Hydrogen Bonding, Solvent Polarity, and the Visible Spectrum of Phenol Blue and Its Derivatives

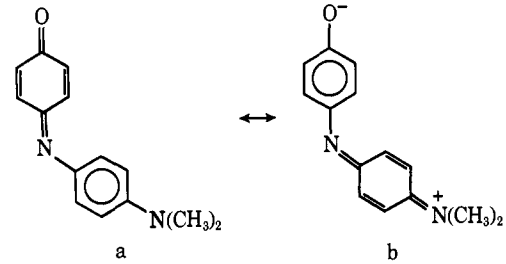
J. Figueras

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received March 4, 1970*

Abstract: Studies of the absorption spectrum of phenol blue (**1**) in solvent mixtures containing hydrogen-bond acceptors and donors show that the position of the absorption maximum of the dye is very responsive to hydrogen bonding. The effect of solvent OH groups resembles an exaggerated solvent effect; there is no evidence for formation of a discrete hydrogen-bonded complex between dye and donor. A good correlation was observed between the amplitude of the unbonded OH absorption at 3615 cm^{-1} (stretching vibration) and the magnitude of the shift of the dye in mixtures of *p*-cresol (as H-bond donor) and DMSO (as H-bond acceptor). The McRae equation[1] relating absorption frequency of a dye solute to refractive index and dielectric constant of the solvent was used to separate effects of intrinsic solvent polarity from effects of extraneous factors such as hydrogen bonding. In this way, an estimate of the effects of hydrogen bonding on λ_{max} was obtained. The model was used to obtain a very satisfactory interpretation for the effects of changes in structure of phenol blue on the magnitude of hydrogen bond induced shifts of absorption spectra. It was shown that (1) the effects of the interaction of phenol blue with solvent OH groups are larger than the effects of changing intrinsic solvent polarity; (2) the interaction may vary in direction and magnitude as a result of changes in dye structure not directly involving the chromophore (*e.g.*, replacement of a proton by a methyl group), and as the consequence of the presence of multiple bonding sites in the dye. We conclude that solvent polarity scales based on shifts in λ_{max} of an indicator dye are of limited value where hydrogen-bond interactions are possible.

Changes in solvent composition induce shifts in the position of the absorption peaks of solutes. Numerous attempts have been made to correlate these shifts with solvent properties such as dielectric constant and refractive index.[1-4] Kosower[2] suggested that spectral shifts of strongly absorbing solutes in various solvents might be used to establish a scale of solvent polarity. It is generally recognized[1-6] that the effect of a solvent on the spectrum of a solute is the resultant of a large number of factors—static factors such as interaction between solvent and solute permanent dipoles, dynamic factors such as dispersion forces, solvent sorting in the case of mixed solvents,[4] and specific interactions such as hydrogen bonding between solute and solvent. We are concerned in this work particularly with the effects of hydrogen bonding between solvent and solute on the absorption spectrum of a large, complex molecule (phenol blue). As is made clear by the work to be described, spectral shifts produced by hydrogen bonding may be very large, as previously suggested,[7] and may occur toward the red (bathochromic) or toward the blue (hypsochromic). Moreover, the direction of the shift produced by hydrogen-bonding solvents with a given chromophore can be reversed by rather small changes in structure of the chromophore, *e.g.*, the replacement of a proton by a methyl group. We conclude that solvent polarity rankings based upon the behavior of a dye indicator—particularly in cases involving possible hydrogen-bond formation—depend upon the structure of the indicator, and may have no general significance.

The dyes chosen for this investigation were phenol blue (**1**) and some of its derivatives, considered later. Phenol blue is a well-known solvatochromic dye; its behavior in various solvents was first commented upon by Brooker and Sprague[8] and was studied quantitatively by McRae.[1] It has a single absorption band in the visible whose intensity ($\epsilon_{max} > 10^4$) and response to substituents[9] are characteristic of a $\pi \rightarrow \pi^*$ transition. Molecular orbital studies[9] indicate that the unshared pair of electrons on terminal nitrogen is delocalized into the chromophore on excitation. It is less certain that an electron surplus appears on the carbonyl oxygen atom in the excited state, although Hückel parameters can be chosen which cause this to occur.[9] According to the resonance interpretation, the ionic structure **1b** makes a larger contribution to the excited state, which implies that terminal nitrogen becomes electron poor and carbonyl oxygen becomes electron rich in the excited state. In terms of resonance theory, hydrogen bonding at carbonyl oxygen should stabilize ionic structure **1b**, reduce the energy of the excited state, and give a bathochromic shift. Hydrogen bonding at terminal nitrogen will constrain the unshared pair of electrons and



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(1) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).
(2) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253, 3261, 3267 (1957).
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(5) L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Amer. Chem. Soc.*, **87**, 2443 (1965).
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(8) L. G. S. Brooker and R. H. Sprague, *J. Amer. Chem. Soc.*, **63**, 3214 (1941).
(9) W. F. Smith, Jr., *Tetrahedron*, **20**, 671 (1964).

increase the transition energy, giving hyposochromic shifts. Molecular orbital studies also indicate that the azomethine nitrogen atom becomes electron rich in the excited state; hydrogen bonding at this atom will theoretically give bathochromic shifts. However, structural modifications of phenol blue, which are discussed later, were made primarily to investigate hydrogen-bonding effects at carbonyl oxygen and terminal nitrogen, and did not permit conclusions about bonding at azomethine nitrogen.

The first section of this paper describes a group of experiments which establish qualitatively that phenol blue shows large bathochromic shifts attributable to interaction between unassociated hydroxyl groups and dye. In the second section, we attempted to estimate quantitatively the effect of this OH interaction on the transition energy of phenol blue and several of its derivatives in hydrogen-bonding solvents.

Results and Discussion

Section 1. The positions of the absorption maximum (in nanometers and kilocalories per mole) of phenol blue in various pure solvents are reported in Table I. Of particular interest are the very large shifts observed when the dye is dissolved in *m*-cresol or trifluoroethanol (TFE), both notably good hydrogen-bond donors.[10-12] If the pure solvents are sufficiently diluted (to 0.2 *M*) with an inert solvent (CCl_4), the smaller spectral changes observed in nonbonding solvents can be reduced practically to zero, while hydrogen-bond donors (TFE, *m*-cresol, *p*-cresol) still give large shifts (see Table I). We have, in a sense, "isolated" the large interaction between phenol blue and hydrogen-bond donors from the other smaller solvent–dye interactions, and can therefore study this interaction more conveniently in the diluted system. The relatively large interaction between diluted hydrogen-bond donors and the dye may be the consequence of solvent sorting[4] promoted by hydrogen-bond formation.

