11.478 (2), and c = 15.023 (4) Å; V = 1877.4 (8) Å^3; Z = 4; ρ_{calc} = 1.615 mg mm^{-3}; λ(Mo Kα) = 0.71073 Å; μ = 0.233 mm^{-1}; F(000) = 952; T = 233 K.

A yellow 0.15 × 0.26 × 0.57 mm crystal, in the shape of an irregular chunk, was used for data collection. Lattice parameters were determined from 30 centered reflections within $26.2 \leq 2\theta \leq 38.1°$. The data collection range of hkl was $0 \leq h \leq 12$, $0 \leq k \leq 13$, $0 \leq l \leq 17$, with $[(\sin \theta)/\lambda]_{max} = 0.59$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to ±2.0% during the data collection. A set of 1923 reflections was collected using an ω scan rate varying from 4.0 to 20.0 deg/min. There were 1752 unique reflections, and 1568 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 294 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and coordinates for the hydrogen atoms bonded to the nitrogen atoms and on the water molecule. All other H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. Final residuals were R = 0.038 and R_w = 0.036 with final difference Fourier excursions of 0.24 and −0.32 e Å^{-3}.

X-ray analysis of molecule 9a: $C_9H_{12}N_8O_8 \cdot 2(CH_3CN)$, FW = 442.4; monoclinic space group $C2/c$; a = 14.281 (9), b = 9.077 (4), and c = 15.813 (9) Å; β = 115.41 (4)°; V = 1851 (2) Å^3; Z = 4 ($^1/_2$ molecule per asymmetric unit); ρ_{calc} = 1.587 mg mm^{-3}; λ(Mo Kα) = 0.71073 Å; μ = 0.125 mm^{-1}; F(000) = 920; T = 295 K.

A yellow 0.49 × 0.36 × 0.20 mm crystal, in the shape of an irregular prism (mounted in a capillary), was used for data collection. Lattice parameters were determined from 25 centered reflections within $19.0 \leq 2\theta \leq 34.7°$. The data collection range of hkl was $0 \leq h \leq 15$, $-9 \leq k \leq 0$, $-16 \leq l \leq 15$, with $[(\sin \theta)/\lambda]_{max} = 0.54$. Three standards, monitored after every 97 reflections, exhibited linear decay of ca. 10% during the data collection. A set of 1368 reflections was collected using a constant ω scan rate of 15.0 deg/min. There were 1213 unique reflections, and 966 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 168 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and coordinates for the hydrogen atoms. Final residuals were R = 0.052 and R_w = 0.046 with final difference Fourier excursions of 0.24 and −0.29 e Å^{-3}.

Acknowledgment. This work was supported by the U.S. Army Research Office and the Office of Naval Research.

Registry No. **1**, 137143-78-3; **2**, 113110-14-8; **3**, 137143-79-4; **4**, 137143-80-7; **5**, 137143-81-8; **6**, 137143-82-9; **7**, 137143-83-0; **8**, 137143-84-1; **9**, 137143-85-2; **9**·$(CH_3)_2SO$, 137143-88-5; **9a**, 137143-89-6; $I_2C{=}CI_2$, 513-92-8; Me_2NH, 124-40-3; $PrNH_2$, 107-10-8; NH_2Ph, 62-53-3; $NH_2C_6H_4$-o-NH_2, 95-54-5; $(NH_2)_2C{=}CH_2$, 107-15-3; $NH_2(CH_2)_3NH_2$, 109-76-2; $NH_2(CH_2)_4NH_2$, 110-60-1; $(NH_2CH_2)_4 \cdot HSO_4$, 137143-87-4; NH_3, 7664-41-7; $(NO_2)_2CCN^- \cdot K^+$, 6928-22-9; PhOH, 108-95-2; $(NO_2)_2(C)_2(NO_2)_2 \cdot 2K$, 32607-31-1.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (35 pages). Ordering information is given on any current masthead page.

Prototropic Control of Organic Photochemistry. Hydrogen Bonding Effects on the Di-π-methane Photorearrangement

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The IR and UV spectra as well as the photochemistry of the isopropyl monoester of dibenzobarrelene dicarboxylic acid **2** were analyzed in detail in several media. A correlation was found between the photochemical results and the spectroscopically detected hydrogen-bonded structures of **2**. An equilibrium between dimeric (**2-HD**) and intramolecularly hydrogen bonded (**2-HI**) structures was detected by IR spectroscopy in nonpolar solvents having weak hydrogen-bond-accepting capabilities. The ratio of the two regioisomeric dibenzosemibullvalene products **3** and **4** formed in the di-π-methane photorearrangement of **2** was found to correlate with such an equilibrium, and it was concluded that intramolecular (**2-HI**) and dimeric (**2-HD**) hydrogen-bonded structures display significantly different photochemical reactivity. The infrared spectra and the photoproduct ratio in polar solvents possessing hydrogen-bond-accepting capabilities (e.g., acetonitrile), on the other hand, turned out to be concentration independent. High regioselectivity was found in the solid state where the dimer **2-HD** is the only species, leading to **4** as the major product. In contrast, **3** was obtained preferentially in aqueous sodium bicarbonate solutions where **2** exists as the carboxylate anion. Supporting evidence regarding the different hydrogen bonding arrangements in **2** was found in the solvent effects on its UV spectra.

