Fundamental Studies on Brooker's Merocyanine

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Abstract: The spectroscopic properties of solvent soluble derivatives of Brooker's simple merocyanine 4-[(1-methyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one, which can in principle exist in two distinct canonical forms, have been assessed both experimentally and theoretically using molecular orbital methods. ^{1}H and ^{13}C NMR evidence in a range of solvents suggests that the merocyanine exists as a resonance hybrid which is weighted toward the zwitterion even in solvents of low dielectric constants. In protic solvents, the large hypsochromic shift observed for the merocyanine in the visible region arises from both a dielectric effect and a hydrogen bonding effect. Theoretically, the PM3/COSMO method gives a reasonable account of the structure and spectroscopic shifts of the merocyanine in aprotic solvents. The large shifts observed arise because solvents with large dielectric constants have a much greater stabilizing effect on the more polar ground state of the merocyanine than they do on the first excited state. While the same method predicts stable hydrogen-bonded structures for a dihydrate and hexahydrate, it is unable to reproduce the known hypsochromic shift for these solvated species. In contrast, a version of the CNDO/S method does predict the correct trends on hydration though the magnitude of the effect is less than that found experimentally.

Introduction

There have been a considerable number of experimental and theoretical studies on the solvatochromic behavior of merocyanines dyes following their discovery by Brooker.[1−3] Many authors have postulated that the origin of the large hypsochromic shift in the spectrum of 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one (**1**) is due to a distinct change in structure from a covalent quinone (**1A**) in pyridine or chloroform to a zwitterion (**1B**) in water or methanol.[2] The extent of this shift is critically dependent on the solvent used for measurement in each case with the highest energy absorption found in water and the lowest one in chloroform with an observed change in colour from yellow to blue[4−8] (Table 1). Although a number of authors have suggested that this shift is proportional to the polarity of the solvent in terms of the dielectric constant, with the highest energy absorption in solvents with high values, the experimental data are not supportive as the absorption maximum in dimethyl sulfoxide ($\lambda = 572$ nm; $\epsilon = 46.7$) occurs at a *longer* wavelength or lower energy than that measured in ethanol ($\lambda = 514$ nm; $\epsilon = 24.6$) whereas the reverse would be expected on the basis of solvent polarity.[4]

Table 1. Experimental Absorption Energies of the Merocyanines **4**, **5**, and **9**[a]

		λ				
solvent	ϵ	**1**[b]	**4**	**2**[f]	**5**	**9**
dioxane	2.21	614[c]	619	626	626	386
chloroform	4.8	620[c] 618[d]	620	633	634	395
pyridine	12.3	605	600	630	632	406
acetone	20.7	585	599	619	620	385
ethanol	24.6	514[e]	521	616	617	402
methanol	32.7	483 490[d]	491	582	601	395
dimethyl sulfoxide	46.7	572	579	617	618	395
water	78.4	442	447	527	526	380
formamide	111.0	494	502	578	581	392

[a] ϵ is the dielectric constant of the solvent (ref 13); λ is the longest wavelength absorption maximum (in nm). [b] Reference 5 except where stated otherwise. [c] Extrapolated values. [d] Reference 8. [e] Reference 11. [f] Reference 10.
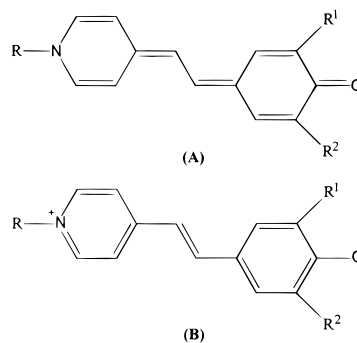
1: R = CH$_3$; R^1 = R^2 = H
2: R = CH$_3$; R^1 = R^2 = *t*-C$_4$H$_9$
3: R = CH$_3$; R^1 = *t*-C$_4$H$_9$; R^2 = H
4: R = *i*-C$_{10}$H$_{21}$; R^1 = R^2 = H
5: R = *i*-C$_9$H$_{19}$; R^1 = R^2 = *t*-C$_4$H$_9$

Recent studies have strongly suggested that one of the main factors which contribute to the large solvatochromic shift is a

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Scheme 1. Numbering Convention for the Merocyanine (**1**)
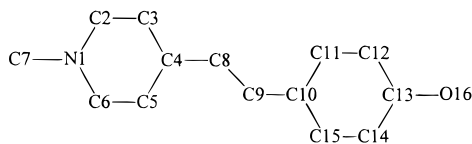
hydrogen-bonding interaction between the oxygen atom of the merocyanine and the solvent[9,10] which is thought to stabilize the zwitterion (**1B**).[9] Indeed, if large alkyl groups are placed *ortho* to the oxygen atom as in the closely related 2,6-di-*tert*-butylmerocyanine (**2**), to impede hydrogen bonding between the lone pair of electrons at the oxygen and the acidic hydrogen of the solvent, the large solvatochromic shift is substantially reduced for many solvents.[10] Thus in moving from chloroform to ethanol, the absorption maximum changes from 618 to 514 nm for the parent merocyanine (**1**), but for the 2,6-di-*tert*-butyl derivative **2**, the shift is considerably smaller from 633 to 616 nm, respectively (Table 1). Furthermore, an almost linear relationship is found between the acidity of the hydrogen bond donor and the absorption energy of the simple merocyanine (**1**) which ranges from 442 nm in water, to 531 nm in *n*-butanol, and to 578 nm in the much weaker hydrogen bond donor, *tert*-butyl alcohol.[9] Similar effects are found for the 2-*tert*-butyl merocyanine **3** for a wide range of hydrogen-bonding alcohols.[11] Resonance Raman scattering spectra of the merocyanine also show an increase in the frequency of two bands near 1560 and 1160 cm^{-1} with increasing hydrogen bond donor acidity, which is claimed to lead to an increase in the relative contribution of the zwitterion (**1B**) versus the quinone form (**1A**), with the first band assigned to a C=C stretching vibration and the second to C-aryl stretching modes.[9]

The structure of the merocyanine has been probed also by ^{1}H NMR spectroscopy in deuterated solvents such as chloroform and methanol though the solubility is extremely low in the former and the results must be treated with caution. In one study the coupling constants of the two *trans* hydrogens at the 8 and 9 ethylidene bridge positions (Scheme 1) were reported to have a single value of at 15.5 Hz in moving from chloroform to methanol,[8] while in another study values of 16.1 Hz were reported for the same protons in methanol but 14.6 Hz in dichloromethane.[9] Both values are consistent, however, with the coupling constants of *trans* protons at a double bond[12] (see later). The possibility that a *cis* conformer of the merocyanine contributes to the large solvatochromic shifts observed in moving from solvents of high to low dielectric constants is therefore discounted.[14−17]

However, no structural conclusions can be drawn from the corresponding ^{1}H NMR chemical shift data as the resonances of the protons at the 8 and 9 positions at 6.9 and 7.7 ppm,

respectively, in methanol, and 6.2 and 7.4 ppm, respectively, in dichloromethane[9] are close to the resonance of the two protons at the double bond in stilbene at 7.0 ppm and to the two vic protons at the 1 and 3 positions in 1,4-diphenylbutadiene at 6.6 ppm.[12]

Furthermore, ^{13}C NMR studies show little change in the resonance position of key carbons of the merocyanine (**1**) with change of solvent from chloroform to methanol.[4] Thus C2 and C6 which are adjacent to a positive nitrogen in the zwitterion (**1B**) and a neutral nitrogen in the quinone (**1A**) show values of 142 and 144 ppm, respectively, in each solvent and C13 which is adjacent to a negative oxygen in the former and neutral oxygen in the latter appears at the same position at 175 ppm in both solvents, respectively.[4] However, the real resonance position has not been properly established for chloroform because of the low solubility, and quoted literature values are extrapolated from methanol/chloroform mixtures.

Recent theoretical studies have claimed, however, that the structure and electronic properties of donor−acceptor polyenes and the merocyanine discussed here show large variations under the influence of applied electric fields such as those produced during electric field induced second harmonic generation.[18,19] By inference it has been assumed that solvents are able to exert similar electric fields which are able to influence the degree of bond length alternation between the two distinct canonical forms of the merocyanine. This change of structure from a covalent form to a zwitterion appears to occur for several related polyenic dyes and appears to be responsible for the different spectral and nonlinear optical properties observed particularly in the change from protic to aprotic solvents.[18,20−22] However, for the merocyanine, this contention is not supported by an analysis based on the Onsager reaction field model which shows that the electric field produced by even the most polar solvents is inadequate to produce the large geometric distortions required to change its structure.[19] Although the predicted structural changes are large under the influence of electric fields, there has been no experimental verification of this effect, for example, by monitoring the change in absorption maximum in a selected solvent with an external applied field.

