Synthesis of pyridinium – indan-1,3-dion-2-ide betaine dyes and use as indicators of carboxylic acids' polarity

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2-[4-(2,4,6-Triarylpyridinium-1-yl)phenyl]indan-1,3-dion-2-ides **5a–d**, (N^+C^-) betaine dyes, were synthesised by reaction of 2,4,6-triarylpyrylium perchlorates **6a–d** with 2-(4-aminophenyl)indan-1,3-dione **7**. The solvatochromic effect of compounds **5** was investigated. The betaines obtained are suitable for polarity determination of carboxylic acids and their anhydrides.

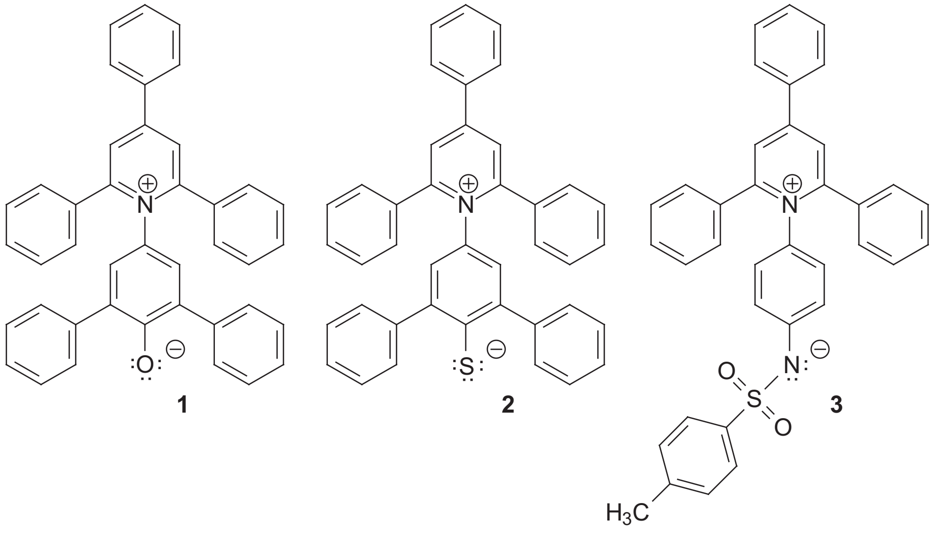
Keywords: betaines, solvent effects, dyes, solvatochromism, pyridinium salts

Pyridinium *N*-phenolate dyes show very large negative solvatochromic effects. For instance, the most intensively investigated and commercially available betaine 5'-(2,4,6-triphenylpyridinium-1-yl)-*m*-terphenyl-2'-olate (Reichardt's dye, **1**) (Scheme 1) is used as a solvent polarity indicator ($E_T(30)$ scale).[1-3] Many structural modifications of **1** have been proposed to improve its properties including solubility in aliphatic hydrocarbons [4,5] or in water.[6,7] Thus the dye **1** and its derivatives are almost perfect polarity indicators for different kind of solvents but not for carboxylic acids. Addition of a trace of an acid to a solution of **1** changes the colour to pale yellow due to protonation of the phenolic oxygen atom of the dye. The protonated form (pyridinium salt) does not exhibit the solvatochromic absorption band. The same disadvantage was observed for thiophenolate **2**[8] and aminide **3**[9] betaine dyes.

Gompper *et al.*[10] synthesised the betaine dye **4** which has the negative charge at a carbon atom (Scheme 2). Proton removal from the corresponding CH-acid of **4** is only possible because of the presence of two electron-withdrawing cyano groups. Unfortunately, no detailed synthetic procedure and solvatochromic properties for this compound are available. Another N^+C^- betaine dye **5a** was described by Utinans and Neilands.[11] This time the negative charge was generated at the C2 atom of the indan-1,3-dione moiety. The authors proposed two potential ways for preparation of **5a** but no synthetic and spectroscopic details were given. The only data mentioned in this paper are λ_{max} in methanol (470 nm) and chloroform (630 nm). Some modifications of **5a** were also undertaken to prepare materials for non-linear optics (NLO) experiments and host–guest polymer films.[12]

CH-acids are often relative strong, much stronger than carboxylic acids.[13] For example, the value of p*K*a for 2-(4-nitrophenyl)indan-1,3-dione was found as 2.31 in 50% ethanol and the appropriate value for 2-(4-trimethylammonium-phenyl)indan-1,3-dione is 2.84.[14] A p*K*a value in the same range should be observed for the conjugated acid of **5a**, therefore betaine dye **5a** should be usable in most carboxylic acid solutions. The aim of the present paper is to reinvestigate the preparation of the compound **5a** and to examine its solvatochromic properties.