1. Introduction

The effects of hydrogen bonding (HB) on the photophysical behavior of the excited states of organic compounds have been widely documented.[1] It has been shown that peculiar photobehavior induced by HB is largely dependent on structural factors. Intramolecular hydrogen bonding (IHB), for instance, may induce strongly shifted emission as in methyl salicylate,[1b,2] photochromism,[3] as in

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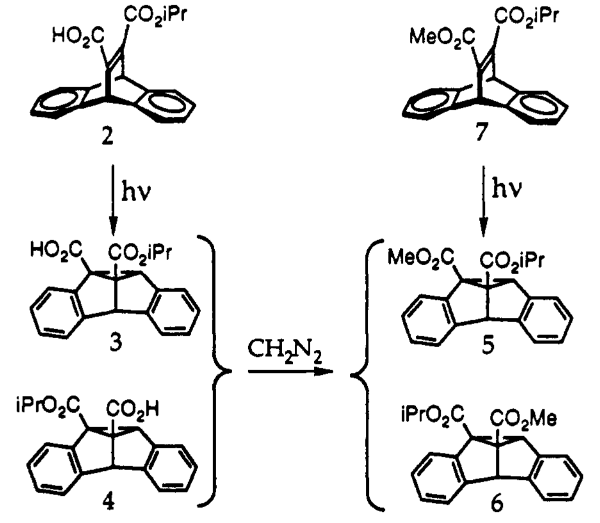
Scheme I



the case of the salicylideneanilines,[3b-d] and an extremely efficient internal conversion as in *o*-hydroxyaryl ketones.[4] An interesting aspect that has emerged from recent studies relates to the possibility of controlling the properties of the excited states. For example, the photophysical behavior of substrates capable of having different HB structures is often very sensitive to the basicity and to the polarity of the surrounding solvent media.[5] With this in mind, it may also be expected that hydrogen bonding could be useful in providing a means of controlling photo*chemical* reactivity. In our recent studies on the solid-state photoreactivity of substituted dibenzobarrelene diesters[6] we had occasion to study the di-π-methane rearrangement[7] of the isopropyl monoester of dibenzobarrelene dicarboxylic acid **2** (Scheme I). It was found that the acid/ester **2** displays a very strong medium-dependent photochemistry which we attributed to different hydrogen-bonded structures.[8] Here, we report in detail on the effect of several media on the photochemistry of compound **2**. Experimental support regarding the various hydrogen-bonding alternatives for **2** is obtained from spectroscopic studies and X-ray crystallographic analysis.

2. Results

2.1. Photochemistry. The acid/ester **2** was prepared by addition of 2-propanol to dibenzobarrelene dicarboxylic acid anhydride (**1**). The latter compound was prepared by addition of acetylene dicarboxylic acid to anthracene according to the method of Diels and Alder.[9] All photolyses were carried out at 313 nm with the filtered output of a medium-pressure Hanovia lamp. Organic solvents such as benzene, acetone, acetonitrile, and 2-methyl-2-butanol, as well as 0.05 M aqueous sodium bicarbonate, and the crystalline solid state were chosen as the photolysis media. The concentration of **2** was varied from 10^{-3} to 10^{-1} M in benzene, acetonitrile, and 2-methyl-2-butanol and was kept constant at 10^{-2} M in aqueous $NaHCO_3$. The dibenzosemibullvalene regioisomers **3** and **4** were found to be the only photoproducts in all reaction media (Scheme I). In order to determine the reaction regioselectivity by quantitative GLC analysis, the photolysis mixtures were treated with excess diazomethane. The mixed acid/esters **3** and **4** were converted quantitatively in this manner into the dibenzosemibullvalene methyl/isopropyl diesters **5** and **6**. The same two compounds were also obtained from photolysis of the methyl/isopropyl diester **7** prepared in a closely related study.[6] The regioisomeric identity of compounds **3** and **4** was deduced by correlating them with the structures of **5** and **6** recently determined by X-ray crystallography.[6c]

Table I. Medium and Concentration Effects on Photoproduct Ratios

medium	concn (M)	% $3^{a,b}$	% $4^{a,b}$
aq $NaHCO_3$	0.01	90	10
benzene	0.001	83	17
benzene	0.003	80	20
benzene	0.006	76	23
benzene	0.01	72	27
benzene	0.03	66	34
benzene	0.06	60	40
benzene	0.1	55	45
MeCN	*c*	50	50
t-BuOH	*c*	50	50
solid state		5	95

[a] The product percentages were obtained by GLC analysis following esterification of the reaction mixtures with diazomethane. [b] The estimated uncertainty in the product percentage is 5%. [c] Product percentage constant within the limits of our detection at concentrations ranging from 0.1 to 0.002 M.

Table II. Quantum Yields of Product Formation from Dibenzobarrelenes 2 and 7 in Benzene[a]

reactant[b]	Φ_3	Φ_4	Φ_5	Φ_6	Φ_T[d]
2 (3.0×10^{-3})	0.066	0.017			0.083
2 (1.0×10^{-2})	0.063	0.026			0.090
7 (1.0×10^{-2})			0.09	0.11	0.20

[a] The estimated uncertainty in the Φ values is ±5%. [b] Concentration of reactant in parentheses (M). [c] Total quantum yield of product formation.

