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Fundamental Studies on the Structure and Spectroscopic Behavior of Phenol Blue

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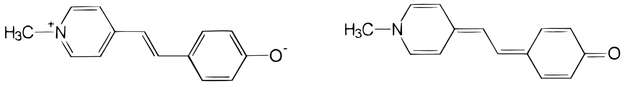
The structure and spectroscopic properties of Phenol Blue [*N*-(4-dimethylaminophenyl)-1,4-benzoquinoneimine (**4**)], which can exist in principle either as a zwitterion (**A**) or as a quinoneimine (**B**), have been assessed both experimentally and theoretically using molecular orbital methods. ^{13}C NMR evidence on the more soluble diethylamino derivative (**6**) strongly suggests that the molecule exists purely as the quinoneimine (**B**) both in protic solvents and in aprotic solvents of low and high dielectric constant. Theoretically, the solvatochromic shift of the dye in aprotic solvents, calculated using the PM3/COSMO method, shows a good correlation with the experimental data and arises because solvents with large dielectric constants exert a much greater stabilizing influence on the more polar excited state than they do on the ground state. In protic solvents, the larger bathochromic shifts observed are attributable to both a dielectric effect and a separate hydrogen bonding contribution from the solvent. In water, Phenol Blue is predicted to form a stable trihydrate which is calculated at the CNDOVS level of theory to absorb at a significantly longer wavelength than the unsolvated structure in line with the experimental data.

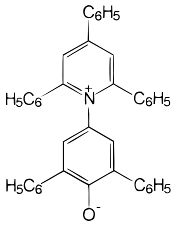
Introduction

Solvent has a pronounced effect on the visible absorption spectra of many polar conjugated organic molecules. In some cases, the absorption moves to shorter wavelength with increasing solvent polarity, while in other cases the reverse is true.[1] For example, both Brooker's merocyanine [1-(4-aza-4-methylphenyl)-2-*trans*-(4-oxyphenyl)ethene (**1**)][2,3] and Reichardt's betaine [(2,4,6-triphenyl-1-pyridinium)-*N*-(2,6-diphenyl-4-phenoxide) (**2**)[4−7] exhibit *negative solvatochromism* with the absorption bands moving from 620 and 731 nm in chloroform respectively to 442 and 453 nm in water. In contrast, both Nile Red [7-diethylamino-3H-1,2-benzophenoxazine-3-one (**3**)][8−10] and Phenol Blue [*N*-(4-dimethylaminophenyl)-1,4-benzoquinoneimine (**4**), also called indoaniline],[8,11−16] exhibit *positive solvatochromism* with the absorption moving in the opposite direction from 484 and 552 nm in hexane to 593 and 684 nm in water, respectively.



A **B**

(1)



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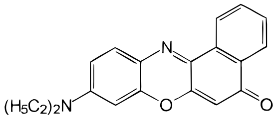

(3)

The large shifts observed for these molecules have been rationalized in physical organic chemistry using multiparameter scales of solvent polarity[1,17,18] which attribute the solvatochromic shift to the sum of a number of effects measured by the parameters such as π^*, α, and β, where the π^* parameter is a measure of the exoergic effects of solute/solvent, dipole/dipole, and dipole/induced dipole interactions, and the α and β parameters are empirical measures of the ability of the bulk solvent to act either as a hydrogen bond donor or hydrogen bond acceptor, respectively. Other more complex scales of solvent polarity have been described,[1] but all of these are essentially empirical and generally rely on the measured interactions or properties of the given solvent with some other substance.

In contrast to this multiparameter physical chemistry approach, we have theoretically modeled the solvatochromic shift of Brooker's merocyanine (**1**) using a simple molecular orbital method combined with a continuum solvation model, which does not invoke a range of empirical solvent parameters.[19] In this approach, we have proposed that the solvatochromic shift can be represented by two distinct effects. The first effect arises from interactions between the molecule and the dielectric field of the solvent, while the second arises from specific hydrogen bonding interactions between the solvent and the lone pair electrons of the exocyclic oxygen. Justification for this treatment is provided experimentally by (a) the smooth change in the position of the low-energy absorption maximum of (**1**) with increasing dielectric constant of aprotic solvents[19a] and (b) the presence in the crystal structure of two distinct water molecules which are hydrogen bonded to the exocyclic oxygen.[20] Although the merocyanine can in principle exist in two canonical forms, it has been universally proposed that the large negative solvatochromic shift observed is attributable to the zwitterionic form (**1A**) in polar solvents and the quinone form (**1B**) in nonpolar solvents. However, our recent experimental and theoretical studies have demonstrated that the molecule exists mainly as a zwitterion (**1A**) in *all* solvents.[19a]

Similar arguments have been proposed to explain the origin of the large positive solvatochromic shift of Phenol Blue where

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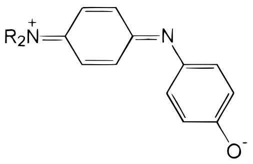
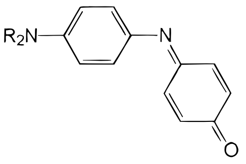
it has been suggested that the contribution of the zwitterion (**4A**) increases with increasing solvent polarity at the expense of the neutral quinoneimine (**4B**). There have been a number of theoretical studies on the structure and spectra of Phenol Blue in the gas phase using the HMO,[21] CNDO/2, and PPP methods,[22−23] and more recently[24] using a combination of the AM1 method[25] for the structure, coupled with the INDO/S method[26] for the calculation of transition energies. In this later study,[24] the relationship of the torsion angle between the aniline and quinone rings and the position of the absorption maximum was explored, where it was found that the absorption shifts to longer wavelength with increasing torsion angle. The same procedure has been applied to calculate the spectra of 23 derivatives of indoanilines and a good correlation has been claimed with experimental data.[27] A similar coupled approach has been used to calculate the molecular hyperpolarizability of Phenol Blue containing either donor or acceptor groups in the quinone ring.[28] Hyperpolarizability calculations have been reported also on two conformers of 4-aminoindoaniline (**5**)[29] but this time using both the PM3 method[30] and density functional theory.[31] The relationship between the π-conjugation size of indoaniline dyes and the spectra has been calculated using the INDO/S method where it has been shown that the absorption moves to shorter wavelength with an increasing number of aromatic rings at the quinone end of the molecule.[32]



(A)



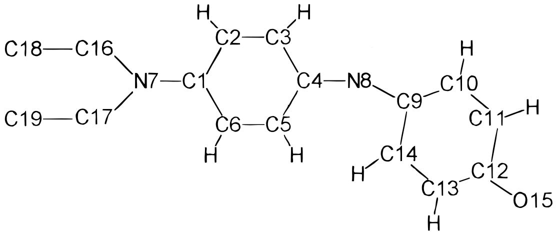
(B)