We found that the best method for synthesis of **5a** is a condensation of 2,4,6-triphenylpyrylium perchlorate **6a** with 2-(4-aminophenyl)indan-1,3-dione **7**. Amine **7** can be prepared by several methods. In our laboratory, the best and most inexpensive method was a two-step procedure: the first step was the reaction of *p*-aminophenylacetic acid with phthalic anhydride leading to 2-(4-acetaminophenyl)indan-1,3-dione[15] and the second one was the hydrolysis of this amide.[16] Amine **7** reacts readily with pyrylium salt **6a** in ethanol solution in the presence of sodium acetate. The red betaine dye **5a** was isolated by filtration in an almost pure form. The dye **5a** is sparingly soluble in common organic solvents but in most cases the solubility is too low for solvatochromic experiments. We prepared three new betaines **5b–d** substituted by methyl groups in pyridinium moiety which are much more soluble in various solvents (Scheme 3). Indicators **5** are unfortunately insoluble in water and in aliphatic hydrocarbons.



Scheme 1 Molecular structure of the betaine dyes **1–3**.

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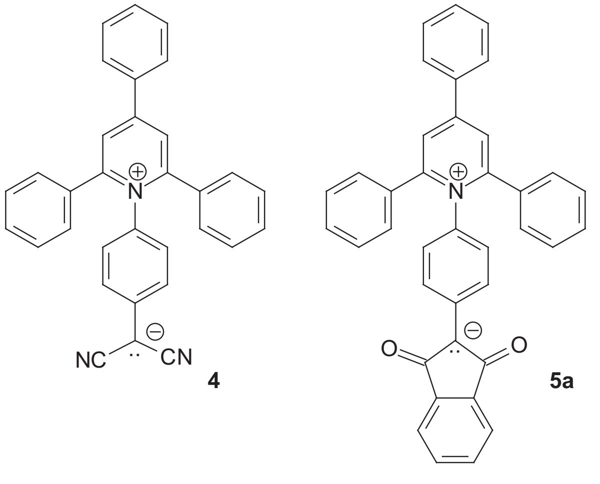


Scheme 2 Molecular structure of the betaine dyes **4** and **5a**.

The solutions of **5** in acetic, propionic, butyric and valeric acids were still coloured. After addition of hydrochloric acid the red tint disappeared. Chloroacetic, trichloroacetic and formic acids protonated betaine dye **5** just as hydrochloric acid. A blue solution of **5** in acetone did not bleach after addition of a variety of benzoic acids, cinnamic acid and iodoacetic acid. It is concluded that betaine dyes **5** can be used as solvent polarity indicators for carboxylic acids of moderate strength and their anhydrides.

For the quantitative description of the solvatochromic effect of betaine **5d**, Visible absorption spectra were measured in 19 HBD (hydrogen-bond donor) and non-HBD solvents of different polarities. The observed ν_{max} [cm^{-1}] were recalculated to E_T(**5d**) [kcal mol^{-1}] according to Eqn (1).

$$E_T(\mathbf{5d})\ [\text{kcal mol}^{-1}] = 2.859 \times 10^{-3} \cdot \nu_{max}\ [\text{cm}^{-1}] \qquad (1)$$

The results obtained are given in Table 1 and illustrated in Fig. 1.

