Spectroscopic Studies on Brooker's Merocyanine

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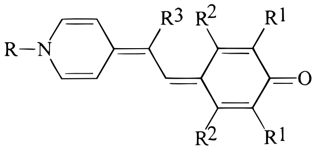
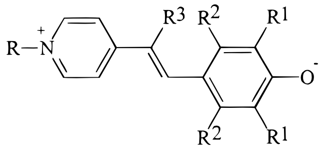
Abstract: The origin of the multiple absorption bands of Brooker's merocyanine, 1-(4-aza-4-methylphenyl)-2-*trans*-(4-oxyphenyl)ethene, found in the visible region of the spectrum in solvents such as chloroform and tetrahydrofuran, has been explored experimentally using ^{1}H and ^{13}C NMR spectroscopy and theoretically using molecular orbital methods. While NMR analysis rules out the presence of a cis conformer, AM1/COSMO calculations in various solvents strongly suggest that there are a number of stable nonplanar conformations of the merocyanine as well as a dimer which are predicted to absorb at longer and shorter wavelengths, respectively, than the favored planar conformer. Spectroscopic analysis at variable temperature is supportive with the intensity of the longer wavelength absorption initially reducing with decreasing temperature, followed by an increase in the concentration of dimers and possibly aggregates. Further support is provided by synthesis of the corresponding nonplanar merocyanine containing methyl groups at the double bond and at the *ortho* positions of the oxyphenyl ring, which absorbs at longer wavelength than its related planar analogue.

Introduction

Merocyanines dyes such as such as 1-(4-aza-4-methylphenyl)-2-*trans*-(4-oxyphenyl)ethene (**1**) have attracted considerable attention since their discovery by Brooker et al.,[1,2] because of their ability to change color from blue in nonpolar solvents to orange-red in protic solvents, with the absorption moving, for example, from 620 nm in chloroform to 447 nm in water.[2] Although this large solvatochromic shift was originally attributed to a distinct change in structure from the covalent quinone (**1A**) to the zwitterion (**1B**), our recent studies on the more soluble merocyanines (**3** and **4**) have suggested that the molecule exists as a resonance hybrid which is weighted toward the zwitterion even in solvents of low dielectric constants.[3] The large shift observed arises from both the dielectric effect of the solvent and its ability to hydrogen bond with the peripheral oxygen atom of the merocyanine,[3] leading to greater stabilization of the more polar ground state over the first excited state in solvents of high polarity.[3,4]



(A)



(B)

1, $R = CH_3$; $R^1 = R^2 = R^3 = H$

2, $R = CH_3$; $R^1 = (CH_3)_3C$; $R^2 = R^3 = H$

3, $R = (CH_3)_2CHC_7H_{14}$; $R^1 = R^2 = R^3 = H$

4, $R = (CH_3)_2CHC_6H_{12}$; $R^1 = (CH_3)_3C$; $R^2 = R^3 = H$

5, $R = R^2 = R^3 = CH_3$; $R^1 = H$

6, $R = CH_3(CH_2)_3CH(C_2H_5)CH_2$; $R^1 = R^2 = R^3 = H$

7, $R = CH_3(CH_2)_3CH(C_2H_5)CH_2$; $R^2 = R^3 = CH_3$; $R^1 = H$

Although good correlations have been claimed between the calculated shifts of Brooker's merocyanine (**1**) and the main experimental absorption band in aprotic solvents with widely differing dielectric constants,[5−9] the visible absorption spectrum is complicated by the presence of distinct shoulders and/or additional absorption bands, which have usually been ignored, particularly in most theoretical discussions. For example, in chloroform, merocyanine **3** shows a main absorption band at 620 nm, with a second absorption at 582 nm, together with evidence of a shoulder at around 540 nm (Figure 1a). The second absorption band has been tentatively assigned in previous studies on the simpler merocyanine **1** to the presence of a cis isomer.[10] However, other studies on the closely related 2,6-di-*tert*-butyl merocyanine (**2**) have questioned this assignment for the additional peak, which appears in both chloroform and ethanol, and suggested on the basis of the emission spectrum that it corresponds to a second, as yet unidentified vibrational form of the merocyanine.[11] While the cis merocyanine is known and has been prepared by photoisomerization of the protonated

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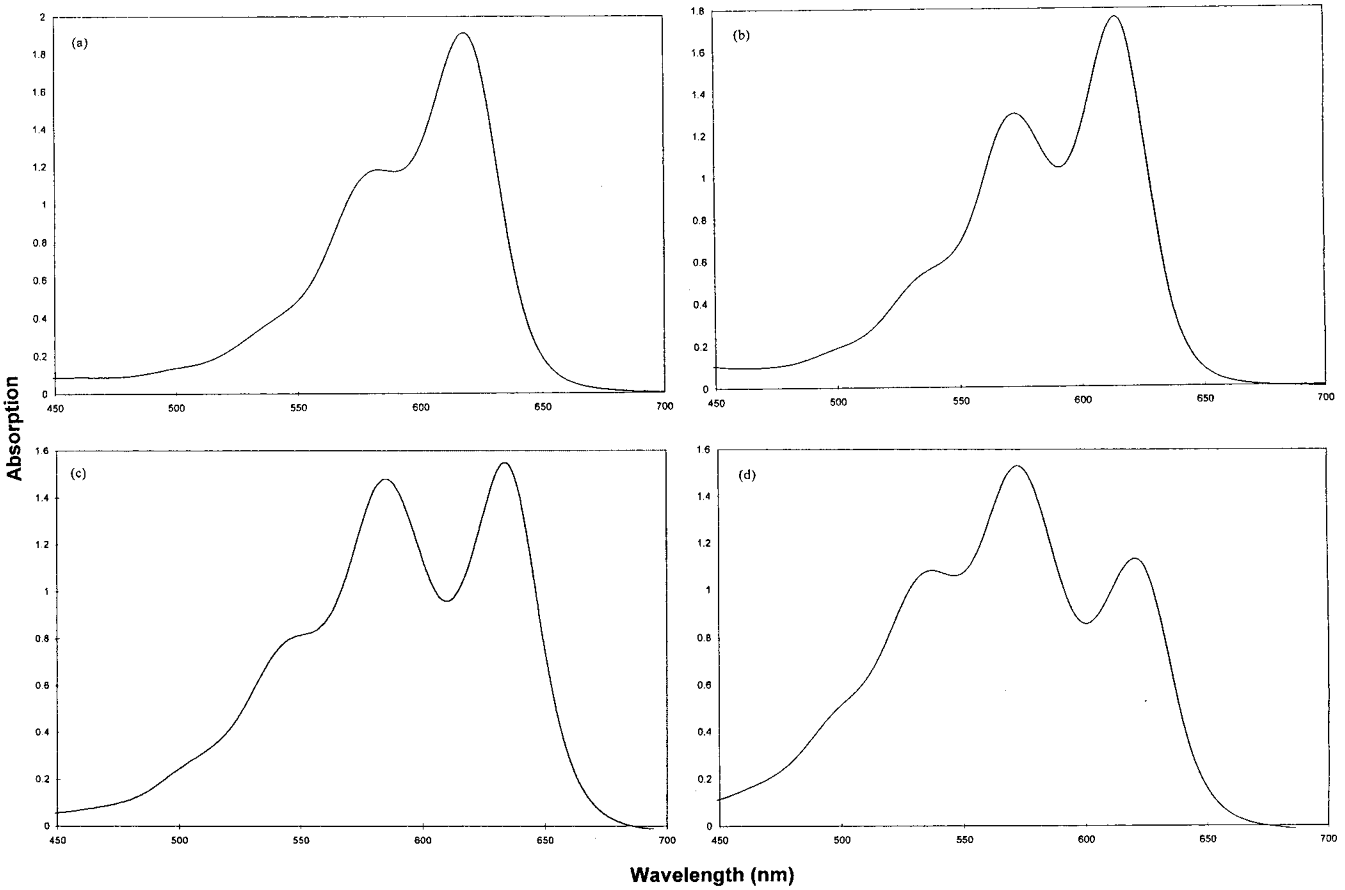

Figure 1. Visible absorption spectra of (a) merocyanine **3** in chloroform, (b) merocyanine **3** in tetrahydrofuran, (c) merocyanine **4** in chloroform, and (d) merocyanine **4** in diethyl ether.

trans isomer of the parent merocyanine **1** followed by deprotonation, there is no direct route via isomerization of the trans merocyanine itself.[12−14]

The possibility that the second absorption band is due to aggregation and 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**.[11] The alternative possibility that there are two or more excited states for the merocyanine in the visible region seems unlikely on the basis of a number of spectroscopic calculations at several different levels of theory which predict one band only.[5−9,15−17]

The present studies have been carried out, therefore, to identify the structure(s) responsible for the other absorption band(s) found in the visible spectra of the merocyanines using a combination of theoretical calculations on **1** and **2** and experimental measurements on more soluble derivatives such as **3** and **4**.

