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Solute–Solvent Interactions in the Ground State and in Electronic Excited States. The Dipolar Aprotic to Polar Protic Solvent Blue Shift of Some Anilines and Phenols

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Abstract: The long-wavelength transition of some anilines, phenols, and their nitro derivatives was found to be blue shifted on transfer from dimethylformamide to methanol solvent. The enthalpies of transfer of the Franck–Condon excited states were then determined by combining calorimetric and spectroscopic data. It was found that enthalpies of transfer of the Franck–Condon excited states were uniformly endothermic into the hydrogen-bonding solvent. An estimate of the solvent transfer enthalpies of the corresponding relaxed excited states was made from fluorescence, absorbance, and calorimetric data. A comparison of the solvent transfer enthalpies of the ground state, the Franck–Condon excited state, and the relaxed excited state was used to evaluate the specific solvation mechanisms causing the blue shift.

The frequently observed solvent effects on the wavelengths of electronic transitions are the sum of the changes in solvation energy of the ground state and changes in the solvation energy of the excited state. Combination of calorimetric and spectroscopic data can separate these two effects, thus shedding some light on the nature of the solvation effects in the ground and excited states, as well as on the nature of the particular electronic transition.[1-3] Recently we reported the results of such a study on the long-wavelength transition of some nitroaromatics.[3] In this transition the dipole moment increases in the excited state transferring negative charge from the aromatic ring to the nitro group. Nevertheless, this transition was found to be blue shifted from a dipolar aprotic to a polar protic solvent. This unexpected result indicated that, as charge is transferred from the aromatic system to the NO_2 group, it strengthens dipole–dipole interactions more than it strengthens the hydrogen bonds to the NO_2 group.

It should be of interest to examine a transition in which the dipole moment also increases, but transfers negative charge in the other direction, namely toward the aromatic ring. An example of such a transition is to be found in the long-wavelength absorption of anilines (corresponding to the 287-nm band of aniline) and phenols (corresponding to the 275-nm band of phenol).[4,5] The solvation of this excited state should be of interest as it bears on the question of the greatly enhanced excited-state acidities of phenols[6] and the reduced basicities of the excited states of anilines,[6b] as well as on the excited states of related biomolecules.[7] Anilines and phenols having a conjugated nitro group would be expected to have a still larger dipole moment increase in the excited state,[8,9] while having the complicating factor of the nitro group solvation effects observed earlier[3] superimposed on the amino or hydroxy group solvation effect. Such compounds are of added interest because their spectral shifts have been used by Kamlet and Taft for their solvatochromic comparison method to construct a scale of solvent hydrogen bond donor and hydrogen bond acceptor abilities.[10] As before[3] the dipolar aprotic–polar protic solvent pair used in this study was dimethylformamide and methanol. These two solvents have very similar dielectric constants and therefore lend themselves well to the study of specific solvation effects.

Results and Discussion

The enthalpy of transfer of a compound from dimethylformamide to methanol, $\delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}}$, is the difference between the heats of solution, $\Delta H_{\text{solvent}}$, of the compound in the two solvents of interest:

$$\delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}} = \Delta H_{\text{MeOH}} - \Delta H_{\text{DMF}}$$

With the spectral solvent shift, $\delta\Delta E^{\text{abs}}_{\text{DMF}\to\text{MeOH}}$, defined in the usual way as the difference in the excitation energies, ΔE^{abs}, in the two solvents:

$$\delta\Delta E_{\text{DMF}\to\text{MeOH}} = \Delta E^{\text{abs}}_{\text{MeOH}} - \Delta E^{\text{abs}}_{\text{DMF}}$$

The energy of transfer of the Franck–Condon excited state, $\delta\Delta H^{\text{F.C. excited state}}_{\text{DMF}\to\text{MeOH}}$, is then readily calculated from the equation

$$\delta\Delta H^{\text{F.C. excited state}}_{\text{DMF}\to\text{MeOH}} = \delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}} + \delta\Delta E^{\text{abs}}_{\text{DMF}\to\text{MeOH}} \quad (1)$$

All but one of the 12 compounds examined were found to be blue shifted into the polar protic solvent (Table I, column 2). Considering the first three amines, one sees that their enthalpies of transfer into the hydrogen bond donor solvent are all endothermic (Table I, column 3). This is mainly a consequence of the greater net interaction[11] of the amino group with the hydrogen bond acceptor solvent (DMF) than with the hydrogen bond donor solvent (MeOH). That this is so is shown by the fact that in the case of *N,N*-dimethylaniline, where the former interaction is necessarily absent, the transfer enthalpy is least endothermic (0.8 kcal/mol). This, however, is still larger than the transfer enthalpy of cumene, 0.11 kcal/mol,[12] which can be used as a model for the difference between the cavity-forming enthalpies in the two solvents[11] plus any solute–solvent interactions[13] not specifically involving the functional group. Thus, even in the absence of a hydrogen bond