The variation in the product ratio as a function of the photolysis media shown in Table I suggests the involvement of different states of protonation of the carboxylic acid functionality. The largest differences in the product distribution were observed in $NaHCO_3$ and in the solid state, where the 3:4 ratio was found to change from 90:10 to 5:95. Intermediate results were obtained in the organic solvents, with significant differences apparently depending on their polarity. No selectivity was observed upon direct irradiation in acetonitrile and 2-methyl-2-butanol or with acetone as a solvent and triplet sensitizer. No changes in the product ratio were observed in these solvents when the concentration of **2** was varied between 0.001 and 0.1 M. In benzene, on the other hand, the **3**:**4** ratio was found to vary steadily from 83:17 to 55:45 at the concentration was changed between 0.001 and 0.1 M.

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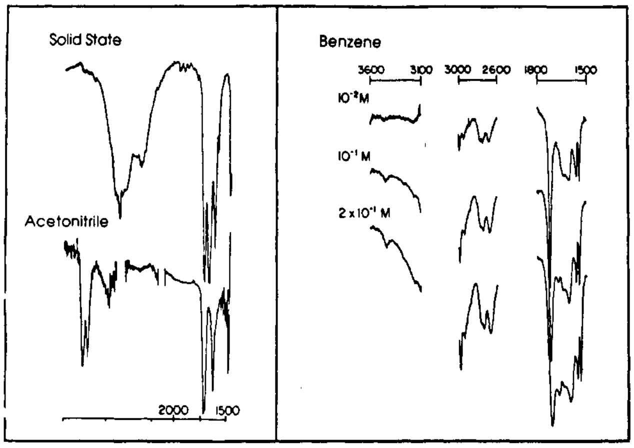


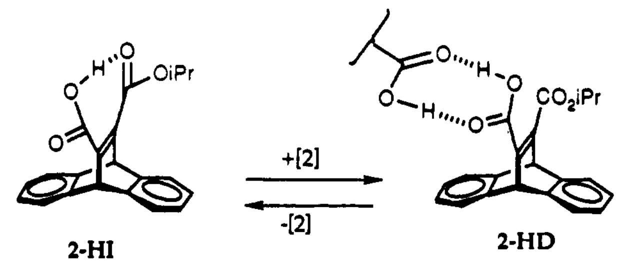
Figure 1. FT–IR spectra of acid/ester 2 in the solid state, in 10^{-2} M acetonitrile, and in 10^{-3}, 10^{-2}, and 2×10^{-1} M benzene. Solution spectra were recorded after solvent subtraction. The regions of strong solvent absorption have been omited for clarity.

The quantum yields of formation of the dibenzosemibullvalene photoproducts **3** and **4** (Φ_3 and Φ_4) were measured in benzene by using a merry-go-round apparatus. Two different concentrations of **2** were chosen (3.0×10^{-3} and 10^{-2} M) such that both solutions remained opaque in 1-cm pathlength cells while giving similar conversion values. The quantum yields were measured in duplicate relative to valerophenone which has a type II quantum yield of 0.30 in benzene.[10] As shown in Table II, an increase in the total concentration of **2** resulted in a small, but easily detectable, increase in the total quantum yield of product formation (ϕ_T) from 0.083 ± 0.003 to 0.090 ± 0.003. Interestingly, such an increment is the combined result of an approximately 60% increase in Φ_4 and a 5% decrease in Φ_3. The quantum yield of product formation from diester **7**, whose product ratio (**5**:**6** = 7:93) was found to be independent of the concentration of **7** in solution,[6b] was found to be about twice as large as that of the acid ester **2** (i.e., $\Phi_7 = 0.20 \pm 0.01$).

2.2. Infrared Spectra. The infrared spectra of the acid/ester **2** were obtained in the weakly or non-hydrogen bonding solvents benzene, chlorobenzene, chloroform, and dichloromethane, in the weak hydrogen-bonding acceptor (HBA) acetonitrile, and in the solid state. The effects of these media on the infrared spectra are manifested mainly in absorptions occurring in the carbonyl (C=O) and hydroxyl (O–H) stretching regions. Variations in the frequency and intensity of these absorptions were found to depend strongly on the hydrogen bonding capabilities of the medium (Figure 1).[11,12] Carbonyl absorptions assigned to the carboxylic acid and ester groups, for instance, appear as a single band in acetonitrile (1727 cm^{-1}, as two bands in the solid state (1724 and 1680 cm^{-1}, and in as many as three different bands, depending on the concentration, in solvents such as benzene (1730, 1692 and 1660 cm^{-1}).