However, the structure of the merocyanine in solution has been calculated by using a variety of molecular orbital approaches with most based on self-consistent reaction field models. An early study using a SCF π-electron bond length optimization method modified by the introduction of solvation term showed a change in structure from the quinone (**1A**) to the zwitterion (**1B**) with increasing solvent polarity coupled with a movement in the predicted transition energies from around 460 to 310 nm.[8] Similar results have been obtained on the same merocyanine with a modified CNDO/S method[4] which uses a solute−solvation interaction factor based on the dielectric constant of the solvent. Here again the calculated geometries and transition energies are found to be highly dependent on the dielectric constant employed and in solvents with low values the quinone (**1A**) is favored with a predicted absorption at 420

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nm, while in highly polar solvents the zwitterion (**1B**) results with a corresponding shorter absorption at 299 nm. The QCFF/SOL method, which incorporates both permanent and induced dipoles for the solvent, suggests that the zwitterion (**1B**) (constructed from optimized fragments rather than the complete molecule) is also favored over the fully optimized quinone (**1A**) in polar solvents, but the spectroscopic results are more consistent with the experimental data if it is assumed that the zwitterion (**1B**) is the dominant species in both polar and nonpolar solvents.[23]

The AM1[24] and PM3[25] methods of the MOPAC program[26] generate the quinone (**1A**) in the gas phase but the use of sparkles (positive and negative charges) positioned above and below the oxygen and nitrogen atoms to simulate a solvent field produces the higher energy zwitterion (**1B**) at the AM1 level.[20,27] More recent calculations using a self-consistent reaction field model using both the INDO/S method[19,28−30] and the AM1/COSMO method[24,31,32] also predict a change in structure with increasing solvent polarity from the quinoid form (**1A**) toward the zwitterion (**1B**) though this is less marked in the former case with only small variations to the C8−C9 and C13−O16 bond lengths which change from 1.408 and 1.267 Å in cyclohexane to 1.385 and 1.275 Å, respectively, in water.[19] As before, this structural change is accompanied by a hypsochromic shift in the transition energies from around 388 to 336 nm for the former case[19] and from 521 to 502 nm for the latter.[32] In summary, therefore, almost all of these calculations predict a quinoid structure at low dielectric constant with *a longer wavelength absorption* than the zwitterionic form which is produced in solvents of high dielectric constant.

However, spectroscopic calculations[27] using both the AM1 and CNDOVS[33] methods on both the quinone (**1A**) and zwitterion (**1B**) strongly suggest that the former will absorb at *a shorter wavelength* than the latter in apparent contradiction to the previous studies described above[4,8,19,32] which predict exactly the opposite trend.

Furthermore, most of the previous studies can be criticized because they have ignored the important *hydrogen-bonding effect* which is partly responsible for the large solvatochromic shift observed for the merocyanine dyes in protic solvents. Indeed, the real dielectric effect can be relatively small as evidenced by the shift in the absorption band of the 2,6-di-*tert*-butyl merocyanine **2** which moves from 633 nm in chloroform to 623 nm in tetramethylurea and then to 617 nm in dimethyl sulfoxide despite a large increase in the dielectric constant from 4.8 to 23.1 to 46.7, respectively.[10]

The present work has been carried out, therefore, to re-assess previous experimental results by using more soluble derivatives containing alkyl groups in both aromatic rings and by extending the range of solvents used both for visible and ^{1}H and ^{13}C NMR spectroscopic analysis. Theoretical calculations have been performed also on the merocyanine at several levels of theory

to resolve the apparent contradiction between different spectroscopic results obtained previously and to investigate the large effect of solvation on the structure both in terms of the dielectric effect and hydrogen bonding.

Methods of Calculation

Molecular orbital calculations were carried out on empirical structures for the merocyanine **1** using the AM1[24] and PM3[25] methods of the MOPAC 93[26] Program with full optimization of all bond lengths, angles, and torsion angles except where stated otherwise. Spectroscopic calculations were carried out on the fixed ground state geometry using the multielectron configuration interaction (MECI) treatment in MOPAC 93 which considers 36 states (20 singlets, 15 triplets, and 1 quintet) between the two highest occupied and two lowest unoccupied molecular orbitals (keywords for the ground state calculation in water: pm3 prec 1scf xyz eps=78.4 ef geo-ok meci singlet c.i.=4 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. In the calculations reported here, the spectroscopic constant of the CNDOVS method was adjusted to 0.78 with the core coefficient of 0.33 retained for the heavy atoms.[33] Solvent effects were considered at the AM1 and PM3 levels using the COSMO method incorporated in the MOPAC 93 program, and also the separate AMSOL[34,35] and the VAMP[36,37] programs. More accurate reference calculations of the ground state were carried out with the extended basis sets[38] of the GAMESS program.[39]

Discussion

Experimental Measurements. All the solvents used for measurement were of the highest purity and dried over molecular sieves because of the hygroscopic nature of the merocyanine. Solutions for NMR and spectroscopic studies were prepared from the anhydrous merocyanine which was dried *in vacuo* over phosphorus pentoxide. This procedure was necessary as even small quantities of water produced large changes in the visible spectra.

1. NMR Results. The contention in the early literature that the merocyanine exists in two distinct forms is not supported by either the ^{1}H or ^{13}C NMR data reported here (Tables 2 and 3). The NMR data obtained in a variety of solvents for the merocyanines synthesized in the current work which contain a long alkyl branched chain at the N1 atom such as 4-[(1-isodecyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one (**4**) and also two *tert*-butyl groups in the other ring such as 4-[(1-isononyl-4(1*H*)-pyridinylidene)ethylidene]-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one (**5**) confirm the previous limited data[8,9] on the less soluble version (**1**).

In the postulated change from the quinone (**A**) to the zwitterion (**B**), the largest electronic effect would be expected at those atoms which are directly connected to either the positive nitrogen or negative oxygen atoms. ^{13}C NMR data on these atoms, therefore, should provide a good indication of the structural changes induced by increasing solvent polarity. In model compounds for the quinone (**A**), such as 1,4-benzo-

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Table 2. ^{1}H NMR Data Obtained for the Merocyanines **1**, **4**, and **5**[a]

| solvent	ϵ	merocyanine	chemical shift (ppm)						coupling constant (Hz)		
			H2	H3	H8	H9	H11	H12	$J_{2,3}$	$J_{8,9}$	$J_{11,12}$
CDCl$_3$	4.8	**4**	7.53	7.08	6.30	7.36	7.31	6.52	6.74	15.32	8.64
		5	7.50	6.89	6.03	7.21			7.06	13.70	
C$_5$D$_5$N	12.4	**4**	8.40	7.87	6.70	7.88	7.69	7.16	7.42	15.16	8.76
		5	8.07	7.34	6.79	7.92	7.59		6.47	14.62	
CD$_3$OD	32.7	**4**	8.48	7.90	6.98	7.81	7.50	6.67	6.04	15.96	8.69
(CD$_3$)$_2$SO	46.7	**4**	8.44	7.75	6.75	7.80	7.40	6.37	6.21	15.49	8.67
		5	8.35	7.82	6.18	7.50	7.17		7.05	14.73	
D$_2$O	78.4	**1**	8.13	7.65	6.79	7.48	7.34	6.57	6.89	16.06	8.71
CH$_3$CONDCH$_3$	191.3	**4**	8.61	7.86	6.86	7.77	7.41	6.55		15.34	7.63
		5	7.78	7.33	6.42	7.72	7.42		7.00	14.79	

[a] Protons at the 5, 6, 14, and 15 positions are essentially equivalent to those at the 3, 2, 12, and 13 positions. ϵ is the dielectric constant of the nondeuterated solvent.