Methods of Calculation

Molecular orbital calculations were carried out on the merocyanines **1** and **2** using the AM1[18] and PM3[19] methods of the MOPAC 93 program[20] with full optimization of all bond lengths, angles, and torsion angles. The effect of solvents of varying dielectric constant (ϵ) on the structures and energies of the merocyanines were assessed using the COSMO[21] method of the same program[20] using tetrahydrofuran ($\epsilon = 7.60$), pyridine ($\epsilon = 12.4$), acetone ($\epsilon = 20.7$), and dimethyl sulfoxide ($\epsilon = 46.7$) (keywords for the calculation in tetrahydrofuran: prec am1 ef xyz geo-ok eps=7.60). Conformational analyses were carried out using mainly the AM1 method by selecting a number of different starting geometries for the optimization by rotating either the left-hand ring (A) and/or the right-hand ring of the merocyanine (B) by 10, 20, and 30° increments relative to the plane formed by atoms C4−C8−C9−C10 (see Chart 1). The starting conformations considered for **1** were as follows.

A: a planar structure but with ring A rotated (C5−C4−C8−C9 = $\theta_1 = \pm 10{-}30°$).

B: a planar structure but with ring B rotated (C15−C10−C9−C8 = $\theta_2 = \pm 10{-}30°$).

AB1: ring A rotated (C5−C4−C8−C9 = $\theta_1 = \pm 10{-}30°$) and ring B rotated in the same direction (C15− C10−C9−C8 = $\theta_2 = \pm 10{-}30°$).

AB2: ring A rotated (C5−C4−C8−C9 = $\theta_1 = \pm 10{-}30°$) and ring B rotated in the opposite direction (C15−C10−C9−C8 = $\theta_2 = \pm 10{-}30°$).

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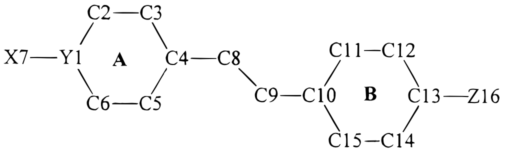
Chart 1. Numbering Convention Adopted for the Merocyanine (**1**, X = C, Y = N, and Z = O) and the Stilbenes (**8**, X = Z = H, Y = C, and **10**, X = Z = OMe, Y = C)



Around 60 representative starting conformations were selected from the total of 192 possible options in addition to the four planar conformations (**P**) in each solvent, but only a limited number were found to be stationary points on the potential energy surface. These were identified by using force calculations on each separate structure (keywords for the calculations in acetone: am1 xyz eps=20.7 force large let isotope), and only those showing positive vibrational frequencies were considered further. Spectroscopic calculations were then carried out with MOPAC93 on the most stable fixed ground-state conformations of **P, A**, **B**, **AB1**, and **AB2** using the multielectron configuration interaction (MECI) treatment (keywords for the ground-state calculation in tetrahydrofuran: am1 prec 1scf xyz eps=7.6 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 of each conformer and the first excited singlet-state energy (same keywords except: root = 2 and open(2,2) added). A series of additional calculations were carried out in the gas phase using the CNDOVS method,[22] which has been parametrized for dyes and is based in part on the older CNDO/S formalism,[23] as an independent check on some of the AM1/COSMO results.

A different conformational approach was considered for the 2,6-di-*tert*-butyl merocyanine (**2**) because the two *tert*-butyl groups here are able to adopt a number of different arrangements in each of the possible planar and nonplanar structures. The conformations explored were carried out on the major planar structure only in the same solvents to assess the effect of the large group on the spectra, and included the following.

P/C: One methyl component of the each of the two *tert*-butyl groups was placed in the molecular plane near the aromatic carbons C11 and C15, respectively, with the remaining two methyl groups of each of the two *tert*-butyl groups symmetrically disposed above and below the molecular plane adjacent to the oxygen atom O16.

P/D: One methyl group of each of the two *tert*-butyl groups was placed in the ring plane as before with both in the vicinity of O16, with the remaining two methyl groups of each of the two *tert*-butyl groups symmetrically disposed above and below the molecular plane near aromatic carbons C11 and C15, respectively.

P/E: One *tert*-butyl group arranged as in **P/C**, with the methyl component of the group placed in the molecular plane near the aromatic carbon C11, and the other *tert*-butyl group arranged as in **P/D**.

Although other conformations are possible, these were considered to be a representative set for the purposes of the present study.

Discussion

NMR Data. A detailed NMR analysis of the merocyanines **3** and **4** in solvents with low dielectric constants, which give two or more strong absorption bands in the visible region, shows no discernible difference in the ^{1}H coupling constants ($J_{8,9}$) between protons H8 and H9 located at the double bond over other solvents which show one main absorption peak only (Figure 1, Table 1). For example, the visible spectrum of **3** in chloroform shows two major absorptions at 582 and 620 nm, with a distinct shoulder at around 540 nm (Figure 1a), yet the ^{1}H NMR spectrum in the same deuterated solvent shows a simple AX pattern of two doublets with a coupling constant, $J_{8,9}$, of 15.3 Hz (Table 1), which compares favorably with values of 14.0−15.7 Hz found for the trans protons in a wide range of 1,2-disubstituted alkenes[24,25] and contrasts markedly with values of 10.0−12.0 Hz found for the cis protons in closely related systems[24,25] which we have previously discussed in depth.[3] A similar AX pattern of two doublets and coupling constant, $J_{8,9}$, of 15.2−15.5 Hz are found in solvents such as deuterated pyridine, dimethyl sulfoxide, and *N*-methylacetamide, but here the two main bands in the visible spectrum, recorded in the undeuterated solvents, merge with increasing dielectric constant so that only a single broad band is observed at 579 and 535 nm, respectively, for the latter cases.

The NMR spectrum of **4** in deuterated chloroform (Table 1) also shows a simple AX pattern of two doublets ($J_{8,9}$ = 13.7 Hz), despite the presence now of two major absorption peaks of almost equal intensity 584 and 634 nm and a shoulder at around 550 nm (Figure 1c). In diethyl ether, the visible spectrum of **4** is better resolved, and the shoulder now becomes a distinct absorption at 537 nm in addition to the longer wavelength absorptions at 572 and 620 nm (Figure 1d). Similar AX patterns are found for **4** in other solvents, such as deuterated pyridine, dimethyl sulfoxide, and *N*-methylacetamide, with $J_{8,9}$ values ranging from 14.6 to 14.8 Hz (Table 1). As the protonated trans and cis forms of the merocyanine **1** show coupling constants ($J_{8,9}$) of 16.2 and 12.1 Hz, respectively,[14] in line with the data discussed for the respective alkenes, the presence of a cis conformer in solutions of the merocyanine **3** can be completely discounted, and the additional absorption bands found in the visible spectra must arise from some other structural attribute.