4 R=CH_3
5 R=H
6 R=C_2H_5

Solvent effects on the spectra of Phenol Blue have been explored using the QCFF/SOL method, which incorporates both permanent and induced dipoles for the solvent.[33] The results suggest that the quinoneimine (**4B**) is favored over the zwitterion (**4A**) (which was constructed from optimized fragments rather than the complete molecule) in both polar and nonpolar solvents, but the predicted absorptions at 437 and 384 nm, respectively,[33] are both too short by comparison with experimental data (see later). More thorough molecular orbital calculations using the INDO/S method coupled with a self-consistent reaction field lead to essentially the same conclusions with the results best interpreted if the quinoneimine is assumed to be favored over the zwitterion in both water and in the gas phase with predicted absorptions at 456 and 383 nm, respectively.[34] However, recent ab initio calculations on the structure of Phenol Blue, coupled with spectroscopic calculations at the INDO/S level, are contradictory and suggest that the zwitterion (**4a**) is more stable than the quinoneimine (**4b**) in polar solvents, with the reverse true in nonpolar solvents.[35]

A number of these studies can be criticized, however, either because the optimized gas-phase structure used for the subsequent INDO/S spectroscopic calculations does not correlate particularly well with experimental data available in the Cambridge Structural Database,[36] especially in relation to the key C1−N7, C4−N8, N8−C9, and C12−O15 bond lengths of the dye (Scheme 1), which will have a marked effect on the calculated transition energies (see later) or because specific hydrogen bonding interactions between protic solvents and the lone pair electrons at the heteroatoms of the dye have been ignored.

SCHEME 1: Numbering Convention for the Indoanilines 4−6



The present work has been carried out to experimentally assess the structure of the dye in solution by synthesizing the more soluble diethylamino derivative (**6**) and analyzing the ^{1}H and ^{13}C NMR spectra in range of protic and aprotic solvents with varying dielectric constants in an attempt to identify the canonical form(s) responsible for the absorption. Theoretical calculations have been performed also on the indoaniline (**4**) at several levels of theory to investigate the large effect of solvation on the structure both in terms of the dielectric effect of the solvent and its hydrogen bonding ability.

Methods of Calculation

Molecular orbital calculations were carried out on empirical structures for Phenol Blue (**4**) using the AM1[25] and PM3[30] methods of the MOPAC 93 Program[37] with full optimization of all bond lengths, angles, and torsion angles except where stated otherwise. The atom numbering convention used is shown above (Scheme 1). The effect of solvents of varying dielectric constant (ϵ) on the structures and energies of the indoaniline (**4**) were assessed at the AM1 and PM3 levels using the COSMO method[38] incorporated in the MOPAC 93 program. In this solvation model, the solute molecule is embedded in a cavity constructed from the intersecting van der Waals spheres of the component atoms surrounded by a dielectric continuum of permittivity ϵ. The surface between the continuum and the solute is then partitioned into a large number of segments and the interaction between the charge density at each segment polarizes the surrounding medium and produces a reaction field which in turn acts on the solute. Typical solvents used in the calculations included tetrahydrofuran ($\epsilon = 7.52$), acetone ($\epsilon = 21.0$), and dimethyl sulfoxide ($\epsilon = 47.2$) (keywords for the calculation in tetrahydrofuran: prec pm3 ef xyz geo-ok eps = 7.52). Spectroscopic calculations were carried out on the fixed ground state geometry using the multielectron configuration interaction (MECI) treatment in MOPAC 93 which considers 100 configurations (50 singlets, 45 triplets, and 5 quintets) between the three highest occupied and two lowest unoccupied molecular orbitals (keywords for the ground state calculation in water: pm3 prec 1scf. xyz eps=80.1 ef geo-ok meci singlet c.i.=5 root=1 vectors), and the transition energy evaluated from the difference between the heats of formation of the modified ground state energy and the first excited singlet state energy (same keywords except: root=2 and open(2,2) added). The spectra were calculated also using the CNDOVS method, which has been specifically developed for dyes and pigments, with the spectroscopic constant adjusted to 0.45 and the core coefficient of 0.33 retained for the heavy atoms.[39] Molecules and crystal structures were displayed and analyzed using the SYBYL molecular modeling package.[40]

TABLE 1: ^{13}C NMR Data Obtained for Structure 6^a

		chemical shift (ppm)									
solvent	ϵ	C1	C2	C3	C4	C9	C10	C11	C12	C16	C18
C_6D_6	2.28	147.5	111.7	126.4	131.3	153.5	139.4	142.5	187.0	44.22	12.68
$CDCl_3$	4.81	148.3	111.7	127.9	131.1	152.8	138.9	142.4	188.0	44.73	12.68
C_5D_5N	13.3	149.0	112.3	127.6	131.3	153.2	139.8	142.9	188.1	44.82	12.81
$(CD_3)_2CO$	21.0	149.1	112.6	128.4	131.6	153.4	139.7	143.2	187.8	45.12	12.85
CD_3OD	33.0	149.0	111.7	127.5		151.5	138.4		187.9	44.24	11.51
$(CD_3)_2SO$	47.2	148.2	111.8	127.9	130.6	151.8	138.4	142.3	186.9	44.15	12.60
$CH_3CONDCH_3$	179.0	149.3	112.8	127.8	130.8	153.1	139.9	143.3	188.1	45.19	12.98

[a] Carbons at the 5, 6, 13, 14, 17, and 19 positions are essentially equivalent to those at the 3, 2, 11, 10, 16, and 18 positions. ϵ is the dielectric constant of the nondeuterated solvent.

TABLE 2: ^{1}H NMR Data Obtained for Structure 6^a

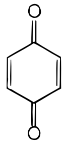
		chemical shift (ppm)								coupling constant (Hz)		
solvent	ϵ	H2	H3	H10	H11	H13	H14	H16	H18	J2,3	J10,11	J13,14
C_6D_6	2.28	6.37	6.98	7.18	6.50	6.47	7.20	2.86	0.82	9.86	9.83	10.05
$CDCl_3$	4.81	6.73	7.07	7.33	6.65	6.57	7.38	3.44	1.23	9.10	9.86	10.15
C_5D_5N	13.3	6.79	7.28	7.34	6.62	6.56	7.46	3.30	1.08	9.86	9.86	10.06
$(CD_3)_2CO$	21.0	6.70	6.94	7.16	6.43	6.38	7.30	3.37	1.07	9.12	9.87	10.19
CD_3OD	33.0	6.82	7.12	7.35	6.60	6.58	7.46	3.50	1.23	9.10	*b*	*b*
$(CD_3)_2SO$	47.2	6.79	7.06	7.30	6.57	6.53	7.38	3.44	1.16	8.88	9.84	10.15
$CH_3CONDCH_3$	179.0	6.74	7.15	7.37	6.61	6.58	7.43	3.48	1.20	9.11	*b*	*b*

[a] Protons at the 5, 6, 17, and 19 positions are essentially equivalent to those at the 3, 2, 16, and 18 positions. [b] Peaks at the 10, 11, 13, and 14 positions in deuterated methanol are inadequately resolved to measure the coupling constants. ϵ is the dielectric constant of the nondeuterated solvent.

