The Ultraviolet Transitions of Benzoic Acid. 4. High-Resolution Spectral Studies of Hydrogen Bonding in the Excited States of the Benzoic Acid Dimer

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Abstract: High-resolution spectral studies of the benzoic acid dimer in host single crystals have been made to investigate the details of the changes in H bonding which occur upon electronic excitation. The principal host crystal used was benzene. An increase of H-acceptor ability in the first singlet state is shown by an anomalous H-isotope shift (a red shift upon deuteration). The occurrence of odd parity dimer modes in fluorescence also supports this conclusion. No odd parity modes appear in phosphorescence, demonstrating that the triplet state is not like the singlet. It is concluded that the triplet H bonding is not very different from that in the ground state while the singlet is forced into an unsymmetrical structure in the vicinity of the H bonds.

I. Introduction

In a previous paper (part 2),[1] low-resolution spectra and solvent shifts have been used to show that the H-acceptor bond of benzoic acid is stronger in the first excited state, ^1L_b, and that of the H-donor bond is weaker. These experimental indications are supported by semiempirical MO calculations. It seemed of importance to us to search for detailed experimental verification of these results in the electronic-vibrational spectra of the benzoic acid dimer. Benzoic acid is one of the simplest compounds in which the effect of an active chromophore (the benzene ring in this case) on the H bonding of carboxyl groups can be investigated. The detailed results obtained indeed show how the electronic changes in the H bonds are related to the chemical properties of the excited molecule.

The statement made in part 2 that the excitation is localized on one ring is confirmed by the results of this high-resolution study.[1] It is also shown that in the singlet state the dimer is much more distorted than in the triplet state, relative to the symmetrical ground state. These results have a direct bearing on the question of the change of acidity of benzoic acid when raised to its excited states.

It is well known that the acidity of aromatic carboxylic acids decreases in the excited states:[2]

$$pK(S_0) < pK(T_1) < pK(S_1)$$

This order reflects an increase in proton affinity which parallels the increase we have found in H bonding as revealed both by the high-resolution spectra reported here and by the results given in part 2.[1]

II. Experimental Section

The principal experimental results were obtained using single-crystal benzene containing benzoic acid dimers in solid solution. It was found that the dimer goes into the crystal in one principal way. The structure of crystalline benzene at 200 K[3] is shown in Figure 1. The long axis of the dimer lies in the *b* direction of the crystal. The benzene unit-cell dimension along the *b* axis[3] (9.67 Å) can accommodate the benzoic acid dimer, whose aromatic ring-center to ring-center distance is 9.68 Å.[4] Thus, polarized spectra can be obtained in which long- and short-axis spectra are separated. The crystals were grown by lowering tubes with tapered ends into water at 0 °C. Concentrations of benzoic acid included in the crystal were on the order of 10^{-4} mole fraction or less. Experimental tests to be described later show that these molecules are truly in solid solution as dimers. The crystals were then removed from the thin-walled glass tubes and oriented, polished, and mounted in a cold room at about −20 °C.[5] The spectra were taken at about 2 K and were recorded photographically using Eastman Kodak 103a-0 plates and a 3.4-m Jarrell-Ash Ebert type spectrograph. A 6-in. grating having 30 000 lines/in. was used in first order. Slit widths were normally 10 μ. The linear dispersion on the plates was 2.5 Å/mm, and the resolution achieved was greater than 100 000. The plates were calibrated with Fe-arc lines and were both measured and microdensitometered. The measured spectrum lines and calibration lines were compared using a computer program which gave the spectrum lines their wavelength and wavenumbers, corrected to vacuum. The program also computed differences, useful in making spectral analyses.

The fluorescence and phosphorescence spectra were taken on a high aperture (f/5 Meinel "C") spectrograph in the second order of the grating. The resolving power was about 25 000. The high aperture permitted shorter exposure times which were necessary because it was observed that benzoic acid in benzene gradually disappears under irradiation. It is possible that benzoic acid decomposes to CO_2 plus benzene, since no spectra of reaction products are found in the photolyzed crystals.

III. Results

A. Description of the Spectra. The polarized absorption spectrum of benzoic acid in benzene is shown in Figure 2. The polarization ratio of the principal lines which are within the linear range of the plate density is $a{:}b = 9{:}1$. Actually the *a* and *c* axes are not always distinguished in the crystal orientation process, but the theoretical ratio $a(c){:}b$ is about 9:1 in either case. The major *b*-polarized line is the benzene-like mode 6b at 557 cm^{-1}. This mode resembles the component of the e_{1u} mode of benzene having a node through the substituent, and it therefore appears at nearly the same frequency as in benzene in its $^1B_{2u}$ state, 522.4 cm^{-1}. All other lines are mainly *a,c* polarized, hence perpendicular to the long axis of the molecule. This is the polarization direction of the electronically allowed transitions. The weak line located 3 cm^{-1} above the origin is probably associated with a ^{13}C impurity. (A dimer with one ^{13}C in the rings has about 12% probability.)

Proof that we are observing only the benzoic acid dimer is provided by the spectra of mixtures of isotopically substituted molecules. Figure 3 shows the absorption spectrum of a 1:1 mixture of undeuterated (d_0) and carboxy-deuterated (d_1) benzoic acid containing the three possible dimers. Four lines of equal intensity are observed at the origin of the absorption spectrum, 35 076.2 + (0.0, 1.6, 23.0, 24.6) cm^{-1}. An expansion of the origin region of this spectrum (bottom of Figure 4) shows this splitting more clearly. If only monomer were present we would see just two lines, separated by the zero-point shift due to one D atom on the carboxyl group (23 cm^{-1}). If electronic excitation were uniformly distributed over the two halves of the excited dimer, we would see three lines with a 1:2:1 inten-

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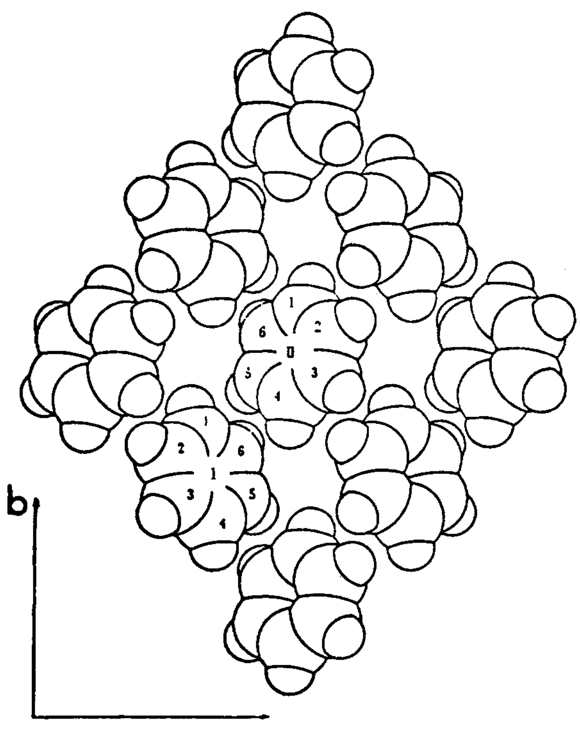

Figure 1. Structure of benzene crystal (Cox et al., ref 3).

