Thermosolvatochromism of Phenol Blue in Polar and Nonpolar Solvents

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Received: July 30, 2003; In Final Form: October 27, 2003

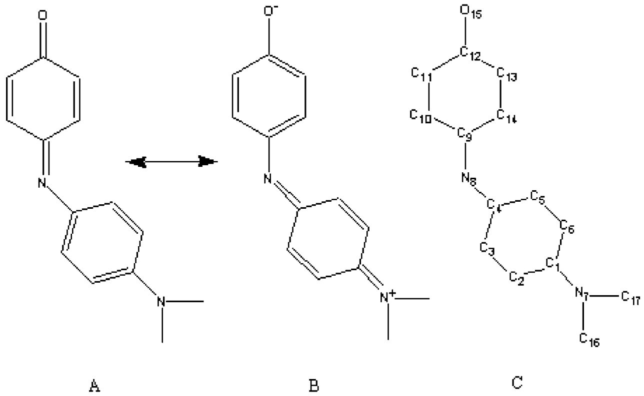
The solvatochromic properties of phenol blue [N-(4-dimethylaminophenyl)-1,4-benzoquinoneimine] have been investigated in polar and nonpolar solvents using variable-temperature ^{1}H NMR and electronic absorption spectroscopy. In acetonitrile, chloroform, and cyclohexane, protons on the quinoneimine ring are inequivalent at all temperatures, while in methanol an exchange process increasingly broadens the signals from these protons as the temperature is raised. The temperature-dependent absorption spectrum of phenol blue in methanol, acetonitrile, chloroform, and cyclohexane is reported, and the observed increase in peak frequency and bandwidth with temperature is found to exceed the predictions of continuum theory. The large increase in dipole moment on excitation results in a strong inductive contribution to the solvatochromism, and leads to large thermochromic shifts even in nonpolar solvents. The possible contributions of solvent-dependent electronic structure, low-frequency intramolecular vibrations, and conformational flexibility to the thermosolvatochromic properties of phenol blue are discussed. Evidence is presented for solvent dependence of the dipole difference $\mu_e - \mu_g$ between the ground and excited electronic states.

1. Introduction

Phenol blue (Scheme 1) is a positively solvatochromic dye[1] of the donor−acceptor polyene type, with interesting nonlinear optical properties.[2] A number of theoretical studies[3−7] have explored its solvent-dependent electronic properties, and the results suggest that the quinoneimine form (**1A**) makes the dominant contribution to the electronic structure of the ground electronic state. The observed red shift of the lowest-energy electronic transition with increasing solvent polarity (λ_{max} shifts from 552 nm in hexane to 684 nm in water[5]) stems from the increase in dipole moment of phenol blue in its excited electronic state, which resembles the zwitterionic resonance structure (**1B**). To the extent that the optical properties of phenol blue are described by the two-state model often employed for push−pull polyenes,[8,9] this molecule is expected to display interesting solvent effects on the frequencies and intensities of vibrations coupled to bond length alternation. Indeed, Hirota et al.[10] have reported red shifts with increasing solvent polarity for two Raman modes of phenol blue assigned to the C═N and C═O stretches. Even more interesting is their report that the putative C═N stretch, and to a lesser extent also the C═O stretch, has a peak frequency which depends on the wavelength used to excite the resonance Raman spectrum. This dispersion in the broad band at about 1450−1500 cm^{-1}, assigned to the C═N stretch, was observed in polar solvents such as methanol, DMSO, and chloroform, but not in nonpolar solvents, where "polarity" in this context is based on the absorption maximum of phenol blue. In methanol, the peak frequency of this vibration was reported to blue shift by 26 cm^{-1} as the excitation wavelength was decreased from 647 to 458 nm, while the more narrow C═O stretch at about 1640 cm^{-1} shifts by only a few wavenumbers over this same range.

Hirota et al.[11] have interpreted these interesting results using a model that considers the absorption line shape of phenol blue to be inhomogeneously broadened by solvent-induced perturbations to the electronic structure. They have presented a theoretical calculation to account for the dispersion, which treats the vibrational and electronic transitions as linearly coupled to the solvent relaxation. A key aspect of their model is that the dispersion is obtained only for Raman modes having vibrational dephasing times shorter than the solvent relaxation time. Painelli and co-workers[12−14] have also presented a model which accounts for a number of interesting solvent effects in push−pull polyenes, including dispersion in the Raman shift and nonlinear solvent response. They have also reported that the C═N stretch of phenol blue, in the *non*resonance Raman spectrum, is broader in more polar solvents.[13] Within the framework of the two-state model, they describe the electronic transition as inhomogeneously broadened by a range of ionicities induced by solvent interactions, where the ionicity represents the percent charge-transfer in terms of the contribution of the zwitterionic structure **1B** to the ground-state wave function.

SCHEME 1



Both of the above models qualitatively capture the observed dispersion of the broad Raman band at ~1480 cm^{-1}. However, it is puzzling that these solvent perturbations to the electronic

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10.1021/jp036235p CCC: $27.50

structure are not also reflected in broadening and dispersion of the carbonyl stretch, since solvent-induced changes in the relative contributions of **1A** and **1B** to the ground-state wave function should produce parallel changes in the C═N and C═O bond orders. In the model of Hirota et al.,[11] the stronger dispersion in the C═N stretch results from its faster vibrational dephasing time. If this is the case, then one wonders what is the physical basis for this faster dephasing time. In the picture due to Painelli et al., on the other hand, larger dispersion and larger solvent-induced broadening is predicted for vibrational modes having smaller excited-state displacements.[13] This seems to conflict with the observed resonance Raman spectra for phenol blue, in which the bands assigned to the C═N and C═O stretches are of comparable intensity.

Phenol blue has been previously observed to exhibit anomalous solvatochromic properties. According to theories which treat the solvent as a dielectric continuum,[15] the absorption maximum and bandwidth of a solvatochromic dye are functions of the solvent dielectric constant ϵ and refractive index n. Figueras[1] reported that hydrogen bonding interactions at the carbonyl and dimethylamino groups lead, respectively, to red and blue shifts of the absorption maximum, resulting in poor correlation with the predictions of continuum theory. In addition, Hirota et al.[16] found that the variance (second moment) of the absorption spectrum is not proportional to the peak frequency, as would be expected from continuum theory. However, this conclusion was based on neglect of the induction contribution to the solvent shift, which will be shown in this work to be large. Both the Hirota[10,11,16] and Painelli[12−14] groups have discussed the importance of solvent-induced heterogeneity of the electronic structure of phenol blue, and recently the latter[17] have pointed out the contribution of conformational degrees of freedom to the absorption width of phenol blue.