The corresponding ^{13}C chemical shifts of merocyanines **3** and **4** in deuterated chloroform show few differences from those found in deuterated *N*-methylacetamide, with similar chemical shifts for most of the carbons with the exception of the resonance of C13, which moves upfield with increasing dielectric constant (Table 2). These results again suggest that the structures of the merocyanines in solution show little change on moving from solvents with low dielectric constants to those with high values, as we have previously discussed.[3] It follows from both the ^{1}H and ^{13}C data, therefore, that the structures responsible for the different absorption bands in solution must be very closely related.

Conformational Studies. In loosely related structures such *trans*-stilbene **8**, an examination of the Cambridge Structural Database[26] shows that the molecule is essentially planar,[27−30] with the phenyl rings twisted by around 3−5° from the plane

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Table 1. ^{1}H NMR Data Obtained for the Merocyanines **3**, **4**, **6**, and **7**[a]

			chemical shift (ppm)						coupling constant (Hz)		
solvent	ϵ	merocyanine	H2	H3	H8	H9	H11	H12	$J_{2,3}$	$J_{8,9}$	$J_{11,12}$
$CDCl_3$	4.8	**3**	7.53	7.08	6.30	7.36	7.31	6.52	6.74	15.32	8.64
		4	7.50	6.89	6.03	7.21			7.06	13.70	
		6	7.46	7.03	6.27	7.36	7.31	6.48	6.49	15.29	8.85
		7	9.24	7.91	(2.21)			4.76	6.64		
C_5D_5N	12.4	**3**	8.40	7.87	6.70	7.88	7.69	7.16	7.42	15.16	8.76
		4	8.07	7.34	6.79	7.92	7.59		6.47	14.62	
CD_3COD_3	20.7	**6**	8.71	8.03	7.09	7.85	7.65	6.88	6.84	15.99	8.65
		7	10.5	9.35	(2.22)	4.83		6.03	6.96		
$(CD_3)_2SO$	46.7	**3**	8.44	7.75	6.75	7.80	7.40	6.37	6.21	15.49	8.67
		4	8.35	7.82	6.18	7.50	7.17		7.05	14.73	
$CH_3CONDCH_3$	191.3	**3**	8.61	7.86	6.86	7.77	7.41	6.55		15.34	7.63
		4	7.78	7.33	6.42	7.72	7.42		7.00	14.79	

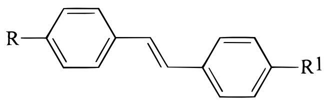
[a] Protons at the 5, 6, 14, and 15 positions are essentially equivalent to those at the 3, 2, 12, and 11 positions. ϵ is the dielectric constant of the nondeuterated solvent. Values in parentheses are the resonances of the methyl hydrogens.

Table 2. ^{13}C NMR Data Obtained for the Merocyanines **2**, **3**, **4**, **6**, and **7**[a]

			chemical shift (ppm)								
solvent	ϵ	merocyanine	C2	C3	C4	C8	C9	C10	C11	C12	C13
$CDCl_3$	4.8	**3**	141.1	120.7	153.8	108.4	144.1	116.6	133.1	120.2	178.6
		4	141.9		147.0	104.3		119.3	135.9		183.5
		6	141.1	120.8	153.9	111.5	144.7	118.6	132.5	120.3	177.4
		7	144.7		164.1	113.3		127.8	134.1		
C_5D_5N	12.4	**3**	145.2	122.5	154.1	110.9	142.1	120.0	134.2	120.2	178.7
		4	143.9	128.7	141.7	105.1	149.8	120.3	138.4		183.7
CD_3COD_3	20.7	**6**	144.3	123.0	155.6	103.9	144.1	116.7	132.9	118.3	178.3
		7	141.1	129.9	193.5	115.8	147.3	122.8	130.1		208.2
$(CD_3)_2SO$	46.7	**3**	143.9	120.4	155.7	111.9	142.6	119.0	132.1	119.7	174.0
		4	143.7		150.3	104.3		115.6	139.4		180.3
$CH_3CONDCH_3$	191.3	**3**	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	41.0		174.1

[a] Carbons at the 5, 6, 14, and 15 positions are essentially equivalent to those at the 3, 2, 12, and 11 positions. ϵ is the dielectric constant of the nondeuterated solvent. Spaces in the table indicate that the resonances could not be resolved.

of the central C4−C8−C9−C10 atoms (Chart 1). The degree of twist increases in substituted derivatives such as 4-(2-(4′-nitrophenyl)ethenyl)phenylcarbamic acid ethyl ester (**9**),[31] where the right-hand ring (B) is twisted 12.3° from the central plane. However, the more symmetrical bis(4-methoxy)-*trans*-stilbene (**10**) exists in two conformations.



8, $R = R^1 = H$

9, $R = NO_2$; $R^1 = NHCO_2Et$

10, $R = R^1 = OMe$

One of these is a stable orthorhombic form,[32] which undergoes a photoinduced conformational change on irradiation to give an unstable twisted monoclinic form.[32] In the former conformer, each aromatic ring is twisted in the same direction by 10.4° below the plane formed by the central atoms C4−C8−C9−C10, with a central C8−C9 bond length of 1.316 Å. However, in the latter, both rings are again twisted in the same direction but here by 30.9° below the plane of the same central atoms.[32] The reduced overlap between the aromatic rings and the ethylenic bridge in this conformation appears to be compensated by a short central C8−C9 bond length of 1.276 Å.

The possibility that the observed absorption bands of the merocyanine in solution arise from the presence of planar and nonplanar conformations, similar to those found for the stilbene **10**, has been explored by calculating the structure of the molecule from several different starting positions using the AM1/COSMO method in both aprotic and protic solvents. For example, the AM1 optimization of a starting structure for the merocyanine **1** in dimethyl sulfoxide, based on the twisted monoclinic form of bis(4-methoxy)-*trans*-stilbene (**10**), gives a twisted structure, where the heterocyclic and phenyl rings are twisted by −30.5 and −21.3°, respectively, to the plane formed by the central C4−C8−C9−C10 atoms. In this conformation, which is only 0.84 kcal mol^{-1} higher in energy than the fully planar structure, the C8−C9 and C13−O16 bond lengths at 1.350 and 1.289 Å differ only slightly from the values of 1.354 and 1.287 Å found in the optimized planar structure in dimethyl sulfoxide (Table 3). A force calculation on the twisted conformer gives positive frequencies only, thus ruling out the possibility that it could be a transition state rather than a genuine stationary point on the potential energy surface. A very similar structure is obtained at the AM1 level in water, but here the twisted conformer is slightly more stable than that found in dimethyl sulfoxide, as shown by the smaller energy difference of 0.57 kcal mol^{-1} relative to the planar structure; again, positive frequencies only are generated from a force calculation. However, in acetone the twisted conformer is predicted to be less stable and now 1.00 kcal mol^{-1} above the planar structure.

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Table 3. Selected Stable Conformers of the Merocyanines **1**, **2** and **5**, Calculated at the AM1/COSMO Level in Aprotic Solvents[a]