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Table I. The Solvent Blue Shift ($\delta\Delta E_{\text{DMF}\to\text{MeOH}}$) of the Long-Wavelength Transition of Anilines and Phenols and the Enthalpy of Transfer of Their Ground States ($\delta\Delta H_{\text{DMF}\to\text{MeOH}}$), Their Franck-Condon Excited States ($\delta\Delta H^{\text{F.C. excited state}}_{\text{DMF}\to\text{MeOH}}$), and Their Relaxed Excited States ($\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}}$) from Dimethylformamide to Methanol (kcal/mol)

compd	$\delta\Delta E_{\text{DMF}\to\text{MeOH}}$	$\delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}}$	$\delta\Delta H^{\text{F.C. excited state}}_{\text{DMF}\to\text{MeOH}}$	$\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}}$
N,N-dimethylaniline	1.07	0.81[a]	1.88	1.7
4-methylaniline	3.71	2.1[a]	5.8	4.2
1-naphthylamine	4.53	2.49[a]	7.02	4.4
2-naphthol	0.79	2.3[a]	3.09	3.1
4-nitro-*N,N*-dimethylaniline	1.6	1.6[a]	3.2	
2-nitro-*N,N*-dimethylaniline	1.6	1.7[a]	3.3	
2-nitroaniline	1.5	2.5[a]	4.0	
4-nitroaniline	1.97	3.6[a]	5.6	7.7
2-nitrophenol	−1.02	2.4[a]	1.4	1.3
4-nitrophenol	1.98	2.7[a]	4.7	6.6
2,4-dinitrophenol	0.38	3.2[a]	3.6	
4-nitrophenoxide ion	7.48	−4.24[b]	3.24	1.25

[a] Reference 12. [b] P. Haberfield, *J. Am. Chem. Soc.*, **93**, 2091 (1971). This is a *single ion* transfer enthalpy.

interaction with the dipolar aprotic solvent, the dipole-dipole interaction of an aniline with the dipolar aprotic solvent is greater than with the polar protic solvent. If, for a compound such as 4-methylaniline, we attribute the net endothermic transfer enthalpy, $\delta\Delta H_{\text{DMF}\to\text{MeOH}}$, to three factors, (1) a positive component caused by the amino N-H to DMF solvent hydrogen bond, (2) a positive component caused by the aniline-DMF dipole-dipole interaction, (3) a negative component caused by the amino N lone pair-MeOH hydrogen bond, then excitation should increase the positive contributions of (1) and (2) and decrease the importance of the negative contribution of (3), thus leading in all three instances to a prediction of a still greater endothermic transfer enthalpy of the Franck-Condon excited state. This was observed (Table I, column 4). How much do factors (1), (2), and (3) contribute to the observed effect?

On the basis of some earlier observations,[2] factor (3) should be most susceptible to Franck-Condon strain. Its contribution should therefore diminish on solvent relaxation. Estimating[3] the enthalpy of transfer of the relaxed excited state from fluorescence data, using the equation

$$\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}} = \delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}} + \frac{1}{2}\,\delta\Delta E^{\text{abs}}_{\text{DMF}\to\text{MeOH}} + \frac{1}{2}\,\delta\Delta E^{\text{fl}}_{\text{DMF}\to\text{MeOH}} \qquad (2)$$

where $\delta\Delta E^{\text{fl}}_{\text{DMF}\to\text{MeOH}}$ is the difference in the fluorescence energies in the two solvents, yields the $\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}}$ in Table I, column 5. It can be seen (Figure 1) that about half of the increase in the excited state transfer enthalpy vanishes on relaxation for 4-methylaniline as well as for 1-naphthylamine. This points to factor (3) as the major contributor to the blue shift. Further support for this view can be seen in the fact that the tertiary amine, *N,N*-dimethylaniline, which should have the weakest hydrogen bond to methanol, exhibits no significant change in its excited state solvent transfer enthalpy on solvent relaxation. The same is true for 2-naphthol, where factor (3) would again be less important because of the weaker basicity of oxygen relative to nitrogen. With factor (3) diminished in these two cases, the blue shift should then be less in these compounds, which is in fact observed.