The concept of solvent-driven changes in electronic structure of donor−acceptor polyenes is not without controversy. Using quantum calculations and accounting for the solvent reaction field, Ratner et al.[7] concluded that even in very polar solvents the reaction field is insufficient to produce large geometric distortions of phenol blue in its ground electronic state. However, the strong solvent dependence of the first hyperpolarizability[2], β, which depends on the dipole moment difference $\mu_e - \mu_g$ between the excited and ground electronic states as well as the intensity and energy of the electronic absorption, argues that the ground- and/or excited-state structure of phenol blue depends on solvent. A recent paper by Serrano and Canuto,[18] who argue that the zwitterionic form of phenol blue makes an increasingly larger contribution to the ground-state structure in more polar solvents, explains the solvent dependence of β as a function of solvent-induced changes in the bond length alternation pattern.

The strong solvatochromism of phenol blue is tied to its large nonlinear optical response through the common dependence of both effects on the dipole moment difference, $\mu_e - \mu_g$. Temperature tuning of bulk solvent polarity results in a thermochromic response which we exploit in this work in order to investigate the importance of solvent-dependent intramolecular properties of phenol blue. If solvent polarity contributes to a range of ground-state electronic structures, such an effect would be diminished at higher temperature and would tend to cause a decrease in width of the absorption spectrum. On the other hand, low-frequency vibrational modes or conformational flexibility (e.g., bending or torsional motion) resulting in a variation in the distance between donor and acceptor groups could lead to an increase in absorption bandwidth with temperature. We employ variable temperature ^{1}H NMR to explore this conformational freedom directly, and find that a temperature-dependent exchange process of phenol blue takes place in methanol solution, but not in acetonitrile, chloroform, or cyclohexane. While the thermosolvatochromic response of phenol blue is found to exceed the predictions of continuum theory, it does not appear that conformational flexibility is the sole source of the discrepancy. We observe that the thermosolvatochromic properties of phenol blue appear to correlate with the solvent-dependence of the first hyperpolarizability, lending credence to the idea that the difference in the ground- and excited-state dipole moments of phenol blue depends on solvent.

2. Experimental Section

Phenol blue was purchased from Aldrich and recrystallized from a 1:1 mixture of ethyl acetate and petroleum ether. Phenol blue was found to undergo reactions in all solvents at different rates, particularly in methanol and chloroform, possibly as a result of acid-catalyzed hydrolytic decomposition.[19,20] It was found that the rate of reaction was slowed, although not eliminated, if the solvent was first distilled over calcium chloride to remove water. Sample integrity was confirmed using absorption spectroscopy. Absorption data were taken over a range of temperatures in cyclohexane, chloroform, methanol, and acetonitrile using a temperature-controlled cell, and were corrected to the concentration of the solution at room temperature. An absorption spectrum was also obtained in a liquid nitrogen temperature glass of 4:1 ethanol and methanol. This was obtained by quickly freezing the solution and using a rapid scan absorption spectrometer. The 77 K spectrum reported here is the average of twenty-five 45 ms scans.

Variable-temperature ^{1}H NMR spectra were obtained at 500.13 MHz with a Bruker DRX500 Avance spectrometer using a 3.5 s acquisition time, 7.5 kHz spectral width, 2 s relaxation delay, 3 μs (40°) pulse width, and 16 or 32 transients. The dynamic NMR full line shape simulations were performed with DNMR3 software (part of SpinWorks package). The temperature dependence of the chemical shifts was determined at low temperature (very slow exchange regime) and then extrapolated to the regions of intermediate and fast exchange.

Geometry-optimized structures of phenol blue were calculated using Hartree−Fock theory implemented with GAMESS software[21] and 6-31G* basis sets. Spectroscopic properties were calculated for the optimized geometry using the CI method in the ZINDO program,[22] which considered 122 singly excited configurations.

3. Results

Quantum Mechanical Calculations. The calculated ground-state geometry of phenol blue is compared to X-ray data in Table 1. In agreement with other quantum chemical studies,[3−7] the bond distances found here suggest that the ground state of the isolated phenol blue molecule is well-represented by resonance structure **1A**. However, there are some interesting discrepancies between the X-ray geometry and the calculated geometry. The experimental solid -state structure of phenol blue is suggestive of approximately equal mixtures of the **1A** and **1B** resonance forms. For example, the C12−O15 bond distance of 1.302 Å is intermediate between the typical lengths of 1.43 Å for a single bond (C−O) and 1.23 Å for a double (C═O) bond. The nearly equal lengths of the C4−N8 and N8−C9 bonds are *both* intermediate between the values for single and double bonds between carbon and nitrogen, and the C2−C3, C5−C6, C10−

TABLE 1: Calculated Geometry of Phenol Blue versus Crystallographic Data[a]

parameter	6-31G*	X-ray[5]
C1−N7	1.392	1.350
C1−C2	1.403	1.417
C2−C3	1.378	1.366
C3−C4	1.390	1.437
C4−C5	1.387	1.432
C5−C6	1.384	1.368
C1−C6	1.398	1.416
C4−N8	1.406	1.366
N8−C9	1.263	1.334
C9−C10	1.478	1.433
C10−C11	1.325	1.344
C11−C12	1.481	1.406
C12−C13	1.486	1.443
C13−C14	1.326	1.374
C9−C14	1.482	1.426
C12−O15	1.197	1.302
N7−C16	1.448	1.470
C2−C1−C6	116.8	117.6
C3−C4−C5	117.6	116.7
C10−C9−C14	116.5	117.5
C11−C12−C13	116.4	120.4
C4−N8−C9	124.1	125.8
C1−N7−C16	118.3	121.6
C2−C1−N7−C16	19.6	−3.3
C2−C1−N7−C17	169.1	−176.2
C3−C4−N8−C9	133.3	160.6
C4−N8−C9−C14	−5.9	−12.4

[a] Bond lengths are in angstroms and angles in degrees. Atoms are numbered as in Scheme 1C.