Table I. λ_{max} of Phenol Blue in Various Solvents, Neat and 0.2 *M* in CCl_4; Dye at 10^{-4} *M*

Solvent	λ_{max} in pure solvent nm	Kcal/mol	λ_{max} (nm) in solvent at 0.2 *M* in CCl_4	Δnm
Anisole	584	48.97	565	0
Acetone	582	49.14	566	1
Acetonitrile	584	48.97	568	3
N,*N*-Dimethylformamide	595	48.06	568	3
Pyridine	596	47.98	565	0
Dimethyl sulfoxide	605	47.19	570	5
Methyl formate	578	49.48	565	0
Benzonitrile	597	47.90	568	3
Nitromethane	591	48.39	567	2
1,2-Dichloroethane	589	48.44	565	0
Methanol	608	47.03	571	6
Butanol	606	47.19	569	4
Trifluoroethanol (TFE)	660	43.33	601	36
m-Cresol	686	41.69	604	39
p-Cresol			603	38
Benzene	575	49.73		
Carbon tetrachloride	565	50.61		
Cyclohexane	552	51.81		

Figures 1–3 show the effects on λ_{max} of adding various concentrations of hydrogen-bond acceptors to solutions of phenol blue in CCl_4 containing 0.2 *M* *p*-cresol. A control curve (the lower one in each case) shows the effects on λ_{max} of phenol blue of adding acceptor in the absence of *p*-cresol. The acceptors were DMSO, acetone, and tri-*n*-octylphosphine oxide (TOPO). The effect of *p*-cresol on the phenol blue spectrum diminishes as the concentration of acceptor increases, giving initially a hypsochromic shift in dye hue. However, as the polarity of the medium increases with higher levels of acceptor, the dye absorption ultimately shifts bathochromically, which accounts for the minimum in the DMSO and TOPO response curves. The shapes of the curves in Figures 1–3 correlate with the relative abilities of the acceptors to hydrogen bond to *p*-cresol; these have been determined to be TOPO > DMSO > acetone from infrared studies.[10-12] Trifluoroethanol gave similar results with dye **1** in competition experiments.

The foregoing results suggest that unbonded hydroxyl is required to produce the large bathochromic shifts described above. This is supported by results of an experiment (Table II) in which phenols bearing acceptor substituents were added to phenol blue solutions. When the acceptor substituent is located meta or para to the phenolic hydroxyl group, the phenol causes a bathochromic shift in the phenol blue spectrum. If the substituent is ortho to the hydroxyl group, the phenol causes little or no shift in the phenol blue spectrum. In the last case, the hydroxyl group is tied up by chelation and is not available to the dye.

Table II. Effect of Substituted Phenols on λ_{max} of Phenol Blue Dye at 10^{-4} *M* in Benzene

Substituent	Phenol concn, g/100 ml	λ_{max} of phenol blue in meta- or para-substd phenol	Presence of ortho-substd phenol
	None	575	575
$-COOCH_3$	0.66	586 (para)	576
-CHO	0.66	588 (meta)	577
$-COCH_3$	0.70	585 (meta)	575
$-NO_2$	1.39	621 (meta, para)	575

Infrared studies support the validity of the assumption that unassociated cresol is primarily responsible for shifting the absorption of phenol blue. The amount of unbonded hydroxyl in a solution containing cresol determines the intensity of the unbonded OH absorption at 3615 cm^{-1}. A correlation between the intensity of this peak and the magnitude of the shift in the absorption maximum of phenol blue was obtained as follows. A calibration curve was determined which related the spectral shift of phenol blue (in kilocalories per mole) to *p*-cresol concentration by measuring λ_{max} of the dye in a series of concentrations of *p*-cresol in CCl_4 solution. Then the absorption of the dye was measured in mixtures containing 0.2 *M* *p*-cresol and various amounts of hydrogen-bond acceptors (acetone, TOPO, DMSO). The *effective* concentration of *p*-cresol which remained unassociated with the acceptor

(10) K. B. Whetsel and R. E. Kagarise, *Tetrahedron*, **18**, 315 (1962).
(11) T. Gramstad, *Spectrochim. Acta*, **19**, 497 (1963).
(12) N. Kornblum, P. J. Berrigan, and Wm. LeNoble, *J. Amer. Chem. Soc.*, **85**, 1141 (1963).

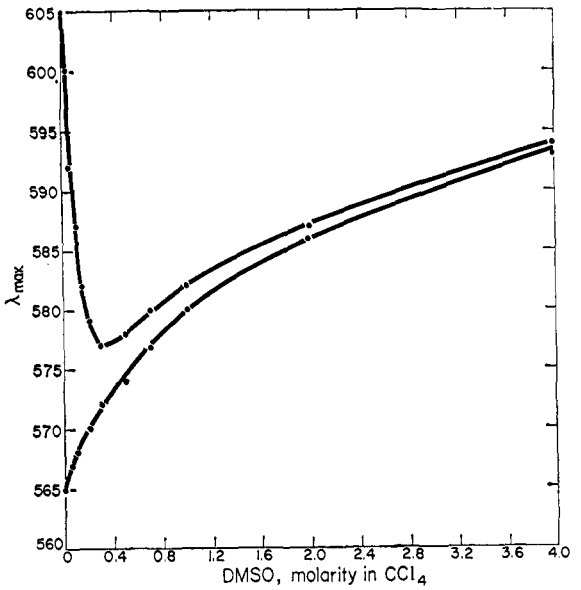


Figure 1. λ_{max} of phenol blue *vs.* DMSO concentration: lower curve, *p*-cresol absent; upper curve, 0.2 *M p*-cresol present.

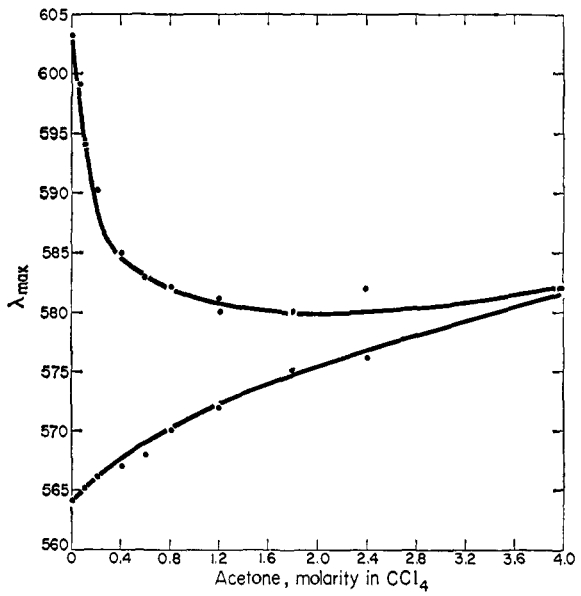


Figure 2. λ_{max} of phenol blue *vs.* acetone concentration: upper curve, *p*-cresol absent; lower curve, 0.2 *M p*-cresol present.

in each case was read from the aforementioned calibration curve. Infrared intensities at 3615 cm^{-1} of the dye–cresol–acceptor mixtures were found to be directly proportional to effective concentrations of *p*-cresol as determined from shifts in dye spectra. The correlation is shown in Figure 4.

