DOI: 10.1002/ejoc.200800355

Differentiating Between Dipolarity and Polarizability Effects of Solvents Using the Solvatochromism of Barbiturate Dyes

Mirko Bauer,[a] Anja Rollberg,[a] Anina Barth,[a] and Stefan Spange*[a]

Keywords: Solvatochromism / Solvent effects / Polarity / Barbiturates / Donor–acceptor systems / Polyenes

Barbiturate dyes containing either a dipolar or polarizable chromophoric system have been synthesized and their solvatochromism investigated. The effect of specific and non-specific solvent interactions on the position of their UV/Vis absorption bands has been evaluated by using the Kamlet–Taft and Catalán solvent parameter sets. Furthermore, the effect on the solvatochromic behaviour of different substitution patterns on the barbiturate moiety has been examined.

Introduction

Solvatochromism[1] has been established as a readily applicable and powerful tool to investigate the influence of numerous polarity effects[2] of the surroundings of a reaction on reaction rates, equilibria or the physicochemical properties of molecules. Therefore, the use of solvatochromic probes has been established to measure the polarity effects of environments comprising not only well-behaved solvents and room-temperature ionic liquids,[3,4] but also inorganic surfaces,[5,6] biomolecules [7–9] and organized media.[10]

In recent decades, the Kamlet–Taft approach[11] has successfully been applied to separate the influence of non-specific chemical interactions, including electrostatic effects (dipolarity/polarizability), from specific interactions, that is, hydrogen-bonding, which are related to the molecular structure of a compound. The commonly used simplified Kamlet–Taft equation applied to the UV/Vis absorption shift ($\tilde{\nu}_{max}$) of a solute is given by Equation (1),[11] where $\tilde{\nu}_{max,0}$ is the solute property of a reference system, for example, a non-polar medium, α describes the HBD (hydrogen-bond donating) ability, β the HBA (hydrogen-bond accepting) ability, π^* the dipolarity/polarizability of the solvents and a, b and s are solvent-independent correlation coefficients that indicate the contribution of the different solvent effects to the UV/Vis absorption shift.

$$\tilde{\nu}_{max} = \tilde{\nu}_{max,0} + a\alpha + b\beta + s\pi^* \qquad (1)$$

One problem of the Kamlet–Taft π^* scale is that the dipolarity and polarizability of the solvent are included in only one parameter. The use of a polarizability correction term $d\delta$[12] is not suitable for solving the problem, because it does not allow differentiation of the polarizability effects between two related solvents, for example, aromatic or halogenated hydrocarbons. Another disadvantage of the Kamlet–Taft parameters is that their determination is not based on a well-defined reference process, rather they are derived from an average of measurements using numerous probes.

Therefore, the search for an alternative solvent polarity scale with well-defined reference processes is required. In recent years, Catalán and co-workers have introduced three alternative empirical polarity scales: SA, SB and SPP, which are formally related to the Kamlet–Taft parameters α, β and π^*, respectively.[13] The advantage of Catalán's concept is that each solvatochromic solvent parameter is based on a pair of well-defined reference homomorph solvatochromic probes. In 2004, Catalán and Hopf reported an important fourth scale: the polarizability parameter SP.[14] This novel scale promises to measure gradual differences in the surrounding's polarizability by the solvatochromic method. One can now formulate another multiparameter equation, analogous to Equation (1), which comprises two parameters for specific and two parameters for non-specific interactions [Equation (2)]. It has, however, been pointed out that the SPP and SP scales are actually not independent of each other.[14] Thus, it seems reasonable to include only one of these parameters at a time when using Equation (2).

$$\tilde{\nu}_{max} = \tilde{\nu}_{max,0} + a\mathrm{SA} + b\mathrm{SB} + s\mathrm{SPP} + t\mathrm{SP} \qquad (2)$$

With this in mind we have designed a range of novel barbiturate dyes that are structurally related but supposed to show different sensitivities towards electrostatic effects. To examine this sensitivity and separate the individual solvation effects, the solvatochromic properties of these dyes were investigated in detail, and the coefficients of the individual interaction contributions were determined by using

---

[a] Department of Polymer Chemistry, Chemnitz University of Technology,
Straße der Nationen 62, 09107 Chemnitz, Germany
Fax: +49-371-531-21239
E-mail: stefan.spange@chemie.tu-chemnitz.de

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

multiple correlation analysis of both Kamlet–Taft's Equation (1) and Catalán's Equation (2). Related barbituric acid derivatives have already been widely used in materials science [e.g., in materials for non-linear optics (NLO)][15–19] and analysis.[20–23] The barbiturate moiety also offers the possibility of a facile variation of its electron-demanding effects as well as its interaction with the surroundings by introducing different substituents. In particular, we wanted to determine whether the free NH functions and those capped by alkyl groups have an effect on the chromophoric π-electron system. Furthermore, 2-thiobarbiturates have been investigated to examine the effects of the more dipolar and polarizable thiocarbonyl moiety.