Table I. Origin Bands of Singlet and Triplet States in Isotopically Substituted Benzoic Acid Dimer in Benzene Single Crystal (cm^{-1})[a]

isotopic species	singlet	Δ	triplet	Δ
d_0	35 076.2		27 458.6	
d_5	35 216.4	140.2	27 560.1	101.5
4-d_1	35 097.1	20.9	27 500.4	41.8
1-d_1-d_0	35 074.7 d_0*-d_1	−1.5	27 458.3	0
	35 076.2 d_0*-d_0		27 458.3	
	35 097.7 d_1*-d_1	21.5	27 464.4	6.1
	35 099.3 d_1*-d_0	23.1	27 464.4	6.1
d_0-d_5	35 076.2 d_0*-d_0		27 459.6	
	35 076.9 d_0*-d_5	0.7	27 459.6	0
	35 215.7 d_5*-d_0	139.5	27 560.3	100.7
	35 217.0 d_5*-d_5	140.8	27 560.3	100.7

[a] The first three rows refer to the homogeneous dimers in benzene from spectra on three different plates. The remaining two sets of entries are for 1:1 mixtures of the isotopically substituted and unsubstituted dimers, all four lines being from one plate. The differences are therefore accurate. The singlet data is from absorption, and the triplet from emission at lower resolution. The d_0-d_0 entries for the singlet are within 0.1 cm^{-1} on three plates, but differ by up to 1.3 cm^{-1} for the triplet. The d_5-d_5 entries happen to differ for both.

sity pattern since in that case the d_0*-d_1 (d_0-half excited) and d_1*-d_0 dimers would be identical. The fact that four lines are observed demonstrates that the dimer is indeed present but that the excitation of the dimer is largely localized on one half of the molecule. This fact had already been deduced from the low-resolution spectra in part 2.[1] An intensity comparison of these four lines in the 1:1 vs. 1:2 $d_0 + d_1$ spectra in Figure 4 leads to their unambiguous assignment as origins of the following species (increasing energy): d_0*-d_1, d_0*-d_0, d_1*-d_1, and d_1*-d_0. The frequencies of the 0-0 lines observed in the isotopically substituted molecules for both singlet and triplet states are given in Table I.

Additional evidence that we are dealing only with dimers comes from the vibrational analysis of the fluorescence. Figure 5 shows the fluorescence spectrum of benzoic acid in a single crystal of benzene. In Table II the principal fluorescence lines are listed and their assignments from infrared and Raman spectra[5,6] are also given. For a dimer, the normal modes are the odd and even combinations of the monomer modes. It is notable that for some modes of benzoic acid both even (as expected) and odd parity dimer vibrations occur in the fluorescence. For example, the mode 6a in benzoic acid monomer has the frequency 405 cm^{-1}, while in the dimer it has an in-phase even parity mode at 420 cm^{-1} and an odd parity mode at 393 cm^{-1}. Both of these latter frequencies appear in the fluorescence spectrum but we see no trace of 405 cm^{-1}. The reason for the appearance of the odd parity component in fluorescence is related to the fact that the excitation is trapped in one half of the molecule. As a result, the molecule in its excited state does not possess a center of symmetry and the odd parity modes

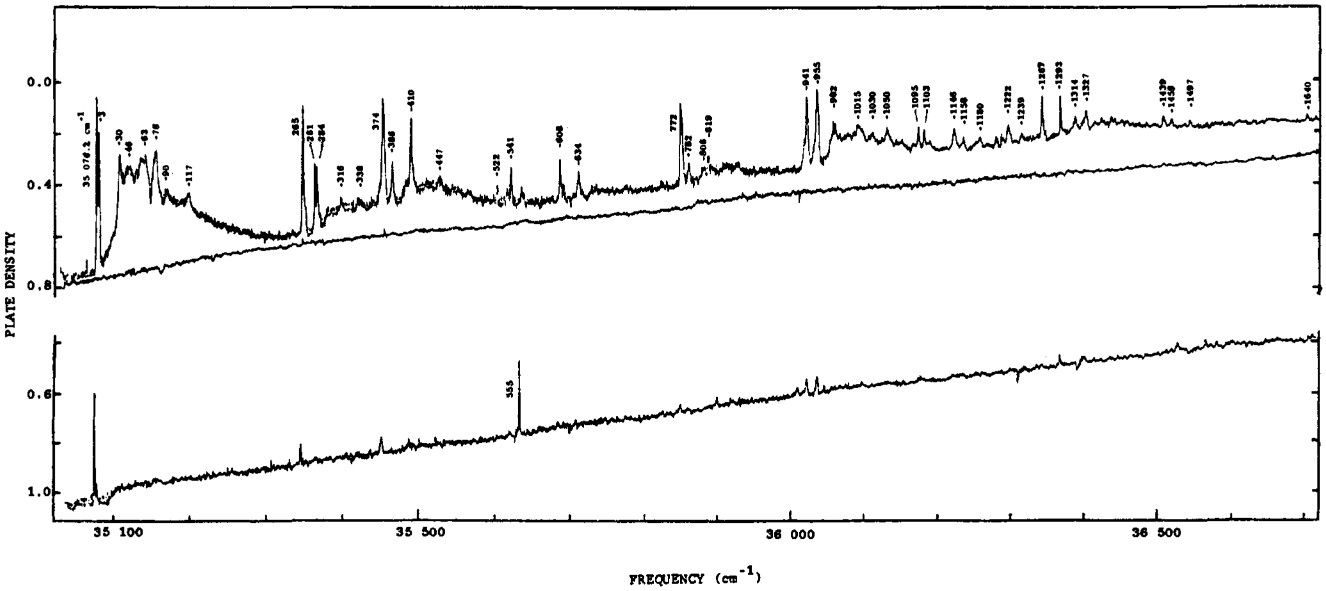

Figure 2. Polarized absorption spectrum of benzoic acid dimer in a single crystal of benzene at 2 K.