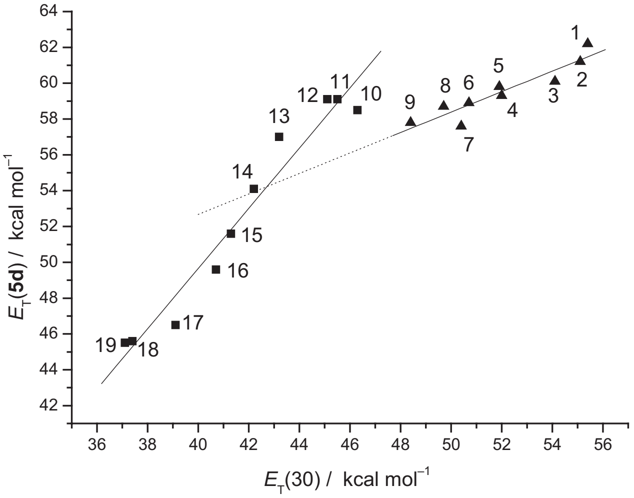


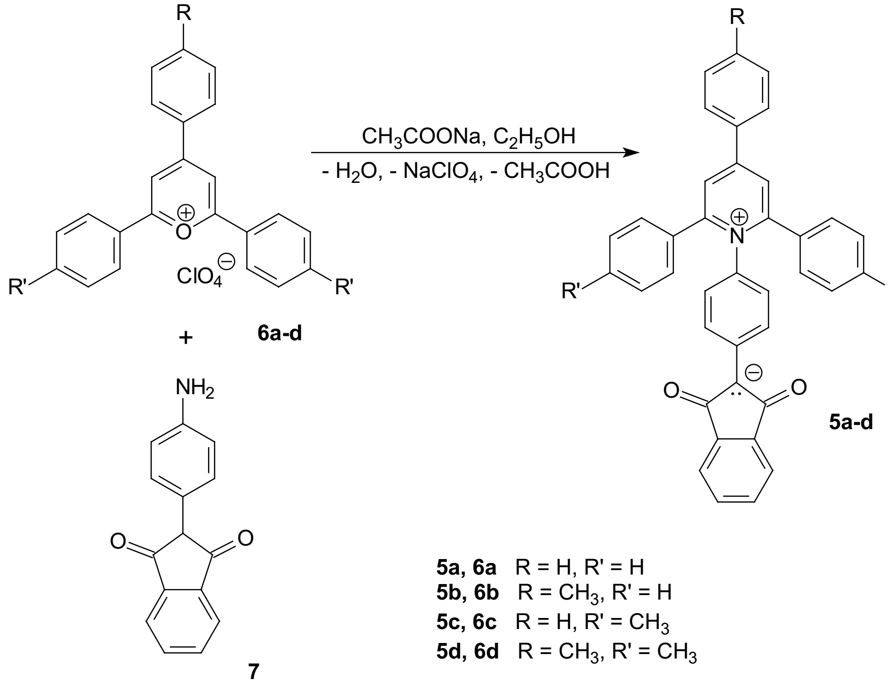
Fig. 1 Linear correlations between the E_T(30) values of standard betaine dye 1 and the E_T(**5d**) values of betaine dye **5d** measured in nine HBD solvents (▲, Eqn (2)) and 10 non-HBD solvents (■, Eqn (3)). Solvents numbering as in Table 1.

Figure 1 reveals that the strong HBD solvents (alcohols) follow a regression line (E_T(**5d**) *vs* E_T(30)) with a slope much smaller than that for the regression line for the non-HBD solvents. The very weak C–H hydrogen-bond donors $CHCl_3$, CH_2Cl_2 and CH_3CN are considered as non-HBD solvents.[7] The "HBD-line" can be described by Eqn (2) and the "non-HBD-line" by Eqn (3).

$$E_T(\mathbf{5d})\ [\text{kcal mol}^{-1}] = 0.571 \cdot E_T(30) + 29.83 \qquad (2)$$
$$(n = 9 \text{ HBD solvents}, r = 0.929, \sigma = 0.594\ [\text{kcal mol}^{-1}])$$

$$E_T(\mathbf{5d})\ [\text{kcal mol}^{-1}] = 1.680 \cdot E_T(30) - 17.57 \qquad (3)$$
$$(n = 10 \text{ non-HBD solvents}, r = 0.976, \sigma = 1.28\ [\text{kcal mol}^{-1}])$$

The specific solvation of betaine dye **5d** in HBD solvents leads to a smaller susceptibility (slope 0.571). The same effect was observed for other betaine dyes possessing hydrogen-bond-accepting sites.[6,7] In the case of compounds **5**, a negative charge is delocalised on five atoms including



Scheme 3 Synthesis of betaine dyes **5a–d**.

