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A solvatochromic derivative of Meldrum's acid

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Abstract

The preparation of the 5-(4-*N*,*N*-dimethylaminobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**2**), a dye derived from Meldrum's acid, is described, and its solvatochromic behaviour compared with that of an analogous derivative of barbituric acid. Dye **2** exhibited positive solvatochromism, being sensitive both to the dipolarity–polarizability and the acidity of the medium.

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Keywords: Solvatochromic dye; Meldrum's acid; Dipolarity–polarizability; Hydrogen-bonding

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1. Introduction

Cyclic 1,3-diones like Meldrum's (2,2,-dimethyl-1,3-dioxane-4,6-dione) and barbituric acid may be used as building blocks for intramolecular donor–acceptor pairs which act as solvatochromic dyes. Thus, condensation of *N*,*N*-dimethylaminobenzaldehyde with *N*,*N*-dimethylbarbituric acid leads to the formation of merocyanine **1**, a compound whose solvatochromic behaviour has been recently described by us [1].

In the present report, the analogous condensation product of this aldehyde with Meldrum's acid was prepared and its solvatochromic behaviour compared with that of compound **1**.

The resulting 5-(4-*N*,*N*-dimethylaminobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **2** exhibited larger charge-transfer transition energies than **1** in the same solvents, spanning a range of positive solvatochromic shifts similar to that of the barbituric derivative. Theoretical calculations were in agreement with the experimental data, allowing a theoretical interpretation of the spectral behaviour of both compounds, supported by the reported X-ray structures of some analogs of **2** [2] (Scheme 1).

2. Experimental

2.1. Materials and methods

The recorded melting point was obtained with a Microthermal capillary equipment, and was not corrected. The IR spectrum was recorded with a Perkin-Elmer 735B apparatus, NMR spectra with a 400 MHz Brüker Avance spectrometer, visible spectra were obtained with a Hewlett Packard Kayak XA spectrophotometer.

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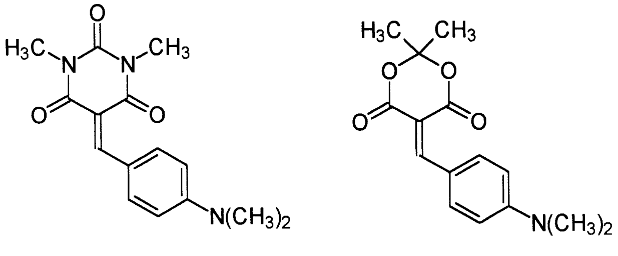

Scheme 1.

All employed solvents were analytically pure and were employed without any further drying or purification. Meldrum's acid and 4-*N*,*N*-dimethylaminobenzaldehyde were purchased from Aldrich.

Theoretical calculations were performed with the Gaussian 98w package [3]. Both compounds had their structures optimized with the semi-empirical AM1 method, starting from structures where the donor aromatic ring and the acceptor dione moiety were not coplanar, in agreement with reported data for analogous systems [2]. Transition energies for both compounds were calculated with the aid of the ZINDO/S option, employing configuration interactions involving singly-excited transitions among the 10 highest occupied and the 10 lowest unoccupied molecular orbitals of the molecules.

2.2. Preparation of dye **2**

A mixture of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) (0.50 g, 3.45 mmol) and 4-*N*,*N*-dimethylaminobenzaldehyde (0.52 g, 3.45 mmol) in acetic anhydride (2 ml) was gently refluxed for 1 h. The resulting cooled mixture was filtered to give the 5-(4-*N*,*N*-dimethylaminobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**2**), in the form of a dark purple solid (0.43 g, 45% yield), recrystallized in acetone/hexane, mp 165–167 °C. Analysis, found N 4.88% calc. for $C_{15}H_{17}NO_4$ N, 5.09%. IR (KBr) 1700, 1600, 1500, 1360, 1280, 1160, 1120 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.74 (s, 6 H, OC(CH_3)$_2$), 3.13 (s, 6 H, NCH_3), 6.66 (d, 2 H, J = 9.5 Hz, Ar-H *ortho* to NMe_2), 8.22 (d, 2 H, J = 9.5 Hz, Ar-H *meta* to NMe_2), 8.27 (s, 1 H, C = CH). ^{13}C NMR ($CDCl_3$) δ 28.1 (C-$\underline{C}H_3$), 40.3 (N-CH_3), 103.6 ($\underline{C}$-CH_3), 105.0 (C-5), 111.1 (C-3′ and C-5′), 120.2 (C-1′), 139.1 (C-2′ and C-6′), 154.6 (C-4′), 159.0 (C-7), 161.6 (C-4), 165.4 (C-6).