The effects of *p*-cresol on absorption intensity and band shape suggest that a distinct hydrogen-bonded complex of dye and cresol does not form. The effect of cresol resembles that of a solvent with exaggerated high polarity (in the sense that DMSO is more polar than CCl_4). Addition of various amounts of *p*-cresol to a solution of phenol blue in CCl_4 leaves the shape of the absorption band unchanged, although absorption intensity increases and the curve is displaced toward longer wavelengths. No isosbestic point is observed. A common intensity–wavelength envelope was obtained (Figure 5) for solutions of phenol blue containing

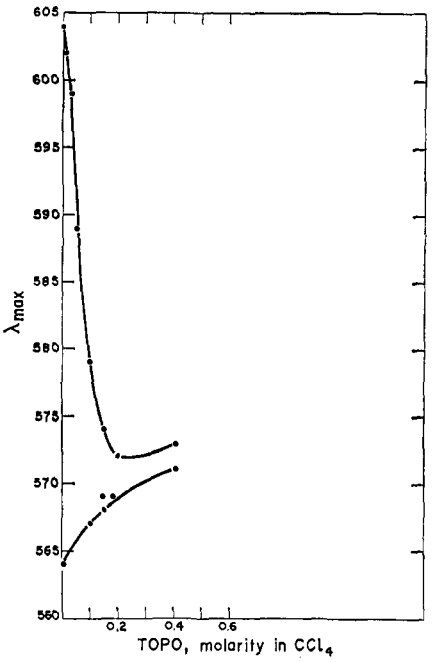


Figure 3. λ_{max} of phenol blue *vs.* TOPO concentration: upper curve, *p*-cresol absent; lower curve, 0.2 *M p*-cresol present.

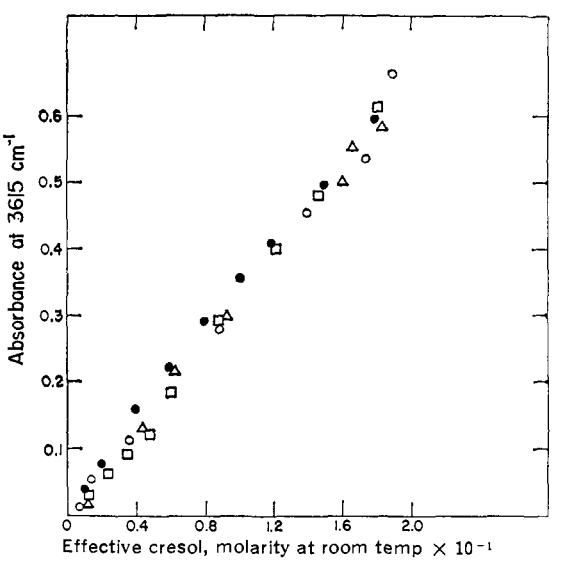


Figure 4. Ir absorbance at 3615 cm^{-1} of various *p*-cresol–H-bond acceptor mixtures *vs.* effective *p*-cresol level based on visible absorption of phenol blue: *p*-cresol concentration series (●); 0.2 *M p*-cresol containing various amounts of DMSO (□), acetone (△), or TOPO (○).

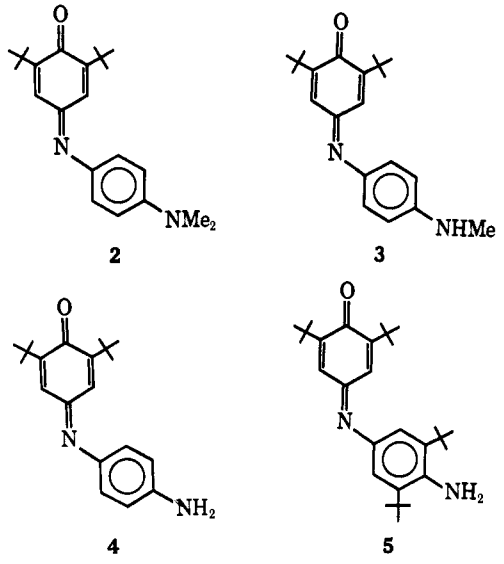
various concentrations of DMSO or *p*-cresol or mixtures of the two. The characterization of the effects of *p*-cresol as an exaggerated solvent effect is supported by the results given in Figure 6 comparing the spectrum of phenol blue in CCl_4 solution in the presence of 4.0 *M* DMSO and in the presence of 0.1 *M p*-cresol; the spectra are almost identical.

Section 2. A. Calculations. We made a quantitative study of hydrogen-bonding effects on spectra using phenol blue and dyes **2**–**5**. These dyes were chosen to give information about the relative importance of carbonyl oxygen and terminal nitrogen as possible bonding sites. The spectra of these dyes were determined in 18 different solvents; transition energies

Table III. Solvent Polarity Parameters[a] and Absorption Data Dyes 1–5 at *Ca.* 10^{-4} *M*

Solvent	$n^{20}D$[b]	*D*	Transition energy, kcal/mol 1	2	3	4	5
Carbon tetrachloride	1.4614	2.24	50.6	52.1	53.8	56.3	53.4
Acetone	1.3588	21.24	49.1	50.5	51.3	53.1	51.5
N,N-Dimethylformamide	1.4319	37.2	48.1	49.5	49.8	51.2	50.4
Pyridine	1.5095	12.3	48.0	49.7	50.2	52.0	51.1
Dimethyl sulfoxide	1.4804	45.5	47.2	48.8	49.1	50.4	49.9
Methyl formate	1.3433	8.5	49.5	50.9	51.9	54.2	52.1
Benzene	1.5011	2.28	49.7	51.1	52.6	55.2	52.6
1,2-Dichloroethane	1.4488	10.38	48.6	50.7	52.7	55.2	52.4
Nitromethane	1.3935	38.57	48.4	50.4	52.0	54.6	52.2
Cyclohexane	1.4266	2.02	51.8	52.7	54.3	56.7	53.8
Acetonitrile	1.3441	37.45	49.0	50.5	51.7	54.1	52.2
Methanol	1.3288	33.62	47.0	49.9	50.5	52.9	51.1
Ethanol	1.3611	24.5	47.2	50.2	50.3	52.3	50.9
Butanol	1.3992	17.68	47.2	49.5	50.2	52.3	51.0
N-Methylformamide	1.3419	171.0	47.4	49.6	50.2	52.0	50.7
Formamide	1.4453	108.7	45.5	49.1	50.4	53.2	51.1
Benzonitrile	1.5289	25.9	47.9	49.7	51.1	53.4	51.4
m-Cresol	1.5398	11.8	41.7	46.4	48.8	55.6	48.1
Trifluoroethanol	1.2903	26.53	43.3	49.3	54.5	60.3	51.5
cis-Dichloroethylene[b]	1.4490	9.20	48.5			55.6	
trans-Dichloroethylene[b]	1.4454	2.14	50.6			56.5	

[a] Data from "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1969; "Digest of Literature in Dielectrics," Vol. 26–29, 1962–1965, Chapter 2; and J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Vol. 2, Elsevier, New York, N. Y., 1965. Refractive indices of DMSO and TFE measured in these laboratories. [b] See text for discussion.



and solvent parameters (refractive indices and dielectric constants) are listed in Table III.