				torsion angle (deg)		bond length (Å)				calcd λ		exptl λ	
structure	solvent	ϵ	conformational type	θ_1	θ_2	C4−C8	C8−C9	C13−O16	ΔH_f	AM1	CNDOVS	I	II
1	tetrahydrofuran	7.6	**P**	0.0	0.0	1.419	1.370	1.271	38.77	591.0	537.9	614	573
			B	0.2	9.7	1.420	1.369	1.272	38.95	594.4	580.0		
			AB2	9.8	−9.2	1.423	1.368	1.272	39.08	618.1	550.1		
			AB1	18.8	20.3	1.428	1.363	1.275	39.81	632.7	572.4		
	pyridine	12.4	**P**	0.0	0.0	1.431	1.361	1.278	34.05	595.1	553.9	600	570 sh
			A	13.7	5.1	1.434	1.360	1.280	34.20	599.1			
			B	0.0	20.0	1.434	1.357	1.280	34.60	604.5	616.8		
			AB1	30.5	29.4	1.441	1.353	1.282	35.70	611.6	634.5		
			AB2	20.1	−19.3	1.437	1.355	1.281	34.87	611.9	640.4		
	acetone	20.7	**P**	0.0	0.0	1.436	1.356	1.284	30.50	578.4	562.7	599	575 sh
			A	20.3	0.4	1.436	1.357	1.283	30.75	582.7	622.8		
			B	6.5	21.1	1.439	1.354	1.284	30.95	582.8	625.0		
			AB1	10.2	9.8	1.437	1.355	1.283	30.57	579.5	610.0		
			AB2	19.3	−17.6	1.440	1.354	1.285	31.15	587.6			
	dimethyl sulfoxide	46.7	**P**	0.0	0.0	1.440	1.354	1.286	27.06	559.2	567.9	579	
			A	10.3	−0.2	1.441	1.353	1.283	27.08	560.7	573.2		
			A	29.9	0.6	1.445	1.351	1.288	27.55	566.2	610.0		
			B	0.2	10.0	1.440	1.354	1.286	27.14	559.0	612.6		
			AB1	30.6	30.1	1.447	1.349	1.289	28.29	563.0	695.0		
2	acetone	20.7	**P/C**	0	0	1.416	1.375	1.259	9.31	602.6		620	578
			P/D	0	0	1.422	1.369	1.261	12.30	615.3			
			P/E	0	0	1.420	1.370	1.261	10.70	610.5			
5	tetrahydrofuran	7.6	**AB1**	44.1	48.1	1.460	1.354	1.283	30.20	702.2	748.0	629	

[a] ϵ is the dielectric constant; ΔH_f is the ground-state heat of formation in kcal mol^{-1}; λ is the absorption maximum in nm, where the experimental values for the two bands I and II are given for structure **3** representing **1**, **4** representing **2**, and **6** representing **5**, respectively.

The PM3 method also predicts stable nonplanar structures for the merocyanine. For example, in acetone the heterocyclic and phenyl rings are twisted now by −32.9 and −12.8°, respectively, to the central plane, but here the twisted conformer is less stable than the planar conformer, compared with the AM1 results, now by 1.55 kcal mol^{-1}. In the absence of solvent, only the planar quinone form of the merocyanine (**1A**) results from structure optimization at the AM1 or PM3 levels, as noted previously.[16,17]

While the starting conformation adopted for the initial structural optimizations was based on the twisted monoclinic form of bis(4-methoxy)-*trans*-stilbene (**10**), there are clearly a large number of other alternative possibilities based on the rotation of either the left-hand ring (conformation **A**) or the right-hand ring (conformation **B**) of the merocyanine while keeping the remainder of the conjugated structure planar, or the rotation of both rings (conformations **AB1** and **AB2**) relative to the central plane formed by atoms C4−C8−C9−C10 (see Methods of Calculation). More thorough calculations were then carried out to explore the conformational hyperspace in a more systematic and rigorous manner by rotating each ring in turn by up to 30° in 10° increments in solvents of differing dielectric constants, such as tetrahydrofuran, pyridine, acetone, and dimethyl sulfoxide, using the AM1 method as an example. The resulting optimized structures from each starting position were subjected to force calculations (described above), and those which did not yield all positive vibrational frequencies were discarded. The remainder, representing conformer types **A**, **B**, **AB1**, and **AB2**, were subjected to subsequent spectroscopic calculations in each of the four solvents (Table 3).

An analysis of the resulting structures on each conformational type showed that the initial torsion angles adopted of 10, 20, and 30° remained substantial after optimization. For example, optimization of conformer **A** in pyridine at an initial 20° twist at the aromatic ring produced a structure which was 0.15 kcal mol^{-1} higher in energy than the fully planar conformer, with a final twist of 13.7° at ring A and a 5.1° twist at ring B (Table 3). Similarly, optimization of conformer **AB2** in acetone at initial twists of 30 and −30° for each aromatic ring relative to the central plane formed by atoms C4−C8−C9−C10 produced a final structure which was 0.65 kcal mol^{-1} higher in energy than the fully planar conformer, with final twists now of 19.3 and −17.6°(Table 1). In a number of other conformers, which gave all positive frequencies, there was little change to the initial starting torsion angles. For example, optimization of conformer **B** in tetrahydrofuran at an initial 10° twist at the aromatic ring produced a structure which was 0.18 kcal mol^{-1} higher in energy than the fully planar conformer, with a final twist of 9.7° at ring B and a 0.2° twist at ring A (Table 3). While these energy differences calculated by the AM1/COSMO method are only approximate, they do indicate the relative stability of one conformer against another in a given solvent. However, the Boltzmann distribution for the relative populations of the planar conformer **P** versus the twisted conformer **B** in tetrahydrofuran (Table 3) yields a ratio of 1.35 in favor of the former, which resembles the intensity of the observed bands of **3**, and particularly **4**, in the same solvent when the ratios of the integrated areas under each peak are considered (Figure 1b,c).

Aggregation Effects. The simple merocyanine **1** is essentially planar in the solid state as a trihydrate[33] and exists mainly as the zwitterion (**B**), with a double bond at C8−C9 and single bonds at C4−C8 and C9−C10 with lengths of 1.346 and 1.441 Å, respectively, versus average values of 1.33 and 1.47 Å found for the same bonds in a series of 1,2-diphenylethenes present in the Cambridge Structural Database.[26] The corresponding bond length of 1.304 Å at C13−O16 appears to lie between the C═O double bond length of around 1.22 Å found in benzoquinone[34] and the C−O single bond length of around 1.33 Å found in hydrated sodium phenoxide.[35] 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. The hydrogen bonds are almost

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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, implying that the merocyanine oxygen is mainly sp^2 hybridized.

In the crystal, the merocyanine molecules are arranged so that the constituent atoms which lie in one plane along the *x* and *y* axes form head-to-tail and tail-to-head dimers with molecules which lie in the plane below.[33] The central double bonds are parallel to one another, with the nitrogen (N1) and oxygen (O16) atoms of one molecule in the first plane positioned over the oxygen (O16′) and nitrogen (N1′) atoms, respectively, of the other in the second plane at internuclear distances of N1−O16′ and O16−N1′ of 3.33 Å in the *z*-direction (the numbers of the second molecule are primed for distinction). The aromatic rings in each plane are, therefore, displaced in the *x*-direction by the C−O bond length so that the bridging carbon, C8, and aromatic carbon, C10, of the first molecule lie over the C10′ and C8′ atoms, respectively, of the molecule below, but at a larger separation distance of 3.61 Å. The net effect of the increased separation distance at the center is that each molecule of the dimer is bowed outward from the nitrogen and oxygen atoms of each component.

The intermolecular separation effectively rules out any covalent bonding between the two units, because the atoms in each plane lie outside the van der Waals contact distances for carbon, nitrogen, or oxygen. The free merocyanine has a large calculated ground-state dipole moment, and if the molecule is partitioned between C8 and C9, a summation of the calculated atomic charges shows that the left-hand side, containing the heterocyclic ring **A**, is positive and the right-hand side, containing the phenolic ring **B**, is negative,[17] resulting in the observed centrosymmetric crystal packing arrangement in the dimer. It follows that the formation of the dimer is a consequence mainly of electrostatic interactions between the oppositely charged ends of each molecular component, which effectively cancels the dipole moment.

In solvents of high dielectric constant, the dimer would be expected to dissociate into single solvated monomers, but in solvents of low dielectric constant, it is possible that the dimer would persist as a discrete entity. Although there are no direct orbital interactions between the two molecules in the dimer, calculations were carried out on a hypothetical dimer, constructed from two planar merocyanine molecules, using the AM1 and PM3 methods coupled with the COSMO routine of MOPAC 93, to assess whether these methods are able to predict aggregation effects. In the empirical starting structure adopted, the N1, C8, C10, and O16 atoms of one molecule in the first plane were positioned over the O16′, C10′, C8′, and N1′ atoms, respectively, of the other in the second plane, as in the crystal structure, but with each intermolecular distance set at around 2.0 Å.