Results and Discussion

We have used two types of solvatochromic dyes that in principle can show all kinds of interactions with a solvent (Figure 1). The barbituric acid moiety, which acts as an electron-withdrawing substituent, was coupled either with two 4-(dimethylamino)phenyl groups, which results in a dipolar structure (**1**), or with a retinyl group, to yield a polarizable all-(*E*) linear polyene structure (**2**).

The solvatochromism of one of the merocyanine-type dyes, **1b**, as well as a related dye has already been studied by Rezende et al.[21a] These dyes show positive solvatochromism as the position of the solvatochromic UV/Vis absorption band is shifted to a lower energy with increasing dipolarity/polarizability and HBD strength of the solvent. However, Rezende reported only on the synthesis and solvatochromism of *N*,*N*-dimethyl-substituted barbituric acid dyes. The alkylated thiobarbiturate dye **1d** is described in a patent, yet no characterization data is given there.[24a] Surprisingly, no information on the NH derivatives of **1** were found in the literature in spite of a patent reference[24b] that names a few related compounds.

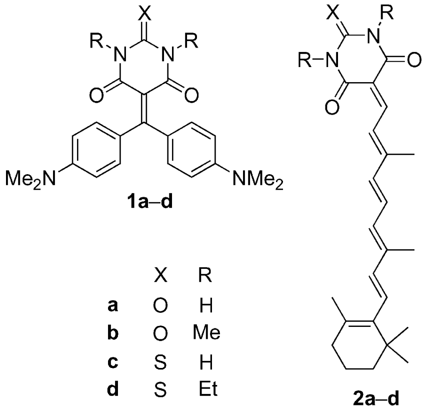


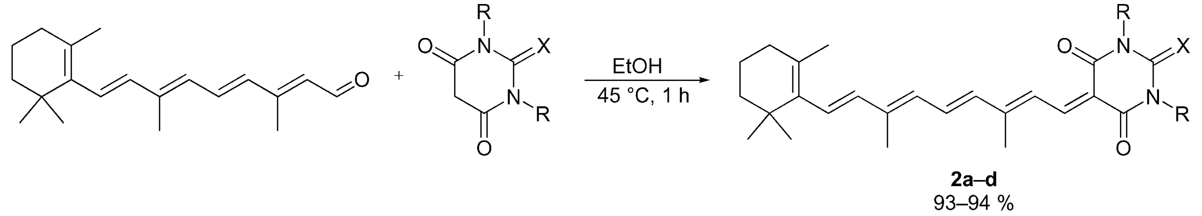
Figure 1. Barbiturate dyes studied in this work.

Electron-poor retinyl dyes related to **2** have already found interest as dyes and NLO materials[25] as well as anticancer drugs.[26] However, no such compounds with barbiturate functions have been reported so far.

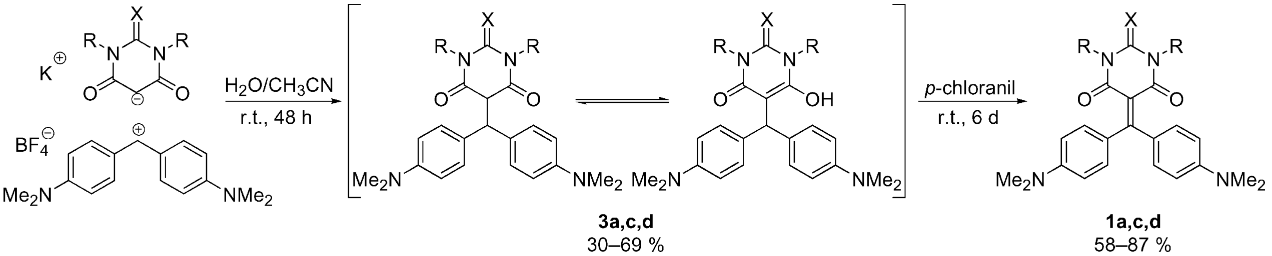
Synthesis

According to the literature, the compounds to be investigated should be readily accessible by aldol condensation of retinal or Michler's ketone with the respective barbituric acid derivatives.[21a,24,27,28]

Although this route proved to be suitable for preparing compounds **2a**–**d** (Scheme 1), the method described by Rezende[21a] for **1b**, heating of Michler's ketone and *N*,*N*-dimethylbarbituric acid at reflux in acetic anhydride/acetic acid, failed for the NH derivatives. Finally, the method of choice involved a two-step reaction starting from Michler's hydrol blue (Scheme 2).[29] The idea for the synthesis of the intermediates **3** was inspired by Mayr's reactivity scale for nucleophiles (for the anion of barbituric acid, $N > 10$ was



Scheme 1. Synthesis of compounds **2a**–**d**.