Discussion

Most of the experimental studies published on Phenol Blue (**4**) have attributed the large solvatochromic shift to a distinct structural change in moving from nonpolar to polar solvents. Indeed, recent resonance Raman spectra of the dye in various solvents ranging from protic solvents such as ethylene glycol to nonpolar solvents such as ethane near their critical densities[41] are highly supportive. For example, both the positions and intensities of the $C{=}N$ and $C{=}O$ stretching bands show large solvent-induced shifts which appear to correlate well with the shift in absorption peak reflecting the dependence of the structure on the solvent used for measurement.[41] Further support is provided also by recent theoretical calculations on Phenol Blue at the ab initio MP2/STO-3G level,[35] which have suggested that the solvatochromic shift arises because the zwitterion (**A**) is more stable in polar solvents than the quinoneimine (**B**), with the reverse being true in nonpolar solvents. However, as our experimental and theoretical studies appear to conflict with these recent studies and with much of the established literature, we will discuss each piece of our evidence in turn.

1. NMR Analysis. In these studies, the diethylamino derivative (**6**) of Phenol Blue was synthesized for both ^{1}H and ^{13}C NMR analysis (Tables 1 and 2) as it was found to be much more soluble in a wide range of solvents than the parent (**4**). In the postulated change from the zwitterion (**A**) to the quinoneimine (**B**), the largest electronic effect would be expected at those atoms which are directly connected to, or in the vicinity of, either the positive nitrogen or negative oxygen atoms. ^{13}C NMR chemical shift data on atoms, C1, C2, and C12, therefore, should provide a good indication of the structural changes induced by increasing solvent polarity and/or hydrogen bonding effects. In model compounds for the right-hand ring of the quinoneimine (**B**), such as 1,4-benzoquinone (**7**) and 4,4-dimethylcyclohexa-2,5-dien-1-one (**8**), the carbonyl carbon resonates at 187.1[42a] and 185.8 ppm,[42b] respectively, in $CDCl_3$, while the imino carbon of 1,4-benzoquinone dioxime (**9**) resonates at 150.4 ppm in $(CD_3)_2SO$ (this work). In model compounds for the left-hand ring, such as *N*,*N*-diethylaniline (**10**), the carbon attached to the nitrogen atom resonates at 147.8 ppm in $CDCl_3$ and those in the two ortho positions of the ring resonate at 111.9 ppm.[43a]



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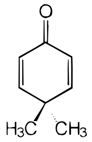

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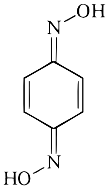

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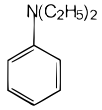

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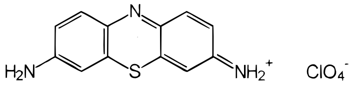


(11)

In contrast, in model compounds for the right-hand ring of the zwitterion (**A**), such as the phenoxide anion, the carbon attached to oxygen now resonates at 168.1 ppm.[42c] However, there are few published spectra of model compounds for the left-hand ring of the zwitterion with the exception of thionin perchlorate (**11**),[43c] though it is difficult here to absolutely assign the resonance of the carbon attached to the exocyclic nitrogen. In aniline, the carbon attached to nitrogen resonates at 146.4 ppm in $CDCl_3$, but on protonation to form the hemisulfate, the resonance of the same carbon moves upfield to 139.8 ppm in $^2H_6$ dimethyl sulfoxide.[43b] There are no resonances between 140 and 150 ppm in the spectrum of thionin perchlorate (**11**) in $^2H_6$ dimethyl sulfoxide,[43c] but we assign the single distinct resonance at 139.0 ppm to the carbon attached to the exocyclic protonated nitrogen of the ring.

An analysis of the ^{13}C chemical shifts for the indoaniline (**6**) shows the resonances for carbon C1 of the anilino ring vary from 147.5 to 149.0 ppm and those for carbons C2 and C6 vary