3. Results and discussion

3.1. Structure and solvatochromic behaviour of **2**

According to the optimized structure of **2**, the aromatic ring is not fully coplanar with the acceptor dione ring, with a torsion angle of ca. 8°. This theoretical prediction is in good agreement with the X-ray structures of two analogs of **2**, the 5-(4-methoxybenzylidene)- and the 5-(4-nitrobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones, for which theoretical calculations employing the AM1 method yielded good results [2].

The length of the C–C double bond which acts as a bridge between the aromatic and the dioxanedione ring is dependent on the nature of the 4-benzylidene substituent. For the 4-nitro derivative, the C5–C7 bond length was 1.345 Å, increasing in the 4-methoxy derivative to 1.356 Å [2] This bond-length increase is in agreement with the donor nature of the methoxy group, and is a good indication of the conjugation between the aryl and the dioxanedione ring in the latter compound, an effect which is absent in the nitro derivative. In the case of compound **2**, with a similar conjugation between the donor and the acceptor moieties, the calculated C5–C7 bond length was practically equal (1.357 Å) to the corresponding value of the methoxylated analog.

The $\lambda_{\max}$ values of the longest-wavelength charge-transfer band of dye **2** are given in Table 1. For the sake of comparison, the corresponding $\lambda_{\max}$ values of compound **1** in the same solvents are also given. As can be seen in Fig. 1, compound **2**, like its analog **1**, showed a positive solvatochromic behaviour. The barbituric acid derivative **1** exhibited consistently smaller transition energies (larger $\lambda_{\max}$ values) than the Meldrum's acid derivative **2** in the same solvent. Dyes **1** and **2** share a common donor group, similarly conjugated to two different acceptor fragments. Their relative transition energies should depend on the relative electron affinities of the acceptor fragments. The pyrimidinetrione moiety of **1** should accommodate a negative charge more easily than the dioxanedione fragment in **2**. The larger transition energies of compound **2** are in line with these expectations, since barbituric acid is stronger ($pK_a = 4.0$ [4]) than Meldrum's acid ($pK_a = 7.3$ [5]).

This result was in agreement with theoretical calculations, which predicted for compound **1** in the gas phase a charge-transfer singlet transition at 377 nm ($f = 0.443$). The same transition for compound **2** had a calculated $\lambda_{\max}$ value of 369 nm, with an oscillator strength of 0.533. Both transitions had, as main contributors, HOMO–LUMO excitations, corresponding to charge transfers from the dimethylamino group to the cyclic 4,6-dione systems.

Table 1
Variation of the $\lambda_{\max}$ value for the longest-wavelength charge-transfer band of dyes **1** and **2** in different solvents

Solvent	$\lambda_{\text{máx}}$ Values, nm		Polarity values		
	Dye **1**[a]	Dye **2**	SPPN[b]	SA[c]	SB[d]
Diethyl ether	446	432	0.694	–[e]	0.562
Ethyl acetate	452	440	0.795	0.000	0.542
Toluene	453	440	0.655	–[e]	0.128
Tetrahydrofuran	–	443	0.838	0.000	0.591
Acetone	459	446	0.881	0.000	0.475
Acetonitrile	458	448	0.895	0.044	0.286
1,2-Dicloroethane	–	450	0.890	0.030	0.126
Dicloromethane	462	449	0.876	0.040	0.178
1-Butanol	–	452	0.892	0.341	0.809
Ethanol	462	451	0.853	0.400	0.658
Methanol	462	452	0.857	0.605	0.545
1-Octanol	–	449	0.867	0.299	0.923
2-Propanol	–	453	0.884	0.283	0.762
1-Propanol	–	451	0.847	0.367	0.727
1-Pentanol	–	452	0.885	0.319	0.860

[a] Data from Ref. [1].
[b] Values taken from Ref. [6].
[c] Values taken from Ref. [7].
[d] Values taken from Ref. [8].
[e] Value assumed equal to 0.000 in the regression.