In tetrahydrofuran ($\epsilon = 7.60$), the AM1/COSMO calculations move the two molecules apart to form a dimeric structure, which is predicted to be 4.38 kcal mol^{-1} higher in energy than the monomer, with a net dipole moment of 0.816 D versus 33.55 D for the free merocyanine.[3] Remarkably, the dimer resembles the crystal structure with average intermolecular distances, N1−O16′ and O16−N1′, and C8−C10′ and C10−C8′, of 3.64 and 4.54 Å, respectively. The dimer, therefore, bows outward near the central positions, as found in the crystal structure, though the predicted intermolecular separations in tetrahydrofuran are somewhat larger. The calculated bond lengths of each component of the dimer show only small differences from those calculated for the monomer, with values at C4−C8, C8−C9, and C13−O16 of 1.422, 1.368, and 1.270 Å, respectively, versus 1.419, 1.370, and 1.271 Å for the same bonds in the merocyanine itself.[3] Electronically, the atomic charge calculated at oxygen reduces from −0.675 in the monomer to −0.588 in the dimer, while that at nitrogen shows a small increase from −0.054 to −0.073, respectively, implying a small but significant electrostatic interaction between the two molecules despite the substantial internuclear separation. A dimer is predicted also by the PM3 method using the same starting structure, but this time it lies only 2.76 kcal mol^{-1} higher in energy than the monomer, with a net dipole moment now of 0.742 D for the former versus 34.96 D for the latter. The average intermolecular nitrogen−oxygen distances, N1−O16′ and O16−N1′, are slightly longer and the C8−C10′ and C10 and C8′ distances are shorter than those predicted by the AM1 method, with values of 3.66 and 4.31 Å, respectively. Both calculated results appear to reproduce the trends in the crystal data, though the longer interplanar distances between the interacting nitrogen and oxygen atoms may be due to the solvent. Although the enthalpy of dimerization is relatively small, the negative entropy associated with the process will reduce the overall free energy, making it more difficult than the calculations suggest, but the positive entropy of solvation may very well cancel this contribution.

However, the possibility that the predicted dimer is simply an artifact of the semiempirical methods and not a true structure cannot be discounted, as a force calculation gives a number of very small negative frequencies. To check this out, calculations were carried out on stilbene **8**, which shows nonbonded parallel stacks of molecules in the crystal which lie over one another symmetrically with a uniform separation distance of 5.66−5.72 Å, depending on the crystal structure data.[27−30] In a hypothetical starting structure for a stilbene dimer, the C1, C8, C9, and C13 atoms of one molecule in the first plane were positioned over the C1′, C8′, C10′, and C13′ atoms, respectively (Chart 1), of the other in the second plane, with each intermolecular distance set at around 2.0 Å. An initial calculation at this separation gave 1,2,3,4-tetraphenylcyclobutane! A repeat calculation at the AM1/COSMO level, again in tetrahydrofuran, at an initial separation distance of 2.5 Å results in the molecules being forced apart to a nonbonding distance in excess of 5.0 Å at each pair of the four molecular positions. No dimer is formed in this case, as the heat of formation of the aggregate at 109.7 kcal mol^{-1} is almost exactly twice the monomer energy of 54.88 kcal mol^{-1}. The two results together strongly suggest that the AM1/COSMO method is, therefore, capable of identifying important intermolecular interactions in polar molecules.

An analysis of the calculated AM1 results obtained for the merocyanine dimer in tetrahydrofuran shows that the effective van der Waals surface area of 183.7 Å^2 is less than twice that of the monomer at 116.4 Å^2 because of the close proximity to one another of the head and tail of each dimer component. The core−core repulsion energy of the dimer at 8462.9 eV is substantially greater than twice the monomer repulsion energy at 2185.9 eV because of the additional interplanar repulsion between the atomic nuclei of the two components. In contrast, the electronic energy of the dimer at −13 456.7 eV is much larger than twice that of the monomer at −4682.9 eV because of the additional interplanar attractive energy between the electrons on the atoms of one component of the dimer and the atomic nuclei of the other component, and vice versa.

The possibility that the shape of the dimer generated in tetrahydrofuran is simply an artifact of the van der Waals radii of the COSMO routine stored in the MOPAC 93 program[20,21] (with values of 1.53, 1.48, and 1.36 Å for carbon, nitrogen, and oxygen, respectively) can be discounted because an AM1 optimization in pyridine ($\epsilon = 12.4$) using the same starting structure, with the molecules separated by 2.0 Å, gives a resulting dimeric structure where the two molecules are again pushed apart, but this time they remain almost parallel to one another, with average N1−O16′ and O16−N1′ distances of 4.33 Å and C8−C10′ and C10−C8′ distances of 4.54 Å. This structure is 2.59 kcal mol^{-1} higher in energy than two separate monomer units. A similar result is obtained in acetone ($\epsilon = 20.7$), where the resulting dimer now shows the same intermolecular distances, increased to 4.71 and 4.74 Å, respectively, with the energy only 1.06 kcal mol^{-1} above the sum of that for two free merocyanine units.

While the formation of a trimer rather than a dimer is unlikely in solutions of low dielectric constants because of its expected large dipole moment, the formation of a tetramer cannot be ruled out, as the alternating head-to-tail arrangement here would effectively cancel the dipole moment in this structure also. To investigate the possibility of tetramer formation, further calculations were carried out on a hypothetical structure constructed from a stack of four planar merocyanine molecules, arranged in an alternating head-to-tail and tail-to-head fashion, with the central double bonds parallel to one another, and with the pairs of three internuclear N−O′ and O−N′ distances set at around 2.0 Å in the *z*-direction as in the dimer. The AM1/COSMO results predict a tetramer which is 1.73 kcal mol^{-1} higher in energy than the monomer, with a net dipole moment of 0.816 D versus 33.55 D for the free merocyanine. In the tetramer, the two central merocyanines are parallel to one another and bowed at the center in a fashion similar to that in the dimer, with both internuclear distances N−O′ and O−N′ of 3.89 Å and average C8−C10′ and C10−C8′ distances of 4.58 Å, respectively. The remaining two merocyanine molecules are arranged so that the nitrogen atoms of each interact with the two oxygens of the internal dimer pair at a distance of 3.87 Å, but the oxygens of these flanking molecules are well removed from the two nitrogens of the internal dimer pair at an average nonbonding distance of 6.30 Å. Although it seems likely that the merocyanine can, in principle, form tetramers in solution, these are less likely to form than dimers on entropic grounds.

The calculated intermolecular separations found in different solvents at the AM1/COSMO level suggests that a dimer is more likely to be formed in solvents with low dielectric constants, such as tetrahydrofuran, than those with higher values, such as acetone. However, while these semiempirical calculations do not correctly predict the true interplanar distances between the dimer components, the trends reported here appear to be reliable and strongly suggest that the merocyanine will at least partially dimerize in solvents of low dielectric constants, leading to differences in absorption over the monomer (see later).

Calculated Spectra. Multielectron configuration interaction (MECI) calculations on the stable twisted conformers of the merocyanine **1** produced in each of the five solvents explored surprisingly predict an absorption band at a *longer wavelength* than that obtained for the fully planar conformer in all cases. Similar trends have been reported for the HOMO−LUMO energy gap[36] when the right-hand ring of the planar zwitterionic form of **1**, generated from a calculation using positive sparkles positioned at the oxygen atom, is empirically twisted by 15−30°. The same phenomenon has been reported also for indoaniline dyes such as *N*-(3-((2-methyl-4-(diethylamino)-phenyl)imino)-6-oxo-1,4-cyclohexadien-1-yl)acetamide,[37] where a rotation of the phenyl ring from 18 to 58° relative to the remaining molecular plane results in a change in the calculated absorption from 476 to 539 nm.

