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SOLVATOCHROMISM OF DYES. PART I. SOLVATOCHROMISM OF MEROCYANINES. DERIVATIVES OF THE 7*H*-INDOLO[1,2-*a*]QUINOLINIUM SYSTEM. A NEW MODEL OF SOLVATOCHROMISM

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A new approximate model of the solvatochromism of merocyanines is presented. In solution merocyanines exist in the electronic ground state as a mixture of three different structures. Since only one longest wavelength band is observed in the UV–visible absorption spectra of such merocyanines, their lowest excited states are roughly assumed to be represented by a single structure. The molar fraction of each of the three structures of merocyanines in the ground state is a function of the solvent polarity. This (VBHB) model has been verified using merocyanines prepared from 5-(hydroxyaryl)-7,7-dimethyl-7*H*-indolo [1,2-*a*] quinolinium perchlorates. The analysis of the experimental data suggests that the three ground-state structures of merocyanines are the vinylogous amide (V) and the betaine as the free (B) or hydrogen-bonded (HB) form.

INTRODUCTION

Solvent polarity is an important but not precisely defined term. Many methods have been reported for solvent polarity determination,[1–3] including the use of solvatochromic dyes. Unfortunately, in some cases, e.g. with the use of merocyanines, the unexpected highly non-linear behaviour of solvatochromism (which is understood as a $\bar{\nu}-\pi$ relationship, where π denotes the solvent polarity) is observed. This problem was studied by Dähne and co-workers,[4–9] but in our opinion without satisfactory conclusions. Phenomena such as the variation of the extent and direction of solvatochromism which occurred on passing from non-polar to highly polar solvents remained unexplained. A similar anomalous behaviour of merocyanines was observed by Flannery,[10] who investigated the kinetics of dark processes in photochromic indolinospiropyrans.

The aim of this paper is to demonstrate that the solvent induces such major changes in the structure of electronic ground states of a merocyanine-like dye that it is possible to distinguish the several precisely defined forms of a dye remaining in equilibrium.

RESULTS AND DISCUSSION

Spectral measurements

The 5-(2- or 4-hydroxyaryl) derivatives of 7*H*-indolo[1,2-*a*]quinolinium salts[11–18] (Scheme 1), after deprotonation with a base, show considerable solvatochromic effects when dissolved in solvents of different polarity.

The variation of the electron-donating properties of the 5-(hydroxyaryl) substituent gives a distinct spectroscopic effect. The investigations were carried out in 60 solvents of polarity ranging from 129·5 to 264·4 kJ mol^{-1} in the E_T parameter scale (see Table 1). Measurements in nitromethane could be carried out only for acidic merocyanines with p$K_a < 6$.[18] The wavenumbers of the longest wavelength absorption for particular merocyanines are given in Table 1.

The extent of solvatochromism given by the shift of absorption bands is non-linear in E_T. Measurement points lie on a curved line which can be considered as consisting of three nearly linear parts (Figures 1–4) in every case except that for **2g** (notation according to Table 1). The points for solvents of polarity < 150 kJ mol^{-1} lie on a line of negative slope, i.e. they represent positive solvatochromism. Within the range of medium polarities (150–200 kJ mol^{-1}), the points follow a flat portion of the plot. Its slope can either be negative (for merocyanines **2e** and **2h**) or positive. The points for highly polar solvents (above *ca* 200 kJ mol^{-1}) depict the third portion of the diagram. It has a positive slope for all merocyanines and hence they show a negative solvatochromism. Such changes in the sign of solvatochromism with solvent polarity may be due to

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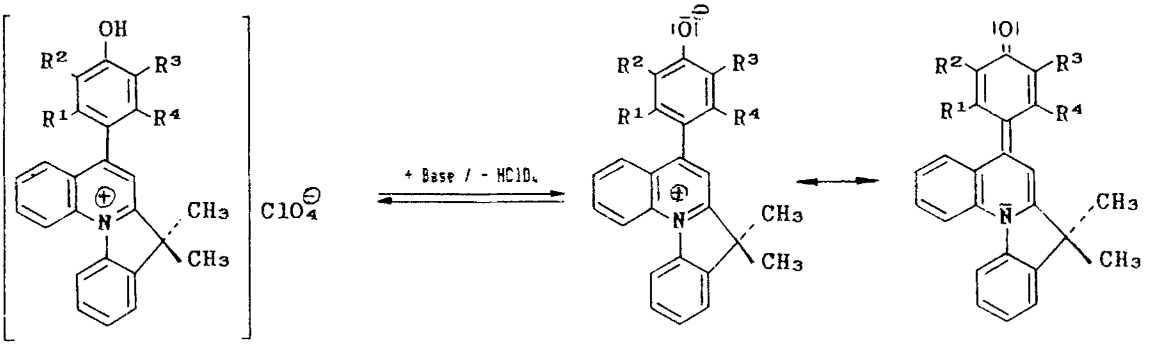
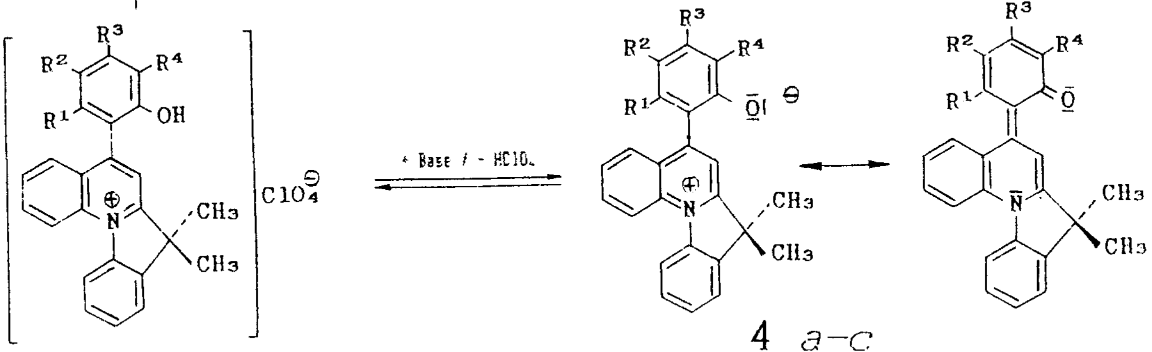