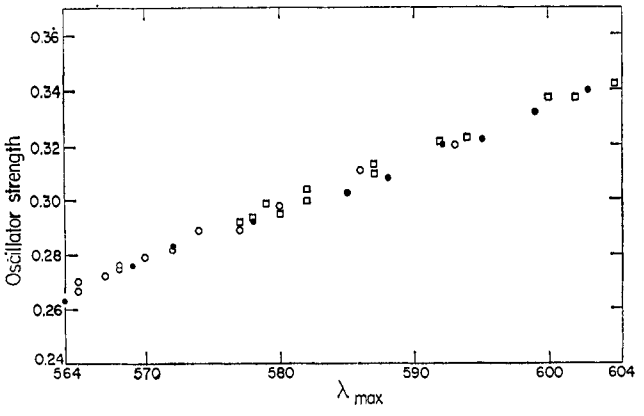


Figure 5. Oscillator strength *vs.* λ_{max} for phenol blue in the presence of various amounts of *p*-cresol (●), DMSO (○), and mixtures of various amounts of DMSO with 0.2 *M p*-cresol (□).

The analysis of solvent effects on the spectra of these dyes was based on the following assumptions.

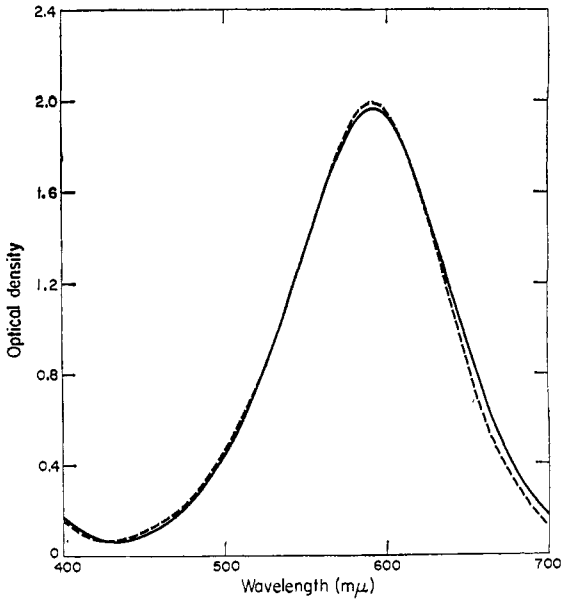


Figure 6. Spectrophotometric curves comparing spectrum of phenol blue in the presence of hydrogen-bonding and nonhydrogen-bonding solvents: solid curve, 4.0 *M* DMSO in CCl_4; broken curve, 0.1 *M p*-cresol in CCl_4.

(1) The total transition energy $E_T = E_I + \Delta E_H$, where E_I is the transition energy the dye would have in the complete absence of hydrogen-bonding effects and ΔE_H is a perturbation in transition energy produced by hydrogen bonding. The transition energy E_I depends only upon the "intrinsic" polarity of the medium. In the absence of hydrogen bonding, $\Delta E_H = 0$ and the response of the dye is affected only by intrinsic solvent polarity.

(2) The part of the transition energy which depends only upon intrinsic solvent polarity is related by a modified form of the McRae equation[1] to macroscopic solvent properties n (refractive index) and D (dielectric constant[13])

$$E_I = \frac{n^2 - 1}{2n^2 + 1}A + \left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right)B + C \quad (1)$$

where A, B, and C are empirical constants dependent upon the nature of the absorber. McRae derived this equation on quantum statistical grounds taking into account interaction of the electron cloud of the solvent with excited and ground state electron distributions of the dye solute.

To apply the mathematical model, an iterative computer routine (described in the Experimental Section) was employed with eq 1 to obtain values of A, B, and C for each dye **1–5**, using absorption data and solvent parameters in Table III. The computer program simultaneously sorted absorption data into a set which fitted eq 1 and a set which did not. A check on the adequacy of the computer routine was provided by McRae's published calculations for phenol blue[1] which were based on semitheoretical estimates for the constants A and B. McRae used two values for A depending upon solvent polarity; in this work, we permitted A to assume one value. In Table IV, we compare his "semitheoretical" parameters for phenol blue with those determined empirically from the iterative computer routine. (McRae's constants in units of cm^{-1} were converted to kilocalories per mole for the comparison.) There is good agreement between the two sets of constants.

Table IV. Constants A and B, Equation 1, Determined for Phenol Blue

	McRae's work[a] (semitheoretical)	This work (empirical)
A, kcal	−35.5, −31.2	−33.0
B, kcal	−5.1	−4.4

[a] See ref 1.

Using the constants A, B, and C for a given dye, we calculated a predicted transition energy $\hat{E}_I$ for each of the 18 solvents. The predicted $\hat{E}_I$ is an estimate of that part of the transition energy which depends only upon intrinsic solvent polarity, $\hat{E}_I$. It follows from assumption 1 that the deviation $\hat{E}_I - E_T$ of the observed transition energy from the calculated value is a measure of the perturbation ΔE_H produced by the hydrogen bonding. For a nonbonding solvent, provided the absorption data fit the McRae equation, $\hat{E}_I$ and E_T will have the same value so that $\Delta E_H = 0$.

(13) The use of macroscopic dielectric constants for studying solvent effects on spectra is controversial (ref 2) because it is assumed that the microenvironment resulting from interaction of a solute with one or more solvent molecules is quite different from the average environment which determines the macroproperty. Midwinter and Suppan (ref 4) have shown, however, that anomalous dielectric constant effects on absorption observed with mixtures of solvents can be quite well accounted for if one allows for solvent sorting in the vicinity of the dye molecule and uses the inhomogeneous composition of the solution around the dye molecule and the *bulk dielectric constants* of the component solvents to calculate an effective dielectric constant. These authors also suggest that solvent shell effects may be less important for large solute molecules, for which the bulk dielectric constant of the solvent is an appropriate parameter for predicting solvent shifts.