The concentration-dependent behavior of the photochemical results observed in benzene was clearly paralleled in the spectra obtained in the same solvent at concentrations ranging from 0.2 to 10^{-4} M. The spectra are consistent with a model involving an equilibrium between intra- and intermolecular hydrogen bonding[11] as shown in Scheme II. The monomeric structure **2-HI** (Scheme II) is favored at low concentrations, and the spectral assignment proposed is supported by (a) the low frequency of the O–H stretch at 2780–2749 cm^{-1}, (b) the carboxylic acid carbonyl band at 1730 cm^{-1}, and (c) a low frequency and relatively weak carbonyl band at 1660 cm^{-1} that corresponds to the intramolecularly hydrogen-bonded ester group.[11] Similar observations have been reported in dilute solutions of several pyrazole-1,2-dicarboxylic acid derivatives studied by Zvatek et al., which also display a similar seven-membered intramolecular H-bonded structure.[12]

Scheme II



Increasing the concentration of **2** in benzene resulted in the growth of a very broad (3600–2400 cm^{-1}) and relatively structureless band as expected for the dimeric structure **2-HD**.[11] The growth of this band was accompanied by that of an intense absorption at 1695 cm^{-1} attributed to the dimerized acid carbonyl. An expected increase in intensity of the free carbonyl ester band of **2-HD** seems to have been compensated by the corresponding decrease in intensity of the band due to the free acid of the monomer. Both of these bands occur at 1730 cm^{-1}, and the spectrum remains unchanged in this region. The spectra of **2-HD** in concentrated benzene solutions (3600–4200, 1695, and 1730 cm^{-1}) compare favorably with that observed in the solid state with bands at 3600–2400, 1680, and 1724 cm^{-1}. In fact, recent X-ray analysis of **2** indicates a dimeric arrangement with inversion centers localized within the dimeric motif of the hydrogen bond as represented in **2-HD**.[13] The monomer–dimer equilibrium is also supported by the linearity of a plot of $[\mathbf{2}]/A_{1660}$ vs A_{1695}/A_{1660}, where [**2**] is the total concentration of **2** ranging from 0.001 to 0.2 M and A_{1660} and A_{1695} are absorbances corresponding to the monomer and dimer, respectively, measured at their respective maxima.[14] A dimerization equilibrium constant of $K \approx 5\ M^{-1}$ was estimated in a qualitative manner from the infrared results with limitations given by the poor resolution in the carbonyl stretching region. The spectra run in chlorobenzene, dichloromethane, and chloroform closely resembled the spectra obtained in benzene solutions. Significant differences were found in the relative position and intensity of the free and intramolecularly bonded carbonyl bands. The relative amount of dimer, as judged qualitatively by its carbonyl band intensity, decreased within the series benzene, chlorobenzene, chloroform, and dichloromethane. At the same time, the stretching frequency of the acid carbonyl group (which is non-hydrogen bonded) was found to decrease in the same series correlating qualitatively with an increase in solvent

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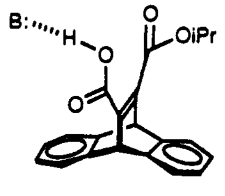
Chart I



2-HM

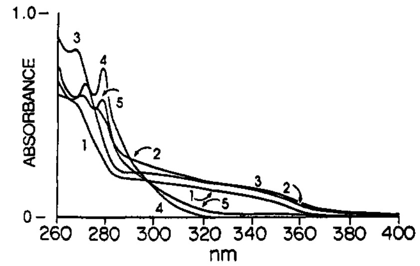


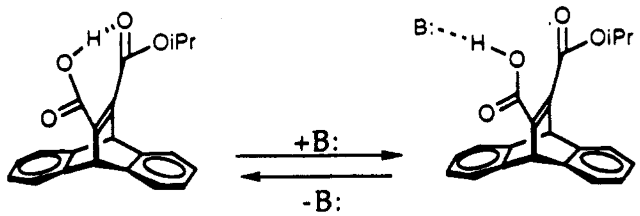
Figure 2. UV absorption spectra of 10^{-3} M solutions of acid/ester 2 in (1) hexane, (2) benzene, (3) chloroform, (4) methanol, and (5) acetonitrile.

polarity defined by the π^* scale of Kamlet, Abboud, and Taft.[15a]

The spectra run in acetonitrile remained unchanged within the concentration range 10^{-3} to 10^{-1} M. This is consistent with the photochemical results, where no changes in the product ratio were observed over the same concentration range. In acetonitrile, the O–H absorption stretching region was clearly indicative of a RC(O)O–H··solvent interaction with sharp absorption maxima at 3632 and 3544 cm^{-1}. We suggest that in this solvent, a single species such as **2-HM** (Chart I) remains stable over the concentration range of our experiments. No difference between the acid and ester carbonyl bands was observed, and a single strong absorption band was detected at 1727 cm^{-1}. It is interesting to note that, in contrast to 2, the much stronger intramolecular H bonds of the closely related monohydrogen maleate and phthalate are known not to be perturbed by solvents as polar and basic as dioxane, dimethyl sulfoxide, and water.[16]

2.3. Ultraviolet Absorption Spectra. Compound 2 exhibits a surprisingly long wavelength absorption band in the 300–380-nm region (Figure 2) in solvents such as hexane, chloroform, dichloromethane, and benzene. In polar solvents such as acetonitrile, methanol, and acetic acid, the spectra presented only a weak absorption tail in the 300–330-nm range. The long-wavelength absorption band in the nonpolar solvent is analogous to the charge transfer band assigned to the intramolecular H bonded form of potassium hydrogen maleate observed by Nagakura.[17] The spectra obtained in acetonitrile, where no intramolecular H bond is detected by IR spectroscopy, compared satisfactorily with the normal spectra of the closely related dibenzobarrelene 11,12-diesters recently studied in our laboratory.[18] The effects of dimerization of the electronic absorption spectra of carboxylic acids have been documented to be largely dependent on the system under consideration, being sometimes almost negligible.[19]

Scheme III



2-HI

2-HM

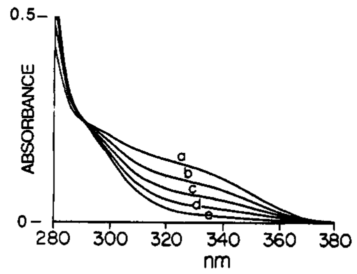


Figure 3. Changes in the absorption spectra of a 10^{-3} M solution of acid/ester 2 upon addition of methanol (M): (a) 0, (b) 0.1, (c) 0.30, (d) 0.6, and, (e) 2.5.