1 a–j

2 a–j

1, 2	R¹	R²	R³	R⁴
a	H	H	H	H
b	H	Cl	Cl	H
c	H	Br	Br	H
d	H	NO_2	H	H
e	H	H	OCH_3	H
f	H	Br	OCH_3	H
g	CH_3	Br	Br	CH_3
h	-CH=CH-CH=CH-		H	H
i	H	NO_2	OCH_3	H
j	H	CH_3	CH_3	H



3 a–c

4 a–c

3, 4	R¹	R²	R³	R⁴
a	H	H	H	H
b	-CH=CH-CH=CH-		H	H
c	H	Br	OCH_3	H

Scheme 1

Table 1. Wavenumbers (1000 cm^{-1}) of longest wavelength absorption bands ($S_1 \leftarrow S_0$ transitions) of merocyanines, measured in solvents of various polarity at 25 ± 0·1 °C

No.	Solvent	Polarity, $E_T(30)$ (kJ mol^{-1})	2a	2b	2c	2d	2e	2f	2g	2h	2i	2j	4a	4b	4c
1	Water	264·4	21·23	21·43	21·24	22·60	19·90	20·00	21·51	18·01	22·08	19·69	20·50	19·70	18·45
2	Formamide	184·8	18·84				17·67								
3	Ethane-1,2-diol	235·9	19·62	19·92	19·72	20·97	18·18	18·30	19·60	16·92	19·58	18·00	19·31	18·00	17·96
4	Methanol	232·6	19·30	19·36	19·23	20·63	17·79	17·81	18·83	16·82	19·10	17·59	19·08	17·28	17·46
5	3-Oxapentane-1,5-diol	225·4	18·92	18·88	18·73	20·07	17·26	17·35	18·35	16·35	18·57	17·20	18·34	17·00	16·98
6	3,6-Dioxaoctane-1,8-diol	224·1	18·22				16·95					17·04		16·60	
7	Ethanol (96%)	217·9	18·50	18·42	18·35	19·70	17·08	17·08	17·46	15·86	18·36	17·04	18·21	16·43	16·74
8	2-Aminoethanol	217·1	18·08	18·15	18·07		16·89	16·94		15·50			17·70	16·80	16·58
9	Benzyl alcohol	212·8	18·10												
10	Propan-1-ol	212·5	17·97	17·88	17·87	19·26	16·78	16·72	16·90	15·60	17·90	16·80	17·56	16·00	16·29
11	Butan-1-ol	210·4	17·75				16·66					16·69			
12	2-Methylpropan-1-ol	205·3	17·76	17·53	17·59		16·62	16·56		15·48	17·68	16·67	17·30	15·82	16·05
13	Propan-2-ol	203·7	17·48	17·45	17·47	18·85	16·56	16·45	15·95	15·47	17·45	16·64	16·95	15·68	15·82
14	Butan-2-ol	197·4	17·35	17·20	17·22		16·48	16·36		15·33	17·33	16·55	16·70	15·40	15·63
15	3-Methylbutan-1-ol	197·0	17·72				16·65					16·67			
16	Cyclohexanol	196·5	17·26	17·20	17·24		16·40	16·34		15·25	17·26	16·49	16·90	15·80	15·68
17	Pentan-2-ol	194·9	17·33				16·45								
18	Nitromethane	194·0		17·57	17·62			16·60			17·50				16·08
19	Acetonitrile	192·8	17·27	17·43	17·42	18·31	16·68	16·52	15·80	15·71	17·32	16·91	16·61	15·10	15·23
20	Dimethyl sulphoxide	188·6	17·09	17·39	17·32	18·30	16·46	16·40	16·00	15·41	17·24	16·64	15·78	14·60	15·05
21	Aniline	185·6	17·27	17·35	17·34		16·36	16·40		15·27			16·40	15·23	15·83
22	Tetramethylene sulphone	184·3	17·33				16·56								
23	2-Methylpropan-2-ol	184·0	17·29				16·54								
24	*N*,*N*-Dimethylformamide	183·5	17·06	17·15	17·16	17·99	16·62	16·37		15·50	17·02	16·82	15·73	14·61	15·01
25	*N*,*N*-Dimethylacetamide	183·1	17·06				16·71								
26	Acetone	176·8	17·22	17·00	17·03	17·73	16·94	16·46	14·78	15·78	16·80	17·13	16·10	14·98	15·09
27	Nitrobenzene	176·0	16·99				16·44								
28	Benzonitrile	176·0	16·99				16·44								

29	2-Methylbutan-2-ol	175·5	17·10	16·66	16·64		16·60	16·25		15·48	16·64	16·77	16·30	15·07	15·41
30	1,2-Dichloroethane	175·5	17·07				16·53					16·78			
31	Butan-2-one	173·1	17·24				17·02								
32	Acetophenone	173·1	17·01				16·41								
33	Dichloromethane	172·2	16·95	16·80	16·84	17·45	16·49	16·18	14·22	15·50	16·84	16·67	15·95	14·68	14·92
34	1,1,3,3-Tetramethylurea	171·8	17·14				16·89					17·14			
35	Hexamethylphosphoric triamide	171·3	17·20				16·92								
36	Cyclohexanone	170·9	17·12	16·85	16·90		16·74	16·40		15·76	16·80				
37	Pyridine	168·5	16·90	16·72	16·76	17·50	16·52	16·18	14·46	15·40	16·70	16·68	15·53	14·40	14·83
38	4-Methylpentan-2-one	165·1	17·21				16·89				16·74				
39	1,1-Dichloroethane	165·1	17·06	16·72	16·75		16·79	16·24		15·78	16·48	16·93	16·18	15·00	15·00
40	Quinoline	165·1	16·92				16·28								
41	Chloroform	163·9	17·06	16·50	16·58		16·38	16·08		15·38	16·27	16·60	15·68	14·42	14·68
42	1,2-Dichlorobenzene	159·7	16·95	16·35	16·44	16·97	16·59	16·10	13·78	15·51	16·07	16·81	15·55	14·42	14·62
43	Fluorobenzene	159·7	17·08				16·91								
44	Iodobenzene	158·8	16·82				16·17								
45	Chlorobenzene	157·1	17·00				16·83			15·67		17·11			
46	Bromobenzene	157·1	16·93				16·79								
47	Tetrahydrofuran	156·7	17·61				17·40								
48	Anisole	155·8	16·94	16·37	16·49	16·94	16·78	16·25	13·90	15·69	16·14	17·10	15·72	14·38	14·77
49	1,3-Dichlorobenzene	155·1	16·92				16·79								
50	Phenetole	152·5	17·03												
51	1,4-Dioxane	150·9	17·57	16·50	16·61	16·91	17·42	16·60	14·00	16·10	16·47	17·62	15·50	14·55	14·82
52	Trichloroethylene	150·4	17·07	16·26	16·35		17·06	16·26		15·87	16·24		15·37	14·42	14·52
53	Diethyl ether	152·5	17·26	16·56	16·68		17·88	16·60		16·10			16·10	14·87	15·20
54	Benzene	144·5	17·42	16·32	16·48	16·67	17·41	16·68	13·50	16·24	16·48	17·68	15·51	14·65	14·69
55	Toluene	142·1	17·66	16·38	16·52	16·67	17·59	16·72		16·24	16·78	17·80	15·80	14·77	14·92
56	Carbon disulphide	136·6	17·11	16·04	16·12	16·28	17·11	16·40	12·90	16·15	16·10	17·39	14·94	14·72	14·38
57	Carbon tetrachloride	136·2	17·73	16·55	16·76		17·73	17·03	13·60	16·55	17·53	18·06	15·46	14·73	14·63
58	Tetrachloroethylene	133·6	17·85	16·41	16·61	16·88	17·46	16·90	13·20	16·47	17·30	17·95	15·20	14·78	14·65
59	Cyclohexane	130·8	18·40	17·20	17·80	18·30	18·38	17·52		17·12	18·03	18·62	16·22	16·38	14·93
60	*n*-Hexane	129·5	18·45	17·40	18·40	18·92	18·57	17·80		17·16	18·10	18·86	17·10	15·55	15·47