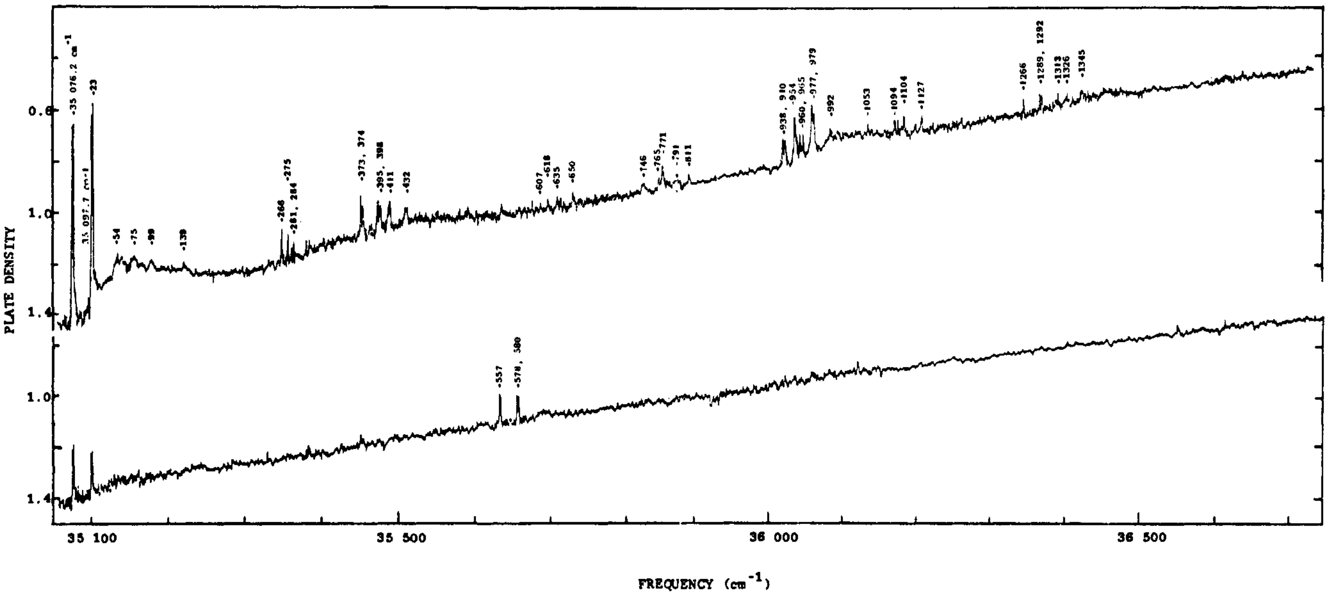

Figure 3. Polarized absorption spectrum of 50% carboxy-deuterated benzoic acid in single benzene crystal at 2 K. The 23-cm^{-1} splitting is the main isotope shift. The 1.6-cm^{-1} splitting is the secondary shift, more clearly shown in Figure 4.

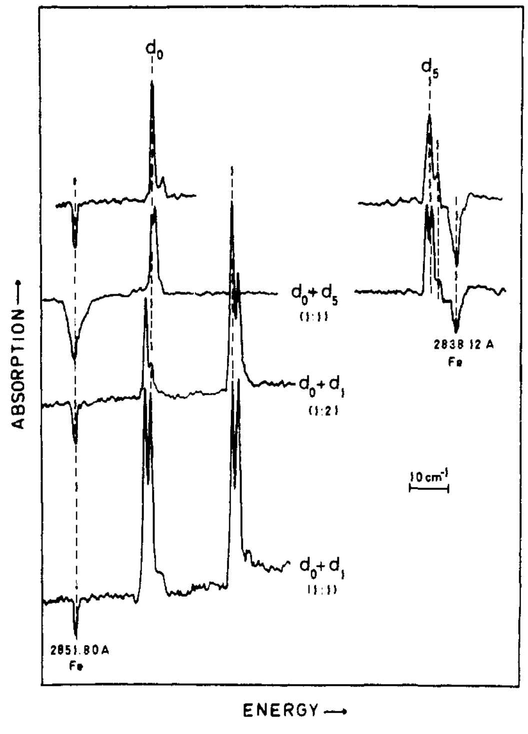

Figure 4. Origin region absorption bands of several deuterated species. From top down: (1) pure d_0 and pure d_5 origin regions compared to nearby iron lines; (2) d_0 + d_5 in 1:1 ratio; (3) d_0 + d_1 (carboxy deuterated) in 1:2 ratio; (4) d_0 + d_1 (carboxy deuterated) in 1:1 ratio.

are not forbidden by selection rules. This point will be discussed later.

B. Analysis of the Isotope Effects. We can get more quantitative information about the H bonds in the excited singlet state of benzoic acid by a further study of the isotope effects shown in Figure 4. The d_5 (ring deuteration) absorption origin is blue shifted 140 cm^{-1} from the d_0 origin. This is the usual shift caused by a reduction of the C-H (or C-D) force constants in the excited state of the benzene ring. In benzene itself this blue shift is 203 cm^{-1} (and note that $5/6 \times 203 = 169$). With a 1:1 mixture of d_0 and d_5 benzoic acid there is a very small (0.7 cm^{-1}) blue shift of the d_0*-d_5 origin relative to d_0*-d_0. This shift shows that, while the excitation is largely confined to the d_0 side of the dimer, there is a change in zero-point energy, ΔE, caused by the deuteration of the unexcited half of the molecule. A similar blue shift of 1.3 cm^{-1} is observed when the d_5*-d_5 molecule absorbs relative to the absorption of d_5*-d_0. From these shifts we can extract the dimer splitting energy, 2ϵ, and the deuteration zero-point energy effect.

We assume that the resonance interaction energy between the dimer halves only causes an appreciable spectral shift in the homogenously deuterated dimers, and thus we neglect second-order effects. Then the 0.7-cm^{-1} splitting between d_0*-d_0 and d_0*-d_1 is the difference between zero-point energy shifts, Δ, and the resonance interaction, ϵ: $0.7 = \Delta - \epsilon$. Similarly the 1.3-cm^{-1} splitting between d_0-d_1* and d_1-d_1* is $1.3 = \Delta + \epsilon$. These give $\epsilon = +0.3$ and $\Delta = 1.0$ cm^{-1}, with an uncertainty of about 0.3 cm^{-1}.