TABLE 2: Dipole Moments and GS → E*n* Transition Moments of Phenol Blue

state	dipole moment (Debye)		transition moment (Debye)	
(energy, cm^{-1})	INDO/S[a]	measured	INDO/S[a]	measured
GS (0)	4.07 (5.33[b])	5.80[c]		
E1 (23,700)	2.10		0.63	
E2 (26,000)	15.77	7.5−9[c]	3.53	4.96[d]

[a] This work. [b] This work, 6-31G*. [c] From ref 5. [d] This work, calculated from the absorption band in methanol at 20.4 °C assuming the entire band is from the GS → E2 transition.

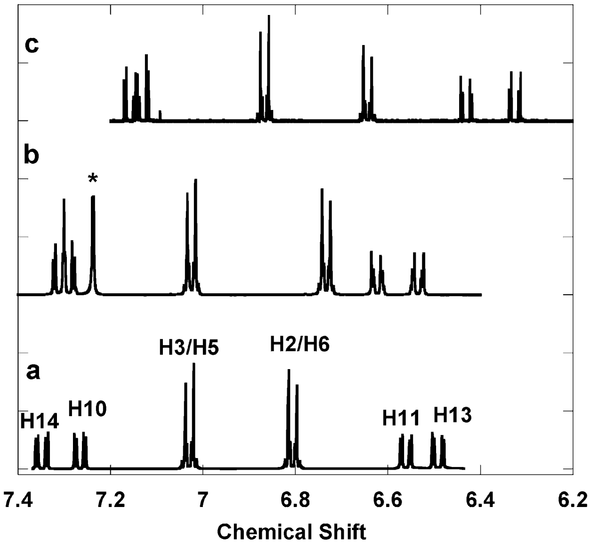

Figure 1. Room-temperature proton NMR of phenol blue in (a) CD$_3$CN, (b) CDCl$_3$, and (c) cyclohexane-d_{12}. The asterisk marks residual protiated solvent, and the assignments (Scheme 1C) are from ref 5.

C11, and C13−C14 bond lengths are similar in length to typical C═C bonds. In contrast, the calculated bond distance for C4−N8 is close to that for a typical C−N bond and the calculated N8−C9 bond distance is that of a C═N bond. Taken with the calculated bond length of the C12−O15 bond (about 1.2 Å), and inspection of the carbon−carbon bond length patterns for the two rings, the calculations support the conclusion that the resonance structure **1A** makes the dominant contribution to the ground electronic state, in agreement with experimental data for the solution-phase molecule. The solid-state structure, on the other hand, evidences significant contributions from both the **1A** and **1B** resonance forms. We expect calculations at the 6-31G* level to do an adequate job of accounting for the electronic structure in these kinds of systems. To the extent that this level of theory is a reliable indicator of gas-phase structure, comparison to the solid-state structure lends support to the idea that the electronic structure of phenol blue can depend on its environment.

INDO/S calculations performed at the optimized geometry reveal two closely spaced electronic states, E1 and E2, which are 23700 and 26 000 cm^{-1} above the ground state, respectively. The transition from the ground to the lower energy excited state has an oscillator strength of less than 0.005, and though the excited state is a mixture of configurations, this weak transition will be referred to here as the n-π^* transition. The calculated oscillator strength of 0.14 for the transition to the second excited state, referred to here as $\pi-\pi^*$, is in reasonable agreement with the measured value of 0.29, obtained in methanol at room temperature. The state dipole moments and transition dipole moments connecting these states to the ground state (GS) are shown in Table 2, from INDO/S calculations. The calculated ground-state dipole moment of 4.1 D (appropriate to the gas-phase molecule) is in fair agreement with the experimentally determined value of 5.8 D.[5] The GS dipole moment calculated at the 6-31G* level, 5.3 D, is in better agreement with experiment than the INDO result. The dipole moment of the E1 state is found to be 2.1 D and is perpendicular to the direction of the ground-state dipole moment. Though the GS → E1 transition is essentially forbidden, it is worth noting that the slight decrease in dipole moment in E1 compared to GS would lead to a only a small shift in the n-π^* transition with solvent polarity. Thus there is little reason to expect this forbidden state to contribute to the solvatochromic behavior of phenol blue. The transition moments of the GS → E1 and GS → E2 transitions were found to be parallel. The E2 state has a calculated dipole moment of 15.8 D, approximately parallel to the ground-state dipole moment and larger by a factor of about four. The calculated transition moment of 3.5 D is in fair agreement with the experimental value of about 5 D (methanol) obtained in this work from the integrated absorbance at room temperature. To summarize, INDO/S calculations support the interpretation of the solvatochromic properties of phenol blue in terms of an increase in dipole moment on excitation. The ground- and excited-state dipole moments will be considered to be parallel in the analysis of the solvatochromism.

NMR Spectroscopy. To explore the possibility of temperature-dependent changes in conformation of phenol blue, variable-temperature proton NMR spectra of phenol blue were measured in the deuterated solvents: methanol, acetonitrile, chloroform, and cyclohexane. Figure 1 compares the room-temperature NMR spectrum of phenol blue in acetonitrile-d_3, choroform-*d*, and cyclohexane-d_{12}. Figure 2 shows the proton NMR spectrum of phenol blue in CD$_3$OD at three different temperatures. The assignments given in Figures 1 and 2 are from ref 5, and the labels designate protons attached to carbons as shown in Scheme 1C. At all temperatures and in all solvents

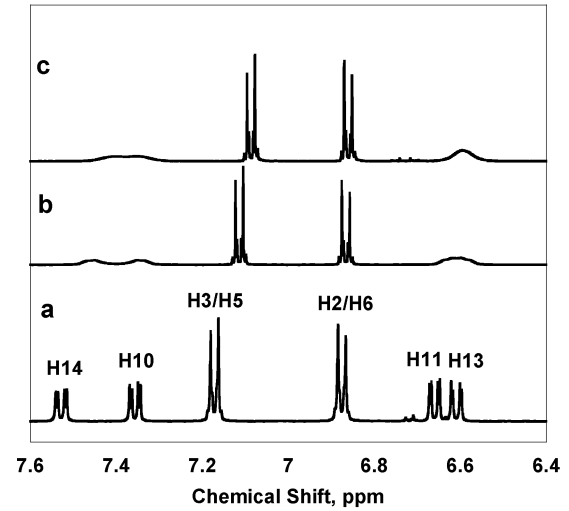

Figure 2. Proton NMR of phenol blue in methanol-d_4 at (a) −74 °C, (b) 25 °C, and (c) 55 °C.