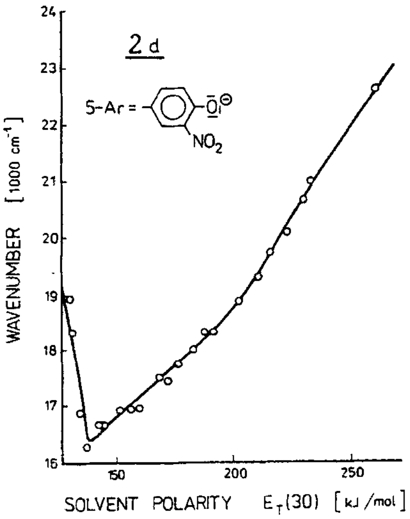


Figure 1. $\bar{\nu}$ vs E_T for the longest wavelength absorption of merocyanine **2d** in various solvents

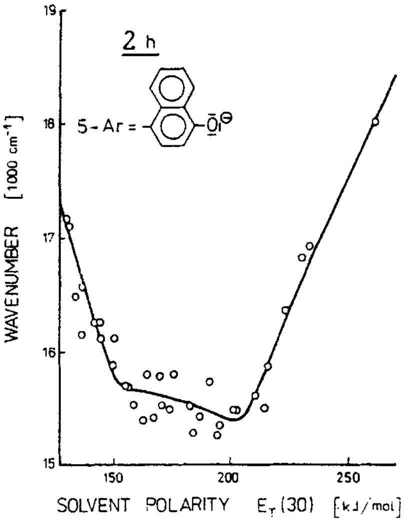


Figure 2. $\bar{\nu}$ vs E_T for the longest wavelength absorption of merocyanine **2g**

changes in the structure of the merocyanines on solvation. The number of possible forms is at least one higher than the number of bends of the function.

The results suggest a solvent-dependent equilibrium between three forms of merocyanines. In our case a maximum of three such forms in equilibrium could be observed. One may accept that these forms are three electronic ground states. Each of the possible ground states produces its own lowest excited state. For simplicity, the structures of the latter are virtually identical,

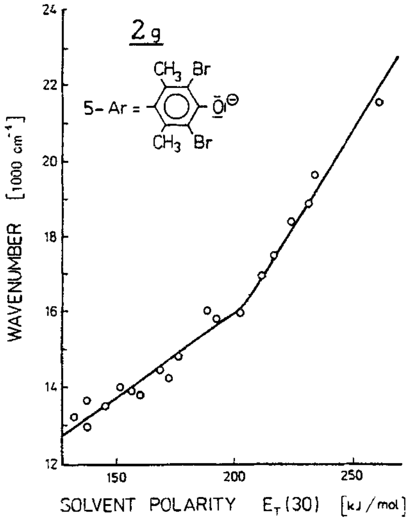


Figure 3. $\bar{\nu}$ vs E_T for the longest wavelength absorption of merocyanine **2h**

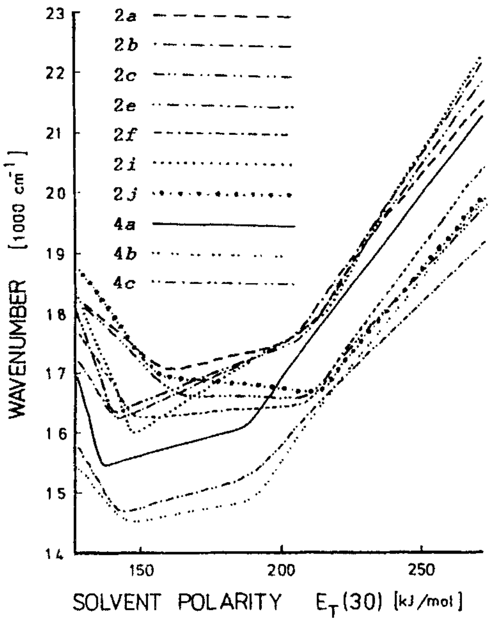


Figure 4. $\bar{\nu}$ vs E_T for the longest wavelength absorption of merocyanines **2a**–**c**, **e** and **f** and **4a**–**c**. The parameters applied are derived from the model proposed in this paper

i.e. there is one lowest excited state common to all possible ground states. This assumption is well rationalized. Merocyanines and betaines are dyes that contain donor–acceptor chromogens. The absorption of light is accompanied by an electron transfer from donor to acceptor. The donor moiety of a betaine dye is identical with the acceptor moiety in a merocyanine dye. Hence the electron transfer in the two dyes proceeds in opposite directions. This suggests that the excited state is intermediate between the ground states of both betaine and merocyanine. Moreover, significantly different excited states would produce a double absorption band from one another. Since only one absorption band is observed, either there is one common excited state or two excited states closely resemble each other. The ground state should be represented by a form of merocyanine with the lowest energy level. Based on that assumption, a mathematical model can be constructed and verified using experimental results given in this paper.