The calculated results obtained here in tetrahydrofuran predict absorptions at 591 and 633 nm for the planar and most twisted conformer, respectively (Table 3), versus the two main experimental absorption bands found for the soluble merocyanine **3** at 573 and 614 nm (Figure 1c, Table 3). A similar picture emerges in acetone, with calculated values of 578 and 588 nm obtained for the planar and most twisted conformer, respectively, of structure **1** (Table 3) versus experimental absorptions at 575 and 599 nm for structure **3** (Table 3). These results strongly suggest that the two absorption bands observed experimentally in the spectra of the merocyanines arise from the presence of both planar and nonplanar conformers, which absorb in a similar region of the spectrum.

Experimentally, the two absorption bands of the merocyanine **3** show the widest separation in solvents of low dielectric constant, with a value of 41 nm found in tetrahydrofuran (see Figure 1b), approximately 30 nm in pyridine (though the bands are much broader here, they overlap, and the second band appears as a shoulder), and 24 nm in acetone, but no apparent separation in dimethyl sulfoxide. The calculated results show the same trends, with predicted separations of 38.7, 16.8, 9.2, and 3.80 nm between the two conformations in the same solvents (Table 3).

However, because the MECI calculations reported here considered the two highest occupied and the two lowest unoccupied molecular orbitals only (giving a total of 36 states involving 20 singlets, 15 triplets, and 1 quintet), independent calculations were carried out on the planar and nonplanar conformers using the CNDOVS method,[22] which considers all the singly excited configurations between the seven highest energy occupied orbitals and the seven lowest energy virtual orbitals. The results appear to confirm the trends found using the MECI routine, with the nonplanar conformers always showing the longest wavelength absorption band (Table 3), though the predicted absorptions in the gas phase occur at a shorter wavelength than those found by the MECI treatment in solvents with differing dielectric constants (Table 3). Thus, while CNDOVS calculations on the planar conformer optimized by the COSMO/MOPAC program in tetrahydrofuran give a predicted absorption of 538 versus 591 nm by the MECI routine, the nonplanar conformer optimized using the same method in the same solvent (**AB1**) gives values of 572 and 632 nm, respectively (Table 3). In all cases, the CNDOVS method mirrors the movement toward a longer wavelength absorption with the change from planar to nonplanar structure (Table 3).

The related solvent, soluble 2,6-di-*tert*-butyl merocyanine (**4**), shows a similar number of absorption bands in the visible region, but these are generally better separated from one another (Figure 1), and by inference most would be expected to arise from the presence of nonplanar conformers also. However, the relative intensities of the major absorptions of **4** are often different from those observed for **3**. For example, in chloroform the visible spectrum of **4** shows two absorption bands of almost equal intensity at 634 and 584 nm (Figure 1c), while that of **3** shows two different intensity bands, with that at 620 nm around twice the size of that at 582 nm (Figure 1a). The possibility that the conformations of the two *tert*-butyl groups in **4** also contribute to the complexity of the absorption spectra has been explored by calculating a number of representative conformations of the two large alkyl groups using the planar structure (**P**) of the

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merocyanine **2** as an example. These include one major conformer, **P/C,** where one methyl component of each of the two *tert*-butyl groups lies in the molecular plane near the aromatic carbons C11 and C15, respectively, with the remaining two methyl groups of each of the two *tert*-butyl groups symmetrically disposed above and below the molecular plane near the oxygen O16 (see Chart 1), and an alternative conformation, **P/D**, where one methyl group of each of the two *tert*-butyl groups still lies in the ring plane, but now both point to O16, with the remaining two methyl groups of each of the two *tert*-butyl groups symmetrically disposed above and below the molecular plane near aromatic carbons C11 and C15, respectively. A third major possible conformer, **P/E**, has the conformation of one *tert*-butyl group arranged as in **P/C** and the other arranged as in **P/D**.

The calculated results obtained for the optimized structures of **2** in different solvents show significant energy differences among the conformers. For example, in acetone, conformer **P/C** is the most stable, with energy differences of −1.39 and −2.99 kcal mol^{-1} relative to conformers **P/E** and **P/D**, respectively (Table 3). Furthermore, MECI calculations show that the conformation of the *tert*-butyl group does have a significant effect on the predicted low-energy absorption band. Thus, the most stable conformer, **P/C,** is predicted to absorb at 603 nm in acetone, while the least stable conformer, **P/D,** is predicted to absorb at 615 nm, with the intermediate conformer, **P/E**, predicted to absorb at 611 nm (Table 3). It follows that the presence of the *tert*-butyl groups has a significant effect on the transition energies of the merocyanine **2**, probably because they tend to insulate the polar oxygen atom from the dielectric field of the solvent and result in a shortening of the C13−O16 bond length from 1.28 Å in **1** to 1.26 Å in **2**. In acetone, the calculated absorption of the favored structure, **P/C**, of merocyanine **2** shows a bathochromic shift of 49 nm over the unsubstituted merocyanine **1**, compared with the experimental shift of 21 nm observed for the main absorption band in the same solvent (Table 3). The overall shift produced in acetone by changing the conformation of the *tert*-butyl groups in **2** is relatively small at 12.7 nm but, nonetheless, comparable to the shift of 9.2 nm produced by rotating the aromatic rings in **1**. In both cases, the variation appears to arise in part from small changes to the bond lengths across the aromatic system, e.g., at the C4−C8, C8−C9, and C13−O16 bonds.

In contrast to the movement of absorption to longer wavelength with reduced planarity, MECI calculations on the dimer of merocyanine **1** show exactly the opposite trends. While the free merocyanine is predicted to absorb at 591 nm at the AM1 level in tetrahydrofuran,[3] the dimer is predicted to absorb at 494 nm. On excitation, the ground-state dipole moment of the dimer after CI increases from 0.857 to 2.469 D, compared with the monomer, which shows a reduction from 32.90 to 24.48 D. This hypsochromic shift with aggregation is strongly supported by independent CNDOVS calculations, which give predicted absorptions of 538 nm for the monomer and 446 nm for the dimer based on the AM1 structures optimized in tetrahydrofuran.

Neither the ^{1}H nor the ^{13}C NMR spectra of the twisted conformers or the dimer would be expected to be significantly different from the planar merocyanine, in line with the experimental results, which are time-averaged scans (Tables 1 and 2). This is especially true for the resonances near the central double bond, C8═C9, where the attached trans carbons C4 and C10 and trans hydrogens H8 and H9 always remain in the same plane in both the planar and twisted structures and dimer with an expected large proton coupling constant, $J_{8,9}$, in all cases. Furthermore, because the protons in the heterocyclic ring A are isolated from those in aromatic ring B and from those at the C8 and C9 positions, their chemical shifts and coupling constants would not be expected to change significantly with rotation or with the formation of the dimer. A similar argument applies to the ^{13}C NMR shifts.

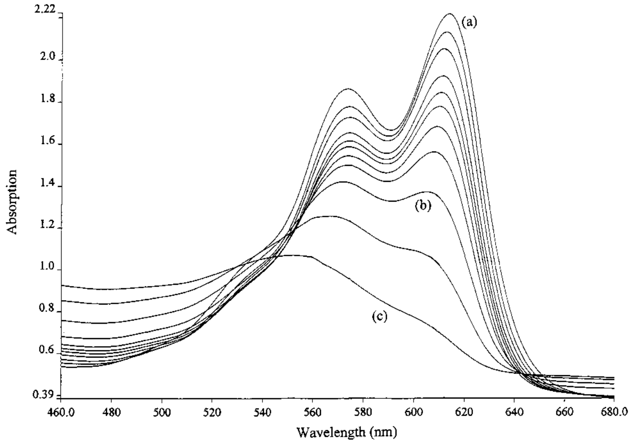

Figure 2. Effect of temperature on the visible absorption spectrum of merocyanine **3** in tetrahydrofuran: (a) 20, (b) −50, and (c) −100 °C.