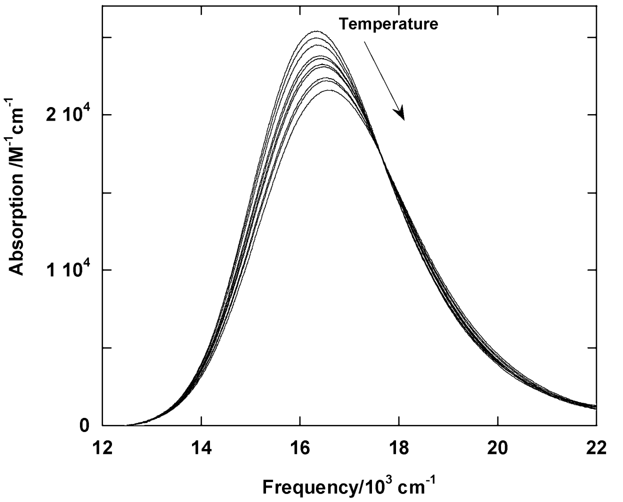

Figure 3. Absorption spectrum of phenol blue in methanol at −4.4, −1.4, 4.4, 15.8, 20.4, 25.8, 30.1, 41.4, 45.0, and 55.2 °C. The peak intensity decreases and blue shifts as the temperature increases.

TABLE 3: Thermosolvatochromic Properties of Phenol Blue

		absorption maximum, cm^{-1} versus temperature, °C		absorption width, cm^{-1} versus temperature, °C	
solvent	ϵ^a	slope, cm^{-1}/°C	intercept, cm^{-1}	slope, cm^{-1}/°C	intercept, cm^{-1}
acetonitrile	37.5	4.58	16960	5.09	3410
methanol	32.7	4.31	16275	4.84	3410
chloroform	4.81	8.27	16580	5.63	3084
cyclohexane	2.02	4.79	18020	3.92	3208

[a] Dielectric constant at 20 °C.

examined, the aromatic protons H3 and H5 are equivalent, as are H2 and H6. This is consistent with free rotation (on the NMR time scale) of the anilino group about the N8−C4 bond, which is a single bond in the putative resonance structure **1A** of the ground electronic state. The signals due to the protons on the quinoneimine ring, H10, H11, H13, and H14, are more interesting. In all solvents except methanol, the signals from these protons shift with temperature but do not broaden. In methanol, the resonances of the quinoneimine protons coalesce as the temperature is raised, in evidence of an exchange process that interconverts H11 and H13, and H10 and H14. In methanol, the signals from these pairs of protons have already coalesced at room temperature, whereas distinct signals are seen in the other solvents at room temperature and all higher temperatures investigated. These data suggest that there is a solvent-dependent barrier to a rearrangement that interconverts the aforementioned pairs of protons, and that this barrier is lower in methanol than in chloroform, acetonitrile, or cyclohexane. Rotation about the C9−N8 bond would interconvert these pairs of protons, as would the bending motion of the C9−N8−C4 group. Rate constants for the exchange in methanol were determined by comparing theoretical and experimental spectra between −75 °C and 55 °C. An Eyring plot was used to determine the enthalpy of activation, $\Delta H^{\ddagger} = 10.0$ kJ mol^{-1}, and the entropy of activation, $\Delta S^{\ddagger} = -187$ J mol^{-1} K^{-1}. The NMR data indicate that a torsion or bending motion interconverts the quinoneimine protons of phenol blue in methanol but not in acetonitrile, chloroform, or cyclohexane.

Absorption Spectroscopy. The solvatochromism of phenol blue has been investigated previously by a number of workers.[1,15,23] Kolling[23] found that in aprotic solvents the transition frequency of phenol blue is a linear function of the Kamlet-Abboud-Taft solvent polarity parameter,[24] π^*. Because solvent polarity can be tuned by varying the temperature, solvatochromic dyes also exhibit thermochromism.[25,26] The absorption spectrum of phenol blue was measured in this work over a range of temperatures in cyclohexane, chloroform, acetonitrile, and methanol. Figure 3 shows the results for methanol, and changes in the absorption maximum and width are summarized for all four solvents in Table 3. In general, the absorption band at ~600 nm shifts to the blue, the bandwidth increases, and maximum molar absorptivity decreases as the temperature is raised. In methanol solution, there is an apparent isosbestic point at about 17 700 cm^{-1} (567 ± 1 nm), which could be indicative of two equilibrating forms of phenol blue in methanol solution. This apparent isosbestic point is unique to methanol solution. For example, in cyclohexane, the crossing points of the absorption spectra in the range from 8 to 72 °C are spread over several hundred wavenumbers. We previously reported an isosbestic point in the temperature-dependent absorption spectrum of betaine-30 (a strongly solvatochromic dye) in methanol, not observed in other solvents.[26] As discussed in ref 26, the presence of an isosbestic point in solvatochromic systems with two equilibrating forms is unexpected because the temperature-tuned solvent shifts for the component spectra would be expected to blur the crossing point. We have speculated that the persistence of an isosbestic point in methanol solution, in the case of betaine-30 which strongly hydrogen bonds to methanol, is explained by the existence of a rather ordered (i.e., not strongly temperature-dependent) solvent shell about the chromophore. The present results suggest that there are also two distinct forms of phenol blue in methanol. However, it is not possible to deduce the nature of the two forms, nor is it possible to rule out the existence of two equilibrating forms, such as geometric isomers, in the other solvents.

The blue-shift with increasing temperature is expected on the basis of the decrease in solvent polarity. The absorption maximum $\tilde{\nu}_{max}$ and full-width at half-maximum $\Delta\tilde{\nu}_{1/2}$ were both found to increase linearly with temperature in all four solvents, with R values exceeding 0.99. The slopes and intercepts for the best fits to $\tilde{\nu}_{max}$ and $\Delta\tilde{\nu}_{1/2}$ versus temperature are given in Table 3. We also note that the integrated absorbance in all solvents decreases with temperature, moreso than expected on the basis of changes in the refractive index, revealing that the transition moment decreases as temperature increases.