Turning to the nitroanilines and nitrophenols, factors (2) and (3) above must be modified to include the NO_2 group-DMF dipole-dipole interaction and the NO_2-MeOH hydrogen bond, respectively. The observed pattern of results (Table I, Figure 2) remains similar except that here the relaxed excited state has an even larger endothermic transfer enthalpy into the hydrogen bond donor solvent than the Franck-Condon excited state. We have observed this behavior previously for simple nitroaromatics[3] and the fact that this is also observed for nitroanilines and nitrophenols supports the contention of Kamlet and co-workers[14] that hydrogen bonding to the nitro groups is a major factor in determining the spectral shifts of these compounds. The sole exception is the interesting, internally hydrogen bonded 2-nitrophenol, which is the one compound exhibiting a red shift in this series. The enthalpy of solvent transfer of the ground state of this compound does not differ significantly from that of similar compounds. The red shift is entirely due to an excited state solvent effect (Figure 3). If this compound is to be regarded principally as a hydrogen bond donor, as suggested by Yokoyama, Taft, and Kamlet,[15] then its transfer enthalpies should be determined mainly by factor (1). Absence of a blue shift in this compound therefore confirms the above conclusion, namely, that factor (3) makes the major contribution to the observed spectral shifts.

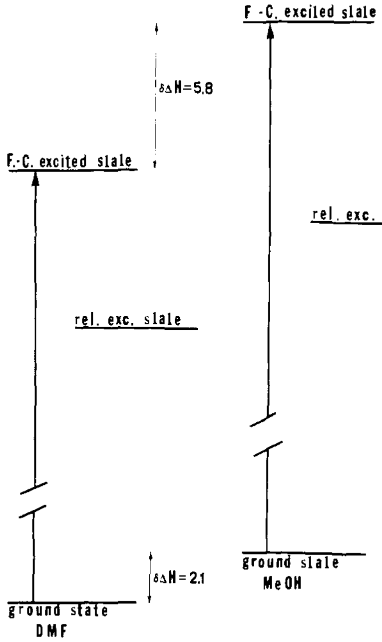

Figure 1. Relative energies (kcal/mol) of the ground states, the Franck-Condon excited states, and the relaxed excited states of 4-methylaniline in a dipolar aprotic solvent (DMF) and in a polar protic solvent (MeOH).

The last example in Table I, 4-nitrophenoxide, was examined in order to have a case where factor (3) clearly dominates the picture. That this is so is evident from its *exothermic* ground state transfer enthalpy (Table I, column 3; Figure 4).

Table II. The Long-Wavelength Absorption Maximum (λ_{max}^{abs}) and the Corresponding Fluorescence Maximum (λ_{max}^{fl}) of Compounds in Dimethylformamide and Methanol (nm)

compd	λ_{max}^{abs} (DMF)	λ_{max}^{abs} (MeOH)	λ_{max}^{fl} (DMF)	λ_{max}^{fl} (MeOH)
N,N-dimethylaniline	301.17	297.80	349.5	346.75
4-methylaniline	301.33	289.99	344.5	342.75
1-naphthylamine	335.74	318.77	416.05	419.8
2-naphthol	333.55	330.51	357.2	353.55
4-nitro-*N,N*-dimethylaniline	398.9[a]	390.3[a]		
2-nitro-*N,N*-dimethylaniline	427.2[b]	417.4[b]		
2-nitroaniline	410.7[b]	402.3[b]		
4-nitroaniline	379.92	370.22	468	424.8
2-nitrophenol	342.26	346.49	406.7	413.5
4-nitrophenol	318.29[c]	311.42[c]	463.5	423
2,4-dinitrophenol	433.8	431.3		
sodium 4-nitrophenoxide	433.03	388.97	477.3	451.0

[a] M. J. Kamlet, R. R. Minesinger, E. G. Kayser, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, **36**, 3852 (1971). [b] Reference 15. [c] This is the major, long-wavelength peak. There is a much weaker peak in DMF at 433 nm and a shoulder in methanol at 382 nm.