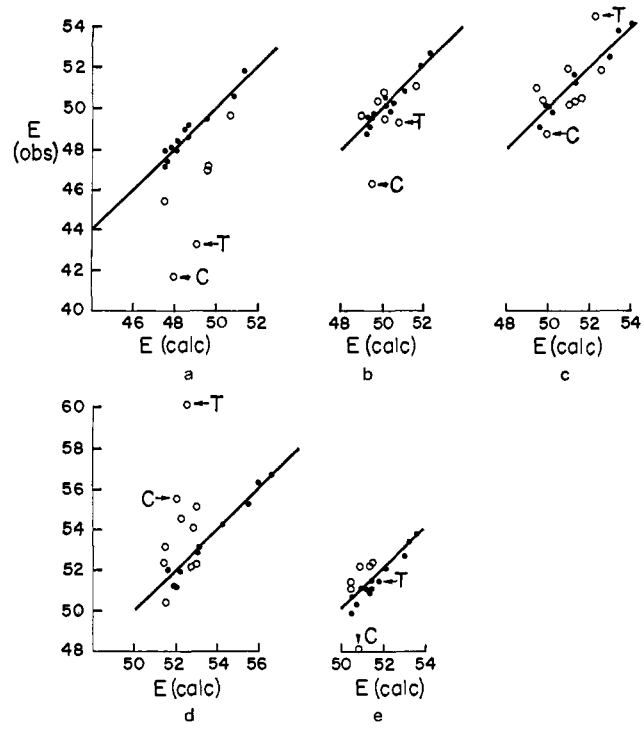


Figure 7. Observed transition energies, E_T, *vs.* those calculated from eq 1 ($\hat{E}_T$) for dyes **1–5**. Points labeled "T" and "C" are for TFE and *m*-cresol solvents. Other points are for the solvents listed in Table III: (a) dye **1**, (b) dye **2**, (c) dye **3**, (d) dye **4**, (e) dye **5**.

Figures 7a–7e show plots of observed transition energies for dyes **1–5** in each solvent *vs.* values of $\hat{E}_I$ calculated from eq 1. Points which fit eq 1 within 0.5 kcal/mol are shown as solid circles; points deviating by more than 0.5 kcal/mol are plotted as open circles. Points labeled "C" and "T" are for *m*-cresol and TFE solvents, respectively. The deviations ($\hat{E}_I - E_T$) for these two solvents are generally large for all of the dyes. Numerical values of these deviations, as well as deviations larger than 0.5 kcal/mol for other solvents, are tabulated for all five dyes in Table V.

Table V. Deviations ($\hat{E}_I - E_T$, kcal/mol) from the McRae Plot for Dyes **1–5**

Solvents	Dyes[a] 1	2	3	4	5
m-Cresol	6.3	3.1	1.1	−3.6	2.6
Trifluoroethanol (TFE)	5.8	1.5	−2.2	−6.7	
Methanol	1.6		1.0		
Ethanol	1.3		1.0	0.6	
Butanol	1.3	0.6	1.0	0.5	
Formamide	2.0		−0.6	−1.6	0.6
Acetonitrile					−1.6
Benzonitrile		−0.7	−0.7	−2.0	−1.2
1,2-Dichloroethane		−0.6	−1.6	−2.2	−1.1
Nitromethane			−1.3	−2.2	−1.1
N,*N*-Dimethyl-formamide				0.8	
Dimethyl sulfoxide				1.0	

[a] Blank entries correspond to deviations less than 0.5 kcal.

B. Characterization of Bonding Sites in Dyes 1–5 (TFE and *m*-Cresol). The deviation ($\hat{E}_I - E_T$) for phenol blue (**1**) in *m*-cresol is reduced by introduction of *tert*-butyl groups ortho to the carbonyl group (dye **2**).

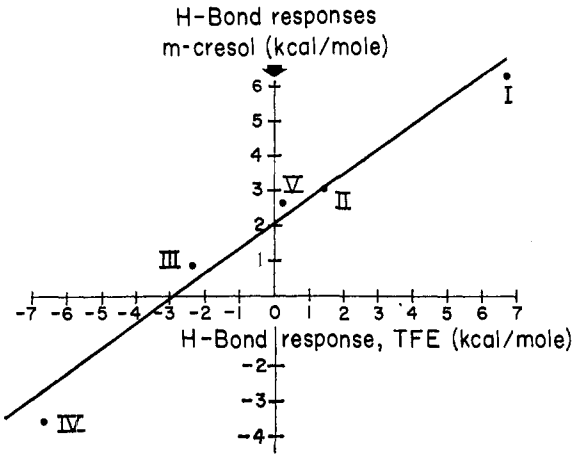


Figure 8. McRae deviations (OH interactions) for dyes **1–5** in *m*-cresol *vs.* those observed in trifluoroethanol (TFE).

This supports the obvious assumption that the carbonyl group is a site of hydrogen bonding. In spite of steric hindrance around carbonyl, dye **2** gives a fairly large deviation (3.1 kcal/mol) in *m*-cresol, the result perhaps of residual bonding at carbonyl or of bonding at the azomethine nitrogen atom, but not at the terminal dimethylamino group, for reasons to be discussed.

The deviations for dyes **2**, **3**, and **4** in *m*-cresol decrease in that order, with a sign reversal for dye **4**. The negative deviation corresponds to a blue-shifting interaction of cresol with dye. Similar results, but larger in magnitude, were observed with TFE. The hypsochromic effect is expected to arise from hydrogen bonding at the terminal amino nitrogen atom. Such blue shifts have been observed previously with sufficiently electron-rich anilines in alcohol solution.[14] This view of the origin of hypsochromic trend in the deviations is supported by the fact that introducing bulky *tert*-butyl groups ortho to the amino group causes sign reversal of the deviation (Table V, compare dyes **4** and **5** in *m*-cresol). Presumably the bulky groups interfere with hydrogen bonding at the terminal amino group and eliminate the hypsochromic effect.

On the basis of this interpretation, we conclude from Table V that the magnitude of the OH interaction at terminal nitrogen increases in the sequence $Me_2N- <$ $MeNH- < NH_2-$. This conclusion was checked by infrared measurements of the intensity of the unbonded OH peak (3615 cm^{-1}) in mixtures of 0.1 *M* *m*-cresol or 0.1 *M* TFE with 0.1 *M* aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline. Per cent reductions in peak amplitude, indicative of a decrease in the amount of unassociated OH, because of bonding to the anilines, are given in Table VI for the aniline–donor mixtures. Although the changes in the unbonded OH peak are small, they are consistent with the deductions from the visible spectral data that the primary amino group in dye **4** is a better hydrogen-bond acceptor than the methylamino or dimethylamino group in dyes **3** and **2**.

Table VI. Per Cent Reductions in Amplitude of the 3615-Cm^{-1} Band for 0.1 *M* *m*-Cresol or TFE on Aniline Additions

Amine	Per cent reduction in peak amplitude *m*-Cresol	TFE
Aniline	17.3	22.2
N-Methylaniline	13.8	14.5
N,*N*-Dimethylaniline	13.8	12.2

(14) E. W. Crandall and J. Olguin, *J. Org. Chem.*, **31**, 972 (1966).