3.2. Correlations with solvent parameters

Spectra of compound **2** were recorded in protic and non protic solvents. The CT transition energies, expressed in wavenumber values, correlated poorly with the dipolarity-polarizability values $\mathrm{SPP^N}$ [6] of the solvents, as can be seen in Fig. 2. This poor correlation pointed to the intervention of other effects to the solvatochromism of the studied dye. As was the case for analog **1**, such deviations were assigned to hydrogen–bond interactions between the protic solvent and the carbonyl oxygens of the dioxanedione group [1]. These interactions have the effect of enhancing charge-transfer from the amino donor group to the acceptor carbonyl oxygens, by partial protonation of the latter by the solvent.

The contributions of the various solvent effects to the observed solvatochromism of compound **2** were evaluated by means of a multiple regression analysis. The CT energies were expressed in terms of three independent contributions, the dipolarity–polarizability, the acidity and the basicity of the solvent. For the first set we employed the $\mathrm{SPP^N}$ dipolarity-polarizability values [6], for the second, the generalized solvent acidity scale SA [7] and for the latter the generalized solvent basicity scale SB [8] of Catalán et al. These scales were chosen because of their convenience, as normalized values for all the solvents employed in this work were available in literature. As might be anticipated, we did not obtain any significant correlation with the solvent basicity SB, but only with the $\mathrm{SPP^N}$ and the SA values. Since the two scales are normalized, the corresponding coefficients of the regression Eq. (1) are a measure of the relative contributions of the two effects to the solvatochromism of **2**

$$\bar{\nu}_{\text{calc.}} = 24830 - 2791\ \mathrm{SPP^N} - 655\ \mathrm{SA}$$
$$N = 15,\quad \mathrm{S.D.} = 131\ \mathrm{cm^{-1}} \tag{1}$$

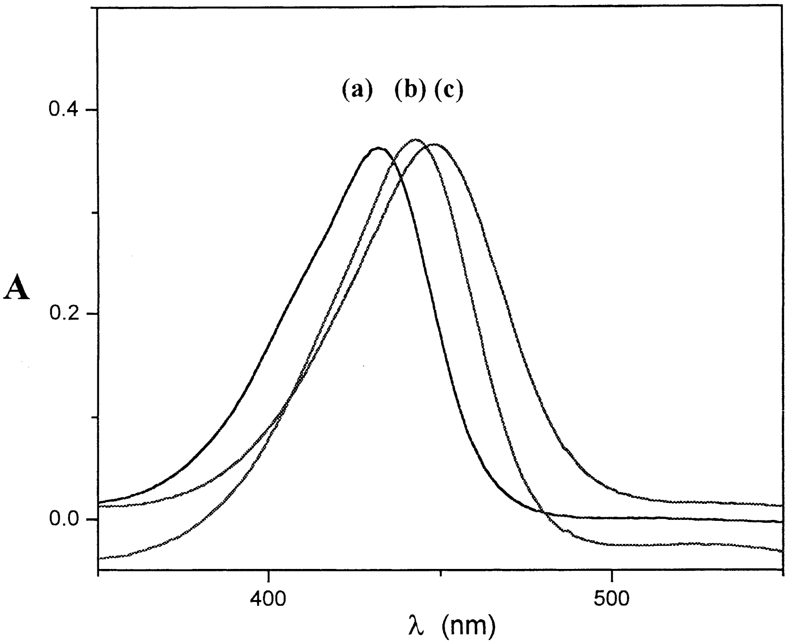

Fig. 1. Variation of the longest-wavelength absorption band of dye **2** (ca. 10^{-5} M) in diethyl ether (a), tetrahydrofuran (b) and acetonitrile (c).