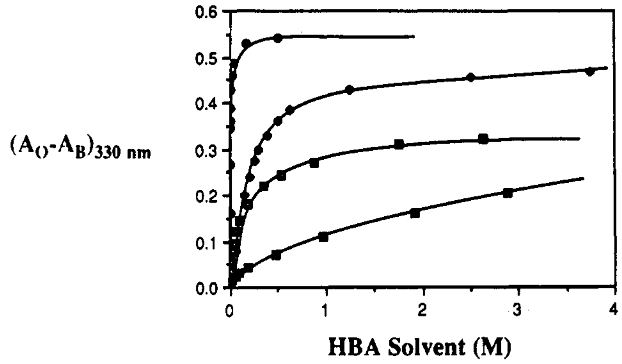


Figure 4. Solvent effects on the optical density at 330 nm of solution of 10^{-3} M acid/ester 2 caused by addition of triethylamine, methanol, acetic acid, and acetonitrile. A_0 and A_B are the absorbance values before and after addition of hydrogen-bonding acceptor (HBA) solvent.

The UV spectra of benzene solutions of 2 at concentrations of 10^{-2}, 10^{-1}, and 2×10^{-1} M, however, showed no significant differences in the 300–400-nm spectral envelope.

2.4. Specific Solvent Effects.[20] We reasoned that an intramolecular H bond such as that proposed for **2-HI** might be disrupted by relatively small amounts of solvents with hydrogen-bond-accepting (HBA) capabilities. Formation of the species **2-HM** (Scheme III), postulated in the presence of polar HBA solvents, should alter the appearance of the observed spectra, since the UV absorption spectra of **2-HI** and **2-HM** are substantially different (vide supra).

The changes in the absorption spectrum of 10^{-3} M **2-HI** in benzene as a function of added methanol are shown in Figure 3. The equilibrium represented in Scheme III is clearly supported by the decreasing absorption of **2-HI** and by the presence of a well-defined isosbestic point at 291 nm. In Figure 4, the results obtained from similar experiments are plotted as the difference in absorption at 330 nm caused by the addition of triethylamine, methanol, acetic acid, and acetonitrile.

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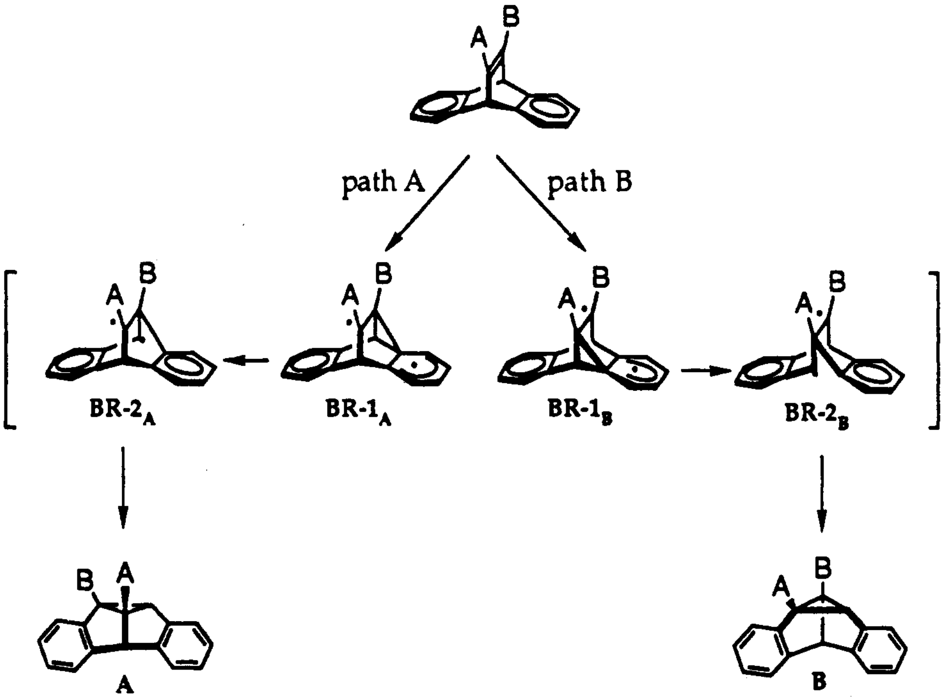
Scheme IV