Table 1 Solvent dependent charge transfer (CT) absorption maxima λ_{max} and the corresponding E_T(**5d**) values of betaine dye **5d** measured in 19 solvents ordered according to decreasing $E_T(30)$ values

No	Solvent	$E_T(30)$/kcal mol^{-1}	λ_{max}/nm	ν_{max}/cm^{-1}	E_T(**5d**)/kcal mol^{-1}
HBD solvents					
1	Methanol	55.4	460	21739	62.2
2	2-Chloroethanol	55.1	467	21413	61.2
3	2,2,2-Trichloroethanol	54.1	476	21008	60.1
4	2-Methoxyethanol	52.0	482	20747	59.3
5	Ethanol	51.9	478	20921	59.8
6	Propan-1-ol	50.7	485	20619	58.9
7	Benzyl alcohol	50.4	496	20161	57.6
8	Butan-1-ol	49.7	487	20534	58.7
9	Propan-2-ol	48.4	495	20202	57.8
Non-HBD solvents					
10	Nitromethane	46.3	489	20450	58.5
11	Acetonitrile	45.5	484	20661	59.1
12	DMSO	45.1	484	20661	59.1
13	DMF	43.2	502	19920	57.0
14	Acetone	42.2	528	18939	54.1
15	1,2-Dichloroethane	41.3	554	18051	51.6
16	Dichloromethane	40.7	576	17361	49.6
17	Chloroform	39.1	615	16260	46.5
18	THF	37.4	627	15949	45.6
19	Anisole	37.1	628	15924	45.5

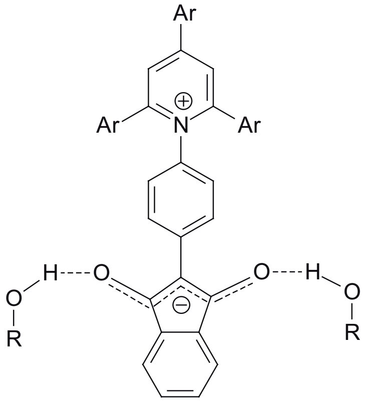
two oxygen atoms. Partial negatively charged oxygen atoms are very good sites for hydrogen bonding (Scheme 4).

The results of solvatochromic measurements for carboxylic acids and anhydrides are presented in Table 2.

It was decided not to calculate $E_T(30)$ values for the carboxylic acids using Eqn (2). We have no knowledge as to whether the carboxylic acids are part of the same family of the HBD solvents as the alcohols or whether they represent a separate family of compounds. In other words, one cannot be sure that Eqn (2) should hold for carboxylic acids. From the values of E_T(**5d**) it appears that acetic acid is slightly more polar than methanol. Other popular polarity scales (Grunwald–Winstein's *Y* scale and Kosower's *Z* scale) place methanol as more polar than acetic acid.[1] This is further evidence for a very complicated nature of solute–solvent interactions. The $E_T(30)$ values for anhydrides, which are always considered as non-HBD solvents, are estimated according to Eqn (3).

The last column of Table 2 gives available literature data for $E_T(30)$. These values are secondary values calculated from Kosower's *Z* scale by means of the correlation equation given in a footnote to Table 2.[1,4]

Table 3 presents the last set of our solvatochromic experiments results. Visible spectra of all the obtained dyes **5a–d** were measured in four solvents of different polarity. It is evident that methyl substituents at the phenyl rings of the pyridinium moiety do not significantly influence the CT band maximum.



Scheme 4 Specific solvation of betaine dye **5** by HBD solvents.