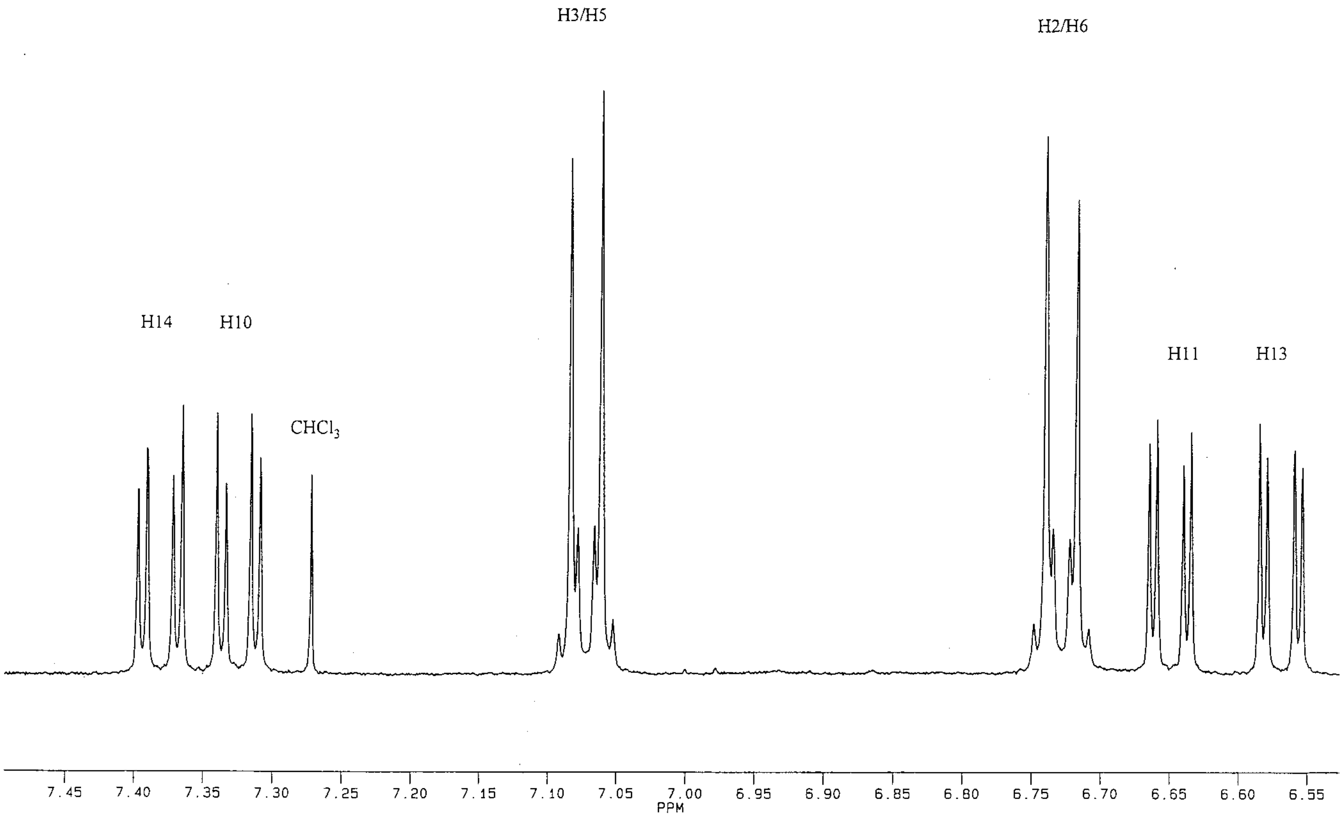


Figure 1. ^1H NMR spectrum of Diethylindoaniline (**6**) in $CDCl_3$ at 50 °C.

from 111.7 to 112.6 with no significant solvent-induced change produced in aprotic solvents either on moving from a low dielectric constant in deuterated benzene ($\epsilon = 2.28$) to deuterated acetone ($\epsilon = 21.0$), dimethyl sulfoxide ($\epsilon = 47.2$), or *N*-methylacetamide ($\epsilon = 179$), or in moving to protic solvents such as deuterated methanol ($\epsilon = 33.0$) where hydrogen bonding effects might have been expected to contribute to a structural change (Table 1). These chemical shifts imply that the anilino ring of the indoaniline (**6**) has very similar aromatic character to that of *N*,*N*-diethylaniline (**10**). Furthermore, the corresponding ^{13}C chemical shift for carbon C12 in the other ring of the indoaniline (**6**) also appears to be unaffected by large changes in the dielectric constant of the solvent used for measurement or the presence of a hydrogen bonding donor and resonates between 186.9 and 188.0 ppm (Table 1) and appears to be identical in character to the carbonyl carbon in benzoquinone. A similar picture emerges for the ^{13}C chemical shift of C9, which appears to be similar to the imino carbon in 1,4-benzoquinone dioxime (**9**) and resonates between 151.5 and 153.5 ppm (Table 1).

The ^1H NMR spectrum of the indoaniline (**6**) shows a number of surprisingly features (Figure 1). Six distinct resonances are present in the aromatic region corresponding to protons H2, H3, H5, H6, H10, H11, H13, and H14 located at the C2, C3, C5, C6, C10, C11, C13, and C14 ring positions (Scheme 1), all of which are influenced by changes in the dielectric constant of the solvent used for measurement (Table 2). In $CDCl_3$, there are two sharp absorptions centered at 6.73 and 7.07 ppm, corresponding to four protons of an AA′BB′ system, which are assigned to the two equivalent protons H2/H6 and the two equivalent protons H3/H5, respectively, on the basis of the shifts found for the ortho and meta protons in *N*,*N*-diethylaniline (**10**) which resonate at 6.65 and 7.20 ppm, respectively, in the same solvent.[43a] The protons in the other ring, however, are not equivalent, with two doublet of doublets centered at 6.65 and 6.57 ppm which we assign to protons H11 and H13 on the basis of the shift found for the four equivalent protons in 1,4-benzoquinone (**7**) which resonate at 6.83 ppm.[43d] There are two further doublets in the spectrum of the indoaniline (**6**) centered at 7.33 and 7.38 ppm (Figure 1) which we assign to protons H10 and H14 on the basis of the shift found for the protons in the poorly resolved spectrum of 1,4-benzoquinone dioxime (**11**).[43e] However, a more detailed examination of the spectrum of (**11**) in $(CD_3)_2SO$ (this work) shows that both trans and cis forms are present in solution, in a ratio of around 2:1; the two unshielded ring protons of each form resonate at similar field to the four equivalent protons in 1,4-benzoquinone (**7**) at 6.70 and 6.73 ppm, respectively, while the two other ring protons which are shielded by the hydroxyl groups resonate at 7.17 and 7.13 ppm, respectively. An analysis of the coupling constants of **6** show that the resonance at 7.38 ppm is clearly coupled to that at 6.57 ppm with $J_{13,14} = 10.15$ Hz, and the resonance at 7.33 ppm is clearly coupled to that at 6.65 ppm with $J_{10,11} = 9.86$ Hz.

The clear separation of the resonances of H11 and H13, and H10 and H14, relative to the resonances of H2/H6 and H3/H5 which are not separated and equivalent, may arise from a number of factors. Recent calculations using density functional theory have claimed that there are two stable conformers of 4-aminoindoaniline (**5**),[29] where the quinone ring is displaced below the plane of the anilino ring with a torsion angle C5−C4−N8−C9 of either 31.5 or 45.2°, and which differ in energy by only 0.5 kcal mol^{-1}. It is possible therefore that the separate resonances observed for H11 and H13, and those for H10 and H14 in diethylindoaniline (**6**), arise because of the presence of two distinct conformers in solution. However, this possibility appears to be unlikely for two reasons: first, the visible absorption spectrum of **6** shows a single band in *all* solvents, whereas other conjugated molecules which are known to have different conformations in solution, such as the merocyanine

TABLE 3: Calculated Geometries of Phenol Blue (4) versus Crystallographic Data[a]