The term diagram (Figure 5) presents an energetic approach to this idea. The solvents of polarity from the lowest value to that given by the point of intersection of the term E_{01} and E_{02} (the E_{01}/E_{02} point) provide positive solvatochromism. Solvents of polarity between the E_{01}/E_{02} and E_{02}/E_{03} points are responsible for solvatochromism being either positive or negative, depending on the merocyanine. Negative solvatochromism is caused by solvents of polarity above the E_{02}/E_{03} point. In the particular ranges of polarity a ground state of merocyanine should be represented by a structure with the lowest energy.

A mathematical model of the observed phenomenon is constructed for this treatment. The fundamental assumption of three ground states and one common lowest excited state relevant to them is followed by four further assumptions:

(i) The energies of particular electron states vary linearly with polarity expressed on the E_T scale. This assumption is credible in view of facts quoted by Reichardt.[19] Moreover, it must be emphasized that there is no contradiction in the overall lack of linearity between the solvatochromic effect and either the E_T or Z parameters. The sum of particular states being linear in E_T is in reality non-linear in the same E_T parameters because their combination involves some non-linear terms, as shown below.

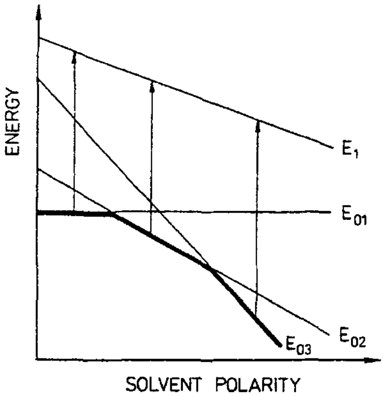


Figure 5. Illustration of a fundamental assumption in the model of merocyanine solvation. E_{01}, E_{02} and E_{03} are energy terms ascribed to three ground states

(ii) The shape of the absorption bands in the spectra corresponding to each of the three merocyanine structures has the character of a Gaussian function with amplitude ε_i and half-width σ_i. Both ε_i and σ_i are independent of solvent polarity.

(iii) The equilibria between merocyanine forms in solutions are not affected by any other factors.

(iv) Because the number of unknowns exceeds the number of available independent equations (any absolute energy value is not given by electronic absorption data), we took the E_{01} term as a base, and consequently both the slope and intercept for the E_{01} term are formally equal to zero. This condition will be discussed in Part II.[20]

Hence one can write that for a given merocyanine the overall population, N, of ground states is constant as the sum of the number of molecules present in a particular ground state n_i with $i = 1$–3:

$$n_1 + n_2 + n_3 = N \tag{1}$$

According to the Boltzmann statistics, the distribution between particular ground states is given by the equations

$$\frac{n_2}{n_1} = \exp\left(\frac{E_{01} - E_{02}}{kT}\right) \tag{2}$$

$$\frac{n_2}{n_3} = \exp\left(\frac{E_{03} - E_{02}}{kT}\right) \tag{3}$$

Equations (1)–(3) give the solution in the following three forms for each of three ground states:

$$n_1 = N \frac{\exp\left(\frac{E_{02} - E_{01}}{kT}\right)}{1 + \exp\left(\frac{E_{02} - E_{01}}{kT}\right) + \exp\left(\frac{E_{02} - E_{03}}{kT}\right)} \tag{4}$$

$$n_2 = N \frac{1}{1 + \exp\left(\frac{E_{02} - E_{01}}{kT}\right) + \exp\left(\frac{E_{02} - E_{03}}{kT}\right)} \tag{5}$$

$$n_3 = N \frac{\exp\left(\frac{E_{02} - E_{03}}{kT}\right)}{1 + \exp\left(\frac{E_{02} - E_{01}}{kT}\right) + \exp\left(\frac{E_{02} - E_{03}}{kT}\right)} \tag{6}$$

The wavenumbers related to the excitation energy from a ground state to the term of the lowest excited state,

E_1, become available from the equations

$$\bar{\nu}_1 = \frac{\Delta E_1}{hc} = \frac{E_1 - 0}{hc} \qquad (7)$$

$$\bar{\nu}_2 = \frac{\Delta E_2}{hc} = \frac{E_1 - E_{02}}{hc} \qquad (8)$$

$$\bar{\nu}_3 = \frac{\Delta E_3}{hc} = \frac{E_1 - E_{03}}{hc} \qquad (9)$$

The shape of an absorption band which consists of three overlapped bands may be described by

$$A = \sum_{i=1}^{3} n_1 \varepsilon_i \exp\left[- \frac{(\bar{\nu} - \bar{\nu}_1)^2}{2\sigma_1^2} \right] \qquad (10)$$

The approximate equality

$$\exp\left[- \frac{(\bar{\nu} - \bar{\nu}_1)^2}{2\sigma_1^2} \right] \approx \exp\left[- \frac{(\bar{\nu} - \bar{\nu}_2)^2}{2\sigma_2^2} \right] \qquad (11)$$

occurs for broad overlapped bands characterized by possibly high σ values. These are approximately the points of intersection of ground-state terms ($E_{01}/E_{02}, E_{02}/E_{03}$). The maximum of the observed absorption band, i.e. of the envelope of three overlapped Gaussian curves, is determined from the differential form of equation (10):

$$\frac{\partial A}{\partial \bar{\nu}} = 0 \qquad (12)$$

Introduction of equation (11) into equation (12) gives equation (13), which provides the calculation of the wavenumber of the maximum of the observed envelope:

$$\bar{\nu} = \frac{\sum_{i=1}^{3} \varkappa_i n_i \bar{\nu}_i}{\sum_{i=3}^{3} \varkappa_i n_i} \qquad (13)$$

where

$$\varkappa_i = \frac{\varepsilon_i}{\sigma_i^2} \times \frac{\sigma_1^2}{\varepsilon_1} \qquad (14)$$

and $\varkappa_i$ is the relative parameter which characterizes the shape of the absorption band. Relevant energy terms for the lowest excited state (E_1) and two remaining ground states (E_{02} and E_{03}) are available from the equations

$$E_1 = a_1 + b_1 \pi \qquad (15)$$

$$E_{02} = a_{02} + b_{03} \pi \qquad (16)$$

$$E_{03} = a_{03} + b_{03} \pi \qquad (17)$$

respectively, where π is the polarity. In this case it represents the polarity expressed in Reichardt's $E_T(30)$ scale.