Experimental

Melting points were determined with a Mel-Temp II apparatus in open capillaries and are uncorrected. Elemental analyses were carried out with a EuroVector EA 3000 analyser. IR spectra were recorded using a Bruker Equinox 55 spectrometer as KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were taken at 500.13 MHz and 125.76 MHz respectively with a Bruker AMX 500 spectrometer in $CDCl_3$ with TMS as internal standard. UV-Vis spectra were recorded on Helios β (Unicam) spectrophotometer with 0.5, 1.0, and 2.0 cm quartz cells. Solvents for the solvatochromic measurements were dried and purified according to literature procedures.[17] Pyrylium salts were prepared by previously described methods: **6a**,[18] **6b**,[19] **6c**[20] and **6d**.[21]

Table 2 CT absorption maxima λ_{max}, the corresponding E_T(**5d**) and $E_T(30)$ values for carboxylic acids and anhydrides

Solvent	λ_{max}/nm	ν_{max}/cm^{-1}	E_T(**5d**)/kcal mol^{-1}	$E_T(30)^a$/kcal mol^{-1}	$E_T(30)^b$/kcal mol^{-1}
Acetic acid	454	22075	63.1	–	51.7
Propionic acid	481	20790	59.4	–	50.5
Butyric acid	483	20704	59.2	–	–
Valeric acid	485	20618	58.9	–	–
Acetic anhydride	466	21459	61.4	47.0	43.9
Propionic anhydride	491	20367	58.2	45.1	–

[a] Calculated by means of the converted Eqn. (3) for anhydrides (non-HBD solvents):
[$E_T(30) = 0.595 \cdot E_T(\mathbf{5d}) + 10.46$]

[b] Literature data[1,4], calculated from Kosower's *Z* values according to the following equation:
[$E_T(30) = 0.752 \cdot Z - 7.87$; r = 0.998 for 15 solvents]

Table 3 Solvent dependent CT absorption maxima λ_{max} of betaine dyes **5a–d** measured in four solvents of different polarity

Compound	Methanol λ_{max}/nm	Acetic acid λ_{max}/nm	Nitromethane λ_{max}/nm	DMF λ_{max}/nm
5a	461	460	494	505
5b	461	457	491	503
5c	462	459	492	503
5d	460	454	489	502

CAUTION: Pyrylium salts are harmful by inhalation, in contact with skin (can act as photosensitisers) and if swallowed. Heating of dry salts may cause an explosion.

Synthesis of betaine dyes (**5a–d**) A suspension of pyrylium salt **6a–d** (1.0 mmol), 2-(4-aminophenyl)indan-1,3-dione **7** (0.3 g, 1.25 mmol) and sodium acetate (0.25 g, 3.0 mmol) in ethanol (15 ml) was stirred and refluxed for 2 h. The red precipitate started to separate in a few minutes (except for **5d**). The mixture was stirred for 2 h at room temperature and then kept overnight in a refrigerator. The solid was filtered off, washed with cold ethanol and diethyl ether. Compounds **5c** and **5d** were recrystallised from ethanol. Betaine dyes **5a** and **5b** (sparingly soluble) were suspended in ethanol (15 ml) and refluxed with stirring for 30 min. Separated products were vacuum dried (*ca* 1 mmHg) at 50–60°C.

2-[4-(2,4,6-Triphenylpyridinium-1-yl)phenyl]indan-1,3-dion-2-ide (**5a**): Yield 0.40 g (76.9%). m.p. 386–387°C. IR (KBr) ν = 1621, 1601, 1584 1547, 1510, 1411 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ [ppm] = 6.68 and 8.69 (2d, *J* = 8 Hz, 4H, AA'BB' system, aromatic H of the ring between pyridinium and indandionide moieties), 7.23–7.39 (m, 14H, aromatic H of the 2- and 6-aryl rings and aromatic H of indandionide moiety), 7.55–7.65 (m, 3H, aromatic *m*- and *p*-H of the 4-aryl ring), 7.87 (d, *J* = 8.5 Hz, 2H, aromatic *o*-H of the 4-aryl ring), 8.11 (s, 2H, aromatic H of the pyridinium ring). $C_{38}H_{25}NO_2$ (527.7): calcd. C 86.5, H 4.8, N 2.7; found C 86.5, H 4.7, N 2.7%.