The sign of ϵ is such as to place the allowed dimer component above the forbidden one, the direction to be expected for the coupling of monomer units by dipoles transverse to the vector joining them. This, of course, agrees with the geometry of benzoic acid dimer and the transition moment of the $^1A \rightarrow {}^1L_b$ transition. The magnitude of ϵ is uncertain, but it is small enough to account for the localization of the excitation.

The isotope shift Δ has the sign expected for an increase of isotopic mass of an electronically excited molecule (a blue shift). This sign results from a decrease of the force constants in the excited state, the direction usually to be expected.

The magnitude of Δ cannot reasonably be accounted for in terms of the mass change of the unexcited half of the molecule. It seems to be a complicated quantity dependent on changes in many frequencies as well as on changes in the description of the normal modes of the dimer between ground and excited states. This point is discussed later.

The substitution of one deuterium atom in the carboxyl group produces an anomalous isotope shift, as shown in Figure 4. There it is seen that the normal blue shift due to the OD bond is 23 cm^{-1} as given by the separation between d_0*-d_0 and d_1*-d_0. However, d_0*-d_1 is 1.6 cm^{-1} to the *red* of d_0*-d_0, and d_1*-d_1 is 1.6 cm^{-1} to the *red* of d_1*-d_0. Using this data we obtain the following results from a calculation similar to the one above: $\epsilon = 0.0$ cm^{-1} and $\Delta = -1.6$ cm^{-1}, again with an

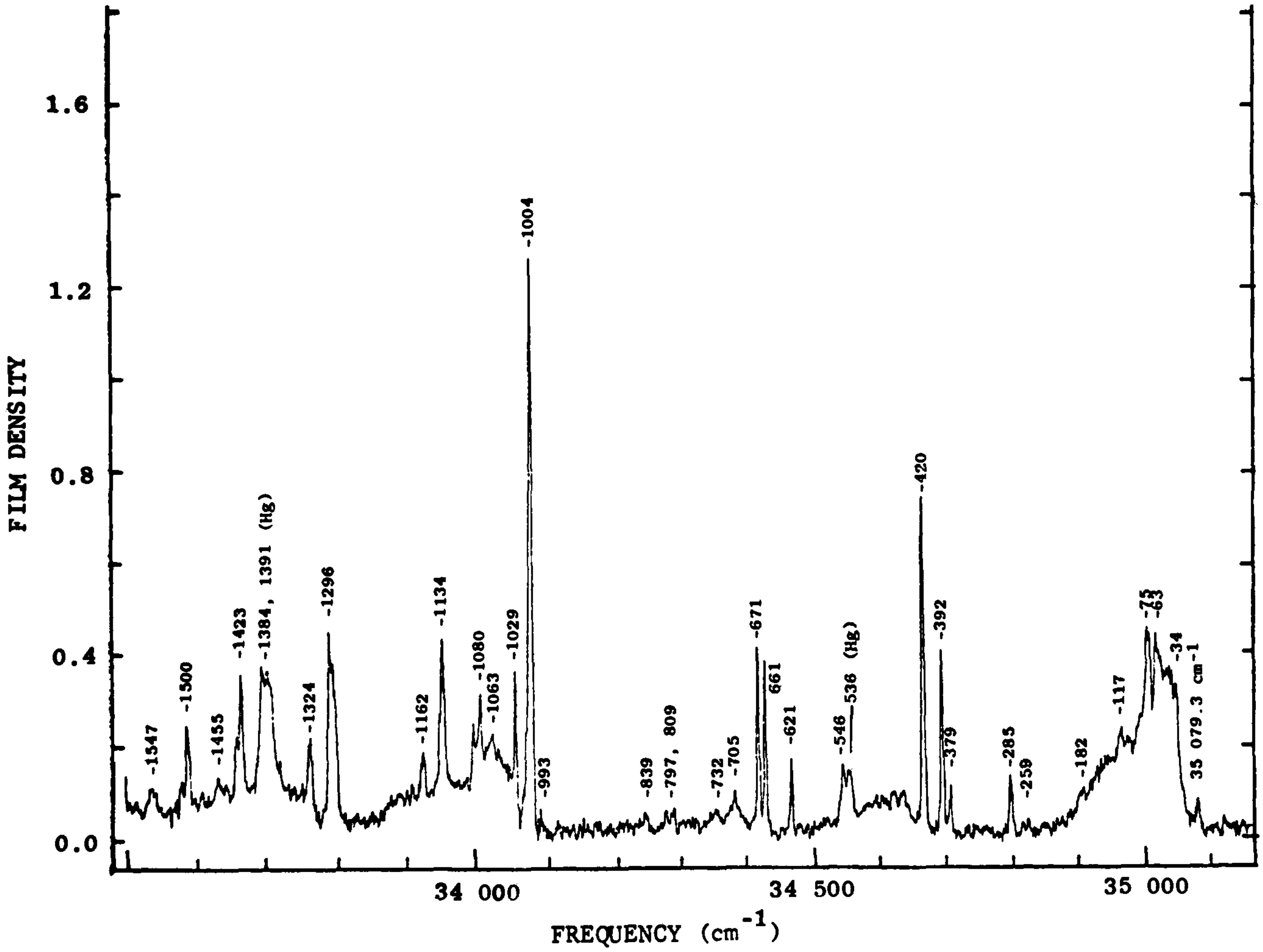

Figure 5. Fluorescence spectrum of benzoic acid dimer in a single crystal of benzene at 2 K. The sharp origin is largely reabsorbed.

error of ±0.3 cm^{-1}. In other words, the presence of a D atom in the H bond to an excited benzoic acid molecule has an isotope shift opposite to that caused by a D atom in the ring or in the OH bond. In this case, Δ is a measure of the contribution of the H bond to the zero-point energy shift caused by deuteration of the unexcited half of the molecule. The simplest interpretation is that the H bond to the carbonyl oxygen on the excited half becomes stronger in the excited state and therefore its contribution to the zero-point energy is greater in the excited state than in the ground state.