The assumption (iv) above can be written as

$$E_{01} = 0 \qquad (18)$$

Although the use of wavenumbers in calculations is convenient, one should remember that for E expressed in cm^{-1},

$$\frac{\Delta E}{kT} = \frac{hc}{k} \times \frac{\bar{\nu}}{T} = 1{\cdot}43879 \, \frac{\bar{\nu}}{T} \qquad (19)$$

The set of equations (6)–(9) and (13)–(19) forms the complete mathematical description of the analysed model. The values of $\varkappa_i$ can be calculated subsequently from the shape of absorption bands in the spectrum of a given merocyanine measured in three solvents belonging to three characteristic ranges of solvent polarity, at a constant dye concentration. It should be kept in mind that the calculated parameters are related to the zero level of E_{01} term as a consequence of equation (18). Particular relative energies can be represented in the form of the following matrix:

$$\mathbf{E}_{\mathrm{rel}} = \begin{bmatrix} E_1^1 & E_{01}^1 & E_{02}^1 & E_{03}^1 \\ E_1^2 & E_{01}^2 & E_{02}^2 & E_{03}^2 \\ \vdots & \vdots & \vdots & \vdots \\ E_1^n & E_{01}^n & E_{02}^n & E_{03}^n \end{bmatrix}_{n \times 4} \qquad (20)$$

Using equation (21) these relative values may be turned into absolute values:1

$$\mathbf{E}_{\mathrm{abs}} = \mathbf{E}_{\mathrm{rel}} + (\mathbf{A}_{n \times 1} + \pi \mathbf{B}_{n \times 1})[1 \;\; 1 \;\; 1 \;\; 1]_{1 \times 4} \qquad (21)$$

Values of column vectors, **A** and **B**, cannot be calculated by means of this method. The original solution of the main part of this problem will be published in Part II.[20]

Results of the application of the proposed model to the series of compounds studied is presented in terms of statistical treatment (see Tables 2 and 3) and graphically (Figures 1–4).

The reliability of the proposed model is proved. Several points (CS_2, CCl_2CCl_2) deviate systematically from the presented relationship. It suggests that the assumed linearity of energy terms against E_T is not obeyed owing to specific solvation effects.

The existence of three structures of the dyes preliminarily assumed for the construction of the above mathematical model obtains additional support both from experiment and from deduction from obvious facts. In highly polar solvents, molecules of the merocyanine type remain under the influence of the permanent dipoles of solvent molecules. It favours the most polar betaine form. Negative solvatochromism specific for this structure proves this assumption. The extent of solvatochromism in the case of merocyanine **2g** is 16·4% higher [equations (15) and (16)] than the Reichardt–Dimroth betaine, which means that this compound is a more sensitive indicator, unfortunately, solely in the case of hydrogen bond-forming solvents.

It is surprising that the classification of solvents forming and not forming hydrogen bonds is ambiguous. For ten of the investigated compounds this limit is situated at a value $E_T(30) = 204{\cdot}35 \pm 5{\cdot}42$ k-

Table 2. Calculated energy levels[a]

Compound	a_1 (cm^{-1})	b_1 (mol cm^{-1} kJ^{-1})	a_{02} (cm^{-1})	b_{02} (mol cm^{-1} kJ^{-1})	a_{03} (cm^{-1})	b_{03} (mol cm^{-1} kJ^{-1})	R[b]	S[c]	n[d]	t test	Deviating points[e]
2a	22846 ±243	−33·8 ±1·5	7208 ±404	−44·8 ±2·4	16075 ±243	−89·2 ±1·5	0·9614	229	59	25·4	−2, −6, −8, +15, +38 +47, +51, −56, +59, +60
2b	24887 ±207	−60·8 ±1·3	11587 ±341	−81·5 ±2·1	21259 ±207	−128·7 ±1·3	0·9863	204	35	32·2	−56, −58
2c	33222 ±256	−120·5 ±1·8	19406 ±335	−138·3 ±2·3	28694 ±256	−184·0 ±1·8	0·9755	256	35	23·9	−29, −56, −58, +60
2d	48638 ±227	−234·2 ±1·6	37053 ±198	−269·1 ±14·6	41776 ±227	−293·6 ±1·6	0·9927	227	22	32·9	−58, +60
2e	23493 ±276	−41·7 ±1·7	6618 ±816	−40·2 ±5·2	16679 ±276	−89·1 ±1·7	0·9178	275	57	16·5	−2, −6, −44, +47, −56, −58
2f	25799 ±200	−64·2 ±1·4	10126 ±453	−68·0 ±3·1	21821 ±200	−124·5 ±1·4	0·9708	200	35	21·8	+51, −56, −58
2g	18518 ±350	−93·8 ±2·0	—[f]	—[f]	22213 ±350	−191·2 ±2·0	0·9886	429	19	23·7	
2h	24726 ±196	−59·4 ±1·2	7864 ±212	−52·1 ±15·1	18717 ±196	−105·2 ±1·2	0·9591	196	35	18·2	−56
2i	32129 ±292	−109·7 ±1·9	20378 ±127	−138·5 ±3·4	29816 ±293	−183·0 ±1·9	0·9728	293	36	23·0	+1, −6, +51, −56, −58
2j	26294 ±245	−59·9 ±1·6	8358 ±89	−53·7 ±2·8	20759 ±245	−112·6 ±1·6	0·9507	245	35	16·5	+51, −56
4a	34981 ±317	−142·9 ±2·1	21222 ±201	−155·5 ±10·6	29846 ±317	−202·1 ±2·1	0·9749	317	33	22·7	
4b	21096 ±309	−44·7 ±1·8	7803 ±515	−53·2 ±3·0	17094 ±309	−102·9 ±1·8	0·9776	273	34	24·6	
4c	24182 ±332	−66·5 ±2·1	11345 ±835	−79·4 ±4·7	17189 ±332	−111·1 ±2·1	0·9293	410	34	13·3	+3, +18, +21, +29, +53

[a] Relative values due to assumption that $E_{01} = 0$. In the case of low and high polarities $x = 1$ was adopted, whereas for medium-polarity solvents $x = 3{\cdot}5$ was taken.

[b] Curvilinear correlation coefficient.

[c] Standard deviation.

[d] Number of experimental points.

[e] Solvents for which a double S value was exceeded. The numbers correspond to the solvents in Table 1. The accompanying sign shows the direction of the deviation.

[f] Lack of experimental data for this term (see text).