Figure 4 shows the absorption spectrum in a 4:1 mixture of ethanol and methanol in liquid solution at room temperature

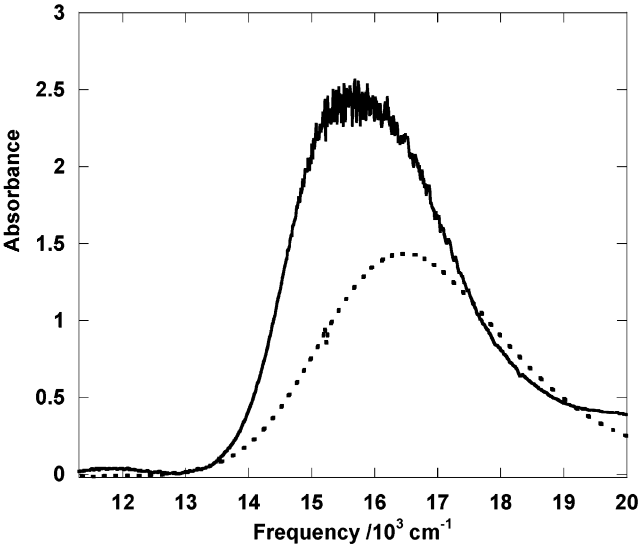

Figure 4. Absorption spectrum of phenol blue in a 4:1 mixture of ethanol and methanol, at liquid solution at room temperature (dotted line) and in the glass phase at 77 K (full line).

TABLE 4: Room Temperature Aborption Maximum $\tilde{\nu}_{\max}$ of Phenol Blue in Various Solvents

solvent	dielectric constant[a]	refractive index[a]	absorption maximum,[b] cm^{-1}
dimethyl sulfoxide	46.7	1.4773	16490
acetonitrile	37.5	1.3416	17120
dimethylformamide	36.7	1.4282	16800
nitromethane	35.9	1.3796	16910
nitrobenzene	34.8	1.55	16520
methanol	32.7	1.3265	16440
benzonitrile	25.2	1.5257	16740
ethanol	24.6	1.359	16500
acetone	20.7	1.356	17170
2-propanol	19.9	1.375	16760
butanol	17.5	1.397	16490
pyridine	12.4	1.507	16770
dichloroethane	10.4	1.442	16930
dichloromethane	8.93	1.421	16940
methylformate	8.5	1.3433	17290
tetrahydrofuran	7.58	1.405	17030
chloroform	4.81	1.443	16820
diethyl ether	4.33	1.35	18030
anisole	4.33	1.5143	17120
carbon disulfide	2.64	1.624	17780
benzene	2.275	1.4979	17380
carbon tetrachloride	2.238	1.4574	17690
1,4-dioxane	2.209	1.42	17500
cyclo hexane	2.023	1.4235	18110

[a] Ref 35. [b] Refs 1 and 23.

and in glassy solution at 77 K. The additional noise in the spectrum at 77 K is due to the high absorbance, the rapid scanning rate, and possibly also to imperfections in the glass. At room temperature the absorption spectrum is similar to that in pure methanol. When the mixture is cooled the absorption band shifts to lower energy and becomes narrower, consistent with the temperature-dependent trends observed in liquid solution. The width of the absorption spectrum $\Delta\tilde{\nu}_{1/2}$ decreases from about 3500 cm^{-1} at room temperature to 2700 cm^{-1} at 77 K, a decrease which is equivalent to the 800 cm^{-1} red shift of $\tilde{\nu}_{\max}$. The increased absorbance at lower temperature is qualitative (no correction was made for the change in sample concentration with temperature), but is consistent with the observed trends in liquid solutions, where the maximum molar absorptivity was found to be generally lower in less polar solvents and at higher temperature. There is no evidence from the spectrum at 77 K that the visible absorption band is a composite of more than one transition, and the underlying vibrational structure remains obscured at this temperature.

We next consider whether temperature-dependent peak frequencies and bandwidths can be explained using continuum theory, which considers the solute molecule to occupy a spherical cavity in a structureless liquid.[15,27−30] The frequency of maximum absorption is

$$\tilde{\nu}_{\max} = \tilde{\nu}^0{}_{\max} + \frac{2\vec{\mu}_g\cdot(\vec{\mu}_g - \vec{\mu}_e)}{hca^3}[f(\epsilon) - f(n^2)] + \frac{(\mu_g{}^2 - \mu_e{}^2)}{hca^3}f(n^2) \quad (1)$$

where $\tilde{\nu}^0{}_{\max}$ is the absorption maximum in the gas phase, a is the cavity radius, h is Planck's constant, c is the speed of light, and μ_g and μ_e are the ground- and excited-state dipole moments. Equation 1 is in cgs-esu units, and the second and third terms account for the orientational polarization and induction effects, respectively. The function $f(x)$ takes various forms, depending on how the polarizability of the solute is treated. Two standard approaches[31] are to neglect the solute polarizability ($\alpha = 0$) or to assume that it is related to the cavity volume by $\alpha = a^3/2$. In the first of these approaches, one uses $f(x) \equiv f_0(x) = (x - 1)/(2x + 1)$, and in the second we take $f(x) \equiv f_{1/2}(x) = (x - 1)/(x + 2)$. At the same level of approximation as eq 1, the solvent reorganization energy is

$$\lambda_{\text{solv}} = \frac{(\mu_e - \mu_g)^2}{hca^3}[f(\epsilon) - f(n^2)] \quad (2)$$

The solvent contribution to the width of the absorption spectrum (fwhm) is given by

$$\Delta\tilde{\nu}_{1/2} \cong 2.355\sqrt{2k_BT\lambda_{\text{solv}}} \quad (3)$$