Experimental Spectra. If conformational effects and dimerization or aggregation are, indeed, responsible for the presence of more than one main absorption in the visible spectrum, then it follows that the population of each conformational level and the dimer or aggregate would be expected to change with temperature to give increasing proportions of the more stable species at lower temperature. Previous studies have shown that the parent merocyanine **1** exhibits thermochromism, with the single broad absorption maximum in ethanol moving from 509 nm at 23 °C to 460 nm at −140 °C.[38] Furthermore, the relative intensities of the multiple absorption bands of **2** found in ethyl acetate and *tert*-butanol show small changes on heating from 25 to 65 °C.[39] In the latter solvent, the color of the solution changes from deep blue at room temperature to purple-red at −196 °C.[39]

Empirically, we have found similar temperature-sensitive results for merocyanine **3**, with the color of a solution in tetrahydrofuran showing a reversible change from purple to red on going from room temperature to −100 °C. Quantitatively, this phenomenon arises because the longer wavelength absorption band at 614 nm, which we have assigned to the twisted conformer(s), reduces in intensity with decreasing temperature relative to the minor absorption band of the planar conformer at 573 nm (Figure 2). At 20 °C the absorption at 614 nm is significantly stronger than that at 573 nm, at −50 °C the intensities of the bands are approximately equal, while at −100 °C the latter is stronger than the former, though both are shifted to shorter wavelength, and there is evidence of an additional broad absorption band at shorter wavelengths (Figure 2). As the temperature of the solution is raised, the original absorption spectrum is restored in full at 20 °C.

This result is fully consistent, therefore, with the presence of both planar and nonplanar conformer(s) in solution at room temperature. Furthermore, because the viscosity of organic solvents such as tetrahydrofuran generally increases strongly with decreasing temperatures, it would be expected that dimerization or aggregation of the merocyanine would be more

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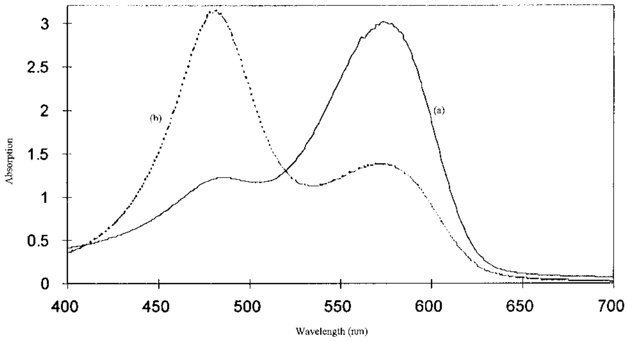

Figure 3. Effect of concentration on the visible absorption spectrum of merocyanine **3** in 2-ethyl-1-hexanol: (a) 25 ppm/40 mm path length cell and (b) 1000 ppm/1 mm path length cell.

favorable at low temperatures, leading to the pronounced but broad absorption observed in the 460−540-nm region (Figure 2), which we assign to the dimer and tetramer on the basis of the calculations described above. These results are supported by previous work, which shows that the aggregation of cyanine dyes is encouraged in solvents with low dielectric constants and high viscosities.[40] In most solvents at room temperature, the formation of dimers or aggregates of the merocyanine can be discounted, as the main absorption bands always obey the Beer−Lambert Law over several orders of concentration.[3,11] However, the viscosities of solvents used for aggregation studies, such as methanol, chloroform, or tetrahydrofuran, are quite small at room temperature, and the merocyanine is, therefore, effectively solvated over a wide concentration range. However, if aggregation effects are responsible for the broad, short-wavelength absorption in tetrahydrofuran at −100 °C, the same effects might be expected at room temperature in more viscous solvents which have a similar low dielectric constant to tetrahydrofuran.

Most common solvents used for spectroscopic measurements have low viscosities but variable dielectric constants;[41] for example, methanol and chloroform have viscosities of 0.55 and 0.54 (given in units of 10^{-3} kg m^{-1} s^{-1} throughout) and dielectric constants of 32.7 and 4.80, respectively, and although there are a number of solvents with higher viscosities which could be used for studying aggregation effects, they generally have large dielectric constants which would discourage the formation of dimers. A typical example is 1,2-ethanediol, which has a large viscosity of 26.1 which would promote aggregation or dimer formation, but its high dielectric constant of 37.7 would exert exactly the opposite effect by stabilizing the monomer. Almost uniquely, 2-ethyl-1-hexanol possesses a large viscosity of 9.8 measured at 20 °C, coupled with a low dielectric constant of 4.40, and solutions of the merocyanine should show a deviation from the Beer−Lambert law with variable concentration if aggregation effects are occurring. This is precisely what is found in practice: the extinction coefficients of solutions of merocyanine **3** in 2-ethyl-1-hexanol no longer show a linear relationship with increasing concentration. At a concentration of 25 ppm, the absorption spectrum of **3** shows a main band centered at 575 nm with a smaller absorption at 482 nm, but on increasing the concentration to 1000 ppm, there is a dramatic change in the spectrum with the latter band now much stronger than the former (Figure 3). We believe that the band at 482 nm arises from the presence of a dimer, as its absorption is close to that predicted theoretically.

Spectroscopic measurements on the *tert*-butylmerocyanine **4** also show absorption bands near the 500-nm region (Figure 1b,c), suggesting that dimers and/or tetramers are formed here also. Molecular modeling studies on the dimer of **1** show that the *tert*-butyl groups can just be accommodated in the interplanar space between each molecule but in certain conformations only, where one methyl component of each group is perpendicular to the ring plane and points outward, with the other two methyl components pointing downward into the space between the molecules. It seems likely, therefore, that aggregation effects are responsible for the shorter wavelength absorptions in this case also, though the interplanar separation distance is likely to be greater in the dimer.

Synthesis of Twisted Merocyanines. The synthetic route to the simple merocyanines **3** and **4** via coupling of an alkyl pyridinium bromide with a 4-hydroxybenzaldehyde generates a mixture of conformers because the rings are able to freely rotate up to 30° in either direction relative to the central C4−C8−C9−C10 plane with no apparent large loss of conjugation between them. However, the introduction of appropriate substituents, such as the methyl group at the central bridging positions, C8 or C9, and/or at adjacent ring positions, such as C3 and C5 or C11 and C15, could, in principle, force the molecule into a nonplanar conformation and thus remove the planar component from the visible spectrum. It should be possible, therefore, to confirm the identity of the predicted nonplanar conformers by synthesis and measurement of the absorption in solution. Molecular modeling studies suggest that the hydrogens of a methyl group inserted at ring position C11 of merocyanine **1** do interact with the hydrogen at the C8 carbon (Chart 1), but in certain conformations only. However, if a further methyl group is introduced at the central C8 carbon, the molecule can no longer adopt a planar conformation, the hydrogens of the methyl groups at C8 and C11 strongly interact, and consequently ring B is forced to rotate to relieve the clash. Synthetically, it is not possible to prepare this specific conformer because in the coupling reaction between *N*-methyl-4-ethylpyridinium bromide and 2-methyl-4-hydroxybenzaldehyde, the aryl methyl group would naturally prefer to occupy position C15, away from the site of clash.

However, if two methyl groups are introduced at the C11 and C15 positions to give 1-methyl-1-(4-aza-4-methylphenyl)-2-*trans*-(2,6-dimethyl-4-oxyphenyl)ethene (**5**), the molecule cannot avoid adopting a nonplanar conformation, though the coupling reaction would be expected to be more difficult to achieve because of steric interactions between the reagents. AM1/COSMO calculations on **5**, starting from a strained planar conformation, where the methyl hydrogens are optimally placed to reduce as much clash as possible, predict a nonplanar conformer of type **AB1** in tetrahydrofuran, with the **A** and **B** rings rotated by 44.1 and 48.1°, respectively. A force calculation gave only positive vibrational frequencies, ruling out the possibility that the structure is a transition state. Because the electronic effect of methyl groups placed into related conjugated systems is generally small, their presence would not be expected to greatly change the position of absorption of merocyanine **5** over **1**; for example, the introduction of two methyl groups into the 5,5′-positions of indigo produces a small bathochromic shift in absorption from 605 to 620 nm with substitution.[42]

Practically, a longer chain alkyl group is preferred at the nitrogen atom of merocyanine **5** to provide better solvent solubility for characterization purposes as in **3** and **4**. The

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(42) See, for example: *Organic Colorants*; Okowara, M., Kitao, T., Hirashima, T., Matsuoka, M., Eds.; Elsevier: Amsterdam, 1988.