Table 3. Scattering of experimental points in relation to expected values in the ranges of standard deviation multiplicity[a]

Compound	n $-3S, +3S$	S cm^{-1}	$-3S, -2S$ (exp./theor.)	$-2S, -1S$ (exp./theor.)	$-1S, 0$ (exp./theor.)	$0, +1S$ (exp./theor.)	$+1S, +2S$ (exp./theor.)	$+2S, +3S$ (exp./theor.)
2a	50	100	1/1	7/7	16/16	15/16	11/7	0/1
2b	33	164	0/1	5/5	11/11	12/11	5/5	0/1
2c	32	156	0/1	6/4	8/11	12/11	5/4	0/1
2d	20	140	0/0	1/3	10/7	6/7	3/3	0/0
2e	55	209	1/1	10/7	11/18	25/18	5/7	3/1
2f	32	113	0/1	5/4	10/11	10/11	7/4	0/1
2g	19	429	0/0	2/3	7/7	8/7	2/3	0/0
2h	35	181	0/1	4/5	14/11	11/11	5/5	1/1
2i	31	141	0/1	5/4	10/11	11/11	5/4	1/1
2j	33	192	1/1	5/5	12/11	12/11	4/5	0/1
4a	33	317	0/1	4/5	12/11	13/11	4/5	0/1
4b	34	273	0/1	8/5	8/11	14/11	4/5	0/1
4c	31	170	2/0	2/4	11/10	10/10	6/4	0/0

[a] Theoretical values according to the Student distribution.

J mol^{-1}, and for three others at 185·5 ± 1·3 kJ mol^{-1}. A common feature of merocyanines for which this limit is situated in the lower region of polarity is an *ortho*-position of oxygen in the aryl part. Since no relationship could be found between the range of this limit and the pK_a values of corresponding hydroxyl compounds,[18] one may assume that a new effect of solvation with the participation of hydrogen bonds has been revealed. In this case coordination of the solvent to the oxygen atom (phenolate anion) should be accompanied by an increase in the steric hindrance, which makes the formation of a planar structure impossible. In ten other compounds this process should not affect the energy barrier of rotation. Then, in the case of a non-planar structure, the π-electron conjugation between the two moieties of the molecule ceases and the electron density on the phenolate oxygen atom remains high and favourable for the formation of strong hydrogen bonds with solvents of lower polarity. Numerous examples are known, including those of the greatest importance for the natural world, in which hydrogen bonds stabilize well defined conformations[21-23] and control reactivity.[24]

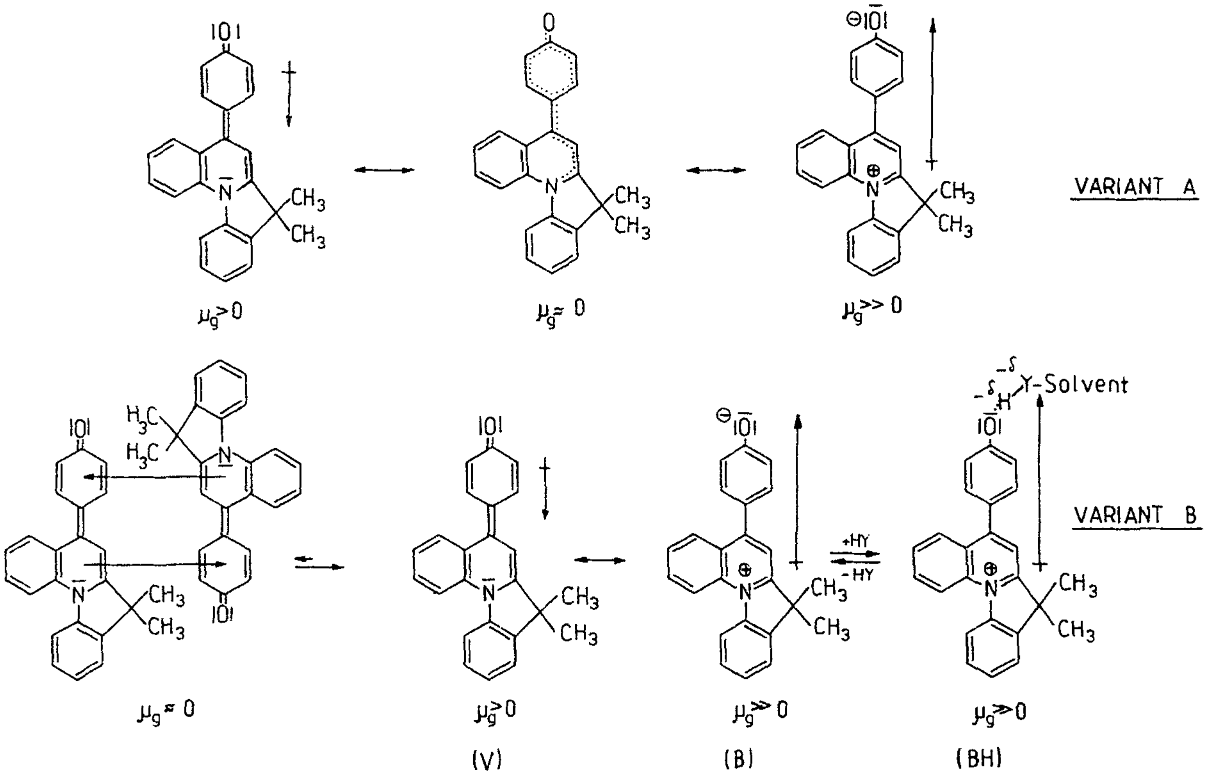
In solvents of lower polarity, the vinylogous amide form prevails. Both betaine and vinylogous amide forms have already been proposed by Dähne *et al.*[4] (Scheme 2, variant A).

Botrel *et al.*[25] investigated the betaine–vinylogous amide equilibrium in their studies of γ-styrylpyridinium betaines. They did this by CNDO/SCI calculations (π and σ) and by interpretation of ^{13}C NMR spectra. Recently, the same equilibrium was investigated by Reichardt *et al.*[26] for dyes in which the system of a *para*-phenylogous γ-pyridone was present.

A further decrease in the solvent polarity leads to a situation in which one molecule of merocyanine may be the object providing the strongest electrical field for another molecule of that dye. This causes aggregation of the dye, particularly at higher concentrations. The formation of dimers with a head-to-tail structure should predominate when the two molecules have identical forms and possibly a head-to-head structure when betaine dimerizes with a vinylogous amide. Because of compensation, the dipole moments of such dimers should be close to zero, and a further reduction in the solvent polarity will aggregate dimers and consequently precipitate the dye from its solution.