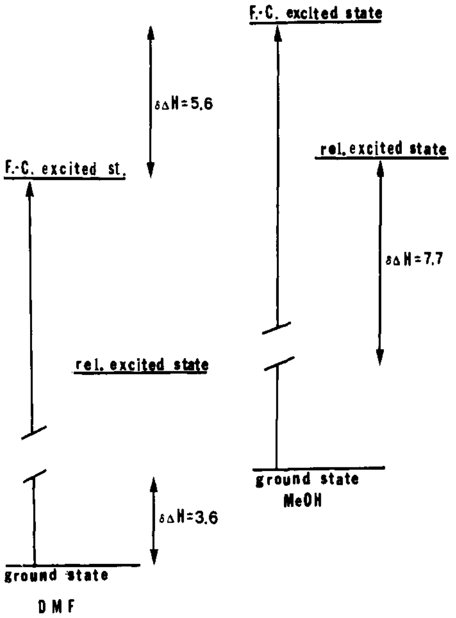

Figure 2. Relative energies (kcal/mol) of the ground states, the Franck-Condon excited states, and the relaxed excited states of 4-nitroaniline in a dipolar aprotic solvent (DMF) and in a polar protic solvent (MeOH).

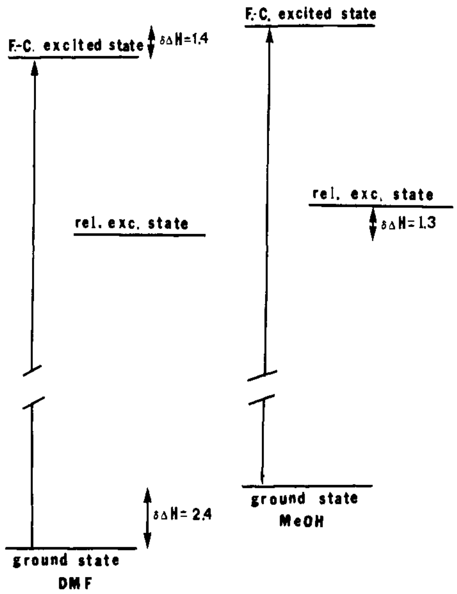

Figure 3. Relative energies (kcal/mol) of the ground states, the Franck-Condon excited states, and the relaxed excited states of 2-nitroaniline in a dipolar aprotic solvent (DMF) and in a polar protic solvent (MeOH).

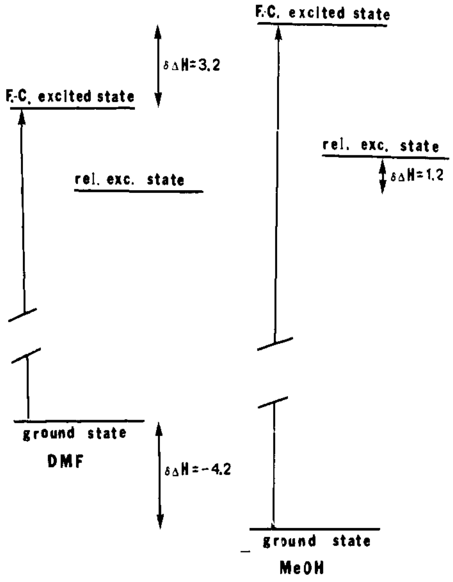

Figure 4. Relative energies (kcal/mol) of the ground states, the Franck-Condon excited states, and the relaxed excited states of 4-nitrophenoxide ion in a dipolar aprotic solvent (DMF) and in a polar protic solvent (MeOH).

On the basis of the above arguments attributing to factor (3) the principal cause of the blue shift, 4-nitrophenoxide should exhibit a very large blue shift as well as a decrease in the excited state solvent transfer enthalpy on relaxation. Both of these phenomena can be clearly seen (Table I, columns 2, 4, and 5).

Experimental Section

Materials. All compounds were commercial samples and were recrystallized or distilled where necessary until their melting point or refractive index agreed with the literature value. Solvents were dried and distilled before use.

Spectroscopic Measurements. Absorption spectra were measured on a Cary 17 spectrophotometer. The wavelength of each absorption maximum was corrected by running the spectrum of holmium oxide glass before or after each set of runs. The values are listed in Table II and are estimated to be accurate to ±0.1 nm or better. Fluorescence spectra were measured on a Perkin-Elmer MPF-2A fluorescence spectrometer. The instrument was calibrated periodically by means of the xenon 467.1-nm peak. Results are listed in Table II. Their accuracy is estimated to be ±1 nm or better.