Several important conclusions can be drawn from the data shown in Figure 4. We note that the amount of solvent needed to disrupt a given amount of **2-HI** is proportional to the solvent hydrogen-bonding basicity β (triethylamine, methanol, and acetonitrile have β's of 0.71, 0.62, and 0.31, respectively).[15a] The hydrogen-bonding basicity of acetic acid is not available, but our results suggest that it is intermediate between the values for methanol and acetonitrile. Attempts to establish the stoichiometry of the solvent interaction with **2** gave simple answers only in the cases of triethylamine and methanol. With triethylamine, an equimolar titration indicates a very strong interaction, most likely involving a complete proton transfer to form the carboxylate anion. The absorption data obtained upon addition of methanol can be correlated with a 1:1 complex by means of a Hildebrand–Bennesi[21] analysis ($K = 4.2\ M^{-1}$). In contrast, and in spite of observing well-defined isosbestic points, the absorption data obtained upon addition of acetic acid and acetonitrile could not be correlated with a simple low integer stoichiometry (1:1[21] or 1:2[22] complexes) indicating complex equilibrium processes. Solvation interactions without hydrogen bonding in the case of acetonitrile, and multiple hydrogen bonding possibilities (i.e., heterodimers) in the case of acetic acid, seem to be two likely solvent interaction alternatives.

3. Discussion

The photochemical transformation of dibenzobarrelenes into dibenzosemibullvalenes is a well-documented example of the di-π-methane rearrangement.[7] The generally accepted reaction mechanism involves the participtation of the triplet excited state followed by the sequential formation of two biradical intermediates, **BR-1** and **BR-2** (Scheme IV). Factors proposed to determine the regioselectivity of the rearrangement of unsymetrically vinyl-substituted dibenzobarrelenes include the following: (a) the relative ability of the substituents on the two vinyl termini (A and B in Scheme V) in stabilizing the adjacent radical centers[7,23,24] and (b) steric effects that may selectively encumber one of the two competing transition states.[24] It has also been proposed that under some circumstances the rearrangement can be understood in terms of an excited state aryl migration which does not require the intermediacy of the first 1,3-biradical (**BR-1**).[23]

With the exception of our recent studies involving the influence of the crystalline solid state,[6,18] the selectivity of the rearrangement, while sensitive to substituent effects,[23,24,27] has been found to be largely independent of the reaction medium. Our observations with the acid/ester **2** represent an example where the medium is capable of altering the photochemical reactivity through changes brought about as a result of different hydrogen-bonding structures. The involvement of three different species is necessary to understand our photochemical results and spectroscopic observations: (a) a monomeric, solvent-bonded structure **2-HM** (Scheme II), predominant at all concentrations in acetonitrile, acetone and 2-methyl-2-butanol; (b) a monomeric, intramolecularly hydrogen-bonded structure **2-HI** (Scheme III), predominant in dilute solutions of nonpolar solvents, which is in equilibrium with a dimeric structure **2-HD**, and (c) **2-HD** itself, which is predominant in concentrated solutions of nonpolar solvents and is unique to the solid state.

The photochemical behavior of **2-HM** in polar organic solvents is characterized by a lack of regioselectivity at all the concentrations studied (0.001–0.1 M). The general reaction mechanism suggests that both the carboxylic ester and solvent-bonded acid groups have very similar radi-

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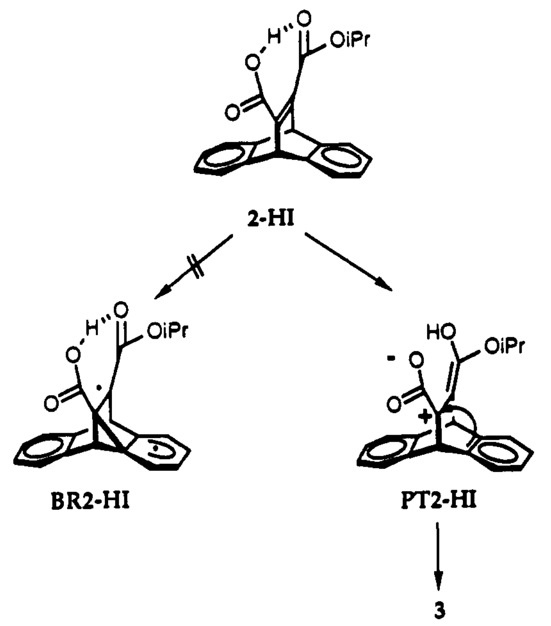
Scheme V



cal-stabilizing abilities. However, removal of a proton to generate the carboxylate anion in $NaHCO_3$ solutions results in increased regioselectivity toward 3. The mechanism of Scheme V suggests that aryl–vinyl bonding occurs next to the carboxylate group positioning the radical center next to the ester substituent.

Data regarding the relative-stabilizing ability of carboxylate anion and carboxylic ester groups is very scarce. Qualitatively, however, it makes sense that a radical center should have a more favorable resonance interaction with an adjacent ester substituent than with a carboxylate anion group. The carbonyl group of the latter, having a very strong resonance interaction with the anionic oxygen, is presumably less "available" for resonance with the unpaired electron of the radical. A simple PMO argument supports this view. The stabilizing interaction between a singly occupied p-orbital on a methylene group and the LUMO of either the COO^- or COOR fragment should be less favorable in the former case owing to the higher LUMO energy of the crboxylate anion (greater SOMO–LUMO separation).