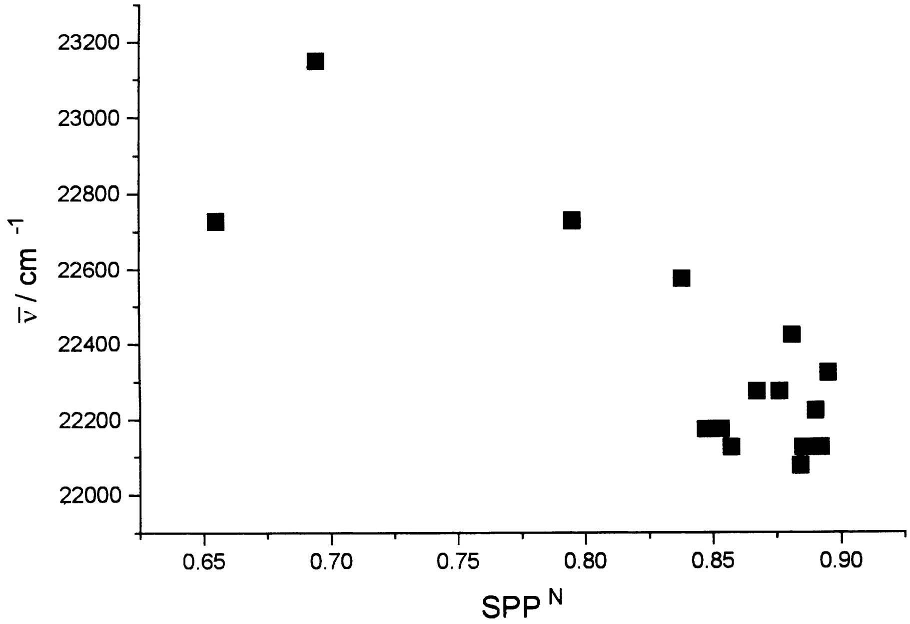

Fig. 2. Variation of the wavenumber values of the longest-wavelength absorption band of compound **2** with the dipolarity–polarizability value SPP^N of the solvent. Wavenumber values, in cm^{-1}, were calculated from the data of Table 1 by the relationship $\bar{\nu} = 10^7/\lambda_{max}$.

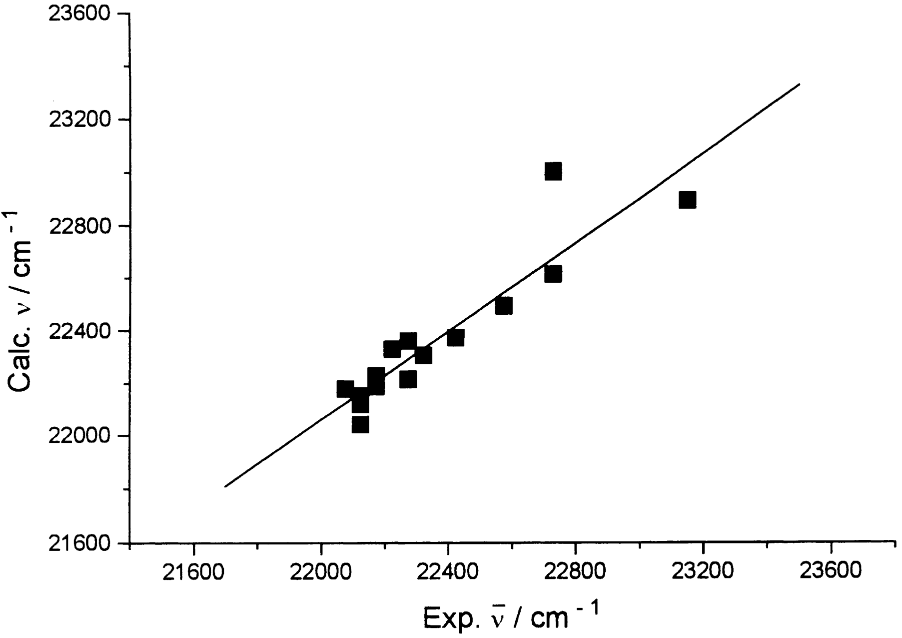

Fig. 3. Correlation between the experimental and the calculated wavenumber values of the CT absorption band of **2** in all employed solvents. Calculated values were obtained with the regression Eq. (1), yielding a correlation coefficient $r = 0.917$ and a standard deviation S.D. = ±131 cm^{-1}. Wavenumber values, in cm^{-1}, were calculated from the data of Table 1 by the relationship $\bar{\nu} = 10^7/\lambda_{\max}$.

It is seen that the solvatochromic behaviour of the dye is governed by dipolarity–polarizability effects, with a significant contribution of hydrogen–bonding interactions of the dye with acidic solvents.

Fig. 3 depicts the correlation between the experimental and the calculated wavenumber values, obtained with the aid of regression Eq. (1). A correlation coefficient $r = 0.917$ was obtained for the corresponding straight line.

In conclusion, both barbituric and Meldrum's acid may act as acceptor fragments, when conjugated with a donor dimethylaminophenyl group, giving rise to dyes with similar solvatochromic behaviour. The positive solvatochromism exhibited by these compounds predominantly reflects the dipolarity–polarizability properties of the medium, being also sensitive to the milieu acidity in protic solvents. Charge-transfer transition energies of the barbituric derivative **1** were systematically smaller than the corresponding energies of the dione analog **2** in the same solvent. This result, born out by theoretical calculations, reflects the greater electron affinity of the barbituric ring system, when compared with the analogous cyclic dione of Meldrum's acid.

Acknowledgements

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