A linear correlation was observed between the deviations ($\hat{E}_I - E_T$) for dyes **1–5** in *m*-cresol and their deviations in TFE (Figure 8). The correlation supports the interpretation that the deviations in these two solvents result from hydrogen bonding, since this capability is common to the two solvents. The approximate correlation line in Figure 8 does not go through the origin and establishes that there is a hypsochromic bias of about 3 kcal/mol in the data for the TFE solutions. This can be interpreted as the result of interaction between TFE and terminal nitrogen which is stronger than that occurring with *m*-cresol; *i.e.*, TFE is a better hydrogen-bond donor. There is indication of this difference in behavior between TFE and *m*-cresol in the infrared data previously discussed (Table VI). A corollary to these results is that phenol blue (**1**) is more strongly hydrogen bonded at the dimethylamino group in TFE solvent than it is in *m*-cresol, which implies that in TFE, phenol blue is hydrogen bonded at least at two sites—carbonyl oxygen and terminal nitrogen.

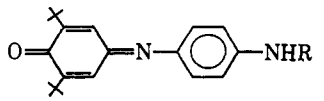
The very different behavior in hydrogen-bonding solvents of the amino dye **4** from that shown by the dimethylamino dye **2** manifests itself also in absorption intensity. Both dyes show increased absorption intensity with increased intrinsic solvent polarity (Table VII, compare cyclohexane and DMSO data), which parallels the behavior of phenol blue noted in Section 1. The two dyes differ in behavior in *m*-cresol or TFE; while the dimethylamino dye **2** shows increased absorption intensity (*vs.* cyclohexane solvent), the primary amino dye **4** shows little or no enhancement of absorption.

Table VII. Oscillator Strengths of Dyes **2** and **4**; Dyes 10^{-4} *M*

Dye	Cyclohexane	DMSO	*m*-Cresol	TFE
2	0.227	0.281	0.302	0.276
4	0.196	0.315	0.222	0.183

The spectral effects of hydrogen bonding at terminal nitrogen—hypsochromic shift and decrease in absorption intensity—bear a close resemblance to the effects produced by an electron-attracting acetyl substituent at that atom (Table VIII). Hydrogen bonding at the amino group of dye **4**—like the acetyl group—constrains the unshared electron pair on terminal nitrogen,

Table VIII. Comparison of Effects of H Bonding and *N*-Acetyl on the Spectrum of Dye **4**



Solvent	R = H (dye **4**) λ_{max}	*f*	R = $COCH_3$ λ_{max}	*f*
DMSO	570	0.315	494	0.162
TFE	474	0.183		

making it less available to the chromophore during excitation.

In summary, dyes **1–5** have at least two bonding sites which interact with solvent OH groups in good donors to give opposite shifts in absorption maximum. Bonding at carbonyl oxygen gives bathochromic shifts; bonding at terminal nitrogen gives hypsochromic shifts. Compounds **2–5** each have a carbonyl group in a similar steric environment; the amount of bathochromic shift from bonding at carbonyl oxygen may be the same for all of them. These compounds differ, however, in substitution around terminal nitrogen, so that the amount of hypsochromic shift from bonding at terminal nitrogen varies from one compound to another. The deviation ($E_I - E_T$) therefore depends upon the extent to which the relatively constant amount of bathochromic shift is offset by the variable amount of hypsochromic shift through the series. Theoretically it should be possible for the opposing spectral shifts to cancel and give a net spectral shift of zero even when the dye is hydrogen bonded. Such apparently is the case for dye **5** in TFE (Table V). An alternative explanation—that dye **5** is not hydrogen bonded at all—is inconsistent with its behavior in *m*-cresol and its position on the graph in Figure 8.

C. Structure Dependence of Solvent Shifts. Using the linear model for solvent effects (assumption 1), we can calculate how much of the difference in transition energy for a dye in two different solvents is due to differences in hydrogen bonding and to differences in intrinsic solvent polarity. A comparison of these effects is given in Table IX for dyes **1–5** in *m*-cresol and TFE *vs.* cyclohexane.

Table IX. Spectral Shifts Due to Intrinsic Solvent Polarity and H Bonding (kcal/mol) in *m*-Cresol and TFE *vs.* Cyclohexane

	Shifts, kcal/mol — Dyes				
	1	**2**	**3**	**4**	**5**
m-Cresol					
Cresol *vs.* cyclohexane	10.1	6.3	5.5	1.1	5.7
Hydrogen bonding	6.3	3.1	1.1	−3.6	2.6
Intrinsic solvent polarity	3.3	3.2	4.4	4.7	3.1
TFE					
TFE *vs.* cyclohexane	7.5	3.4	−0.2	−3.6	2.3
Hydrogen bonding	5.8	1.5	−2.3	−6.7	0.2
Intrinsic solvent polarity	1.7	1.0	2.0	3.1	2.1

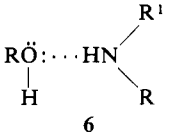
TFE *vs.* cyclohexane. These data show that the responses of dyes **1–5** to hydrogen bonding are much more structure dependent than are their responses to differences in intrinsic solvent polarity.

D. Hydrogen Bonding in Aliphatic Alcohols. The aliphatic alcohols give much smaller deviations from the McRae relationship (Table V) than TFE or *m*-cresol solvents. We attribute this to the effects of self-association of aliphatic alcohols, which decrease the amount of free OH required for interaction with dye (Section 1). Results of competition experiments with ethanol *vs.* *m*-cresol and TFE using phenol blue as an indicator (Table X) show that ethanol acts as a hydrogen-bond acceptor toward *m*-cresol and TFE (indicator shifts *hypsochromically* on adding ethanol to a solution containing *m*-cresol or TFE), but *m*-cresol and TFE do not act as acceptors to each other (indicator shifts *bathochromically* on adding TFE to a solution containing *m*-cresol). Ethanol appears to be a better hydrogen-bond acceptor than TFE or *m*-cresol and should therefore be more self-associated than the latter two solvents. Other authors[15] have suggested that fluorinated alcohols are markedly less associated than ordinary alcohols. The proton-accepting tendencies of the solvent (basicity) must play a role in the interaction of solvents and solutes, inasmuch as solvent molecules compete with solutes as hydrogen-bond acceptors. Mukherjee and Grunwald[16] suggested that TFE is a better hydrogen-bond donor than ethanol because of higher *acidity;* presumably this would be true for phenols also. However, phenol blue gives a bathochromic shift in 0.2 *M* acetic acid of only 3 nm, compared with 39 nm in 0.2 *M* *m*-cresol (CCl_4 diluent) and McRae[1] found that phenol blue absorbed at about the same wavelength in methanol and pure acetic acid. These results are much more easily explained in terms of self-association of solvents than in terms of relative acidities.