Scheme 2. Synthesis of compounds **1a**,**c**,**d**.

estimated[30a]) and electrophiles (E = –7.0 for Michler's hydrol blue cation[30b]). The rate constant k for the recombination reaction, estimated to be about $10^3\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ from Equation (3),[31] provides a solid background for the retrosynthesis.

$$\log k_{20\,^{\circ}\mathrm{C}} = s(N + E) \tag{3}$$

The recombination products **3**, being sensitive to air and light, were isolated as slightly coloured solids in reasonable yields. The ^{1}H NMR spectrum of **3a** in [D$_6$]DMSO shows two doublets at δ = 4.2 and 4.7 ppm, and its ^{13}C NMR spectrum shows two signals at δ = 52 and 53 ppm, which shows that this compound exists only in the triketo form. Remarkably, the thiobarbiturates **3c** and **3d** are present in their enol form in [D$_6$]DMSO, as indicated by ^{13}C NMR peaks at δ = 97 and 93 ppm, respectively, and a single singlet at $\delta \approx$ 5.0 ppm in the ^{1}H NMR spectra. Finally, oxidation of **3a**,**c**,**d** was accomplished with *p*-chloranil in water to yield **1a**,**c**,**d** as intensely coloured solids.

Solvatochromism

The solvatochromism of the novel dyes was studied in 13–30 solvents for which the solvent parameters of Kamlet–Taft and Catalán are available (see Tables 1 and 2). The UV/Vis spectra of these compounds showed no dependence on the dye concentration, and thus the formation of dimers or higher aggregates can be neglected.

In aprotic solvents, compounds **1a**,**c**,**d** show a single absorption band in the visible region. However, in protic solvents this band is considerably broadened and is split into two bands in more acidic media (Figure 2). This effect can probably be attributed to protonation reactions and is in accordance with the observations made by Rezende et al. for **1b**.[21a] His semiempirical calculations showed that this protonation is likely to occur at the carbonyl moieties. Our solvatochromic investigations indeed confirm that HBD solvents interact mainly with the carbonyl moieties and not with the dimethylamino groups (see below). In the cases of split bands, the UV/Vis band at longest wavelength was used for the correlation analysis.

Table 2. Solvent polarity parameter sets of Kamlet–Taft[34] and Catalán[13,14] for the solvents in Table 1.

	Kamlet–Taft			Catalán			
Solvent	α	β	π^*	SA	SB	SPP	SP
n-Hexane	0.00	0.00	–0.04	0.000	0.056	0.519	0.6164
Triethylamine	0.00	0.71	0.14	0.000	0.885	0.617	0.6603
1-Butanol	0.84	0.84	0.47	0.341	0.809	0.837	0.6742
Ethyl acetate	0.00	0.45	0.55	0.000	0.542	0.795	0.6558
Tetrahydrofuran	0.00	0.55	0.58	0.000	0.591	0.838	0.7139
Benzene	0.00	0.10	0.59	0.000	0.124	0.667	0.7929
Methanol	0.98	0.66	0.60	0.605	0.545	0.857	0.6079
TFE	1.51	0.00	0.73	0.893	0.107	0.908	0.5431
Acetonitrile	0.19	0.40	0.75	0.044	0.286	0.895	0.6448
Dimethyl sulfoxide	0.00	0.76	1.00	0.072	0.647	1.000	0.8295

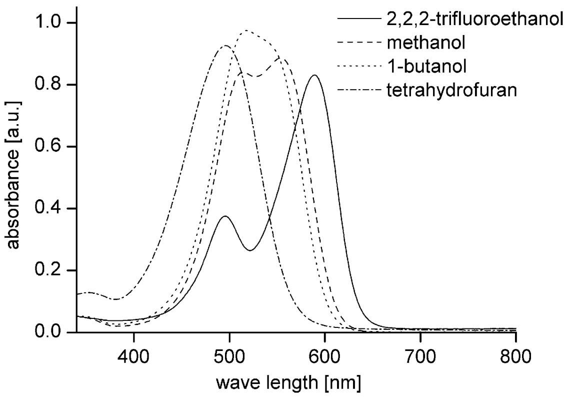


Figure 2. UV/Vis absorption spectra of **1a** in different solvents.