It can be noted that in variant B (Scheme 2), an increase in the dipole moment of merocyanines parallels an increase in the solvent polarity. Both the first and third forms of merocyanines in variant A should possess a permanent dipole moment, and the second form (see Scheme 2) should be close to zero. Assuming a defined state of energy of the intermediate cyanine and not a mixture of molecules representing two different alternative electron structures remaining in equilibrium, lack of parallelism in the solvent polarity and dipole moment of merocyanines makes the Dähne proposal uncertain.

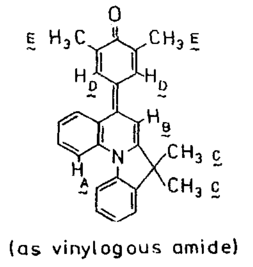
Additional evidence supporting the proposed structures comes from the properties of merocyanine **2g** which is not planar. Based on molar absorptivities in the spectra of **2g** (log $\varepsilon = 4{\cdot}09$) and of **2c** without steric hindrance in acetonitrile (log $\varepsilon = 4{\cdot}69$) the angle of twist of both rings (60°) could be found using the Braude equation.[27] The plot of the wavenumbers for the longest wavelength absorption of this merocyanine versus the solvent polarity (Figure 2) shows no inflection within the range of low polarity. This proves that the ground state of this merocyanine is represented by two possible forms, i.e. two types of betaine or betaine and vinylogous amide. In this case, the vinylogous amide form should be neglected since lack of coplanarity makes the formation of the double bond



Scheme 2

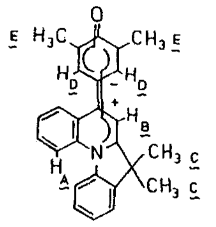
between the aryl and indoloquinoline parts impossible. This point of view is supported by data from ^{1}H NMR measurements on the readily soluble merocyanine **2j** (Table 4 and structure below).

The change from CCl_4 to $CDCl_3$ moved chemical shifts of the D and E protons by about 0·16 ppm towards lower field. The signals then remained almost stable. This could be expected, since the quinoid, vinylogous amide form shows a lower magnetic anisotropy than the benzene form because of a lack of the ring current. Very strong shifts of signals of the A and B protons indicate substantial changes in the electron density. Consequently for the discussed version the indolo[1,2-*a*]quinoline moiety in CCl_4 is an electron donor whereas in the polar solvent it is an electron acceptor. The shift of the signals of proton C towards lower field observed by the change in CD_3CN for CD_3OD may have the same origin. The involvement of the *n*-type electrons of the oxygen atom in the formation of an oxonium cation in CF_3COOH caused an additional shift of signals of proton E to lower field. Evidently, in acidic solvents a hemicyanine is formed.



(as vinylogous amide)

classical notation



newly proposed notation

Table 4. Assignments of chemical shifts in the ^{1}H NMR spectra of merocyanine **2j**

	^{1}H NMR chemical shift (ppm)				
Solvent	H_A	H_B	H_C	H_D	H_E
CCl_4	8·110	6·822	1·615	7·335	2·042
$CDCl_3$	8·336	7·123	1·623	7·498	2·208
CD_3CN	8·522	7·560	1·622	7·460	2·227
CD_3OD	8·997	7·960	1·749	7·497	2·252
$CD_3CN + HClO_4$	9·172	8·185	1·789	7·435	2·345
CF_3COOH	9·280	8·140	1·940	7·460	2·500

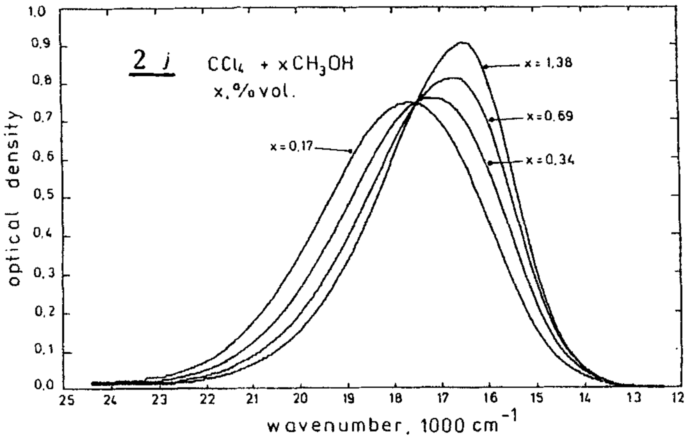


Figure 6. UV–visible absorption spectra of merocyanine **2j** recorded in CCl_4 solutions containing variable amounts of added methanol

The UV–visible spectral studies of merocyanine **2j** in various solvents provided further evidence for the existence of two structures in equilibrium. Thus merocyanine **2j** in CCl_4 solution is violet. The addition of more polar solvents such as DMF, DMSO, acetonitrile or methanol to such solutions turns the colour blue, but on further addition of these solvents the violet colour returns. The spectra recorded with increasing concentration of methanol reveal the existence of an equilibrium as shown by an isosbestic point (see Figure 6).

Temperature-dependent spectroscopic studies of merocyanines in the range 288–333 K in methanol, anisole and carbon tetrachloride revealed approximately the same temperature effect. For merocyanine **2b** to 390 cm^{-1} bathochromic shift appears in methanol, an insignificant hypsochromic shift of less than 150 cm^{-1} is observed in anisole and a distinct hypsochromic 380 cm^{-1} shift is noted in carbon tetrachloride. These results prove solely the expected fact of a decrease in effective polarity of a solvent with the rise in temperature. The kT product for room temperature is 2·5 kJ mol^{-1}, which is almost negligible if one takes for comparison the 125 kJ mol^{-1} change in energy on going from hexane to water. The negligible role of temperature is illustrated in Figure 7, which shows the relationship between wavenumbers and E_T calculated for a few temperatures in the range 150–4800 K. Significant changes are visible in Figure 7 only at temperatures too high for the existence of organic compounds. In conclusion, measurement conditions in various solvents at 15 and 60 °C produced changes that follow those predicted by the presented model.