C. Comparison of Triplet and Singlet States. The isotope shift in the triplet state resulting from deuteration of the OH bond is only 6 cm^{-1} to the blue, compared to 23 cm^{-1} in the singlet state. This shift is principally caused by a change in the OH force constants between ground and excited states, and thus this force constant must change much less in the triplet than in the excited singlet. Assuming that only one normal mode is strongly involved in the OH symmetry coordinate an estimate of the change in excited state OH frequency can be made for each state.[7]

$$\Delta = \frac{1}{2}(1 - p)[\omega_e'' - \omega_e']$$

where $p = (\mu/\mu^i)^{1/2}$, μ = reduced mass of the OH bond, i = deuterated species, and ω_e'' (ω_e') = frequency of the OH stretch in the ground (excited) state. The result is a 44-cm^{-1} drop for the triplet and 168 cm^{-1} for the singlet, about 1.2 and 5% if the ground-state value is 3400 cm^{-1}. Lines in this region of the fluorescence or phosphorescence spectra could not be assigned to the OH frequency because of the many combination bands. Nevertheless, the zero-point shifts show that in the triplet state the carboxyl region is much less electronically excited than it is in the singlet state. The triplet excitation and emission spectra could not be observed with sufficient resolution to observe any difference between d_0*-d_0 and d_0*-d_1 triplet origins, so they are under 1 cm^{-1} apart.

The vibrational structure of the triplet emission is also quite different from that of the singlet. Figure 6 shows the phosphorescence of benzoic acid-d_0 in a matrix of benzoic acid-d_5. Instead of the mode 6a at 420 cm^{-1} one sees a medium-strong band at 409 cm^{-1} which corresponds to the a_2 mode 16a$_g$. There is no evidence for 6a$_g$. In the fluorescence of this same crystal, by way of contrast, one sees 420 and 392 cm^{-1}, the 6a$_g$ and 6a$_u$ modes. In benzoic acid-d_0 in benzene there is a complicated group of lines in the phosphorescence spectrum, 412.5, 420, 435.4, 439.5, 433.8 cm^{-1} (Figure 7). The 412.5 cm^{-1} could be 16a$_g$ and 420 cm^{-1} could be 6a$_g$. There is no evidence for 6a$_u$ expected at 392 cm^{-1}. The complexity of this group of lines is partly caused by the 23-cm^{-1} site splitting. The high intensity of 16a also makes the interpretation of this region difficult. There is a possibility that the 6a and 16a modes can interact in the mixed crystalline environment. In d_5-d_5 benzoic acid 16a is 356 and 6a is 415 cm^{-1}, and therefore they are separated from each other. The fluorescence from this compound in benzene shows 410 and 379 cm^{-1}, presumably the 6a$_g$ and 6a$_u$ lines, and no trace of 356 cm^{-1}. The phosphorescence, on the other hand, shows a strong line at 361 cm^{-1}; presumably this is 16a. There are also weak lines at 393, 402,

Table II. Fluorescence Spectrum of Benzoic Acid-d_0 in Benzene

rel int[a]	frequency, cm^{-1}[b]	frequency diff, cm^{-1}	assignment[c]	Raman freq	IR freq
vw	35 079.3	0.0	origin (reabsorbed)		
m	35 045.1	34.2	lattice		
m	35 016.6	62.8	lattice	64	
m	35 004.0	75.4	H-bond op bend		71
w	34 962.5	116.5	C-X torsion		111
vvw	34 820.2	259.1	C-X ip bend	274	
w	34 794.3	285.0	C-X ip bend		293
w	34 700.8	378.5	?		
m	34 687.4	391.9	6a′		388
s	34 659.7	419.5	6a	422	
w	34 543.4	535.9	Hg line		
w	34 533.4	545.9	scissor		546
w	34 458.2	621.1	6b	616	
m	34 418.5	660.9	i.p. fund. (ipf′)	660	
m	34 408.5	670.8	i.p. fund. (ipf)		671
vs	34 075.2	1004.1	12	1001	
m	34 050.4	1028.9	19a	1028	
w	34 023	1056	ipf′ + 6a′		
m	33 945.4	1133.9	C-X stretch	1134	1130
w	33 917.2	1162.1	6b + scissor		
			15	1157	
m	33 783.2	1296.2	COOH	1292	1306
w	33 755.7	1323.6	2(ipf′)		
m	33 695.0	1384.3	Hg line		
m	33 687.9	1391.4	Hg		
m	33 656.8	1422.5	12 + 6a		
w	33 650.4	1428.9	COOH		1429
w	33 579.2	1500.1	18a		1498
vw	33 531.8	1547.5	12 + scissor		
vw	33 491.4	1587.9	8b	1587	
w	33 381.5	1697.9	C=O		1708
m	33 074.2	2005.1	2(12)		

[a] Relative intensity, qualitatively estimated from the microdensitometer tracing of photographic film. vvs = very, very strong; vs = very strong; s = strong; m = medium; w = weak; only the stronger lines are listed here. [b] Vacuum corrected values. The root mean square deviation is 1.5 wavenumbers. [c] The vibrational notations are Wilson's for benzene-like modes plus i.p. fund. = in-plane fundamental; o.p. fund. = out-of-plane fundamental; C-X = ring-substituent motion.

and 416 cm^{-1}. No trace of $6a_u$ 379 cm^{-1} appears. The line at 416 cm^{-1} could be 6 a_g but it is weak, and could very well be 393 + 20 cm^{-1}, a site-shifted line. Thus there appears to be good evidence that 6a cannot occur in the triplet-singlet spectrum by the same mechanism as in the singlet-singlet spectrum and is always very weak. This is an important conclusion because it means that the principal mode which interacts with the carboxyl region is not excited in the triplet-singlet process. It confirms the other conclusions which show that in the triplet state the carboxyl region is much less perturbed than in the singlet. The appearance of 16a instead of 6a as the prominent mode is an example of a common feature of the triplet state of benzoic acid, namely, that out-of-plane modes are more important than in the singlet. This feature will be discussed in another place.[6]

Further evidence showing the difference between singlet and triplet states is provided by the low-frequency modes which involve the relative motion of the two halves of the dimer, the "dimer modes".[8] There are present in absorption, fluorescence, and phosphorescence between 80 and 140 cm^{-1}. One can see from Figures 5 and 7 that the dimer modes are much weaker relative to the origin line in phosphorescence than in fluorescence, and also that the lattice modes from about 30 to 80 cm^{-1} are much weaker. The detailed structures of the spectra in the 30-190-cm^{-1} region also differ considerably. We hope, in a later paper, to be able to present exact assignments for these features. At present we conclude that the spectra are in agreement with the idea that the interaction involving the H bonds is weaker in the triplet than in the singlet. We also see that only single quanta of the dimer modes have appreciable strength, so that a massive distortion of the dimer in either the triplet or the singlet state does not occur.