The regioselectivity observed in the solid state is opposite to that observed in $NaHCO_3$ solutions, and dibenzosemibullvalenes 3 and 4 are formed in the former medium in a 5:95 ratio. Previous studies on the photorearrangement of dibenzobarrelenes in the solid state have indicated the importance of intermolecular steric control.[6] We have postulated that large amplitude motions are required during the first aryl–vinyl bonding step of the reaction mechanism and that these motions may involve one of the two vinyl groups in unfavorable intermolecular contacts. It has been proposed that movement of the group that minimizes the intermolecular repulsive interactions is favored in the solid state. Infrared spectroscopy and X-ray crystallographic analysis show that **2-HD** is the only species present in the crystal.[13] The two reaction alternatives for **2-HD** involve either movement of the ester group or movement of the acid group engaged in the dimeric hydrogen bond. The results indicate that motion of the ester group is favored over motion of the hydrogen-bonded acid group (95:5). It should be noted that, according to the reaction mechanism, the preferred biradical intermediate contains a radical center next to the hydrogen bonded acid carbonyl. Interestingly, it has been postulated that the radical-stabilizing abilities of hydrogen bonded carbonyl groups should be decreased, making this pathway less favorable.[26] However, the alternative of having the dimeric hydrogen bonds disrupted is probably much less favorable in the solid state.

In benzene solutions, an equilibrium involving the intra- and intermolecular hydrogen-bonded species **2-HI** and **2-HD** (Scheme II) is clearly supported by infrared spectroscopy. A long-wavelength UV absorption band, unique to spectra obtained in nonpolar solvents, correlates with the presence of **2-HI**, and its assignment as a charge-transfer transition is consistent with observations reported in the literature.[17] The assignment of **2-HI** is further supported by specific solvent effects which involve disruption of the intramolecular hydrogen bond. The UV spectra in benzene solutions containing equimolar triethylamine or as little as 1–5% v/v of the hydrogen-bonding acceptor solvents methanol, acetic acid and acetonitrile, change toward the spectrum of solvent-bonded **2-HM**.

The concentration dependence of the photochemical results in benzene indicate that the overall rate of product formation is greater than the rate of equilibration. In such a case, the product ratio should be determined by the relative amounts of **2-HI** and **2-HD** at any given concentration and by the quantum yields of product formation from each of the two species. Our photochemical results indicate that the reactivity of **2-HI** can be interpreted qualitatively in terms of a highly selective (~3.4 = 85:15) but relatively inefficient ($\Phi = 0.09$) rearrangement. The reactivity of the dimer, **2-HD**, seems to tend toward that of the solvent-bonded monomer **2-HM**. The reaction appears to be much less selective (3:4 = 50:50) and somewhat more efficient, as an increase in the quantum yield with increasing concentration indicates (Table II). The preferential formation of dibenzosemibullvalene 3 from **2-HI** indicates the involvement of an initial aryl–vinyl bonding step at the carbon center next to the acid group (Scheme V). However, according to previous observations reported in the literature,[26] intramolecular hydrogen bonding should be expected to decrease the radical stabilizing ability of the ester carbonyl group and disfavor the corresponding biradical intermediate (**BR2–HI**).[26] An alternative explanation which incorporates the results observed in the UV spectra suggests that selectivity may arise via a modified mechanism which involves a proton transferred excited state, **PT2-HI** (Scheme V). Such a species would present the conditions for a regioselective, positive charge-initiated, 1,2-aryl shift leading to 3. This rearrangement would be analogous to the well-studied ground-state carbocationic rearrangement of dibenzobarrelenes.[28]

An important question that remains to be answered concerns the multiplicity of the excited state from which reaction occurs in **2-HI**. All the documented examples of the di-π-methane rearrangement of substituted dibenzobarrelenes have been proposed to occur from triplet excited states. In general, the multiplicity of the rearrangement can be established indirectly through comparisons of sensitized and direct irradiations. Such an approach was not attempted in this case, as it would be expected that common triplet sensitizers (benzophenone, xanthone, etc.) would disrupt the intramolecular hydrogen bond required for the unusual reactivity of **2HI**. While the clear correlation between the spectroscopic and photochemical behavior suggests the involvement of a proton-transferred

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J. Org. Chem. 1992, 57, 247-252

species, such initial reaction could occur from either singlet or triplet excited states. Work aimed at elucidating the detailed nature of the ground and excited state dynamics is currently in progress.

4. Experimental Section

General Procedures. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer. The spectra of solid samples were obtained in KBr pellets. Solution spectra were solvent-subtracted and were obtained in NaCl cells. ^{1}H NMR spectra were determined on a Varian XL-300 instrument at 300 MHz using TMS as the internal standard. Ultraviolet absorption spectra were measured on a Perkin-Elmer Lambda-4 apparatus with data acquisition and processing carried out with the Perkin-Elmer PECUV software. Capillary GLC analyses were performed on a Hewlett-Packard 5890 A gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3392 A integrator. Spectral-grade solvents obtained from BDH were dried by refluxing them with metallic sodium, calcium hydride, or phosphorous pentoxide as appropriate.

Analytical Photolyses. Solutions of acid/ester **2** (1 mL) in 3-mL Pyrex tubes were degassed by at least three freeze–pump–thaw cycles and photolyzed for 1 h with the output of a 450-W medium-pressure Hanovia lamp. An ethereal solution (1 mL) containing a large excess of freshly prepared diazomethane was added to the resulting mixtures after the solvents had been rotary evaporated to dryness. Solid samples, photolyzed in 0.4-mm i.d. Pyrex tubes both as single crystals and powders were directly dissolved in the diazomethane solution. In all cases, the diazomethane–acid mixtures were allowed to stand overnight and then analyzed by GLC.