parameter	AM1	PM3	AM1/COSMO	PM3/COSMO	AM1/COSMO#	PM3/COSMO#	TEYGOT (**12**)
C1−N7	1.404	1.444	1.410	1.448	1.380	1.400	1.350
C1−C2	1.418	1.404	1.418	1.404	1.424	1.414	1.417
C2−C3	1.385	1.386	1.385	1.387	1.381	1.381	1.366
C3−C4	1.414	1.400	1.415	1.400	1.418	1.409	1.437
C4−C5	1.411	1.400	1.411	1.400	1.413	1.403	1.432
C5−C6	1.386	1.386	1.387	1.387	1.383	1.382	1.368
C1−C6	1.417	1.404	1.415	1.403	1.422	1.413	1.416
C4−N8	1.406	1.426	1.404	1.429	1.399	1.412	1.366
N8−C9	1.300	1.300	1.300	1.303	1.300	1.305	1.334
C9−C10	1.481	1.472	1.484	1.473	1.484	1.473	1.433
C10−C11	1.340	1.388	1.342	1.340	1.342	1.342	1.344
C11−C12	1.473	1.481	1.469	1.476	1.469	1.472	1.406
C12−C13	1.475	1.484	1.470	1.478	1.470	1.474	1.443
C13−C14	1.340	1.338	1.342	1.339	1.343	1.341	1.374
C9−C14	1.476	1.469	1.476	1.469	1.475	1.464	1.426
C12−O15	1.238	1.219	1.248	1.231	1.248	1.234	1.302
N7−C16	1.440	1.481	1.450	1.485	1.437	1.474	1.470
C2−C1−C6	117.3	118.8	117.5	119.0	117.2	118.3	117.6
C3−C4−C5	117.6	119.8	117.8	120.1	117.6	118.9	116.7
C10−C9−C14	114.9	117.4	115.0	117.7	114.8	117.1	117.5
C11−C12−C13	115.4	116.4	116.2	117.4	115.9	117.2	120.4
C4−N8−C9	124.0	125.8	124.8	125.6	125.9	131.4	125.8
C1−N7−C16	117.6	116.5	115.5	116.0	120.2	121.5	121.6
C2−C1−N7−C16	−18.5	−25.0	−21.8	−26.1	0.0	0.0	−3.3
C2−C1−N7−C17	−165.9	−160.1	−161.7	−159.5	180.0	180.0	−176.2
C3−C4−N8−C9	−139.5	−126.4	−145.6	−126.1	−152.1	−165.3	160.6
C4−N8−C9−C14	4.3	1.8	5.3	1.4	6.3	2.2	−12.4

[a] Bond lengths in angstroms, angles in degrees. All COSMO results were obtained using a dielectric constant of 80.1 in the calculation. The # sign indicates that torsion angles C2−C1−N7−C16 and C2−C1−N7−C17 were constrained during the optimization (see text). Data for structure **12** is taken from the Cambridge Structural Database (Refcode TEYGOT, ref 45).

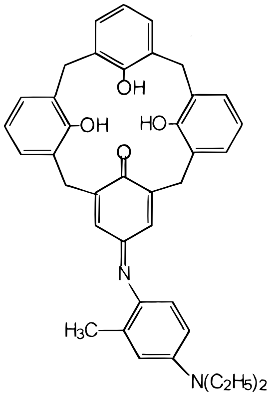
(**1**), generally show a number of separate absorption bands, particularly in solvents of low dielectric constant;[19b] second, an analysis of the ^{1}H NMR spectra of **6** at both +50 °C and −65 °C shows no change to the relative intensities of the pair of the absorptions either at 6.5−6.7 ppm or those at 7.3−7.4 ppm relative to the intensities found at room temperature, though there is a small downfield shift of around 0.04−0.07 ppm with decreasing temperature. There is no change observed either for the resonances of the methylene or methyl protons which resonate at 3.45 and 1.25 ppm, respectively, with decreasing temperature. Overall, these results effectively rule out the possibility that the aromatic resonances are due to more than one stable conformer in solution as the relative populations would be expected to show a marked change in moving from −65 °C to +50 °C.

The most likely explanation for the separate resonances of the protons in the quinoneimine ring lie with the nonplanar character of the molecule. Because the quinoneimine ring is twisted around the C4−N7 bond (see later), H14 points downward and lies below the plane of the anilino ring and H10 points upward and lies above the plane so that both will experience a deshielding effect from the π-electrons of the anilino ring resulting in a downfield shift, with the former more effected than the latter because it lies closer. However, H13 and H11 are too far away from the anilino ring to experience a deshielding effect by the π-electrons and these resonances fall in the same region as those for benzoquinone. Overall, the variable temperature results strongly suggest that the quinone ring is rigidly locked into one conformation only as there is no apparent broadening of the resonances of either H10, H11, H13, or H14 on moving from −65 to +50 °C.

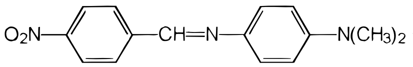
As expected, solvent has a pronounced effect on the chemical shifts of all the ring protons (Table 2), and although the doublet for H2/H6 varies from 6.37 ppm in deuterated benzene to 6.82 ppm in deuterated methanol, these shifts are similar to those observed for the ring protons of many other polar organic molecules, which have only one formal structure[42−44] and arise because the protons are in direct contact with the solvent. The coupling constants between protons at the 2- and 3-positions of the molecule, $J_{2,3}$, have similar values to those found in the same positions of *N*,*N*-diethylaniline (**10**), while those for 10- and 11-positions, $J_{10,11}$, are comparable to those found in 4,4-dimethylcyclohexa-2,5-dien-1-one (**8**). Solvent induces very little change to the values and there appears to be no correlation with varying dielectric constant (Table 2).

2. Structural Considerations. The Cambridge Structural Database[34] reveals a number of structures related to Phenol Blue, but only two of these contain the 1,4-benzoquinoneimine moiety coupled with a donor substituent in the left-hand phenyl ring. The first of these is a calixarene derivative, 5-(4′-diethylamino-2′-methylphenylimino)-25,26,27-trihydroxycalix(4)aren-28-one (**12**)[45] (R-factor = 8.5%), which contains a ring of 2-hydroxybenzyl groups attached at both the C11 and C13 positions of the indoaniline structure as shown. This crystal structure shows C1−N7, C4−N8, N8−C9, and C12−O15 bond lengths of 1.350, 1.366, 1.334, and 1.302 Å, respectively (Table 3), with an estimated standard deviation in bond length between the heavy atoms of 0.01−0.03 Å.[34] The relatively long C12−O15 bond length appears to lie between the C═O double bond length of around 1.22 Å found in benzoquinone[46] and the C−O single bond length of around 1.33 Å found in hydrated sodium phenoxide.[47] Furthermore, the C4−N8 bond length appears to lie between the single C−N bond length of 1.42 Å and N═C double bond length of 1.26 Å found in the central positions of 4-nitrobenzylidene-4′−*N*,*N*-dimethylaminoaniline (**13**).[48]

The anilino ring is approximately planar with a trigonal sp^2 hybridized nitrogen at N7 with the other nitrogen N8 lying in the same ring plane. The quinoneimine ring is twisted, however, with torsion angles C3−C4−N8−C9 and C4−N8−C9−C14 of 160.6° and −12.4° respectively (Table 3). The carbonyl oxygen, O15, is strongly hydrogen bonded to the two hydroxy groups of the 2-hydroxybenzyl substituents which form the calixarene ring at distances of 1.661 and 1.714 Å, respectively.