IV. Discussion

A. Relation of Acid-Base and H-Bonding Properties. Benzoic acid is both an acid and a base. The first singlet excited state shows an increase of affinity for the first proton (hydroxyl) of 7.3 kcal/mol and an increased affinity for a second proton (at the carbonyl) of 10 kcal/mol compared to the ground state.[1] These changes represent a decrease in acidity and an increase of basicity, respectively. The increase of affinity for H atoms in the excited state is paralleled by the changes in H bonding. Thus in part 2 we showed that there is a decrease in H-donor bond strength of the OH and an increase in H-acceptor bond strength of the carbonyl oxygen in the ^1L_b state.

The high-resolution study reported here gives direct evidence of the increase in H-bond strength at the carbonyl oxygen through the anomalous isotope shift. This result is not specific to benzoic acid dimer, but should apply to any H acceptor at the carbonyl oxygen, as was concluded in part 2. Here, however, this conclusion is reached by showing that there is an unexcited half of the dimer, and this half is expected to act as any H donor in the H bond to the carbonyl. The proton shift is in the direction of making an excited protonated benzoic acid molecule and an unexcited, deprotonated molecule.

The high-resolution study has also shown several ways in which the singlet and triplet states differ. The H-bond changes in the triplet state are much less than in the singlet. These

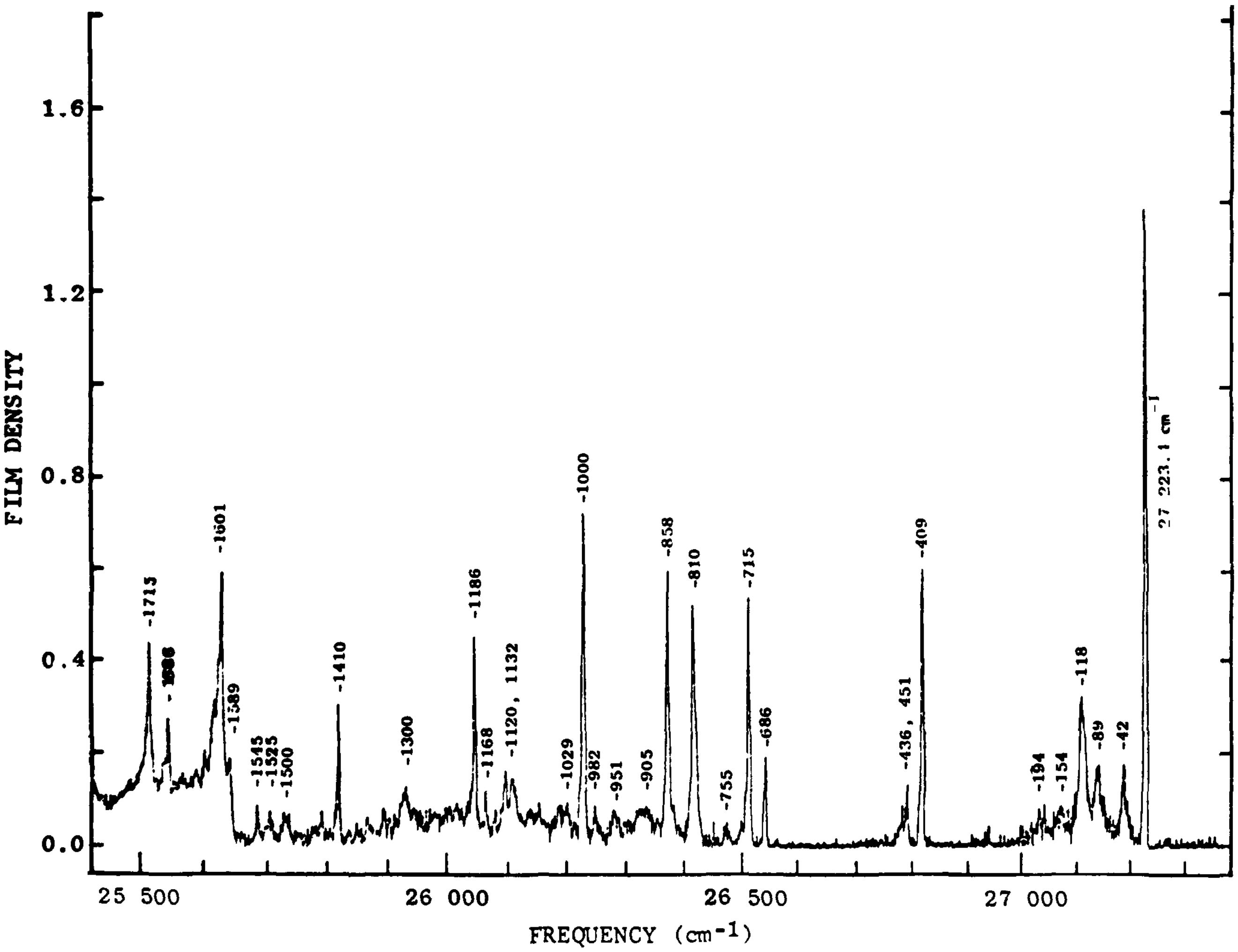

Figure 6. Phosphorescence of benzoic acid-d_0 in a single crystal of benzoic acid-d_5 at 2 K.

differences parallel the excited state acidity measurements, referred to in the Introduction.

B. The Excited-State Potential. Although we have shown clearly that only one half of the benzoic acid dimer participates fully in the electronic excitation, one would also like to know more about the excited-state potential surface, particularly the part having to do with the protons.