Additional UV–visible measurements were performed in order either to confirm or to exclude the existence of a dimer as the main form of merocyanine present in solvents of low polarity. The measurements were performed in cyclohexane, carbon tetrachloride

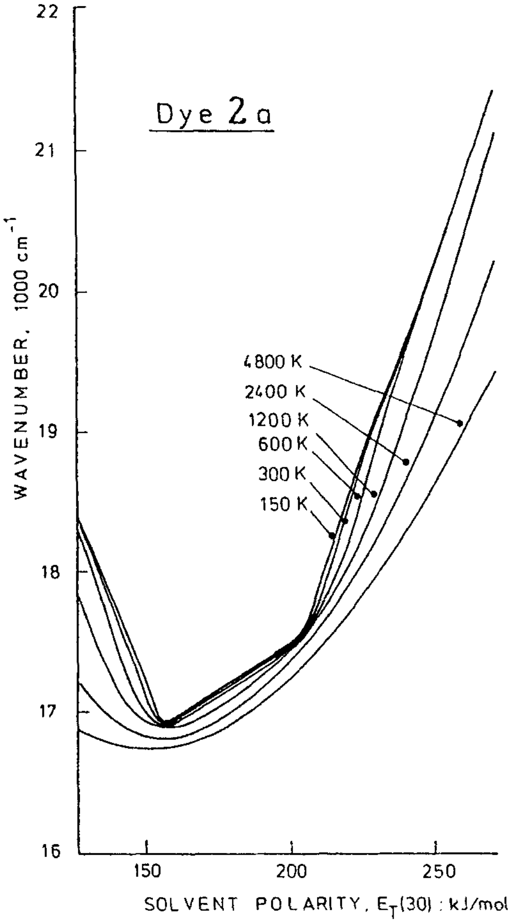


Figure 7. $\tilde{\nu}$ vs E_T at various temperatures calculated for merocyanine **2a**

and acetonitrile using free, pure merocyanine **2j** and varying the dye concentrations in the solvents from 3×10^{-3} to 3×10^{-6} mol l^{-1}. The dye in acetonitrile behaved differently to that in carbon tetrachloride and cyclohexane. In the first instance, the overall shape of the last absorption band, the molar absorptivity and the energy of the corresponding electron transition remained constant. In the other two cases the extent of the observed changes was greater in cyclohexane than in CCl_4. Dilution of the dye solution produced a decrease in the oscillator strength by 27% in cyclohexane and 10% in CCl_4. The dilution was accompanied by a hypsochromic shift of the band by 500 cm^{-1} in cyclohexane and 120 cm^{-1} in CCl_4. Moreover, a decrease in the half-width of 450 cm^{-1} (from 4430 to 3980 cm^{-1}) was observed in cyclohexane, whereas in the other solvents this parameter was independent of concentration and equal to 2950 and 4000 cm^{-1} in acetonitrile and CCl_4, respectively. These results confirm that in the range of the lowest polarities (cyclohexane), merocyanines exist in the form of dimers or higher aggregates but the concentration of these forms is comparatively low. They readily disappear on dilution.

If in the range of low polarities the dyes were mainly in the dimeric form, the cleavage of the dimer should be reflected by a strong bathochromic shift. This means that the position of the absorption maximum of the dye should approach a value extrapolated towards low polarities of the central section of the $\bar{\nu}$–$E_T(30)$ curve. Reichardt's solvatochromic indicator barely exists in the betaine form. The hypothetical vinylogous amide-like structure would possess a remarkably high energy and therefore it does not exist. Thus, the relevant $\bar{\nu}$–E_T diagram is presented by a linear relationship. This is obvious because simultaneously it is a base of the E_T scale.

Dähne's merocyanine can exist as the vinylogous amide solvated either by aprotic or protic (hydrogen bonding) solvents. Therefore, one inflection is observed in the $\bar{\nu}$–E_T diagram. Following Dähne and co-workers' concept,[4,28] the lowest electronic transition should correspond to the intersection of the betaine and vinylogous amide states, E_{01}/E_{02}. Botrel *et al.*[25] also support this point of view. Both approaches are based on the model of the dye molecule which resides within the cavity in a continuous solvent. They neglect the possibility of the formation of strong solvates and, therefore, they draw conclusions which even qualitatively do not fit the experimental data. The lowest transition energies for dyes **2e** and **2h** are usually observed at the point of intersection for both types of solvated betaines, E_{02}/E_{03}.

The merocyanines considered here represent a general case in which three different structures are taken, depending on both the kind and polarity of the solvent. We have obtained various data which suggest that two similar inflections can be observed for the merocyanines studied by Botrel *et al.*[25] and for other compounds such as stilbazoles. These data will be presented in a subsequent paper.

EXPERIMENTAL

Dyes. 5-(2- or 4-hydroxyaryl)-7,7-dimethyl-7*H*-indolo[1,2-*a*]quinolinium perchlorates were prepared and purified following literature methods.[11–18] The purity of all investigated dyes was established by thin-layer chromatography [Kieselgel Alufolien 60 F_{254} plates (Merck), eluted with butan-2-one–acetic acid–*n*-propanol (2 : 2 : 1, v/v)]. The properties of these compounds were reported elsewhere.[18]

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Solvents. Most of the solvents used were of Uvasol grade from Merck of spectrofluorimetric and spectroscopic purity (Table 1, Nos 4, 7, 11, 13, 15, 19, 20, 22, 24, 26, 30, 33, 37, 41, 47, 51 and 53–60) and some were purified on an aluminum oxide packed column (Table 1, Nos 9, 18, 27, 28, 44 and 48–50). The other solvents were purified by appropriate methods. Some of them were distilled just before use (Table 1, Nos 8, 21, 36, 40 and 52). Such purification was carried out directly prior to their use.

Measurements. Absorption spectra were recorded at 25 ± 0·1 °C for 10^{-5} M solutions using Specord UV–visible and Specord M40 spectrophotometers (Carl Zeiss Jena) with 1- or 5-cm quartz cells. Merocyanines were generated from given quinolinium salts in DMSO solutions by addition of an excess of anhydrous potassium carbonate. DMSO solutions (1 μl of dye solution dissolved in 2 ml of solvent) were dissolved in required solvent. This procedure was adopted when it was confirmed that the same results were obtained by using pure merocyanines without DMSO. In several investigations, including ^{1}H NMR studies and concentration measurements by UV–visible spectrophotometry, pure merocyanines were used. The maximum error in the wavenumber at the absorption maximum was 20 cm^{-1}. A cell of adjustable optical length from 1 μm to 1 cm was used in concentration measurements. All calculations and plots were carried out by means of an HP 9820A programmable calculator (Hewlett-Packard).

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