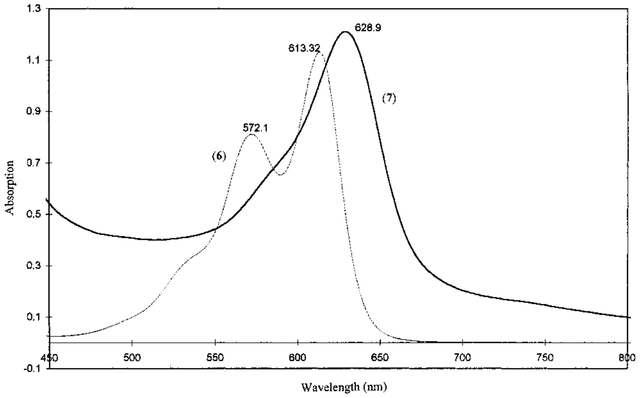

Figure 4. Comparison of the visible absorption spectra of merocyanines **6** and **7** in tetrahydrofuran.

preparation of the sterically hindered merocyanine, 1-methyl-1-(4-aza-4-(2-ethylhexyl)phenyl)-2-*trans*-(2,6-dimethyl-4-oxyphenyl)ethene **7**, was accomplished in this case by coupling *N*-(2-ethylhexyl)-4-ethylpyridinium bromide with 2,6-dimethyl-4-hydroxybenzaldehyde in propanol during 72 h reflux. The product was characterized by an accurate mass measurement and by its NMR spectra. In the ^{1}H NMR spectrum of the corresponding simpler 1-(4-aza-4-(2-ethylhexyl)phenyl)-2-*trans*-(4-oxyphenyl)ethene (**6**), doublets are observed for the protons at C8 and C9, with a coupling constant, $J_{8,9}$, of 15.1 Hz in deuterated acetone, but in the twisted analogue **7**, only a singlet is observed, as expected for the proton at C9 (Table 1). While the ^{13}C NMR spectra of both **6** and **7** show chemical shifts similar to those of **3** and **4** for most of the carbons, particularly for C2, which is adjacent to nitrogen, surprisingly, the resonance of carbon, C13, which is adjacent to oxygen, is much further downfield in both **6** and **7** for reasons which are not entirely clear (Table 2).

The visible spectrum of the twisted merocyanine **7** shows one main absorption band in tetrahydrofuran, compared with two bands for the corresponding simpler merocyanine **6** (Figure 4). In the latter, **6**, the longer wavelength absorption at 613 nm is attributable to one or more twisted conformers, while the band at 572 nm is assigned to the planar conformer. The introduction of methyl groups at the central carbon, C8, and at the 3- and 5-positions of the phenyl ring would be expected to eliminate the planar conformer and move the absorption band at 613 nm to longer wavelength by a margin similar to that found for indigo, as described above. The observed spectrum of **7** is fully consistent with this hypothesis, with a single strong absorption band now at 629 nm (Figure 4), though there is an unexpected residual absorption in the 450−550-nm region which we attribute to some form of aggregation.

Conclusions

The visible absorption bands of Brooker's merocyanine (**1**) found in solvents such as chloroform and tetrahydrofuran are thought to arise from the presence of both planar and nonplanar conformers in solution as well as dimers and possibly tetramers. AM1/COSMO calculations in various solvents suggest that the stable nonplanar conformers absorb at a longer wavelength and are up to 1.65 kcal mol^{-1} above the lowest energy planar conformer. In contrast, dimerization or aggregation of the merocyanine monomers produces a hypsochromic shift. Spectroscopic analysis at variable temperature is supportive, with the intensity of the longer wavelength absorption reducing with decreasing temperature. The absorption of the corresponding twisted merocyanine (**7**) is found to occur at a longer wavelength than the planar analogue (**6**), in line with the predicted results.

Experimental Section

Visible spectra were measured using a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrometer and a matched pair of quartz cells of 10 mm path length except where stated otherwise. 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 whenever possible. Hygroscopic/protic solvents required the addition of tetramethylammonium hydroxide to keep the merocyanine in conjugate base form. All spectra were run generally at room temperature, in solvents of the highest purity (spectroscopic grade and dried over molecular sieves) where possible. Variable-temperature work was carried out using a double-glazed absorption cell constructed by inserting a shortened NMR tube into a quartz cuvette fitted with a rubber septum. The air space around the cell was flushed with dry argon to ensure that no condensation could form inside the cuvette. Precooled solutions of the merocyanine were transferred to the NMR tube, the temperature was measured, and the spectra were rapidly recorded.

^{1}H and ^{13}C NMR spectra were measured in deuterated solvents (Sigma-Aldrich) using a Bruker AC400 spectrometer. In some solvents, 10 000−20 000 scans were required in order to obtain the necessary resolution for the ^{13}C spectra.

The pyridinium salts were prepared by refluxing the 4-alkylpyridine with the corresponding branched-chain alkyl halide (Sigma-Aldrich). The *N*-alkylpyridinium salts were condensed with the corresponding 4-hydroxybenzaldehyde (Sigma-Aldrich) using literature procedures.[43,44] Purity was determined by thin-layer chromatography on silica gel UV_{254} (Sigma-Aldrich). The 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.[45] The actual final melting point was found to be highly dependent on the rate of heating.

1-*trans*-[4-(*N*-(2-Ethylhexyl)pyridyl)]-2-(4-phenolato)ethene (6). *N*-Alkylation of 4-methyllpyridine (1.21 g, 13 mmol) with 2-ethylhexyl bromide (2.51 g, 13 mmol), by refluxing in dry 1-propanol (2 mL) for 3 h, yielded 4-methyl-*N*-(2-ethylhexyl)pyridinium bromide, which was used without further purification. Condensation with 4-hydroxybenzaldehyde (0.51 g, 4 mmol) in dry 1-propanol (6 mL) with piperidine (0.25 mL, 2.5 mmol) during 24 h gave the corresponding benzyl alcohol, which was dehydrated and deprotonated by suspending the solid in 25 mL of ethanolic KOH (0.2 M) and warming gently. The hydrophobic merocyanine which precipitated out of solution was filtered off and purified on a basic alumina column using a mixture of diethyl ether and methanol as eluent, to give blue/purple crystals with a metallic luster. The product was dried over P_2O_5 in a vacuum to yield a dark red amorphous powder, which rapidly turns scarlet in air (1.22 g, 73%); mp 240−245 °C.

1-Methyl-1-*trans*-[4-(*N*-(2-ethylhexyl)pyridyl)]-2-[4-(3,5-dimethyl)phenolato)]ethene (7). *N*-Alkylation of 4-ethylpyridine (3.04 g, 28 mmol) with 2-ethylhexyl bromide (5.49 g, 28 mmol), by refluxing in dry 1-propanol (2.5 mL) for 3 h, yielded 4-ethyl-*N*-(2-ethylhexyl)-pyridinium bromide, which was used without further purification. Condensation of the product (0.41 g, 1.4 mmol) with 2,6-dimethyl-4-hydroxybenzaldehyde (0.21 g, 1.4 mmol) in dry 1-propanol (1.7 mL) with piperidine (0.1 mL, 1 mmol) during 72 h gave the benzyl alcohol, which was dehydrated and deprotonated by suspending the solid in 7 mL of ethanolic KOH (0.2 M) and warming gently. The hydrophobic merocyanine which precipitated out of solution was filtered off and purified on a basic alumina column using a mixture of diethyl ether and methanol as eluent, to give a blue/green powder with a metallic luster after drying over P_2O_5 in a vacuum (0.39 g, 63%); mp 250−253 °C.

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