The deficiencies of continuum theory are well-known: It is based on a point dipole approximation, and higher order multipolar interactions, dispersion forces, and changes in polarizability on excitation are neglected, and the predicted solvent shifts depend strongly on the poorly defined cavity radius a. Nevertheless, the theory has been applied successfully to explain trends in the solvent-dependent absorption (and emission) spectra of a number of solvatochromic dyes.[32−34] The solvatochromic properties of phenol blue have been previously analyzed using eq 1, employing the function $f_{1/2}$ for the orientation term and f_0 for the induction term.[1,15] In this work, we opted to use a consistent form of $f(x)$ for both terms. The absorption maxima for phenol blue in 24 different solvents were taken from refs 1 and 23 (see Table 4), and the best fit to eq 4 was found using linear regression:

$$\tilde{\nu}_{\max} = A + B[f_{1/2}(\epsilon) - f_{1/2}(n^2)] + Cf_{1/2}(n^2) \quad (4)$$

The best fit parameters were found to be: $A = 18900 \pm 500$ cm^{-1}, $B = -1760 \pm 250$ cm^{-1}, and $C = -4340 \pm 1650$ cm^{-1}. Replacing $f_{1/2}(x)$ by $f_0(x)$ led to a similar quality fit and similar physical conclusions, so the rest of the analysis will be based on the present results. Similarly, if we exclude solvents with large quadrupole moments (benzene and dioxane) or hydrogen bonding solvents (alcohols) from the analysis, there is no significant improvement in the fit and similar parameters A, B, and C are obtained. Figure 5 shows the calculated (best fit

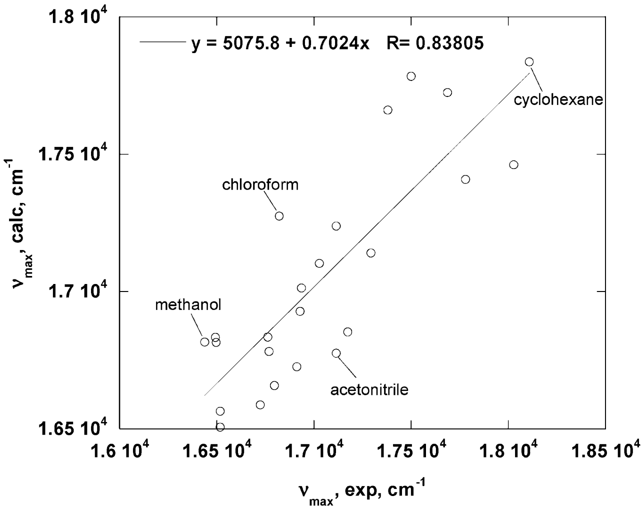

Figure 5. Calculated (best fit to eq 4) versus experimental peak frequency of phenol blue.

to eq 4) versus experimental peak frequency. We find $\tilde{\nu}_{\max}(\text{calc}) = 5076 + 0.7024\tilde{\nu}_{\max}(\text{exp})$ with a correlation coefficient of only 0.84. For comparison, analysis of Stokes shift data for a variety of solvatochromic dyes[33] was reported to give correlation coefficients R in the range 0.70 to 0.97, based on fits to the orientation term only. Figure 5 does not reveal any clear trend that would explain the physical basis for deviations from the simple model. For example, though hydrogen bonding may lead to an additional blue-shift not accounted for by eq 1, the data point for chloroform deviates more than that for the stronger proton donor methanol. We conclude that the solvatochromic model used here does a fair job of accounting for solvatochromism of phenol blue, and therefore may be used to make qualitative predictions about the thermochromic response.

The value of A from linear regression is identified with the gas-phase absorption maximum, and the coefficients B and C can be used to derive the ratio of the excited- and ground-state dipole moments, $\mu_e/\mu_g \approx 3.9$. The value of $\tilde{\nu}^0_{\max} \approx 18\,900$ cm^{-1} derived from the solvatochromic data is somewhat lower than the calculated absorption maximum of 26 000 cm^{-1}, while the dipole moment ratio is in good agreement with theory. However, taking into account the uncertainties in the coefficients B and C, the dipole moment ratio ranges from about two to seven. The dipole moment ratio extracted from the solvatochromic shift data is independent of the cavity radius. Assuming $a = 4.8$ Å as in ref 3, the ground- and excited-state dipole moments are estimated to be 2.4 and 9.2 D, respectively, compared to the values of 4.1 and 13.8 D from our quantum mechanical calculations. An experimental value of $\mu_g = 5.8$ D was given in ref 5.

We next examine whether the temperature dependence of the dielectric constant ϵ and refractive index n can explain the temperature dependence of the absorption maximum and line width of phenol blue. The temperature-dependent dielectric constants were taken from ref 35, and the refractive index at each temperature was estimated using room-temperature values of n and dn/dT from ref 36 (except for methanol where dn/dT was taken from ref 37) assuming that n is a linearly decreasing function of temperature. Neglecting the temperature dependence of the cavity radius as well as that of the ground- and excited-state dipole moments, eq 4 was used along with temperature-dependent values of ϵ and n to estimate the expected peak frequency shift from 0 to 50 °C in acetonitrile, chloroform, methanol, and cyclohexane. As shown in Table 5, the experimentally observed blue shift as temperature is raised from 0 to 50 °C exceeds the prediction of continuum theory by factors ranging from about two (methanol) to four (cyclohexane). However, the calculated values appear to capture the enhanced thermochromic shift in chloroform relative to the other three solvents. The enhanced thermosolvatochromic response in chloroform can be traced to the large size of the induction term and the somewhat larger value of dn/dT in this solvent compared to the other three.

TABLE 5: Thermochromic Shifts of Absorption Maximum and Halfwidth, in cm^{-1}: Predictions of Continuum Theory Compared to Experiment[a]

solvent	$\Delta\tilde{\nu}_{\max}$, exp	$\Delta\tilde{\nu}_{\max}$, calc	$\Delta(\Delta\tilde{\nu}_{1/2})$, exp	$\Delta(\Delta\tilde{\nu}_{1/2})$, calc
acetonitrile	230	67	255	161
chloroform	414	145	282	11
methanol	216	102	242	161
cyclohexane	241	63	196	0

[a] $\Delta\tilde{\nu}_{\max}$ is the peak frequency at 50 °C minus that at 0 °C, and $\Delta(\Delta\tilde{\nu}_{1/2})$ is the fwhm at 50 °C minus that at 0 °C.