Table 3. ^{13}C NMR Data Obtained for the Merocyanines **4** and **5**[a]

solvent	ϵ	merocyanine	chemical shift (ppm)								
			C2	C3	C4	C8	C9	10	C11	C12	C13
CDCl$_3$	4.8	**4**	141.1	120.7	153.8	108.4	144.1	116.6	133.1	120.2	178.6
		5	141.9		147.0	104.3		119.3	135.9		183.5
C$_5$D$_5$N	12.4	**4**	145.2	122.5	154.1	110.9	142.1	120.0	134.2	120.2	178.7
		5	143.9	128.7	141.7	105.1	149.8	120.3	138.4		183.7
CD$_3$OD	32.7	**4**	145.5	122.6	156.4	115.0	143.9	121.8	132.8	121.2	175.5
(CD$_3$)$_2$SO	46.7	**4**	143.9	120.4	155.7	111.9	142.6	119.0	132.1	119.7	174.0
		5	143.7		150.3	104.3		115.6	139.4		180.3
CH$_3$CONDCH$_3$	191.3	**4**	143.7	122.1			144.7	114.7	132.6	119.9	171.7
		2	145.4		152.3	106.6	141.5	117.7	141.0		174.1

[a] Carbons at the 5, 6, 14, and 15 positions are essentially equivalent to those at the 3, 2, 12, and 13 positions; ϵ is the dielectric constant of the nondeuterated solvent.

quinone (**6a**) and 4,4-dimethylcyclohexa-2,5-dien-1-one (**7a**), the carbonyl carbon resonates at 187.1 ppm[40a] and 185.8 ppm,[40b] respectively, in CDCl$_3$, while the heterocyclic carbons adjacent to the nitrogen atom in the related 1-aza-1,4-dimethylcyclohexa-2,5-diene (**8**) resonate at 129.9 ppm.[41] The introduction of *tert*-butyl groups into the ortho positions of benzoquinone to give the 2,6-di-*tert*-butyl derivative **6b** has little effect on the carbonyl resonance which moves to 187.7 ppm.[40a]

(6)   **(7)**   **(8)**
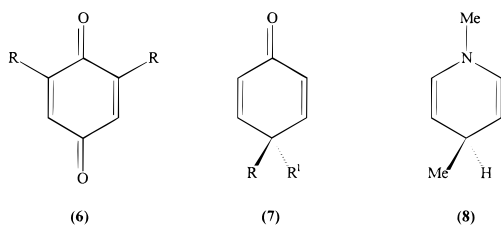
a: R = H   **a**: R = R^1 = Me
b: R = *t*-Bu   **b**: R = Me; R^1 = Et

In contrast, in model compounds for the phenyl ring of the zwitterion (**B**), such as the phenoxide anion, the carbon attached to oxygen now resonates at 168.1 ppm,[40c] while in model compounds for the heterocyclic ring of the zwitterion, such as 1-methylpyridinium iodide, the heterocyclic carbons adjacent to the nitrogen atom resonate at 146.1 ppm (this work).

An analysis of the ^{13}C chemical shifts for the merocyanine **4** show that the resonances for carbon C2 in the heterocyclic ring vary from 141.1 to 145.5 ppm with no apparent correlation with the solvent polarity (Table 3). These chemical shifts imply that the heterocyclic ring is mainly aromatic in character. However, the corresponding ^{13}C chemical shift for carbon C13 in the

phenyl ring of the merocyanine **4** in solvents of low dielectric constants such as chloroform or pyridine (Table 3) at around 178.7 ppm suggest that the real structure is a resonance hybrid of the two canonical forms (**A**) and (**B**) in all solvents as one of us has previously suggested.[27] The crystal structure of the simple merocyanine **1**[42] is supportive as the C13−O16 bond length of 1.30 Å lies between the C=O double bond length of around 1.22 Å found in benzoquinone[43] and the C−O single bond of length of around 1.33 Å found in hydrated sodium phenoxide,[44] though the oxygen atom of the merocyanine, O16, is strongly hydrogen bonded to at least one water molecule (see later). However, as the solvent polarity is increased further, the C13 resonance moves to 174.0 in dimethyl sulfoxide-d_6 and then to 171.7 ppm in *N*-methylacetamide-*d* (Table 3), suggesting that the carbon−oxygen bond is lengthening toward the value found in sodium phenoxide.[44]

An analysis of the proton coupling constant of the two *trans* hydrogens at the 8 and 9 ethylidene bridge positions (Scheme 1) for merocyanine **4** show only very small variations in deuterated solvents in moving from chloroform to pyridine, methanol, dimethyl sulfoxide, water, or *N*-methylacetamide with values ranging from 15.16 to 16.06 Hz despite a very large change in dielectric constant from 4.8 to 191.3 (Table 2). Furthermore, these small changes show no correlation at all with the dielectric constant of the solvent or its hydrogen-bonding ability. For example, in aprotic solvents the coupling constant changes from 15.32 Hz in chloroform to 15.49 Hz in dimethyl sulfoxide, and in protic solvents the value increases initially from 15.96 Hz in methanol to 16.06 Hz in water but then falls to 15.34 Hz in *N*-methylacetamide (Table 2). ^{1}H NMR data[12]

(40) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: New York, 1988; (a) p 310; (b) p 270; (c) p 315.
(41) Dekoning, A. J.; Bubzelaar, P. H. M.; de Bie, M. J. A.; Boersma, J. *Tetrahedron Lett.* **1980**, *21*, 2105.
(42) De Ridder, D. J. A.; Heijdenrijk, D.; Schenk, H.; Dommisse, R. A.; Lemiere, G. L.; Lepoivre, J. A.; Alderweireldt, F. A. *Acta Crystallogr., Sect. C Cryst. Struct. Commun.* **1990**, *46*, 2197.
(43) van Bolhuis, F.; Kiers, C. T. *Acta Crystallogr., Sect.B* **1978**, *34*, 1015.
(44) Sielar, J.; Pink, M.; Zahn, G. Z. *Anorg. Allg. Chem.* **1994**, *620*, 743.

on model compounds for the zwitterion (**B**) which contain a single double bond show that the coupling constants reported for the *trans* protons in a wide range of 1,2-disubstituted alkenes lie in the range from 14.6 to 15.7 Hz. In contrast, the corresponding data on model compounds for the quinone (**1**) which contain two double bonds connected by a single bond, such as those in 1,4-disubstituted butadienes, show that the coupling constants of *the vic* protons (i.e., those at the C2 and C3 positions of the butadiene) lie in the range 10.4−11.2 Hz. It follows that the central bond of the merocyanine is almost certainly a double bond *in all six solvents* because of the large coupling constant observed.

A similar picture emerges from the proton coupling constant of the merocyanine **4** at the 2,3-positions with small variations observed over the six solvents adopted for measurement with values ranging from 6.04 to 7.42 Hz (Table 2) compared with values of 6.63 Hz for 1-methylpyridinium iodide (this work) and 7.78 Hz for 1-aza-1,4-dimethylcyclohexa-2,5-diene (**8**) for the same ring positions.[41] Again the small variations observed for the merocyanine show no correlation with either dielectric constant of the solvent or its hydrogen-bonding ability. The corresponding proton coupling constant for the same merocyanine (**4**) at the 11,12-positions again shows small variations from 7.63 to 8.76 Hz (Table 2) compared with values of 8.61 and 10.50 Hz for the coupling constants at 2,3-positions in the rings of sodium 4-vinylphenolate (this work) and 4-ethyl-4-methyl-cyclohexa-2,5-dien-1-one (**7b**),[45] respectively.

However, the ^{1}H NMR chemical shifts of both merocyanines do show some small changes with increasing dielectric constant (Table 2). Thus the doublet for H8 varies from 6.30 in chloroform to 6.86 ppm in *N*-methylacetamide while that for H9 varies from 7.36 to 7.77 ppm in the same solvents. These shifts are similar to those observed for the ring protons of many other polar organic molecules, which have only one formal structure,[12] and arise because the protons are in direct contact with the solvent.

Overall, it is concluded from the weight of NMR evidence that the true structure of the merocyanine in solution strongly resembles the zwitterion (**4B**) because of the presence of a central double bond coupled with the presence of two aromatic rings. However, the corresponding NMR results for the di-*tert*-butylmerocyanine (**5**) are somewhat different from those for the simpler merocyanine (**4**) (Tables 2 and 3). While the ^{13}C chemical shift for carbon C2 in the heterocyclic ring of **5** is similar to that of **4** with values ranging from 141.9 to 145.8 ppm, carbon C13 in the phenyl ring resonates further downfield at around 183.6 ppm in solvents of low polarity suggesting that this carbon is quinoid in character with a shorter C13−O16 bond length (Table 3). However, the proton coupling constant of the two *trans* hydrogens at the 8 and 9 ethylidene bridge positions (Scheme 1) are 1.6 Hz smaller than those found for merocyanine (**4**) in all the six deuterated solvents (Table 2), but still strongly consistent with the presence of a double bond. The corresponding proton coupling constant for the same merocyanine (**5**) at the 2,3-positions of the heterocyclic ring are very similar to that of **4** and suggest that the overall structure again resembles the zwitterionic form (**B**) with the exception of the C13−O16 region of the molecule.

The introduction of two *tert*-butyl groups into the ortho positions of benzoquinone has virtually no effect on the carbonyl resonance (see above), probably because the C=O bond length is relatively short at 1.22 Å[43] and the interactions between the two oxygen lone pair electrons and the freely rotating *tert*-butyl

(45) Barner, R.; Boller, A.; Borgulya, J.; Herzog, E. G. *Helv. Chim. Acta* **1965**, *487*, 94.