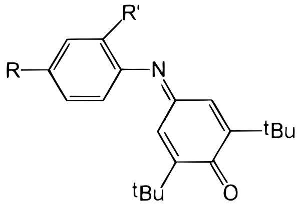


(12)



(13)

The second relevant crystal structure, 4-(2-hydroxy-4-methylphenylimino)-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one (**14**),[49] (R-factor = 5.2%) contains three molecules in the asymmetric unit, with average C4−N8, N8−C9, and C12−O15 bond lengths of 1.409, 1.302, and 1.222 Å respectively, with an angle C4−N8−C9 of 124.0°, which are fully consistent with the quinoneimine form (**B**) of the molecule. Two further related structures, 4-(2-acetoxy-4-nitrophenylimino)-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one (**15**)[50] and 4-(4-bromophenylimino)-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one (**16**),[51] also appear in the quinoneimine form (**B**) with C4−N8, N8−C9, and C12−O15 bond lengths of 1.402, 1.305, and 1.234 Å for the former and 1.417, 1.294, and 1.244 Å for the latter, respectively.



14 R = CH_3 ; R' = OH
15 R = NO_2 ; R' = $OCOCH_3$
16 R = Br ; R' = H

Previous calculations on 4-aminoindoaniline (**5**)[29] in the gas phase using the PM3 method gave a structure with C1−N7, C4−N8, N8−C9, and C12−O15 bond lengths of 1.425, 1.421, 1.302, and 1.219 Å, respectively. We have obtained similar results on Phenol Blue (**4**) at the PM3 level where the same bonds have values of 1.444, 1.426, 1.300, and 1.219 Å, respectively, and also using the AM1 method, where these bonds now have values of 1.404, 1.406, 1.300, and 1.238 Å, respectively (Table 3). However, the C1−N7 bond length appears to be far too long by comparison with crystallographic data on related compounds, and furthermore, the nitrogen atom, N7, is sp^3 hybridized, with the methyl groups inclined at average torsion angles C2−C1−N7−C16/C6−C1−N7−C17 of 22.5° and 16.3° below the anilino ring plane for the PM3 and AM1 methods, respectively. An even larger overestimation of the C1−N7 bond length of Phenol Blue has been reported recently at the MP2/STO-3G level with a calculated value of 1.48 Å, coupled with similar nitrogen hybridization problems, where the alkyl carbons, C16 and C17, are calculated to lie 10.4° and 61.1° above and below the ring plane, respectively, at the HF/STO-3G level.[35] At the MP2/6-31G* level, there is no significant improvement to the nitrogen hybridization, as the alkyl carbons, C16 and C17, now lie 3.4° and 49.1° above and below the ring plane, respectively.[35] This erroneous sp^3 hybridization at N7 will result in reduced conjugation between the dimethylamino group and the left-hand ring and is probably responsible for the relatively small calculated dipole moment of 2.7 D at the MP2/STO-3G level,[35] and our values of 4.39 and 5.32 D at the PM3 and AM1 methods, respectively, versus the reported experimental value of 5.80D.[52]

In our previous studies[19a] on the merocyanine (**1**), we found significant improvements in the bond lengths when a dielectric field was imposed during the structure optimization using the COSMO routine present in MOPAC 93. Accordingly, we have repeated the structure optimization of the Phenol Blue using the dielectric constant of water (Table 3). At the PM3 level, the calculated bond lengths surprisingly show few differences from the gas-phase results with values for the C1−N7, C4−N8, N8−C9, and C12−O15 bond lengths of 1.448, 1.429, 1.303, and 1.231 Å. The nitrogen atom, N7, remains sp^3 hybridized, with the methyl groups now inclined at an average torsion angle of 23.3° to the anilino ring plane. The AM1 method also produces similar small changes over the gas-phase structure (Table 3). The presence of solvent, therefore, has little effect on the hybridization of the nitrogen atom, N7, and the C1−N7 bond length is still too long resulting in a substantial underestimation of the π-electron-donating ability of the dimethylamino group, which would be expected to have a marked effect on the excited state properties of the dye. We found a similar overestimation of the length of the C−NMe_2 bond length in donor−acceptor azobenzenes which is attributable to the parametrization adopted for the nitrogen atom in both methods.[39]

To overcome the hybridization problems associated with both methods, further optimizations were carried out on Phenol Blue in water with the structure constrained so that the dimethylamino group was forced to lie in the plane of the anilino ring by setting the C2−C1−N7−C16 and C6−C1−N7−C17 torsion angles to 0°. This procedure resulted in a significant improvement in the C1−N7 bond length to give values of 1.380 and 1.400 Å for the AM1 and PM3 methods, respectively, which are now much closer to the expected value of 1.36−1.39 Å for the C−N bond length of donor−acceptor arenes containing a conjugated dialkylamino group[36] such as the C−NMe_2 bond in 4-nitrobenzylidene-4′-*N*,*N*-dimethylaminoaniline (**13**),[48] which has a value of 1.387 Å. The other calculated distances for the C4−N8, N8−C9, and C12−O15 bonds of 1.399, 1.300, and 1.248 Å, respectively, at the AM1 level, and 1.412, 1.305, and 1.234 Å, respectively, at the PM3 level, now show a very good correlation with the average experimental data of 1.409, 1.300, and 1.233 Å, respectively, reported for the same bonds in **13**, **14**, and **15**. The constrained structures are both higher in energy than those produced by complete optimization of all variables, with the former typically 1.28 kcal mol^{-1} above the latter at the AM1 level.

TABLE 4: Effect of the Dielectric Constant of Aliphatic Aprotic Solvents on the Experimental Absorption Maximum of Diethylindoaniline (6) Compared with the Experimental and Calculated Values for Phenol Blue (4)[a]

solvent	ϵ	$\lambda\ (\mathbf{6})_{\mathrm{expt}}$	$\lambda\ (\mathbf{4})_{\mathrm{expt}}$	$\lambda\ (\mathbf{4})_{\mathrm{calc}}$
cyclohexane	2.02	563	552	461.7
diethyl ether	4.27	571	554	496.7
ethyl acetate	6.08	583	572	540.5
tetrahydrofuran	7.52	588	587	551.6
cyclohexanone	16.1		587	576.1
acetone	21.0	593	582	580.4
acetonitrile	36.6	597	584	585.6
N,*N*-dimethylformamide	38.3	605	595	585.8
dimethyl sulfoxide	47.2	614	605	586.9
propylene carbonate[b]	66.1		598	588.1
ethylene carbonate[c]	89.8	609		590.2
N-ethylacetamide	135.0	609		590.1
N-methylacetamide	179.0	609		589.7

[a] ϵ is the dielectric constant of the solvent (ref 54); λ is the long-wavelength absorption maximum (in nm). Experimental data for Phenol Blue (**4**) is derived from literature sources (refs 8, 11−16). [b] 4-Methyl-1,3-dioxolan-2-one. [c] 1,3-Dioxolan-2-one.