Similarly, continuum theory can be used to estimate the increase in fwhm as temperature is raised. The absorption line shape contains contributions from Franck−Condon active vibrational modes. If one neglects the contribution of low-frequency vibrational modes ($h\nu < k_BT$) to the line shape, the temperature-dependence of the fwhm is entirely due to solvent broadening. Equations 2 and 3 were used to estimate the increase in fwhm $\Delta(\Delta\tilde{\nu}_{1/2})$ as the temperature is raised from 0 to 50 °C. The solvent reorganization energy was first found from

$$\lambda_{\text{solv}} = D[f_{1/2}(\epsilon) - f_{1/2}(n^2)] \tag{5}$$

where the parameter $D = B - C$ was obtained from the fitting parameters for eq 4. Equation 3 was then used to calculate $\Delta\tilde{\nu}_{1/2}$ at 0 and 50 °C. The resulting increases in fwhm are compared to experiment in Table 5. In all cases the experimental increase in fwhm is greater than predicted, but the deviations are greatest for the least polar solvents. Experimentally, the largest increase in spectral width is observed in chloroform; however, because $\epsilon \approx n^2$, continuum theory predicts only a small change. This comparison suggests that there are other contributions to the temperature-dependent line width in addition to changes in bulk solvent polarity.

Fluorescence Spectroscopy. Measurement of the intrinsic fluorescence of phenol blue was complicated by the presence of impurities. Though some literature reports have referred to phenol blue as nonfluorescent, others have reported the use of phenol blue as a fluorescent polarity probe.[38] In this work, two sources of fluorescence were identified as being from an impurity in the chemical as received and from a reaction product that resulted upon standing. Freshly recrystallized phenol blue exhibits very weak fluorescence, assumed to be intrinsic, that peaks at about 650 nm in methanol and in chloroform. The low fluorescence yield is easily understood from the quantum mechanical calculations, which place the weakly allowed n-π* transition below the strong $\pi-\pi$* responsible for the solvatochromism in absorption.

4. Discussion

The absorption maximum of phenol blue shows a strong thermochromic shift to higher frequency as temperature is increased in all four solvents examined. The large increase in dipole moment in the excited electronic state results in a significant contribution from induction, and thus even in nonpolar solvents there is a significant blue shift as temperature is raised. The neglect of the induction term in ref 16 may have contributed to the poor correlation that was observed for the width and peak frequency of the solvent-dependent absorption spectrum. The large difference between μ_e and μ_g contributes to the large hyperpolarizability reported for phenol blue.[2]

As shown in Table 5, dielectric continuum theory appears to qualitatively account for the solvent trends observed, i.e., larger thermochromism in chloroform than in acetonitrile, methanol and cyclohexane. However, in all cases the observed thermochromic shifts from 0 to 50 °C are more than twice as large as predicted using eq 1. In the case of protic solvents, decreased hydrogen bonding at higher temperatures would be expected to result in an additional blue shift, however, the discrepancy holds for aprotic as well as protic solvents. It is unlikely that the discrepancy between the calculated and experimental thermochromic shifts reported in Table 3 is the result of neglecting the temperature dependence of the cavity radius a in eqs 2 and 3. The cavity radius depends on the van der Waals volume of the solute, which is independent of temperature, though it may be considered to include the first solvation shell as well. At most, the magnitudes of the constants B and C, which are inversely proportional to the cavity volume, would decrease with temperature in proportion to the thermal expansion of the solution. This effect would be largest for chloroform as the change in density with temperature $d\rho/dT$ is larger than that of the other three solvents. If instead of keeping B and C constant, these parameters at 0 °C and 50 °C are scaled in proportion to the density, the thermochromic shift in chloroform is estimated to be 230 cm^{-1}, compared to 145 cm^{-1} when the cavity radius is taken to be independent of temperature. This approach, which clearly overestimates the temperature dependence of the cavity radius, results in a predicted thermochromic shift which is still smaller than the experimental shift of 414 cm^{-1}. Thus the enhanced thermochromic shift compared to the continuum theory prediction is not a result of neglecting the change in density of the solvent.

Implicit in all these arguments is the assumption that the ground- and excited-state dipole moments are independent of solvent and temperature, except to the extent that they change in response to the solvent reaction field as accounted for by the $f_{1/2}$ terms in eq 4. Solvent-induced changes to the electronic structure would confound the correlation between the absorption frequency and solvent dielectric properties. In the present study, we find the transition moment μ_{ge} varies with solvent (vide infra), thus there is evidence that the electronic structure does depend on solvent. In addition, Morley and Fitton[5] performed quantum mechanical calculations incorporating solvent effects on the closely related diethylindoaniline dye (phenol blue is dimethylindoaniline) and found that both the ground and excited-state dipole moments are larger in more polar solvent, but the increase is larger for the excited-state dipole moment. If indeed the dipole moment difference increases with increasing solvent polarity, such an effect would result in enhanced solvatochromic and thermosolvatochromic shifts compared to predictions which consider the dipole moments to be constant. Solvent-dependent state dipole moments could account for some of the scatter observed in Figure 5. In fact, the reported solvent dependence of the first hyperpolarizability β of phenol blue provides direct evidence for solvent-dependent state dipole moments. In the two-state model,[39] the first hyperpolarizability is given by

$$\beta = \frac{3(\mu_{ge})^2(\mu_e - \mu_g)}{2(h\nu_{ge})^2} \tag{6}$$

where μ_{ge} and $h\nu_{ge}$ are the transition dipole and transition energy, respectively. The experimental value of β for phenol blue in cyclohexane is about 15% of the value in chloroform.[2] From the integrated absorbance, we find $\mu_{ge} = 4.3$ D in chloroform and 4.8 D in cyclohexane. (Recall that $\mu_{ge} = 5.0$ D in methanol.) Taking these values along with the observed transition energies, the first hyperpolarizability of phenol blue would be about 6% *larger* in cyclohexane than in chloroform if the dipole difference is independent of solvent. This comparison strongly suggests that the dipole difference $\mu_e - \mu_g$ of phenol blue is much larger in chloroform than in cyclohexane. This could explain why the experimental solvatochromic shift in chloroform deviates positively from the best fit to eq 4, as shown in Figure 5. On the basis of the present study as well as the resonance Raman data of Hirota at al.,[10] chloroform appears to masquerade as a more polar solvent than would be expected on the basis of its bulk dielctric constant, and we have now traced this effect to enhanced dipole moment difference in chloroform solution.