Table 4. Effect of the Dielectric Constant of Aprotic Solvents on the Low-Energy Absorption Band of the Merocyanines **4** and **5**[a]

solvent	ϵ	4 λ	4 $\Delta\lambda$	5 λ	5 $\Delta\lambda$
dioxane	2.2	619		626	
diethylamine	3.6	619	0	624	−2
diethyl ether	4.3	614	−5	620	−6
ethyl acetate	6.0	611	−8	625	−1
tetrahydrofuran	7.6	614	−5	628	2
pyridine	12.3	600	−19	632	6
acetone	20.7	599	−20	620	−6
N,*N*-dimethylformamide	36.7	591	−28	620	−6
acetonitrile	37.5	574	−45	617	−9
dimethyl sulfoxide	46.7	579	−40	618	−8
ethylene carbonate	89.6	549	−70	614	−12
N-methylacetamide	191.3	535	−84	614	−12

[a] ϵ is the dielectric constant of the solvent (ref 13); λ is the absorption maximum and $\Delta\lambda$ is the absorption position relative to that found in dioxane (in nm).

Table 5. Effect of the Dielectric Constant of Protic Solvents on the Low-Energy Absorption Band of the Merocyanines **4** and **5**[a]

solvent	ϵ	4 λ	4 $\Delta\lambda$	4 $\Delta\lambda_\epsilon$	4 $\Delta\lambda_H$	5 λ	5 $\Delta\lambda$
dioxane	2.2	619				626	
tert-butyl alcohol	10.9	582	−37	−11.0	−26.0	627	1
n-butanol	17.5	536	−83	−6.5	−76.5	624	−2
methanol	32.7	491	−128	−31.5	−96.5	601	−25
ethanediol	37.7	483	−136	−36.0	−100.0	579	−47
water	78.4	447	−172	−66.0	−106.0	526	−100
formamide	111.0	502	−117	−76.0	−41.0	581	−45
N-methylformamide	182.4	516	−103	−83.5	−19.5	598	−28
N-methylacetamide	191.3	535	−84	−84.0	0.0	614	−12

[a] ϵ is the dielectric constant of the solvent (ref 13); λ is the absorption maximum; $\Delta\lambda$ is the absorption position relative to that found in dioxane; $\Delta\lambda_\epsilon$ is the dielectric component of the shift; $\Delta\lambda_H$ is the hydrogen bonding component of the shift (all in nm).

groups are small. However, in the merocyanine **5**, the potentially longer C13−O16 bond length (1.30 Å in the crystal structure of **1**[42]) would result in a larger interaction between the same lone pair electrons and the *tert*-butyl hydrogen atoms, and as a consequence the bond is compressed and the ^{13}C resonance moves downfield.

2. Visible Spectra. The large hypsochromic shift, which is observed in the visible spectrum of the merocyanine **4** in moving from chloroform to methanol (Tables 4 and 5), in common with other merocyanines (Table 1), does not appear to arise, therefore, from a distinct change of structure though the small changes observed in the NMR spectra may reflect very small variations. Furthermore, the possibility that aggregation contributes to the solvatochromic behavior by the formation of dimers or other more complex structures can be discounted as the solutions always obey the Beer−Lambert law over several orders of concentration as noted previously for **2**.[10] However, the 2,6-di-*tert*-butyl derivative **5**, in common with the limited previous results on **2**,[10] does not show the large hypsochromic shift found in aprotic solvents for the simpler derivative (**4**). Thus in moving from solvents with small dielectric constants such as dioxane to those with larger values such as *N*,*N*-dimethylformamide and then to ethylene carbonate, the absorption band for **5** shifts by only −12 nm with an average value for each unit increase in the dielectric constant of approximately −0.14 nm (Figure 1, Table 4). It follows that in aprotic solvents the two *tert*-butyl groups are exerting a considerable effect on the spectroscopic properties of the merocyanine by partly insulating the oxygen atom from the electrostatic field generated by the solvent.
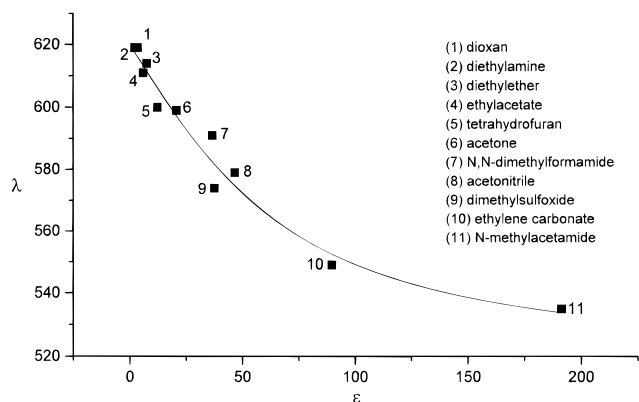
Figure 1. Experimental absorption energies (λ, nm) vs dielectric constant of merocyanine **4** in aprotic solvents.

However, there is a much greater shift in the absorption band of the same merocyanine (**5**) in methanol to 601 nm (Table 5), even though the dielectric constant of this solvent at 32.7 is much smaller than that of ethylene carbonate (Table 4). It appears, therefore, that there are weak hydrogen-bonding interactions between the negatively charged oxygen of the merocyanine (see later) and the acidic hydroxyl hydrogen of methanol, which are mainly responsible for the movement in the absorption to shorter wavelength. With the smaller water molecule, which can be accommodated in the cavity between the oxygen atom and the *tert*-butyl groups, and form a hydrogen bond, the absorption now shifts by 100 nm to a much shorter wavelength of 526 nm (Table 5). The dielectric effect exerted by water would be expected to be similar to that of ethylene carbonate and interpolation of data from the variation of shift with dielectric constants (Figure 1) leads to an expected dielectric shift in water of around 11 nm, leaving a hydrogen-bonding contribution of around 89 nm for the merocyanine (**5**). Applying the same principles to formamide, which shows an overall shift of 45 nm, gives a larger dielectric contribution of 15 nm and a hydrogen-bonding contribution of 30 nm. Thus in protic solvents such as water and formamide, which are relatively small molecules, the hypsochromic shift observed arises *primarily* from the *hydrogen-bonding interaction* between the solvent and the merocyanine oxygen atom.

That hydrogen-bonding interactions are more important than changes to the dielectric constant of the solvent is further demonstrated by the shifts observed for the 2,6-di-*tert*-butyl merocyanine **5** in substituted formamides. In the change from formamide, to *N*-methylformamide, and then to *N,N*-dimethyl-formamide, the absorption band shifts from 581 to 598 nm and finally to 620 nm, respectively (Tables 4 and 5), despite an initial large increase in the dielectric constant from 111.0 to 182.4 and a subsequent sharp fall to 36.7. Formamide is clearly the strongest hydrogen bond donor followed by *N*-methylformamide which appears to have similar strength to methanol. *N,N*-Dimethylformamide is unable to form hydrogen bonds with the merocyanine and the absorption band here is at 620 nm and close to that found in dioxane (Table 4).

In the unhindered soluble merocyanine **4**, the peripheral oxygen atom is more exposed to the dielectric field of the solvent and is able to form hydrogen bonds more readily; as a consequence, the shifts observed are correspondingly larger. Thus the absorption band moves from 619 nm in dioxane to 502 nm in formamide and to 516 nm in *N*-methylformamide (Table 5) through a combination of hydrogen bonding and the dielectric effect, but in *N,N*-dimethylformamide (Table 4) the movement is much smaller due to the dielectric effect alone with the absorption here at 591 nm.

The effect of the dielectric constants of aprotic solvents on the absorption are considerably more marked for this merocyanine (**4**) than the hindered derivative (**5**) with much larger shifts observed in moving from solvents with low dielectric constants to those with larger values. Thus the absorption moves from 619 nm in dioxane to 579 nm in dimethyl sulfoxide through to 549 nm in ethylene carbonate (Table 4) to give an overall shift for **4** of −70 nm versus only −12 nm for **5**. However, the shift observed for *N*-methylacetamide ($\epsilon = 191.3$) suggests that dielectric effect saturates as the absorption here is found at 535 nm representing a maximum shift relative to dioxane of −84 nm (Figure 1, Table 4). Although this solvent has an acidic hydrogen, crystallographic data suggests that it is unlikely to form hydrogen bonds with the oxygen of the merocyanine, because in the favored trans conformation (either alone[46] or in the presence of metal salts[47]), the hydrogen is partly shielded by the adjacent methyl hydrogens on the carbonyl carbon and acts essentially as an aprotic solvent.