2-{4-[4-(4-Methylphenyl)-2,6-diphenylpyridinium-1-yl]phenyl}indan-1,3-dion-2-ide (**5b**): Yield 0.48 g (75.0%). m.p. >400°C. IR (KBr) ν = 1617, 1601, 1549, 1509, 1413 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ [ppm] = 2.50 (s, 3H, CH_3), 6.66 and 8.68 (2d, *J* = 8 Hz, 4H, AA'BB' system, aromatic H of the ring between pyridinium and indandionide moieties), 7.20–7.50 (m, 16H, aromatic H of the 2- and 6-aryl rings, aromatic H of indandionide moiety and aromatic *m*-H of the 4-aryl ring), 7.79 (d, *J* = 8.5 Hz, 2H, aromatic *o*-H of the 4-aryl ring), 8.09 (s, 2H, aromatic H of the pyridinium ring). $C_{39}H_{27}NO_2$ (541.7): calcd. C 86.5, H 5.0, N 2.6; found C 86.45, H 5.0, N 2.7%.

2-{4-[2,6-Bis(4-methylphenyl)-4-phenylpyridinium-1-yl]phenyl}indan-1,3-dion-2-ide (**5c**): Yield 0.36 g (66.0%). m.p. 358–359°C. IR (KBr) ν = 1618, 1606, 1585, 1544, 1510, 1415 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ [ppm] = 2.29 (s, 6H, CH_3), 6.71 and 8.70 (2d, *J* = 8 Hz, 4H, AA'BB' system, aromatic H of the ring between pyridinium and indandionide moieties), 7.08 and 7.13 (2d, *J* = 8.5 Hz, 8H, AA'BB' system, aromatic H of the 2- and 6-aryl rings), 7.19 and 7.32 (two dd, J_1 = 5 Hz, J_2 = 3 Hz, 4H, AA'BB' system, aromatic H of indandionide moiety), 7.55–7.65 (m, 3H, aromatic *m*- and *p*-H of the 4-aryl ring), 7.84 (d, *J* = 8.5 Hz, 2H, aromatic *o*-H of the 4-aryl ring), 8.03 (s, 2H, aromatic H of the pyridinium ring). $C_{40}H_{29}NO_2$ (555.7): calcd. C 86.5, H 5.3, N 2.5; found C 86.6, H 5.3, N 2.6%.

2-{4-[2,4,6-Tris(4-methylphenyl)pyridinium-1-yl]phenyl}indan-1,3-dion-2-ide (**5d**): Yield 0.45 g (78.9%). m.p. 364–365°C. IR (KBr) ν = 1622, 1606, 1584, 1552, 1509, 1412 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ [ppm] = 2.27 (s, 6H, CH_3), 2.48 (s, 3H, CH_3), 6.71 and 8.68 (2d, *J* = 8 Hz, 4H, AA'BB' system, aromatic H of the ring between pyridinium and indandionide moieties), 7.05 and 7.12 (2d, *J* = 8.5 Hz, 8H, AA'BB' system, aromatic H of the 2- and 6-aryl rings), 7.16 and 7.30 (two dd, J_1 = 5 Hz, J_2 = 3 Hz, 4H, AA'BB' system, aromatic H of indandionide moiety), 7.40 and 7.74 (2d, *J* = 9 Hz, 4H, AA'BB' system, aromatic H of the 4-aryl ring), 7.98 (s, 2H, aromatic H of the pyridinium ring). ^{13}C NMR ($CDCl_3$) δ [ppm] = 21.3 (CH_3), 21.6 (CH_3), 102.2 (C2), 117.8, 123.5, 124.8, 126.3, 127.7, 129.1, 129.6, 129.7, 129.9, 130.8, 140.7, 141.3, 143.8, 155.4, 157.7 (aromatic C), 191.9 (C=O). $C_{41}H_{31}NO_2$ (569.7): calcd. C 86.4, H 5.5, N 2.5; found C 86.5, H 5.4, N 2.5%.

We are grateful to Dr Sebastian Leśniewski from the Department of Physical Chemistry, Jagiellonian University for help with the visible absorption spectra measurements.

Received 7 February 2008; accepted 28 April 2008
Paper 08/5090 doi: 10.3184/030823408X324698

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