The standard treatment of the dimer is of some help in understanding the potential surface of benzoic acid dimer. In this case it is best to start with the uncoupled monomers. The excited-state wave functions become products over those of the two halves of the dimer:

$$\Psi_a{}^e = \psi_a{}^e\psi_b{}^0 X_a{}^e X_b{}^0 X(q + d)$$

$$\Psi_b{}^e = \psi_a{}^0\psi_b{}^e X_a{}^0 X_b{}^e X(q - d)$$

where a, b denote the two halves of the dimer; ψ_a, ψ_b are the electronic wave functions of the monomer units; X_a, X_b are the vibrational wave functions of these units (a product over all modes within the unit); $X(q)$ is the wave function describing the vibration in a critical coordinate q which leads to trapping of excitation. The best simple description of q would be to call it the B_u, ν_3' dimer mode,[8] in which the two monomer units counterrotate so as to compress one H bond and stretch the other. The presence of excitation on one unit will induce displacements in all normal modes, and in particular will cause q to change to $q \pm d$, where $q + d$ represents a lowered energy configuration for the a unit and $q - d$ for the b unit. We can take account of a small electronic coupling energy ϵ in a perturbation calculation using this basis to get a potential curve for q. One finds the secular equation

$$\begin{vmatrix} \frac{k}{2}(q + d)^2 - e & \epsilon \\ \epsilon & \frac{k}{2}(q - d)^2 - e \end{vmatrix} = 0$$

where only the q dependence has been included, and ϵ is the exciton splitting energy. This equation generates the potential curve for q shown in Figure 8. As ϵ becomes large compared to $1/2kd^2$ the double minimum disapppears and the electronic dimer splitting dominates the energy-level scheme. The molecule would then become centrosymmetric and should obey selection rules for this symmetry.

If ϵ were zero we would have an electronic degeneracy, which would be an accidental one in C_{2h} or D_{2h}, but the distortion converts this electronic degeneracy to a configurational one, as in the Jahn–Teller effect.

In the case of benzoic acid dimer, we have shown that ϵ is very small in the singlet state and the molecule is distorted. The intensities of fluorescence transitions to the even and odd parity modes of the ground state are determined by the square of the transition moment integral $\langle\Psi^e|M|\psi^0\rangle$. The ground-state function ψ^0 is symmetric and can be represented crudely as

$$\Psi^0 = \psi_a{}^0\psi_b{}^0(X_a{}^u X_b{}^0 \pm X_a{}^0 X_b{}^u)X(q)$$

where $X_a{}^u$ is a vibration of one half of the dimer and the +, −

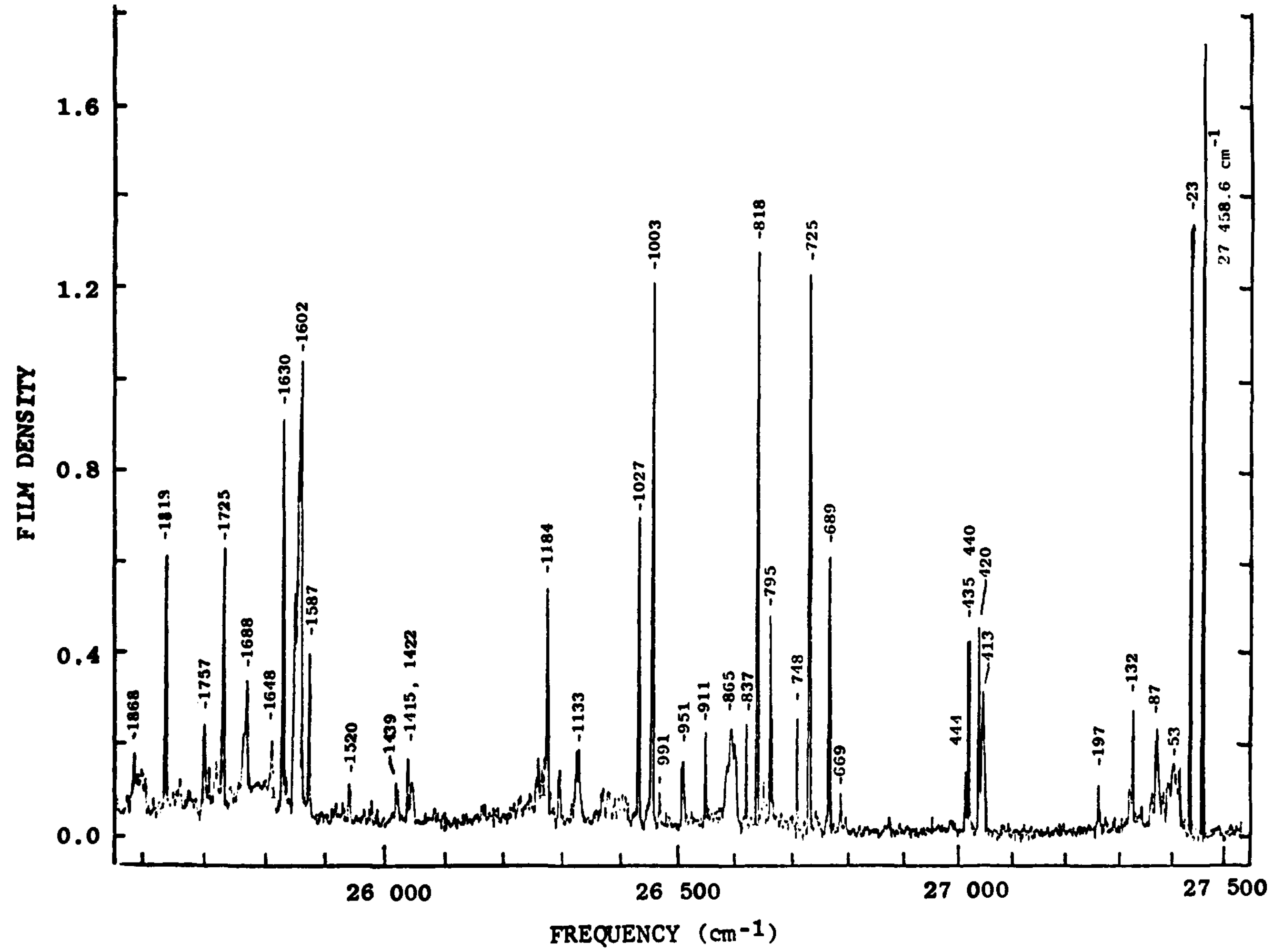

Figure 7. Phosphorescence of benzoic acid dimer in a single crystal of benzene at 2 K.