The overall shift of −172 nm observed for merocyanine **4** in water relative to dioxane (Table 5), therefore, is composed of a hydrogen-bonding component and a dielectric component which can be derived, in principle, from the shifts observed in aprotic solvents (Figure 1). Interpolation of the graphical data for the shifts in water gives a dielectric component of −66 nm to leave a hydrogen-bonding component of −106 nm (Table 5). This method can be extended to other solvents such as formamide to give a dielectric component of −76 nm and a hydrogen-bonding component here of around −41 nm. The estimated hydrogen-bonding shifts (in nm) for protic solvents follow the expected order with water (−106) > ethanediol (−100) > methanol (−96.5) > *n*-butanol (−76.5) > formamide (−41.0) > *tert*-butyl alcohol (−26.0) > *N*-methylformamide (−19.5).

Theoretical Results. 1. Structural Aspects. An analysis of the Cambridge Structural Database[47] shows that the simple merocyanine (**1**) is essentially planar in the solid state as a trihydrate[42] and exists mainly as the zwitterion (**B**) with a bond length of 1.304 Å at C13−O16 which lies between the C=O double bond length of around 1.22 Å found in benzoquinone[43] and the C−O single bond length of around 1.33 Å found in hydrated sodium phenoxide.[44] The corresponding bonds at C8−C9 and at C4−C8 (or C9−C10) show mainly double and single bond character with lengths of 1.346 and 1.441 Å, respectively (Table 6), versus 1.32 and 1.47 Å for the same bonds in 1,2-diphenylethylenes.[47] There are two water molecules intermolecularly hydrogen bonded to the oxygen atom of the merocyanine **1** with O16−OH2 distances of 2.63 and 2.74 Å. Although the positions of the hydrogen atoms in the intermolecular hydrogen bonds are not usually very accurate by X-ray analysis, the low structural *R*-factor of 4.8% coupled with the accurate O16−OH2 distances suggest that the reported O16−HOH bond distances of 1.59 and 1.75 Å are reliable.[42] The hydrogen bonds are almost linear with O16−H−OH angles of 169.8 and 179.6°, respectively, with the bonded hydrogens 11.0 and 12.1° below the merocyanine plane; each forms an angle of 118.7 and 120.8°, respectively, with O16 and C13. The merocyanine oxygen therefore is mainly sp^2 hybridized. The nearest water molecule to the oxygen atom of the merocyanine **1** is highly polarized so that one H−O bond containing the hydrogen-bonded hydrogen is longer than the other with values of 1.05 and 0.87 Å,

(46) Hamzaoui, F.; Baert, F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, *50*, 757.

(47) Cambridge Structural Database, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 2EW, U.K.

Table 6. Calculated Gas Phase Geometries of the Merocyanine **1** versus Crystallographic Data

parameter[a]	6-31G**	DFT[b]	PM3	AM1	AM1[c]	X-ray[d]
C7−N1	1.450	1.478	1.473	1.436	1.456	1.479
N1−C2	1.369	1.395	1.406	1.388	1.367	1.347
C2−C3	1.337	1.371	1.355	1.364	1.398	1.361
C3−C4	1.455	1.455	1.448	1.450	1.405	1.407
C4−C5	1.455	1.458	1.447	1.446	1.405	1.405
C5−C6	1.337	1.372	1.354	1.365	1.400	1.359
N1−C6	1.368	1.393	1.406	1.388	1.367	1.353
C4−C8	1.359	1.409	1.363	1.366	1.451	1.441
C8−C9	1.432	1.417	1.432	1.425	1.344	1.346
C9−C10	1.355	1.411	1.360	1.364	1.448	1.439
C10−C11	1.456	1.454	1.452	1.449	1.404	1.404
C11−C12	1.333	1.372	1.342	1.347	1.384	1.370
C12−C13	1.474	1.481	1.478	1.471	1.426	1.421
C13−C14	1.473	1.477	1.478	1.469	1.426	1.414
C14−C15	1.334	1.373	1.342	1.346	1.385	1.379
C15−C10	1.456	1.455	1.453	1.454	1.406	1.408
C13−O16	1.205	1.261	1.223	1.242	1.297	1.304
C7−N1−C2	122.2	120.8	120.8	121.6	121.4	120.5
C7−N1−C6	120.2	121.1	119.5	120.2	120.1	120.0
C2−N1−C6	117.6	117.8	119.7	118.2	118.5	119.4
C3−C2−N1	122.7	121.9	120.7	121.9	121.5	121.2
C2−C3−C4	121.9	122.3	121.3	121.5	120.5	121.2
C3−C4−C5	113.1	113.7	116.1	114.8	117.5	115.7
C3−C4−C8	120.8	120.6	121.0	120.3	119.3	120.5
C5−C4−C8	126.1	125.7	122.9	125.0	123.3	123.8
C6−C5−C4	121.3	121.8	121.5	121.3	119.9	121.0
C5−C6−N1	123.4	122.4	120.6	122.3	122.1	121.4
C4−C8−C9	125.6	126.6	123.1	125.2	124.7	125.3
C8−C9−C10	127.5	127.7	123.8	126.2	125.3	128.1
C9−C10−C11	123.7	123.8	122.3	124.2	122.8	124.2
C9−C10−C15	120.2	119.6	120.5	119.7	119.0	119.3
C11−C10−C15	116.1	116.6	117.3	116.1	118.1	116.5
C10−C11−C12	122.3	122.0	121.1	122.5	121.2	121.9
C13−C12−C11	121.9	122.0	121.2	121.8	121.3	121.9
C12−C13−C14	115.6	115.2	116.2	115.5	116.9	116.4
C12−C13−O16	122.0	122.3	121.9	122.3	121.6	121.6
C14−C13−O16	122.4	122.4	121.8	122.2	121.5	122.0
C15−C14−C13	121.5	121.8	121.4	121.7	120.9	120.9
C10−C15−C14	122.7	122.3	121.9	122.4	121.5	122.4
C3−C4−C8−C9	180.0	179.9	179.9	179.9	179.9	176.2
C4−C8−C9−C10	179.9	179.9	180.0	180.0	179.6	179.9
C8−C9−C10−C15	180.0	179.9	180.0	180.0	179.8	176.2
heat of formation[e]	g	h	49.418	59.784	79.28	
dipole moment[f]	13.89	15.744	10.12	12.13	19.81	

[a] Bond lengths in angstroms and angles in degrees. [b] Density functional theory. [c] Sparkles present at 3.0 Å. [d] Reference 42. [e] Heats of formation in kcal mol^{−1}. [f] Dipole moments in Debyes. [g] Total energy −666.998848 au. [h] Total energy −671.104297 au.

respectively, compared with values of 0.99 and 0.92 Å for the corresponding bonds in the other water molecule.

Previous calculations on the structure of the merocyanine using the semiempirical AM1 method[20,27] and the ab initio STO-3G[48] or 3-21G[27] basis sets with full optimization of all variables in the gas phase gave the planar quinone structure (**1A**) in all cases with relatively short C4−C8 and C9−C10 bond lengths corresponding to double bonds, a much longer C8−C9 distance corresponding to a single bond, and a short C13−O16 bond length of 1.24 Å which is slightly longer than that found in benzoquinone[43] at 1.22 Å.

However, as a dielectric field is imposed on the calculated structure either by using a series of point charges[20,27] or by using a reaction field method such as the QCFF/SOL,[23] COSMO,[32] or INDO/S,[19] there is a gradual change in structure toward the zwitterionic form with increasing dielectric constant. These results imply that the bond lengths of the merocyanines and related structures can change significantly under the influence of the dielectric field of the solvent as proposed by Marder et al.[18] However, the experimental evidence from NMR spectroscopy in a variety of solvents presented above is not

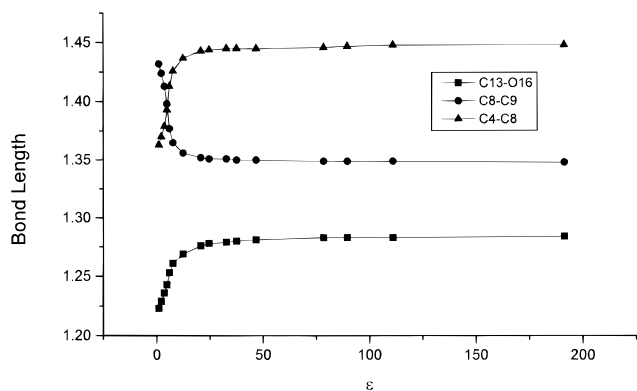(48) Docherty, V. J.; Pugh, D.; Morley, J. O. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1179.

supportive and points to a real structure which is mainly zwitterionic in character even in solvents of low dielectric constant such as chloroform. None of the theoretical methods developed so far have been able to reproduce the experimental structure in nonpolar solvents, and furthermore, the important hydrogen-bonding effects which occur in protic solvents have been ignored.