The increase in absorption width with temperature was also found to exceed the predictions of continuum theory, especially for chloroform and cyclohexane, where $\epsilon \approx n^2$. It has been previously noted that continuum theory fails to correctly describe the temperature dependence of the solvent reorganization energy.[40] Experimentally, the largest increase in line width is observed in chloroform, and the significant increase in fwhm in cyclohexane cannot be attributed to changes in bulk solvent polarity. There are evidently additional temperature-dependent contributions to the line width, such as conformational disorder, low-frequency Franck−Condon active vibrations, and solvent-induced inhomogeneity in the electronic structure. Our NMR data implicate large amplitude bending or torsion only in methanol solution, for which the increase in fwhm with temperature is not particularly anomalous. The large temperature-dependence of the fwhm in nonpolar cyclohexane is difficult to explain in terms of a distribution of ground-state electronic structures, and at any rate such an effect would be smaller at higher temperature leading to a decrease in width. We are led to conclude that low-frequency vibrations of phenol blue contribute to the absorption width and its increase with temperature. In unpublished work, we have found the potential energy curves for bending of the C9−N8−C4 group and for relative rotation about the C9−N8 bond are both displaced in the excited electronic state. Thus these bending and torsional modes are Franck−Condon active and should contribute to the absorption line width.

The NMR data provide evidence of an exchange that interconverts pairs of protons on the quinoneimine ring when phenol blue is dissolved in methanol, but not in acetonitrile, chloroform, or cyclohexane. Bending of the C9−N8−C4 group and/or internal rotation about the C9−N8 bond could be responsible for this exchange. The negative entropy of activation strongly suggests a solvated transition state. We speculate that hydrogen bonding between methanol and phenol blue contributes to the lower barrier to bending in that solvent. Hydrogen bonding at the carboxyl group is expected to increase the electron withdrawing ability of the quinoneimine moiety, while hydrogen bonding at the diethylamino terminus would decrease the electron donating ability of that group. Both of these effects would result in less double bond character for the C═N bond, and thus a lower barrier to exchange of the quinoneimine protons, whether by bending or internal rotation. It is worth noting that the largest bandwidth and largest dispersion of the putative C═N stretch in the resonance Raman spectrum of phenol blue was observed in methanol solution.[10]

We also measured variable temperature ^{1}H NMR spectra of phenol blue in perdeuterated ethanol and found no broadening. Thus it appears that the interaction between phenol blue and methanol is quite specific. The closely related compound N-(4-diethylaminophenyl)-1,4-benzoquinoneimine or diethylindoaniline was also studied by variable-temperature ^{1}H NMR in several solvents,[5] including methanol-d_4. In that work, it was remarked that no apparent broadening of the protons on the quinoneimine ring was observed in the temperature interval −65 to 50 °C. Since this compound differs from phenol blue only in having a diethylamino rather than dimethylamino group on the aromatic ring, it is surprising that such different results were obtained. The difference in the barrier to exchange of quinoneimine protons in these two compounds could result from differences in the electronic structure and/or differences in hydrogen bonding with the solvent. As reported in ref 5, the absorption maximum of the diethylamino derivative is red-shifted compared to phenol blue in the same solvent, for example by about 350−400 cm^{-1} in acetonitrile, cyclohexane, and chloroform. This suggests that the electronic structures of the two compounds are different. In this study as well as that of ref 5, it was noted that in all solvents the ^{1}H NMR signals shift to higher field with increasing temperature and decreasing solvent polarity.

Finally, we consider briefly the possible connection between the present results and the dispersion and width of the resonance Raman band for the C═N stretch, reported by Hirota et al.[10,11,16] In ref 16, the C═N stretch was reported to be relatively broad (on the order of 30 cm^{-1} in methanol), and the line width was found to decrease with decreasing solvent polarity as judged by the frequency of the phenol blue absorption band. In the strongly hydrogen bonding solvent *m*-cresol, the breadth of the C═N stretch was too large to be determined.[9] In contrast, the resonance Raman band assigned to the C═O stretch, which has a solvent-dependent peak frequency like that of the C═N stretch, shows only small dispersion and has a much smaller line width (about 15 cm^{-1} in methanol[41]). In addition, it was reported that the width of the C═O stretch is fairly independent of solvent.[10] As noted previously, if the width and dispersion of the C═N stretch are related to the solvent-dependent distribution of ionicities, then parallel effects would be expected for the C═N and C═O Raman bands. The absorption line widths of phenol blue are not appreciably broader in polar than nonpolar solvents. For example, the fwhm is similar in chloroform and cyclohexane, but dispersion in the C═N Raman frequency is observed in the former but not the latter. This argues against the idea that there is a distribution of ground-state electronic structures in more polar solvents.

Low-frequency vibrations can serve to dephase higher frequency vibrational modes to which they are coupled.[42] Torsional motion or bending involving the C9−N8−C4 group can reasonably be expected to couple more strongly to the C═N bond than to the C═O bond. Perhaps this coupling contributes to the larger line width for the C═N stretch compared to that of the C═O bond in both resonance and nonresonance Raman spectra.[10,13] Alternatively, in a slow-modulation picture, conformational heterogeneity along the bending or torsion coordinate contributes to the line width of the C═N stretch and perhaps also to the observed dispersion in its peak frequency as the excitation wavelength is varied. As suggested by the NMR results reported here, the internal motion responsible for exchange is of much larger amplitude in methanol than in other solvents, consistent with the observation that the width of the C═N stretch is greatest in methanol, compared to chloroform, acetonitrile, and cyclohexane.

5. Conclusions

Analysis of the thermosolvatochromic response of phenol blue suggests that the electronic structure of phenol blue, and in particular the dipole difference $\mu_e - \mu_g$, is solvent dependent. Dielectric continnum theory fails to capture the increase in width of the absorption spectrum with increasing temperature, revealing a considerable contribution from low-frequency Franck−Condon active torsional and/or bending motions to the spectrum. We suggest that these low-frequency motions may contribute to the enhanced width and dispersion of the C═N stretch, compared to the C═O stretch, that has been reported in the Raman spectrum of phenol blue.

Acknowledgment. The support of the National Science Foundation (CHE-0202784) is gratefully ackowledged. We thank Prof. Richard Williams for helpful comments concerning the NMR spectra.

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