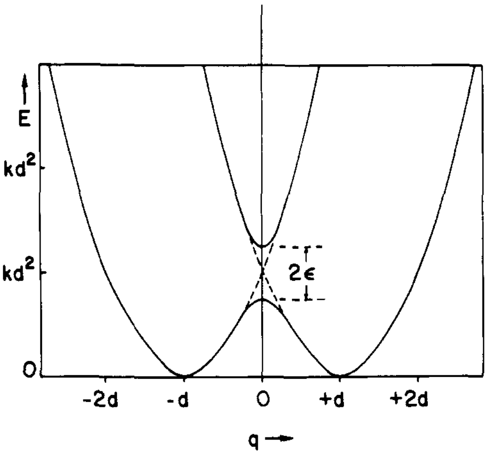

Figure 8. Potential curve for the dimer mode q in the ^1L_b state. d is the displacement at the energy minimum; ϵ is the dimer resonance energy.

signs indicate even and odd parity combinations of the monomer modes to give the modes of the dimer.

The excited-state function ψ^e is a solution of the secular equation, a linear combination of ψ_a^e and Ψ_b^e with one of them predominating. In the limiting case the transition-moment integral becomes

$$\langle \Psi_a^e | M | \Psi^0 \rangle = \langle \psi_a^e | M | \psi_a^0 \rangle \times \langle X_a^e X_b^0 | X_a^u X_b^0 \pm X_a^0 X_b^u \rangle \langle X(q + d) | X(q) \rangle$$

Evidently both even and odd parity vibrations would be equally excited, and the dimer modes would also be excited in this limiting case as shown by the presence of the corresponding Franck-Condon factors.

The ν_3', B_u mode in which the displacement d occurs must be mixed with the various odd parity modes seen in the spectrum, and as the odd component of 6a. It does not appear prominently by itself in the fluorescence. We have to conclude from these facts that ν_3' does not contribute much to the mapping of ground and excited states onto each other, but that 6a and several other modes do so much more effectively. This is certainly reasonable since most of the geometry changes occur in the region of greatest electronic excitation, namely, the rings.

A more careful description of the normal modes of the dimer would be needed for an accurate calculation of the intensity of the various odd parity modes. The limiting case just considered, however, illustrates all the qualitative results found experimentally.

The electronic coupling parameter ϵ can be estimated in two ways. One uses the integrated intensity and the dipole-dipole coupling approximation. With $f = 0.014$ and $R_{AB} = 9.68$ Å (distance between ring centers) the interaction energy is 4.9 cm^{-1}. In the second, the Davydov splitting in the neat crystal is used,[5] a value of 18 cm^{-1}. The source of Davydov splitting is the interaction between nearest benzene rings of two halves of different dimers about 4 Å apart. There are four translationally inequivalent rings which contribute. Dividing by four and reducing the result by the cube of 4.0/9.68 gives 0.32

cm^{-1}. The first estimate must be reduced by the Franck-Condon factor of the 0-0 band, about 0.1, so it becomes 0.5 cm^{-1}, and therefore close to the second estimate. These estimates are in accord with the maximum experimental values we have found, about 0.3 cm^{-1}.

The small value of ϵ establishes an upper limit to the rate of excitation transfer between dimer halves of about 10^{10} s^{-1}. This is enough for the molecule to make many vibrations while in the distorted configuration and accounts for the sharp lines observed in the spectra.

V. Conclusions

In this series of papers we have used low- and high-resolution ultraviolet spectroscopy and standard molecular quantum mechanical methods to provide a description of the excited states of the simplest aromatic carboxylic acid. We began by establishing the amount of charge transfer from ring to carboxyl group and other properties of the excited states (part 1).[9] Using MO methods and solvent shifts, we then established the changes in the strengths of H-donor and H-acceptor hydrogen bonds in the excited states (part 2).[1] Luminescence studies in variously H-bonded systems were then used to show how the hidden $^3n\pi$ state could be located (part 3).[10] In the present paper (part 4), the effect of H bonding on the geometry of the excited molecule was studied particularly for the ^1L_b state but also for the ^3L_a state. The trapping of the excitation on one monomer unit was established, and the relationship between the increased H-acceptor strength and the increased basicity of the excited state was pointed out. The spectroscopic evidence also clearly shows why in the triplet state the acidity change is less than in the singlet.

The technique of using single-crystal solid solutions made it possible to do high-resolution spectroscopy in these H-bonded molecules. A certain amount of luck is involved in getting a host-guest combination to work, but it should be possible to apply the method to other H-bonded systems.

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Photochemistry of 1,5-Diaryl-1,5-diketones

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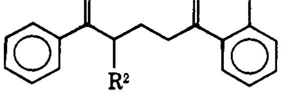
Abstract: The photochemistry of ketones **1–3** has been examined in solution at room temperature by using quantum yield and laser flash photolysis techniques. Triplet energy migration between the two chromophores leads to complete excitation equilibration. In the case of **3**, two triplet states have been characterized, reflecting the syn and anti conformations of the *o*-methylbenzoyl chromophore. The biradicals produced in the triplet decay have lifetimes of ca. 50 ns in wet acetonitrile, for **1** and **2** and 430 ns in the case of **3**, where it results from abstraction of the benzylic hydrogens. Biradicals are produced from **2** with a quantum yield of 1.0; however, the product yields are considerably lower, even in polar hydroxylic solvents. The effect is attributed to strong intramolecular hydrogen bonding in the biradical.

Systems bearing two chromophores of the same type and similar excitation energies are of interest because of the energy migration processes which their photochemistry frequently reflects.[2-4] In particular, several 1,5-diketones have received some attention[5-9] because they can be regarded as the smallest units from polymer systems [e.g., poly(phenyl vinyl ketone)][5,10,11] which still retain the basic properties of the latter.

In this paper we examine the photochemistry of **1–3** with the aim of understanding the processes which control the rates and efficiencies of their photocleavage, the migration of the triplet excitation energy between the two chromophores, the role and lifetimes of the biradicals produced by intramolecular hydrogen abstraction, and, in the case of **3**, the importance of photoenolization.



1, $R^1 = R^2 = H$
2, $R^1 = H$; $R^2 = CH_3$
3, $R^1 = CH_3$; $R^2 = H$

The combination of product studies, quantum yield and quenching experiments, and laser flash photolysis provides a detailed understanding of their photochemistry and elucidates similar photoprocesses in polymers.

Results

Synthesis. Ketones **1–3** were prepared by reaction of the appropriate enamines with vinyl aryl ketones according to reaction 1.

This procedure has been found to give better yields and cleaner products than a direct Friedel–Crafts reaction on the glutaric acid derivative. Products were purified by vacuum distillation, recrystallization, or preparative gas chromatography, as appropriate. In comparison with our earlier experience with other aromatic ketones, we found **1–3** unusually difficult to purify sufficiently to obtain reproducible quantum yields and triplet lifetimes.

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