We have re-examined the structure optimization of the merocyanine using both the AM1/COSMO and PM3/COSMO methods of the MOPAC 93 program and find that the change from the quinone (**A**) toward the zwitterion (**B**) occurs relatively early on with an increasing dielectric constant of the solvent so that the major change has occurred at a value of around 10 (see, for example, the PM3 results in Figure 2). At low dielectric constant, we believe that both methods erroneously predict that the structure is the quinone (**A**). The limiting effect of the solvent appears to occur at a dielectric constant of 30 as a further increase does not markedly change either the C13−O16, C8−C9, or C9−C10 bond lengths further (Figure 2). The resulting structures at both the AM1 and PM3 levels in water is mainly zwitterionic with C4−C8, C8−C9, and C9−C10 bond lengths of 1.446, 1.349, and 1.445 Å for the former and 1.441, 1.353, and 1.438 Å for the latter, respectively (Table 6), and both show

Figure 2. Calculated bond lengths (Å) vs dielectric constant for the merocyanine **1**.

Figure 3. Experimental absorption energies (λ, nm) for merocyanine **4** vs calculated absorption energies (nm) for merocyanine **1** in *N*-methylacetamide (1), ethylene carbonate (2), dimethyl sulfoxide (3), acetonitrile (4), *N*,*N*-dimethylformamide (5), acetone (6), pyridine (7), and tetrahydrofuran (8).

a good correlation with the experimental values of 1.441, 1.346, and 1.439 Å, respectively, found in the crystal structure.[42] The calculated C13−O16 bond lengths of 1.287 and 1.283 Å, respectively, in both structures are somewhat shorter than that found in the crystal at 1.304 Å, but the latter is probably longer than expected because of hydrogen-bonding between O16 and two water molecules as described above.

As all previous calculations have strongly suggested that the merocyanine exists as the quinone in the gas phase, a further calculation has been carried out at the more accurate 6-31G** level to assess the effect of a larger basis set on the structure. However, the results give an even more quininoid structure than those produced with either the STO-3G or 3-21G basis sets with calculated C8−C9 and C13−O16 bond lengths now of 1.432 and 1.205 Å, respectively (Table 6). In contrast, an optimization using the density functional theory program produces different results. The molecule was optimized with the DGAUSS program,[49] incorporating the double-zeta basis set including polarization functions (DZVP) and nonlocal BLYP functionals. The structure now begins to resemble the zwitterion with a C13−O16 bond length of 1.261 Å although the central C4−C8, C8−C9, and C9−C10 bond lengths have approximately the same length with values of 1.409, 1.417, and 1.411 Å, respectively (Table 6). These results suggest that the real structure in the gas phase may also be a zwitterion and it follows that none of the conventional molecular orbital methods at the Hartree−Fock level are able to reproduce the correct geometry.

2. Spectroscopic Results. Although neither the AM1/COSMO or PM3/COSMO method appears to reproduce the correct structure of the merocyanine at low dielectric constants, the methods do give reasonable structures at larger values. Accordingly, spectroscopic calculations were carried out on the optimized structures at a range of dielectric values, and the results are compared with experiment (Table 7). The transition energy between the ground state and first excited singlet calculated using a 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 zwitterion on excitation which has been shown to result in a substantial reduction in the gas phase dipole moment from 19.8 D in the ground state to 11.2 D in the first excited singlet state at the AM1 level.[27] The larger the dielectric constant of the solvent the greater the stabilization of the ground state over the first excited state leading to larger transition energies. The absorption bands in aprotic solvents
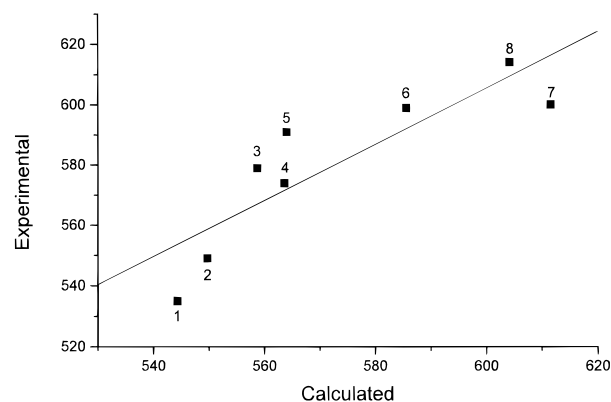
of high dielectric constant are predicted, therefore, to occur at shorter wavelength (i.e., higher energy) than those obtained in aprotic solvents of low dielectric constant, in line with the experimental results. Thus the calculated absorption at the AM1 and PM3 levels in solvents with large dielectric constants such as ethylene carbonate ($\epsilon = 89.6$) at 543 and 550 nm, respectively, compare favorably with the experimental value of 549 nm (Table 8, Figure 3). Likewise, the calculated absorption in solvents of lower dielectric constant such as pyridine ($\epsilon = 12.3$) at 595 and 612 nm, respectively, also show a good correlation with the experimental value of 600 nm (Table 8, Figure 3). However, at very low dielectric constants such as that for dioxane ($\epsilon = 2.2$), the relationship no longer holds and the calculated values occur at much *shorter* wavelengths than expected (Table 8) because the optimized structure reverts to the quinonoid form (**1a**) with the central C8−C9 bond length at 1.42 Å (Figure 2). In ethyl acetate ($\epsilon = 6.0$), the optimized structure begins to revert to the zwitterionic form (**1B**) with the central C8−C9 bond length now at 1.38 Å (Figure 2). If this structure is taken as a representation of the limiting zwitterionic structure in solvents of low dielectric constant, and the absorption energies recalculated in solvents of low dielectric constant using this frozen geometry, the calculated values occur at much *longer* wavelengths than expected (Table 8). These discrepancies almost certainly arise in solvents of low dielectric constant because COSMO is primarily a theory for *high* dielectrics designed for conductors ($\epsilon = \infty$).

Given that the merocyanine is a resonance hybrid which is weighted toward the zwitterion at dielectric constants above 10, where the COSMO spectroscopic calculations appear to work satisfactorily (Table 8), the explanation for the origin of the large hypsochromic shifts observed with increasing values lies with differential stabilization of the ground and first excited state by different solvents. In moving from pyridine ($\epsilon = 12.3$) to ethylene carbonate ($\epsilon = 89.6$), the heat of formation of the merocyanine in the ground state after MECI, calculated using the PM3/COSMO method, falls from 25.78 to 15.86 kcal mol^{-1}, to give stabilization energy of −9.92 kcal mol^{-1} for the more polar solvent (Figure 4). This change in solvent polarity results in an increase in the dipole moment from 38.4 D in the ground state to 42.1 D in the excited state, an overall increase of 3.62 D. However, the corresponding heat of formation in the same solvents for the first singlet excited state after MECI falls from 72.53 to 67.88 kcal mol^{-1}, respectively, giving a net stabilization energy for the excited state of only −4.65 kcal mol^{-1} for the more polar solvent (Figure 4). Here the dipole moment changes

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**Table 7.**   Calculated Geometries of the Merocyanine **1** in Solution versus Crystallographic Data