Table X. Effects of Mixed Hydroxylic Solvents on the Spectrum of Phenol Blue Dye at 10^{-4} *M*

Added solvent	λ_{max}	λ_{max} +0.2 *M* ethanol
None	565	
p-Cresol	605	596
TFE	601	592
p-Cresol + TFE	615	

Steric hindrance around the carbonyl group weakens the already small interaction of dyes with alcohols (Table V); the dimethylamino dye **2** shows no significant deviation in alcohol solvents. The bathochromic deviations shown by the analogous methylamino dye **3** (and to some extent by dye **4**) must, therefore, originate in interactions between the terminal NH function and solvent. This is supported by the disappearance of the interaction as the result of steric hindrance around the amine group (dye **5**). We suggest that the bathochromic deviations for dyes **3** and **4** are the result of hydrogen bonding in which the dye serves as donor (**6**). Such bonding would increase electron density



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around nitrogen and disperse positive charge around nitrogen in the excited state (see **1b**). This interpretation is consistent with the aforementioned acceptor properties of aliphatic alcohols and the presence of NH groups as potential donors in dyes **3** and **4**.

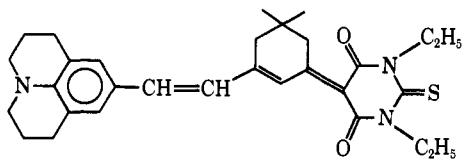
E. Interpretation of the Deviations from Eq 1 for Other Solvents (Table V). Formamide falls between the weak donor alcohols and the strong donors TFE and *m*-cresol; dye **1** gives a modest bathochromic deviation and dyes **3** and **4** give modest hypsochromic deviations. Steric hindrance around the amino group

(15) J. E. Berger, L. R. Dawson, and H. C. Ekstran, *J. Phys. Chem.*, **64**, 1458 (1960), and references cited therein.
(16) L. M. Mukherjee and E. Grunwald, *ibid.*, **62**, 1311 (1958).

eliminates the hypsochromic effect of bonding at terminal nitrogen (formamide acting as donor); compare dyes **4** and **5**, Table V. *N*-Methylformamide—a solvent which represents an extreme variation in dielectric constant (D = 171)—gives spectral results with all five dyes which fit the McRae equation. The absence of deviation from the McRae equation for this solvent may be the consequence of strong self-association and a lesser tendency for NH groups to donate hydrogen bonds compared with OH groups. *N*,*N*-Dimethylformamide (and DMSO also) gives significant, bathochromic deviations only with dye **4**, which could arise from hydrogen bonding with the dye acting as donor, as discussed above in the case of aliphatic alcohols (see **6**).

The remaining solvents listed in Table V—acetonitrile, benzonitrile, 1,2-dichloroethane, and nitromethane—afford data which do not fit within the framework of interpretation offered so far. None of these solvents is a hydrogen-bond donor, yet all show significant hypsochromic deviations with dye **4**, just as *m*-cresol does. Moreover, significant hypsochromic deviations are observed with dye **2** in benzonitrile and 1,2-dichloroethane, cases in which hydrogen bonding is unlikely. The inexplicable deviations were not eliminated by inclusion of a second-degree term in eq 1, the "quadratic Stark effect," which was omitted by McRae as an approximation. The possible importance of uncompensated dipole moment as a factor determining the behavior of these solvents was indicated by the fact that *cis*-1,2-dichloroethylene gave a deviation of −1.6 kcal/mol from the McRae relationship, whereas the trans isomer gave zero deviation. These unexplained deviations underscore the fact that the treatment in this paper is approximate and probably incomplete.

F. Correlations with Brooker's Red-Shifting Merocyanine VII. Brooker, *et al.*,[5] proposed merocyanine dye **7** (Brooker's VII) as a solvent property indicator because it shows unprecedented, large solvent shifts.



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We related the solvent shifts observed with dyes **1**–**5** to those shown by the proposed reference dye **7** by calculating the linear correlation coefficient[17] between Brooker's data and our data for 11 different solvents (Table XI). Good correlations were obtained for dyes **1**, **2**, and **5**, and a statistically significant one for dye **3**. On the other hand, the absorptions of dye **4** were essentially uncorrelated with those of dye **7**. The reason for this lack of correlation is probably that dye **4**, with a primary amino group, can act as a hydrogen-bond donor, whereas dye **7** can function only as an acceptor.

Table XI. Correlation Coefficients, r. Transition Energies of Dyes **1**–**5** *vs.* Those of Dye **8** for 11 Solvents

Dye	r
1	0.981
2	0.971
3	0.827
4	0.254
5	0.936

In view of the high correlation between the solvent responses of phenol blue (**1**) and dye **7**, it is not surprising to find that dye **7** shows a very large response to hydrogen bonding. The deviation from the McRae equation for dye **7** in *m*-cresol is 8.5 kcal/mol (calculated from Brooker's published data).[5,18] Analysis of the total spectral shift for dye **7** in *m*-cresol *vs.* cyclohexane gives 8.5 kcal/mol for the hydrogen-bonding shift and 7.9 kcal/mol for the shift due to change in intrinsic solvent polarity. Both kinds of shifts for dye **7** are considerably larger than those shown by dyes **1**–**5** (Table IX).

Experimental Section

Dyes **1** and **4** were prepared by the oxidative condensation of suitable *p*-phenylenediamines and phenols using ammonium persulfate as oxidant, following the procedure of Vittum and Brown.[19] Dyes **2**, **3**, and **5** were obtained from the BF_3-catalyzed condensation of 2,6-di-*tert*-butylbenzoquinone with appropriate *p*-phenylenediamines. This condensation was described in a recent article for the preparation of Schiff bases,[20] and its utility in the preparation of azomethine dyes will be described in detail in a forthcoming publication.[21] All dyes were of chromatographic purity, purified by column chromatography or giving one spot on a thin layer chromotographic plate, and had acceptable elemental analyses.

Solvents were Eastman Reagent Chemicals or Eastman Spectro Grade materials and were dried and stored over Linde 4A Molecular Sieves. *m*-Cresol and *p*-cresol were Eastman Practical Chemicals, distilled before use. Anilines used for the infrared studies were freshly distilled Eastman Reagent compounds.

Infrared spectral measurements were obtained with a Beckman Model IR-12 high-resolution infrared spectrophotometer; sample temperature in this instrument was 35°. Visible absorption spectra were determined at room temperature with a Hardy model spectrophotometer manufactured by the General Electric Co. To determine the correlation between the infrared and the visible spectral data as discussed in Section 3, it was necessary to correct for the difference in temperature at which these spectral measurements were made. This was done by measuring the spectrum of phenol blue in carbon tetrachloride containing various known amounts of *p*-cresol using a Beckman Model DB recording spectrophotometer and a cell thermostated to 35°. Measurements on these solutions were also made at 25° and a calibration curve was constructed for correcting spectral data obtained at room temperature to 35°.