TABLE 5: Estimated Effect of the Dielectric Constant and Hydrogen Bonding Ability of Acidic Solvents on the Experimental Absorption Maximum of Diethylindoaniline (6)[a]

solvent	ϵ	λ	$\Delta\lambda$	$\Delta\lambda_{\epsilon}$	$\Delta\lambda_{\mathrm{H}}$
cyclohexane	2.02	563			
chloroform	4.81	609	46	13	33
tert-butyl alcohol	12.5	607	44	24	20
propan-2-ol	19.9	615	52	29	23
cyclohexanol	15.0	623	60	26	34
ethanol	25.3	635	72	32	40
ethanediol	41.4	646	83	38	45
water	80.1	684	121	46	75
formamide	111.0	643	80	46	34
N-methylformamide	189.0	612	49	46	3
N-methylacetamide	179.0	609	46	46	0

[a] ϵ is the dielectric constant of the solvent (ref 54); λ is the long-wavelength absorption maximum; $\Delta\lambda$ is the shift in absorption relative to that found in cyclohexane; $\Delta\lambda_{\epsilon}$ is the estimated dielectric component of the shift; $\Delta\lambda_{\mathrm{H}}$ is the hydrogen bonding component of the shift (all in nm).

3. Analysis of Solvatochromic Shifts. The spectrum of Phenol Blue has (**4**) been measured in a number of aprotic solvents, but most of these are clustered in the dielectric constant range of around 2 (cyclohexane) to 47.2 (dimethyl sulfoxide).[8,11−16] However, the greater solubility of the diethylindoaniline (**6**) allows a more thorough analysis of the effect of solvent on the spectroscopic shift and we have now extended the range of experimental measurements to include less common solvents such as ethylene carbonate, *N*-ethylacetamide, and *N*-methylacetamide which have dielectric constants of 89.8, 135, and 179, respectively (Table 4). Although each of the *N*-alkylacetamides possesses an acidic hydrogen atom and could be considered as protic solvents, crystallographic data on *N*-methylacetamide strongly suggests that it is unlikely to form hydrogen bonds with the oxygen of the indoaniline (**6**), because in the favored trans conformation (either alone[53] or in the presence of metal salts[36]), the hydrogen is partly shielded by the adjacent methyl hydrogens on the carbonyl carbon, and the *N*-alkylacetamides therefore act essentially as aprotic solvents as we have previously pointed out.[19a]

Overall, the effect of the dielectric constants of aprotic solvents are considerably less marked for this molecule (**6**) than the results we obtained for the merocyanine (**1**), with much smaller shifts observed, this time in the opposite direction, in moving from solvents with low dielectric constants to those with much larger values. Thus, the absorption moves from 563 nm in cyclohexane ($\epsilon = 2.02$) to 593 nm in acetone ($\epsilon = 21.0$) through to a value of 605 nm in *N*,*N*-dimethylformamide and then to 609 nm in ethylene carbonate ($\epsilon = 89.8$) (Table 4). However, the dielectric effect saturates fairly quickly as there is no further shift observed in moving to *N*-ethylacetamide ($\epsilon = 135$) or to *N*-methylacetamide ($\epsilon = 179$). The result for dimethyl sulfoxide (Table 4) appears to be anomalous and possibly arises because of the presence of small amounts of water which are very difficult to remove completely. Thus, the maximum shift due to the dielectric effect of the solvent is around 46 nm (Table 4).

In contrast, the shifts observed in protic solvent are much larger, and arise from a combination of a distinct hydrogen bonding component, and a dielectric component, which can be derived in principle from the shifts observed in aprotic solvents (Table 4). Thus, the observed absorption of the indoaniline (**6**) at 684 nm in water (Table 5) represents a total shift of 121 nm relative to cyclohexane of which 45 nm is estimated to arise from the dielectric effect of the solvent by interpolation of the data given in Table 4; the shift due to hydrogen bonding, therefore, is much larger at 76 nm. This method can be extended to other solvents such as formamide where the dielectric component remains at 46 nm but the hydrogen bonding component is now smaller at 34 nm. The estimated hydrogen bonding shifts (in nm) for protic solvents follow the expected order with water (76) > ethanediol (45) > ethanol (40) > cyclohexanol ≈ formamide (34) > 2-propanol (23) > *tert*-butyl alcohol (20) > *N*-methylformamide (3) (Table 5).

4. Spectroscopic Calculations. A series of spectroscopic calculations were carried out on the structure of Phenol Blue (**4**) where the dimethylamino group was constrained to lie in the anilino ring plane (as discussed above) at a range of dielectric values using the PM3/COSMO method, and the results were then compared with the experimental data. The transition energy between the ground state and first excited singlet calculated using the multielectron configuration interaction treatment (MECI) is found to be highly dependent on the dielectric constant of the solvent adopted for the two independent calculations. This arises because of the large change in the electronic properties of the molecule on excitation as indicated by the change in the dipole moment in cyclohexane from 8.13 D in the ground state to 19.5 D in the first excited singlet state. The larger the dielectric constant of the solvent, the greater the stabilization of the excited state over the less polar ground state leading to smaller energy gap between the two states. The absorption bands in aprotic solvents of high dielectric constant are predicted, therefore, to occur at longer wavelength (i.e., lower energy) than those obtained in aprotic solvents of low dielectric constant, fully in line with the experimental results. Thus, the calculated absorption at the PM3 level in solvents with large dielectric constants such as propylene carbonate ($\epsilon = 66.1$) at 588 nm, compares favorably with the experimental value of 598 nm (Table 4). In solvents with very low dielectric constants such as cyclohexane, the transition energy is overestimated, but nonetheless lies in the correct direction, with a calculated value of 462 nm versus the experimental value of 552, respectively (Table 4). This overestimation almost certainly arises in solvents of low dielectric constant because COSMO is primarily a theory for *high* dielectrics designed for conductors ($\epsilon = \infty$). However, the correlation between theory and experiment improves dramatically with increasing dielectric constant, and in acetone ($\epsilon = 21.0$), the values almost coincide (Table 4). The initial effective dielectric constant in the COSMO routine which produces a reasonable spectroscopic shift occurs at a value of around 6.08 (Table 4).

The origin of the large bathochromic shifts observed with increasing values of the dielectric constant lies with differential stabilization of the ground and first excited state by different solvents. In moving from cyclohexane ($\epsilon = 2.02$) to ethylene carbonate ($\epsilon = 89.6$), the heat of formation of the indoaniline in the ground state after MECI, calculated using the PM3/COSMO method, falls from 36.97 to 27.99 kcal mol^{-1}, to give stabilization energy of -8.98 kcal mol^{-1} for the more polar solvent. However, the corresponding heat of formation in the same solvents for the first singlet excited state after MECI falls from 98.90 to 76.54 kcal mol^{-1}, respectively, giving a net stabilization energy for the excited state of 22.36 kcal mol^{-1} for the more polar solvent. The change induced by the increase in solvent polarity is reflected in the dipole moments which change from 8.13 in the ground state to 19.5 D in the excited state in cyclohexane and from 11.1 to 24.9 in ethylene carbonate. Thus, solvents with large dielectric constants have a much greater stabilizing effect on the more polar excited state of Phenol Blue than they do on the ground state.