Quantum Yields. Quantum yields of product formation in benzene were measured in duplicate at concentrations of **2** of 3×10^{-3} and 10^{-2} M. Photolyses were carried out in a temperature-controlled water bath with the filtered 313-nm line of the medium-pressure Hanovia lamp. The formation of acetophenone by type II cleavage of 0.1 M valerophenone solutions was measured in parallel irradiations for actinometric purposes.[10] The samples were carefully degassed by repeated freeze–pump–thaw cycles and photolyzed under a positive nitrogen atmosphere.

2-Propyl 12-Carboxy-9,10-ethenoanthracene-11-carboxylate (Dibenzobarrelene 2). Dibenzobarrelene dicarboxylic acid anhydride (5 g, 18.3 mmol), prepared by the method of Diels and Alder,[5] was suspended in 50 mL of freshly distilled 2-propanol and refluxed for 4 h. The excess 2-propanol was evaporated from the resulting solution and the solid residue recrystallized from a mixture of acetonitrile–hexane to yield 6.05 g (99%) of the title compound: mp 176–77 °C; IR (KBr pellet) 3400–2200, 1724, 1680, 1625, 1202 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.50–6.90 (m, 8 H), 6.15 (s, 1 H), 5.78 (s, 1 H), 5.20 (hept, 1 H, J = 7 Hz), 1.40 (d, 6 H, J = 7Hz); HRMS (EI) m/e for $C_{21}H_{18}O_4$ calcd 334.1205, found 334.1204.

Preparative Photolysis of Dibenzobarrelene Acid/Ester 2. A solution containing 200 mg (0.6 mmol) of **2** in 200 mL of acetonitrile was photolyzed in an immersion well for 12 h with the Pyrex-filtered output of the 450-W Hanovia lamp. Nitrogen was bubbled through the solution for 15 min before and during the photolysis period. The solvent was rotary evaporated, and an excess of diazomethane was directly distilled onto the photolysis residue. After standing for 12 h, the resulting mixture was chromatographed (silica gel, petroleum ether:EtOAc = 19:1) to yield 145 mg (70%) of a colorless oil containing a mixture of compounds **5** and **6**. Separation of **5** and **6** could be achieved in low yield by fractional recrystallization from diethyl ether.

8c-Methyl 8b-(2-propyl) 4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*cd*]pentalene-8c,8b-dicarboxylate (5): mp 139–141 °C; IR (KBr pellet) 1735, 1253 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.35–7.05 (m, 8 H), 5.24 (m, 1 H), 5.05 (s, 1 H), 4.45 (s, 1 H), 3.70 (s, 3 H), 1.32 (d, 3 H, J = 7 Hz), 1.30 (d, 3 H, J = 7 Hz); MS (EI) 348, 306, 260, 202. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79, found: C, 75.90; H, 5.93.

8b-Methyl 8c-(2-propyl) 4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*cd*]pentalene-8c,8b-dicarboxylate (6): mp 110–112 °C; IR (KBr pellet) 1737, 1717, 1248 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.35–7.05 (m, 8 H), 5.07 (s, 1 H), 5.05 (m, 1 H), 4.49 (s, 1 H), 3.88 (s, 3 H), 1.22 (d, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 7 Hz); MS (EI) 348, 316, 261, 202. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79, found: C, 75.90; H, 5.93.

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Differences in Reactivity of Stabilized Carbanions with Haloarenes in the Initiation and Propagation Steps of the $S_{RN}1$ Mechanism in DMSO

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The photostimulated reaction of acetone (**2**), acetophenone (**5**), and anthrone (**8**) enolate ions with iodobenzene (**1**) in DMSO gave good yields of substitution products by the $S_{RN}1$ mechanism. On the contrary, the monoanions of acetylacetone, diethyl malonate, and nitromethane (**10**) did not react under irradiation. However, the photostimulated reaction of **1** with **10** in the presence of **2** or pinacolone enolate ions gave 1-phenyl-2-nitroethane as a substitution product. The formation of this product can be explained if one assumes that the radical anion formed in the coupling reaction of phenyl radical with **10** fragments to give benzyl radical and nitrite ion. Benzyl radical then couples with **10** to give ultimately the observed product. From competition experiments the relative reactivity determined for the coupling reaction of different anions with phenyl radicals in the propagation cycle of the $S_{RN}1$ mechanism is as follows: monoanion of β dicarbonyl compounds (unreactive) $\ll$ **2** (1.0) < **5** (7.5) < **8** (16.5). The difference in reactivity observed experimentally is explained on the basis of the pK_a (HOMO energy) of the anions and on the change in the π energy that takes place in the coupling reaction. With reference to the initiation step (electron transfer from the carbanion to **1**), the reactivity increases as the pK_a of the conjugated acid of the nucleophile increases.

The radical mechanism of aromatic nucleophilic substitution, or $S_{RN}1$, is a well-known process by which a substitution is produced on a nonactivated adequately substituted substrate.[1] The propagation steps are shown