid as a proton donor that is responsible for the wavelength and intensity decrease of the benzoic acid absorption bands. The increased electron density on the carboxyl group hinders the intramolecular charge-transfer process[3] and reduces its contribution to the benzenoid states. Likewise, the decrease in σ density on the carbonyl oxygen of benzoic acid acting as a proton acceptor aids the charge-transfer process and is responsible for the increase in wavelength and intensity of the benzoic acid absorption bands.

The spectral changes that occur upon self-association of benzoic acid can be caused by exciton-type interaction of the two chromophores as well as by hydrogen bonding. A simple dipole–dipole model predicts a blue shift of less than 1 cm^{-1} for the ^1L_b transition[15] and a red shift of 280 cm^{-1} for the ^1L_a transition.[10] Clearly, dipole–dipole interaction does not account for the behavior of the ^1L_b band whereas it does play an important role in the ^1L_a state. The observed increase in ^1L_a intensity upon dimerization is 45%. Our hydrogen-bonding model predicts a 14% increase and the dipole–dipole model (using configuration interaction) accounts for a 28% increase.[10]

The strength of the hydrogen bonding of benzoic acid is affected in turn by the electron density distribution in each state. The molecular orbital calculations show that excitation of the hydrogen-bonded complexes of benzoic acid results in an increase in electron density on the carboxyl group (Table IV). The increase in density is greater in the ^1L_a state than in the ^1L_b state and in both states there is a larger increase in density on the carbonyl oxygen, which is more conjugated to the aromatic π system, than on the hydroxyl oxygen. On the basis of electrostatic considerations the benzoic acid donor hydrogen bond should be weakened and the acceptor hydrogen bond should be strengthened in the excited states. Moreover, the effect on the acceptor bond should be greater. The strength of the hydrogen bond in each excited state can be determined, knowing the ground-state enthalpy, from the frequency shift of the absorption origin of the complex from the origin of monomer.[16] The changes in hydrogen-bond enthalpies upon excitation of benzoic acid to the ^1L_b state are listed in Table V. These experimental results confirm the calculated weakening of the benzoic acid donor and strengthening of the acceptor bond upon excitation.

Benzoic acid acts simultaneously as a proton donor and acceptor when it dimerizes or when it is solvated in ethanol; yet relative to the monomer there is a red shift of the spectrum for the dimer and a blue shift for the complex with ethanol. Because of the small (<1 cm^{-1}) dimer interaction mentioned earlier, the excitation is essentially localized on one half of the dimer while the other benzoic acid molecule acts as a nonexcited hydrogen-bonding partner. The red shift upon dimerization indicates that, although the donor and acceptor bonds are equal in strength in the ground state of the dimer, the acceptor bond (involving the conjugated carbonyl oxygen) of the excited dimer half has a much greater effect on the absorption spectrum. The blue shift for the ethanol complex is related to the fact that ethanol is a much weaker proton donor and a slightly stronger proton acceptor than benzoic acid as a hydrogen-bonding partner.

The absorption changes upon complete proton removal from[17] or addition to[18] benzoic acid have been reported in the literature. The wavelength and intensity changes that occur are similar to the corresponding donor and acceptor hydrogen bonding cases except that the effects are much larger, of course. From the published changes in pK upon excitation[19,20] we have determined that the loss of a proton at the hydroxyl oxygen becomes less favorable by 7.3 kcal/mol in the ^1L_b state and the enthalpy for loss of a proton at the carbonyl oxygen

Table VI

bond	calcd moment,[a] esu	obsd moment,[b] esu	Q
C=O	5.85×10^{-18}	2.3×10^{-18}	0.39
O—H	4.6×10^{-18}	1.5×10^{-18}	0.33

[a] A charge difference of one electron is assumed. [b] C. P. Smyth, *J. Phys. Chem.*, **59,** 1121 (1955).

becomes less favorable by 10.0 kcal/mol in the same excited state. These data further verify the calculated increase in basicity caused by the transfer of electron density to the carboxyl group in the excited state, with the transfer being greater to the carbonyl oxygen than to the hydroxyl oxygen.

IV. Conclusion

We have combined the spectroscopic data with molecular orbital calculations to investigate in more detail the hydrogen-bonding properties of benzoic acid. Confidence in the theoretical computations is obtained by their ability to reproduce the observables. From these calculations we have learned in detail the changes in the electron distribution of benzoic acid with changes in hydrogen bonding.

The presence of the aromatic ring alters the hydrogen-bonding properties of the carboxylic acid. The phenyl group is a source of electron density, and the density on the carboxyl oxygens is greater than in the case of formic acid (Figure 1). This increased density weakens the donor bond of the aromatic acid and strengthens the acceptor bond. We have noted the changes in hydrogen bonding in the excited states of benzoic acid where there is a further transfer of electron density from the ring to the carboxyl group.

The dependence of the $\pi\pi^*$ states of benzoic acid on the role of the molecule as a proton donor or acceptor in hydrogen bonding has been stressed. These relationships and the influences of hydrogen bonding on the $n\pi^*$ states are also important in determining the emission properties of the molecule (part 3). The more subtle influences of hydrogen bonding on the electronic states of benzoic acid are revealed in the high-resolution spectra.[15]

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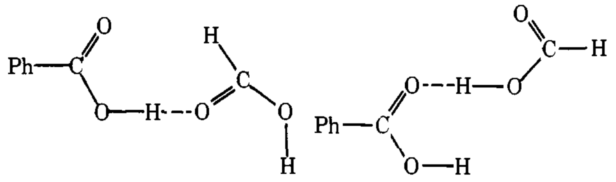
V. Appendix

Molecular Orbital Calculations. INDO. Standard[21] bond lengths and bond angles were used for the benzoic acid and formic acid molecules with the exception of the Ph-COOH bond. The experimental[22] Ph-COOH bond length was chosen because this distance depends on the substituent. The distance between the hydrogen-bonded oxygen atoms was also set at the experimental value measured for the dimer of benzoic acid in the crystalline state.[22] The O-H bond length for the hydroxyl group involved in hydrogen bonding was determined from a plot of this distance as a function of the O· · ·O distance.[23]

Even though a complete geometry search for each molecule and complex would be desirable in order to compare the results for the most stable conformation of each system, it is informative to examine the properties of the complexes in fixed geometries. The geometries used for the donor and acceptor complexes are shown below.



Pariser–Parr–Pople. Expressions 1 and 2 were evaluated for benzoic acid (Table VI). Q_{CT} was estimated from a plot of Q_{CT} as a function of O· · ·O distance.[24] When $R_{O...O} = 2.64$ Å (the experimental distance for the benzoic acid dimer), $Q_{CT} = 0.235$. $\gamma_{\dot{O}\dot{O}}$ and $\gamma_{\ddot{O}\ddot{O}}$ are just the one-center repulsion integrals—15.23 and 18.82, respectively. The calculated changes in the core potential using the above values for the parameters are $\Delta W_{don} = -4.58$ eV and $\Delta W_{acc} = +3.66$ eV. The other input parameters chosen for the Pariser–Parr–Pople program are listed in Table II of part 1.

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