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The Effect of Temperature on the Structure of Gaseous Molecules. 4. Molecular Structure and Barrier to Internal Rotation for Diboron Tetrabromide

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Abstract: The molecular structure of B_2Br_4 has been investigated by electron diffraction at nozzle temperatures of 23, 90, 150, and 305 °C. The molecule has a staggered equilibrium conformation (symmetry D_{2d}), with the following distances (r_a), angles, and root mean square amplitudes of vibration at room temperature: $r(\text{B–B}) = 1.689\ (16)$ Å, $r(\text{B–Br}) = 1.902\ (4)$ Å, $\angle\text{BrBBr} = 120.7\ (3)°$, $\angle\text{BBBr} = 119.8\ (2)°$, $l(\text{B–B}) = 0.0552$ Å (calculated from force field), $l(\text{B–Br}) = 0.0526\ (61)$ Å, $l(\text{B}\cdots\text{Br}) = 0.0948\ (110)$ Å, $l(\text{Br}\cdots\text{Br in BBr}_2) = 0.0744\ (36)$ Å; the parenthesized uncertainties are estimated 2σ. The average rotational barrier for the four temperatures based on a hindering potential assumed to have the form $2V = V_0(1 - \cos 2\phi)$ was found to be $V_0 = 3.07$ ($2\sigma = 0.33$) kcal/mol, higher than in either B_2Cl_4 (staggered) or B_2F_4 (planar). The estimated value of the torsional frequency is 18 cm^{-1}. The structure is discussed in comparison with those of B_2F_4 and B_2Cl_4, and a prediction for B_2I_4 is made.

Introduction

Previous gaseous electron-diffraction investigations in this laboratory on B_2F_4[1] and B_2Cl_4[2] have yielded values both for the structural parameters of the molecules and for the barriers hindering internal rotation. B_2F_4 was found to be a slightly hindered rotor with a potential barrier of about 0.42 kcal/mol and to have a potential minimum when the BX_2 groups are eclipsed (symmetry D_{2h}). B_2Cl_4, however, was found to have a potential minimum in the staggered conformation (symmetry D_{2d}) and a considerably higher barrier of about 1.85 kcal/mol.

Our continuing interest in the diboron tetrahalides has led us to a similar investigation of B_2Br_4. The molecule was known to be structurally similar to the others, i.e., two BX_2 groups joined by a B–B bond. Moreover, interpretations of spectroscopic data[3] strongly suggested the equilibrium conformation to be staggered (D_{2d} symmetry) in all three phases and thus to have a higher barrier to internal rotation than either B_2Cl_4 (staggered in the gas[2,4,5] and liquid,[4-6] eclipsed in the solid[4,7]) or B_2F_4 (eclipsed in all three phases[1,8,9]). Our particular interest was in the magnitude of the barrier, which we felt could be measured to good accuracy by electron diffraction, and in the geometrical details of the structure for comparison with B_2Cl_4 and B_2F_4. The description of our results follows.

Experimental Section

Samples of B_2Br_4 were prepared and purified for us by Dr. David Kohler and Professor David Ritter of the University of Washington using known procedures.[10] Decomposition of B_2Br_4 into BBr_3 and a blackish solid of unknown composition was observed by these investigators to occur at a rate of about 28% per h at 38 °C in the gas phase at 5 Torr. To minimize this decomposition our samples were stored in liquid nitrogen baths between experiments.

In some early diffraction experiments the ground glass joints between the sample bulbs (equipped with Teflon vacuum stopcocks) and the injection nozzle were sealed with a silicone-base grease. This proved unacceptable owing to reaction at the seal producing, apparently, $SiBr_4$ as a contaminant. The grease was replaced with a single wrap of 0.08-mm thick Teflon tape and the joint externally packed with Dux-Seal. For one set of experiments at high temperature (305 °C) the glass joint was replaced with a Monel Swagelok fitting having a Nylon front ferrule and used in conjunction with a newly designed nozzle.[11] During all diffraction experiments the sample bulbs were maintained at temperatures between 7.0 and 11.5 °C. A slow discoloration suggestive of some decomposition was noted, but no evidence of impurity was found in the diffraction data.

Diffraction photographs were made in the Oregon State apparatus with an r^3 sector at four different nozzle-tip temperatures (23, 90, 150, and 305 °C) using 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1. Exposures were made for 30-210 s with pressures in the apparatus of 1.3×10^{-6} to 1.7×10^{-6} Torr at nozzle-to-plate distances of 75.017-75.161 (long camera) and 30.011-30.151 cm (middle camera). Undiffracted beam currents were 0.31-0.44 μA with wavelengths of 0.056 58-0.057 26 Å calibrated in separate experiments from diffraction patterns of CO_2 ($r_a(\text{CO}) = 1.1646$ Å, $r_a(\text{O}\cdots\text{O}) = 2.3244$ Å). Remarkably, as in B_2F_4[1] and BeB_2H_8,[12] many of the plates were ruined by stains and streaks if developed immediately after exposure. As before, the problem was avoided by allowing the undeveloped plates

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