parameter[a]	PM3/COSMO		AM1/COSMO		AM1/AMSOL		X-ray[b]
	EPS = 4.8	EPS = 78.4	EPS = 4.8	EPS = 78.4	SM4	SM2	
C7−N1	1.477	1.477	1.446	1.453	1.436	1.454	1.479
N1−C2	1.390	1.373	1.379	1.369	1.388	1.375	1.347
C2−C3	1.369	1.388	1.378	1.394	1.364	1.385	1.361
C3−C4	1.428	1.403	1.433	1.412	1.450	1.420	1.407
C4−C5	1.427	1.405	1.429	1.409	1.446	1.418	1.405
C5−C6	1.368	1.385	1.378	1.394	1.365	1.388	1.359
N1−C6	1.389	1.376	1.378	1.369	1.388	1.375	1.353
C4−C8	1.393	1.446	1.395	1.441	1.366	1.422	1.441
C8−C9	1.398	1.349	1.394	1.353	1.425	1.367	1.346
C9−C10	1.387	1.445	1.390	1.438	1.364	1.419	1.439
C10−C11	1.434	1.404	1.434	1.409	1.450	1.417	1.404
C11−C12	1.353	1.375	1.358	1.378	1.347	1.370	1.370
C12−C13	1.459	1.427	1.454	1.430	1.470	1.442	1.421
C13−C14	1.460	1.428	1.455	1.431	1.470	1.443	1.414
C14−C15	1.353	1.377	1.357	1.376	1.346	1.369	1.379
C15−C10	1.435	1.406	1.438	1.413	1.454	1.422	1.408
C13−O16	1.243	1.283	1.259	1.287	1.242	1.276	1.304
C7−N1−C2	120.3	120.4	121.3	120.8	121.6	121.0	120.5
C7−N1−C6	119.6	119.0	120.0	119.7	120.2	119.6	120.0
C2−N1−C6	120.1	120.6	118.7	119.5	118.2	119.4	119.4
C3−C2−N1	120.5	120.3	121.6	121.1	122.0	121.0	121.2
C2−C3−C4	120.9	120.1	121.1	120.4	121.5	120.9	121.2
C3−C4−C5	116.9	118.5	115.8	117.4	114.7	117.0	115.7
C3−C4−C8	120.7	120.2	120.0	119.1	120.3	119.1	120.5
C5−C4−C8	122.4	121.3	124.3	123.4	124.9	123.9	123.8
C6−C5−C4	121.1	120.3	121.0	120.3	121.3	120.3	121.0
C5−C6−N1	120.4	120.1	121.8	121.3	122.3	121.4	121.4
C4−C8−C9	122.8	122.6	124.8	124.6	125.1	124.9	125.3
C8−C9−C10	123.7	123.1	125.9	125.4	126.2	125.7	128.1
C9−C10−C11	121.8	121.3	123.5	123.1	124.2	123.1	124.2
C9−C10−C15	120.3	119.7	119.6	118.9	119.7	119.4	119.3
C11−C10−C15	118.0	119.0	116.9	118.0	116.1	117.5	116.5
C10−C11−C12	121.8	121.2	122.0	121.4	122.3	121.7	121.9
C13−C12−C11	120.8	120.4	121.4	121.0	121.9	121.3	121.9
C12−C13−C14	117.0	118.0	116.3	117.1	115.5	116.6	116.4
C12−C13−O16	121.5	121.0	121.9	121.4	122.3	121.7	121.6
C14−C13−O16	121.5	121.0	121.9	121.4	122.2	121.6	122.0
C15−C14−C13	121.0	120.5	121.3	120.9	121.7	121.0	120.9
C10−C15−C14	121.5	120.9	122.1	121.5	122.5	121.9	122.4
C3−C4−C8−C9	179.9	179.9	179.9	179.9	179.8	180.0	176.2
C4−C8−C9−C10	180.0	180.0	180.0	179.9	180.0	179.9	179.9
C8−C9−C10−C15	180.0	180.0	180.0	179.6	179.9	180.0	176.2
heat of formation	36.248	17.384	43.737	25.970	59.970	41.407	
dipole moment	24.44	42.25	25.521	41.25	12.125	35.425	

[a] Bond lengths in angstroms and angles in degrees. Heats of formation in kcal mol^{-1} and dipole moments in Debyes. [b] Reference 42.

by only 0.94 D from 24.8 D in the ground state to 25.7 D in the excited state. Thus solvents with large dielectric constants have a much greater stabilizing effect on the more polar ground state of the merocyanine than they do on the first excited state.

Similar hypsochromic 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. Previous calculations on the conjugate acid of the merocyanine (**9**) at the AM1 level in the gas phase[27] gave a reasonable correlation with crystallographic data on the merocyanine camphor-10-sulfonate[50] and 4-toluenesulfonate[51] anions with the C13−O16 bond length at 1.364 Å versus experimental values of 1.360 and 1.352 Å, respectively, but the calculated C8−C9 bond length was less satisfactory at 1.359 Å versus experimental values of 1.331 and 1.300 Å, respectively. At the PM3/COSMO level in water (ϵ = 78.4), the results are slightly improved with C8−C9 and C13−O16 bond lengths now of 1.345 and 1.366 Å, respectively (Table 6). MECI calculations on the structures obtained at both

the AM1 and PM3 levels using the energy differences between the ground and first excited singlet state, again in water, give transition energies of 435 and 434 nm, respectively, versus an experimental value of 380 nm (Table 1); neither method, therefore, is able to reproduce the very large shift observed experimentally.

(**9**)
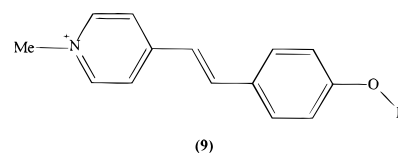
The transition energy of the merocyanine calculated at the CNDOVS level using singly excited configurations is dependent on the value of the spectroscopic constant used in the calculation[33] (see Methods of Calculation). If this is adjusted to reproduce the expected transition energy of 553 nm at a dielectric constant of 78.4 in the absence of hydrogen-bonding contributions (see Figure 1) for either the AM1 or PM3 optimized structures, the predicted transition energy of the conjugate acid (**9**) at 384 nm now shows an excellent correlation with the experimental value of 380 nm (Table 1).

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Fundamental Studies on Brooker's Merocyanine

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Table 8. Calculated Absorption Energies of Merocyanine **1**[a] versus Experimental Values for Merocyanine **4**

		$\lambda_{calculated}$			
solvent	ϵ	AM1	PM3	$\lambda_{experimental}$	structure[b]
gas	1.0	496.7	491.8		o
		753.3	761.2		f
dioxane	2.2	497.4	499.4	619	o
		690.5	700.1		f
diethylamine	3.6	507.9	571.1	619	o
		641.2	651.1		f
diethyl ether	4.3	530.1	533.0	615	o
		622.6	632.2		f
chloroform	4.8	547.6	549.8	620	o
		611.4	620.8		f
ethyl acetate	6.0	577.1	598.6	611	o
tetrahydrofuran	7.6	591.1	604.2	614	o
pyridine	12.3	595.5	611.6	600	o
acetone	20.7	578.4	585.6	599	o
N,N-dimethylformamide	36.7	563.9	564.0	591	o
acetonitrile	37.5	563.4	563.6	574	o
dimethyl sulfoxide	46.7	559.2	558.7	579	o
ethylene carbonate	89.6	542.8	549.7	549	o
formamide	111.0	540.7	547.8	502	o
N-methylacetamide	191.3	537.9	544.3	535	o

[a] ϵ is the dielectric constant of the solvent (ref 13); λ is the lowest energy absorption band (in nm). [b] o = fully optimized and f = frozen geometry for the optimization with eps = 6.0.
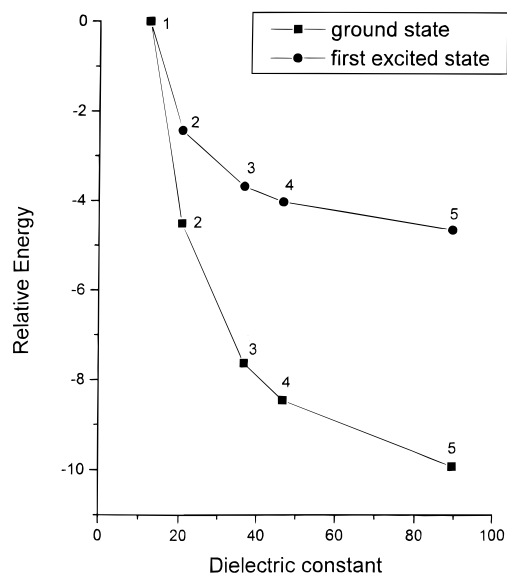

Figure 4. Calculated ground and first excited state energies (kcal mol^{-1}) for merocyanine **1** in acetone (2), *N,N*-dimethylformamide (3), dimethyl sulfoxide (4), and ethylene carbonate (5) relative to the values calculated in pyridine (1).

The hydrated merocyanine would be expected to show a similar but smaller hypsochromic shift to that produced on protonation to the conjugate acid (**9**) as the two oxygen lone pair electrons would be expected to form strong hydrogen bonds with water as seen in the crystal structure.[42] Initial calculations on hydrated merocyanines which contain hydrogen bonds between the oxygen of the merocyanine and one or two water molecules at the AM1/COSMO level in water (ϵ = 78.4) gave only weakly bonded complexes with O16···H$_2$O distances of around 2.10 Å versus distances of approximately 1.57 and 1.75 Å found in the hydrated crystal structure. (This overestimation of the intermolecular hydrogen-bonding distances is a weakness of the AM1 method[52] which extends also to the intramolecular hydrogen-bonding distances found between the phenolic hy-

drogen and either the carbonyl oxygen in salicylaldehyde or the imino nitrogen in salicylaldoxime,[53] with calculated values of 2.02 and 2.11 Å, respectively, versus experimental values of 1.70 and 1.83 Å, respectively[54,55].)