Similar bathochromic effects on the transition energies would be expected from increasing dielectric constants of protic solvents, but here the position is complicated by the formation of hydrogen bonds with the solvent. In our previous studies on the merocyanine (**1**), we found that the PM3 method gave a much better account of hydrogen bonding of water to the lone pair electrons at exocyclic oxygen atom than the AM1 method with calculated $O\cdots H_2O$ distances of 1.77 Å for the former versus 2.10 Å for the latter.[19a] In principle, while there are three possible sites for hydrogen bonding in Phenol Blue, at N7, N8, and O15, the sp^2 lone pair electrons at the former site are conjugated with the ring system and are less likely to form strong hydrogen bonds with the solvent. However, the lone pair electrons at N8 and O15 (two in this case) readily form intermolecular hydrogen bonds with water (or any other protic solvents), though the ^{13}C NMR data in methanol (Table 1) suggests that the bonding has little effect on the electronic structure of the molecule. Optimization of a trihydrate structure with one water molecule attached to N8 and two to O15 using the PM3/COSMO method in water gives a resulting structure with two $O15\cdots H_2O$ hydrogen bond lengths of 1.795 Å and one $N8\cdots H_2O$ hydrogen bond length of 1.843 Å with O15−H−O and N8−H−O angles of 171° and 160°, respectively. The presence of the three intermolecular hydrogen bonded water molecules result in very small changes to the overall geometry of the indoaniline in line with the NMR data, with the length of the terminal C1−N7 and C12−O15 bonds changing to 1.399 and 1.236 Å, respectively, from their values of 1.400 and 1.234 Å in the absence of the attached water molecules.

MECI calculations on the PM3 structure of the nonhydrated indoaniline itself in water gives a predicted transition energy of 589 nm, which is close to the experimental value of 598 nm expected for an aprotic solvent with the same dielectric constant as water (Table 4). Surprisingly, however, the presence of three bonded water molecules has little effect on the predicted transition energy of the indoaniline trihydrate which only moves to 596 nm.

However, spectroscopic calculations at the CNDOVS level on the PM3 structures, using a larger configuration space, but this time with 50 singly excited configurations, give predicted transition energies of 596 nm for the indoaniline alone, and 652 nm for the trihydrate. This shift of 56 nm, which is caused solely by the presence of three hydrogen bonded water molecules, reflects the experimental shift of 76 nm for the diethylindoaniline (**6**) (Table 5). At the valence electron level, the indoaniline has 43 occupied orbitals in the ground state, and on excitation, the first singlet excited state after configuration interaction, S$_1$, is found to be composed mainly of the expected $\pi-\pi^*$ HOMO−LUMO transition but also includes a significant additional transition from a lower occupied molecular orbital, Ψ_{38}, to the LUMO. If the contributions of other transitions with coefficients smaller than 0.1 to the excited singlet state are ignored, then

$$S_1 = 0.95\psi_{43-44} - 0.26\psi_{38-44}$$

A similar picture emerges for the trihydrate which has 55 occupied orbitals in the ground state, to give an excited state here of the following composition:

$$S_1 = 0.95\psi_{55-56} + 0.27\psi_{50-56}$$

An analysis of the composition of both of the lower occupied molecular orbitals of higher energy, Ψ_{38} and Ψ_{50}, show that while they are constructed from a number of π atomic orbitals, they significantly contain large contributions from σ orbitals on N8. For example, molecular orbital Ψ_{38} includes the following contributions from N7 and N8:

$$0.25\phi_{pz}\ (N7) + 0.27\phi_{s}\ (N8) + 0.72\phi_{py}\ (N8)$$

It follows that the two transitions, ψ_{38-44} and ψ_{50-56}, are essentially n$-\pi^*$ in character, and hydrogen bonding to the σ orbitals at N8 will have a marked effect on the transition energy. Overall, therefore, the large positive experimental dielectric and hydrogen bonding shifts of around 45 and 76 nm, respectively, found in moving from cyclohexane to water (Table 5), are well reproduced by the calculated dielectric shift of around 50 nm modeled by COSMO (relative to the limiting dielectric constant of 6.08, Table 4) and the hydrogen bonding shift of 56 nm modeled by the CNDOVS method. The failure of the MECI routine in our version of MOPAC93 to reproduce the same trends is due to the restricted configuration space adopted which only considers 100 configurations (50 singlets, 45 triplets, and 5 quintets) between the three highest occupied and two lowest unoccupied molecular orbitals.

Conclusions

NMR evidence on the soluble diethylindoaniline (**6**) in both protic solvents and aprotic solvents suggests that Phenol Blue (**4**) exists solely as the quinoneimine (**B**). These results contrast markedly to our previous work on Brooker's merocyanine (**1**) which showed that the structure is weighted toward the zwitterion (**A**). In aprotic solvents, the solvatochromic shift of Phenol Blue, calculated using the PM3/COSMO method, shows a good correlation with the experimental data, and arises because solvents with large dielectric constants are able to differentially stabilize the polar excited state. In protic solvents, such as water, the PM3/COSMO method using limited MECI calculations satisfactorily models the dielectric effect of the solvent, but a larger configuration interaction treatment may be necessary to reproduce the further bathochromic shift associated with the formation of a stable hydrogen bonded trihydrate.

Experimental

Visible spectra were measured using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer and a matched pair of quartz cells of 10 mm path length. Solutions of diethylindoaniline (**6**) were prepared at a concentration of 20 ppm, and recorded at room temperature in solvents of the highest purity (spectroscopic grade and dried by appropriate methods prior to use) where possible. IR spectra were measured using a Perkin-Elmer FT-IR 1725X spectrometer, using a KBr disk. ^{1}H and ^{13}C NMR spectra were measured in deuterated solvents (Sigma-Aldrich) using a Bruker AC400 spectrometer. *N*-methylacetamide-*d* was prepared as we have described previously.[19a]

***N*-(4-Diethyaminophenyl)-1,4-benzoquinoneimine (6).** The preparation was carried out by oxidative condensation of *N*,*N*-diethyl-1,4-phenylenediamine and phenol using silver chloride as the oxidizing agent according to the literature procedure.[55] However, it was necessary to purify the product by chromatography on a silica column using a mixture of petroleum ether and acetone as eluent, to give green crystals with a metallic luster after drying over P_2O_5 in vacuo: mp 107−108 °C; IR (KBr) 2926, 1627, 1609, 1585, 1510, 1466, 1406, 1373, 1355, 1274, 1176, 1152, 1074, 872, 823 cm^{-1}.

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