Oscillator strengths were determined using the relationship

$$F = 4.31 \times 10^{-9} \int \epsilon d\nu$$

where the integral is the area under the absorption band in frequency space. This area was approximated by numerical integration, using digitized spectrophotometric data and a digital computer.

A FORTRAN program was developed to obtain a least squares fit of absorption data in various solvents to the McRae equation (1). The program sorted the data into two sets: those which fitted the McRae relationship within 0.5 kcal/mol, and those which deviated from the relationship by more than this amount. An iterative

(17) O. L. Davies, "Statistical Methods in Research and Production," Oliver and Boyd, London, 1957, p 191.

(18) Dye 7 gave absorption data which fit eq 1 within 0.5 kcal/mol for the following 11 solvents: cyclohexane, carbon tetrachloride, *p*-xylene, ethyl acetate, acetonitrile, acetone, 2-butanone, butanol, nitromethane, dimethyl sulfoxide, and *N*,*N*-dimethylformamide. Nine solvents gave deviations from eq 1 larger than 0.5 kcal/mol (deviations in parentheses): *m*-cresol (8.5), nitrobenzene (−2.0), methanol (2.9), benzonitrile (−2.0), ethanol (1.4), pyridine (−1.2), propanol (0.8), chloroform (2.0), and benzene (0.6).

(19) P. W. Vittum and G. H. Brown, *J. Amer. Chem. Soc.*, **68**, 2235 (1946).

(20) M. E. Taylor and T. L. Fletcher, *J. Org. Chem.*, **26**, 940 (1961).

(21) J. Figueras, P. W. Scullard, and A. R. Mack, to be published.

scheme was used to effect this sorting as follows. On the first pass, all of the absorption data were used to obtain a first estimate of constants A, B, and C. These estimates were used in eq 1 to back-calculate predicted values of the transition energies $\hat{E}\mathrm{t}$. The standard deviation between observed and calculated transition energies was obtained. If the standard deviation was less than 0.5 kcal/mol, processing terminated; otherwise the difference $|\hat{E}\mathrm{t} - E_T|$ was calculated for each solvent and the solvents were sorted into two classes depending upon whether the difference $|\hat{E}\mathrm{t} - E_T|$ was (1) larger than the standard deviation or (2) less than or equal to the standard deviation. Absorption data for solvents falling in the second class were then used to recalculate a new set of constants A, B, and C, and this new regression equation was used to calculate a new standard deviation and a new set of differences $|\hat{E}\mathrm{t} - E_T|$ and sorting into two classes was done again. This was continued until the regression gave a standard deviation less than 0.5 kcal/mol. Three to five regression trials sufficed to effect the regression analysis and sorting; standard deviations actually obtained were *ca.* 0.3 kcal/mol.

Statistical analysis of the regression results gave the following probabilities that random variation alone would produce the observed number of successful predictions by eq 1 (see Figures 7a and 7b): dye **1**, 0.02; dye **2**, 0.05; dye **3**, 0.44; dye **4**, 0.48; dye **5**, 0.08; dye **7**, 0.02. The predictions for dyes **1**, **2**, **5**, and **7** are therefore highly statistically significant. The predictions for dyes **3** and **4** are inconclusive. Taking all six experiments as a whole, the probability is about one part in 10,000 that four events out of six with probabilities of about 0.05 would occur on a random basis. This analysis shows that the computer routine can identify significant mathematical structure and that the observed successes did not result from fortuitous selection of random events. The inconclusive predictions for dyes **3** and **4** arise from an assignable cause—a factor of structure (occurrence of an N–H bond) not present in the other dyes. This assignment of cause for dyes **3** and **4** is made possible by the highly significant correlations obtained with the other four dyes.

Acknowledgments. Visible spectral measurements were obtained by Mr. Franc Grum, of these laboratories. Miss Thelma J. Davis and Mr. John Robertson, also of these laboratories, made the infrared measurements. The tetra-*tert*-butyl dye **5** was supplied by Dr. Peter W. Scullard. The author expresses his appreciation for their assistance, and thanks Dr. William H. Lawton for his help in the statistical analysis of the results.

Electronically Excited Aromatic Carbonyl Compounds in Hydrogen Bonding and Acidic Media

Richard Rusakowicz, Gary W. Byers, and Peter A. Leermakers*

Contribution from the Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457. *Received September 18, 1970*

Abstract: In 85% H_3PO_4 several aromatic carbonyl compounds display remarkable though often weak fluorescence at room temperature (Table I) and long but multiple component phosphorescent decay times at 77°K (Table III). By subjecting benzophenone to extremes, namely nonpolar, weakly hydrogen bonding solvents and strongly acidic solvent glasses, and then many intermediate solvent conditions, a model for aromatic carbonyl solvation has been established in which the excited state (1) possesses n,π^* character in nonpolar and weakly hydrogen bonding solvents, (2) exhibits enhanced π,π^* character in very polar hydrogen bonding solvents, and (3) attains a protonated π,π^* state in strongly acid media.

It has been reasonably established that nearly complete reversal of excited state energy levels occurs in certain molecules which are very sensitive to moderate changes in solvent polarity and hydrogen bonding. For example, the fluorescence intensity of quinoline in solvents benzene, ethanol, and water is enhanced in the ratio 1:50:1000, respectively. The authors concluded that the lowest n,π^* state in solvent benzene is replaced by a nearby π,π^* state in water.[1] Singlet state inversion is apparently also a property of acridine[2,3] and pyrene 3-aldehyde[4] whose fluorescence behavior is similar to quinoline. Sensitivity to moderate variations in solvent polarity is often an indication that the lowest π,π^* energy level is almost isoenergetic with the n,π^* energy level. Within the triplet manifold, observations of multiple-component phosphorescence for indanone,[5] butyrophenone,[6] acetophenone,[7] and substituted acetophenones,[8,9] again indicates strong dependence on solvent with respect to the relative energies of n,π^* and π,π^* states. Here, however, triplet energy level reversal has been definitively documented only for butyrophenone[6] and acetophenone.[7]

It is a reasonable thesis that, in general, aromatic carbonyl compounds may be affected by polar, hydrogen bonding solvents, but to varying degrees depending upon the solvent system. To obtain complete inversion of n,π^* and π,π^* states, stronger hydrogen bonding solvents are required which may even lead to protonation of the carbonyl oxygen. In the present paper, through the use of very polar hydrogen bonding solvents and both weak and strong acid glasses at 77°K, we report a detailed examination of the excited singlet and triplet states for a number of carbonyl systems.

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(9) R. N. Griffin, *ibid.*, **7**, 175 (1968).