In contrast, the PM3/COSMO method appears to correct this deficiency, and an optimization on the dihydrate in water (ϵ = 78.4) gives a structure with two O16···H$_2$O hydrogen bond lengths of 1.765 Å and C13−O16−H and O16−H−O angles of 111 and 168°, respectively. The presence of the two intermolecular hydrogen-bonded water molecules results in small changes to the overall geometry of the merocyanine with the central C8−C9 and C13−O16 bond stretched to 1.349 and 1.287 Å, respectively, from their values of 1.346 and 1.283 Å in the absence of the attached water molecules. Experimentally, the two lone pair electrons residing on the oxygens of each of the two complexed water molecules of the merocyanine dihydrate would be expected to form additional hydrogen bonds with four further water molecules to give a hexahydrate. A further PM3/COSMO optimization on the merocyanine hexahydrate in water gives a structure with the two O16···H$_2$O hydrogen bond lengths now shortened to around 1.744 Å, with four additional (O16···H$_2$O)···H$_2$O hydrogen bonds predicted at distances of 1.767 Å.

MECI calculations on the PM3 structure of the nonhydrated merocyanine itself in water gives a predicted transition energy of 551 nm which is extremely close to the experimental value of 553 nm expected in an aprotic solvent with the same dielectric constant as water (Figure 1). Surprisingly, however, the presence of attached water molecules at the oxygen atom of the PM3 structure has little effect on the transition energy with both the dihydrate and hexahydrate in water giving calculated transition energies of 554 and 551 nm, respectively. In contrast, spectroscopic calculations at the CNDOVS level on the PM3 structures, again using singly excited configurations only, give predicted transition energies of 529 nm for the dihydrate and 510 nm for the hexahydrate versus 553 nm for the merocyanine in the absence of two water molecules (Table 7). The marked discrepancy between the two methods is difficult to rationalize especially since the atomic orbital components of the molecular orbitals involved in the CI treatment are located at the same atoms. However, since the lowest energy absorption after configuration interaction treatment is composed mainly of the transition of an electron from the HOMO to the LUMO, a picture of the molecular orbital energies and atomic orbital coefficients might shed light on the discrepancy between the two methods.

At the PM3 level, the energy gap between the HOMO and LUMO is calculated to be 187.2 nm for the merocyanine alone versus 188.0 nm for the dihydrate, i.e., an exact trend to that calculated after MECI. At the CNDOVS level using the same structures, the corresponding energy gap between the HOMO and LUMO is calculated to be 321.2 nm for the merocyanine alone versus 307.9 nm for the dihydrate, i.e., the absorption moves to shorter wavelength as found by the CI treatment. In attempt to resolve the discrepancy, self-consistent optimizations were attempted with the 3-21G basis set in water using the Tomasi method[56] coded in the GAMESS program,[39] but the method would not converge for the hydrated merocyanine. Finally, because the structure optimization of the merocyanine

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in the absence of water at the 3-21G level produces the quinone (**A**),[27] single-point calculations were carried out with the 3-21G basis set on the PM3 structures to evaluate the energy gap between the HOMO and LUMO. The results obtained gave a difference of 210.4 nm for the merocyanine alone versus 192.6 nm for the dihydrate, strongly suggesting that the presence of water does indeed shift the absorption to shorter wavelength.

Overall, however, the large experimental shift of around 105 nm expected in moving from a solvent with the same dielectric constant as water (predicted absorption of 553 nm from Figure 1) to the hydrated molecule (experimental absorption of 447 nm, Tables 1 and 5) is not reproduced in any of the calculations reported here though the CNDOVS result does appear to predict the correct trend.

Conclusions

^{1}H and ^{13}C NMR evidence in a range of solvents suggests that Brooker's merocyanine exists as a resonance hybrid which is weighted toward the zwitterion even in solvents of low dielectric constants. The large hypsochromic shift observed in the visible region for the merocyanine in protic solvents arises from both a dielectric effect and a hydrogen-bonding effect. In aprotic solvents, the PM3/COSMO method gives a reasonable account of the structure and spectroscopic shifts of the merocyanine, but in protic solvents, the same method is unable to reproduce the known hypsochromic shifts associated with the formation of stable hydrogen-bonded species such as a dihydrate and hexahydrate. In contrast, the CNDOVS method does predict the correct trends on hydration though the magnitude of the effect is less than that found experimentally.

Experimental Section

Visible spectra were measured using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer and a matched pair of quartz cells of 10 mm pathlength. Solutions of the merocyanine were made up to a concentration 20 ppm, but where solubility disallowed a matched pair of 100 mm quartz cells were used and lower concentration solutions prepared. A stock solution of the merocyanine was prepared from the anhydrous merocyanine (dried *in vacuo* over P_2O_5) in methanol (1×10^{-3} mol dm^{-3}). All solutions were prepared from this same stock solution, with the methanol completely removed under vacuum before new solutions were prepared by addition of dry solvent. Solutions were kept in the dark wherever possible. All spectra were run at room temperature, in solvents of the highest purity (spectroscopic grade and dried over molecular sieves) where possible. Hygroscopic/protic solvents required the addition of tetramethylammonium hydroxide to keep the merocyanine in conjugate base form (see text).

IR spectra were measured using a Perkin Elmer FT-IR 1725X spectrometer, using NaCl plates and a CaF$_2$ solution cell. ^{1}H and ^{13}C NMR spectra were measured in deuterated solvents (Sigma-Aldrich, except for *N*-methylacetamide-*d*) using a Bruker AC400 spectrometer.

In some solvents 10000−20000 scans were required to obtain the necessary resolution for the ^{13}C spectra.

The pyridinium salts were prepared by refluxing γ-picolene (Sigma-Aldrich) with the corresponding branched-chain alkyl halide (supplied by Zeneca). The *N*-alkylpyridinium salts were condensed with the corresponding *p*-hydroxybenzaldehyde (Sigma-Aldrich) according to literature procedures.[58,59] Purity was determined by thin-layer chromatography on silica gel UV$_{254}$ (Sigma-Aldrich). Melting points of the unhindered merocyanines proved difficult to pinpoint due to phase changes of the crystals, which is in agreement with the findings of Minch and Shah.[60] The actual final melting point was found to be highly dependent on the rate of heating.

4-[1-Isodecyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one (4). *N*-Alkylation of γ-picolene (3.00 g, 32 mmol) with isodecyl bromide (7.07 g, 32 mmol), by refluxing in dry 2-propanol (5 mL) for 5 h, yielded *N*-isodecylpyridinium bromide which was used without further purification. Condensation with 4-hydroxybenzaldehyde (1.22 g, 10 mmol) in 15 mL of dry ethanol with piperidine (1 mL, 10 mmol) gave the corresponding benzyl alcohol, which was dehydrated and deprotonated by suspending the solid in 50 mL of aqueous KOH (0.2 M) and warming gently. The hydrophobic merocyanine which precipitated out of solution was further recrystallized from hot ethanol−aqueous KOH to give blue/purple crystals with a metallic lustre. The product was dried over P_2O_5 in vacuum to yield a black amorphous powder, which rapidly turns scarlet in air (1.84 g, 60%): mp 150−155 °C; IR (KBr) 3035, 1643, 1564, 1509, 1467, 1318, 1204, 1148,-1041, 977 cm^{-1}.

3,5-Di-*tert*-butyl-4-[1-isononyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one (5). *N*-Alkylation of γ-picolene (3.00 g, 32 mmol) with isononyl bromide (6.60 g, 32 mmol), by refluxing in dry 2-propanol (5 mL) for 5 h, yielded *N*-isononylpyridinium bromide, which was again used without further purification. Condensation with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (2.34 g, 10 mmol) in 15 mL of dry ethanol with piperidine (1 mL, 10 mmol) as before gave the benzyl alcohol, which was dehydrated and deprotonated by suspending the solid in this case in 50 mL of ethanol−ammonia solution. The hydrophobic merocyanine which precipitated out of solution was further recrystallized from hot ethanol−ammonia to give a dark-green powder with a metallic lustre after drying over P_2O_5 in vacuum (3.70 g, 85%): mp 235−237 °C; IR (KBr) 3035, 1646, 1609, 1567, 1509, 1477, 1429, 1381, 1350, 1323, 1261, 1213, 1164, 1096, 1019, 961 cm^{-1}.

N-Methylacetamide-*d*. *N*-Methylacetamide (5.00 g, 68 mmol) and excess deuterium oxide (5.47 g, 0.27 mol) were gently heated under reflux conditions for 12 h. Vacuum distillation removed excess D$_2$O and water products, leaving a mixture of deuterated and undeuterated *N*-methylacetamide which crystallized when cooled to room temperature. The product was dried over P_2O_5 in vacuum to yield translucent crystals. Analysis by mass spectrometry (EI) showed that deuteration was 30% successful: mp 23 °C; ^{1}H NMR (CDCl$_3$) 8.10 (broad s), 2.77 (s), 2.01 (s) ppm; ^{13}C NMR (CDCl$_3$) 171.7, 26.1, 22.7 ppm.

JA971477M

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