For the retinal-type dyes **2a**–**d** there is also one absorption band, yet there is no indication of proton transfer [only in 2,2,2-trifluoroethanol (TFE) does a small shoulder in the UV/Vis spectrum appear, see Figure 3]. Nevertheless, reasonable correlations are only obtained when several solvents, for example, triethylamine and chlorinated solvents,

Table 1. UV/Vis absorption maxima of compounds **1** and **2** in selected solvents and the extent of the solvatochromic shift.

Solvent	$\tilde{\nu}_{\max}$ [10^{-3} cm^{-1}]							
	1a	**1b**[a]	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**
n-Hexane	[b]	21.10[c]	[b]	19.76	[b]	21.37[c]	19.61	19.96[c]
Triethylamine	21.46[c]	–	19.96[c]	19.38	21.41[d]	20.16[d]	19.01[d]	23.81[d]
1-Butanol	19.31[e]	19.01	18.55[e]	18.02	20.33	20.83	19.16	18.87
Ethyl acetate	20.04	20.00	18.87	18.59	20.88	20.79	19.57	19.27
Tetrahydrofuran	20.16	19.84	18.98	18.52	21.10	21.28	19.69	19.34
Benzene	19.53	–	18.66	18.59	19.96	20.33	18.87	19.01
Methanol	18.05[f]	18.05[f]	17.36[f]	17.15[e]	20.49	21.01[d]	19.27	19.01
TFE	16.98[f,g]	17.06[f,g]	16.58[f,g]	16.64[f,g]	18.73[g]	19.49	17.54[g]	17.79[g]
Acetonitrile	19.42	19.53	18.55	18.18	20.58	21.23	19.27	19.23
Dimethyl sulfoxide	19.31	19.01	18.25	17.86	20.33	20.00	19.38	18.52
$\Delta\lambda$ [nm]	123	112	102	96	61	58	67	61
$\Delta\tilde{\nu}$ [cm^{-1}]	4481	4032	3376	3163	2415	1901	2337	2166

[a] Data from ref.[21a] [b] Substance is insoluble. [c] Solvent with the highest hypsochromic shift. [d] Value excluded from correlation. [e] Broad maximum. [f] Spectrum shows two maxima. [g] Solvent with the highest bathochromic shift.

are excluded from the correlation analyses. The reason for the deviation of these solvents is not clear yet and requires further investigation. It might for instance be due to a reaction with the solvent leading to differently coloured products (see, for example ref.[32]). As the colour of ethanolic solutions of these dyes slowly fades over a few days only when exposed to light, some photoisomerization in certain solvents cannot be ruled out.[33]

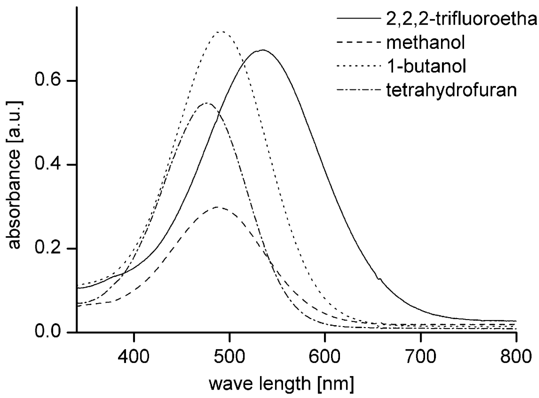


Figure 3. UV/Vis absorption spectra of **2a** in different solvents.

The influence of solvent properties on the shift of $\tilde{\nu}_{max}$ has been evaluated by means of multiple regression analyses using the solvent polarity parameter sets of Kamlet–Taft[34] and Catalán.[13,14] For comparison, the data for **1b** from ref.[21a] have also been included in these analyses. The best-fitting correlation results are summarized in Tables 3 and 4.

Table 3. Values of the solvent-independent correlation coefficients *a*, *b* and *s* for the Kamlet–Taft equation [Equation (1)], wavenumber of a reference system ($\tilde{\nu}_{max,0}$), correlation coefficient (*r*), standard deviation (*sd*), significance (*f*) and the number of solvents (*n*) for compounds **1** and **2**.

	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*r*	*sd*	*f*	*n*
1a	20.94	–1.62	0.84	–2.21	0.97	0.23	<0.0001	22
1b	21.12	–1.58	–	–2.05	0.98	0.20	<0.0001	13
1c	19.73	–1.26	0.49	–1.81	0.96	0.21	<0.0001	23
1d	19.65	–1.06	–	–1.84	0.98	0.15	<0.0001	26
2a	20.67	–0.87	1.28	–1.04	0.83	0.33	<0.0001	27
2b	21.22	–0.53	–	–1.00	0.67	0.47	0.0003	30
2c	19.50	–0.77	1.29	–1.33	0.86	0.31	<0.0001	30
2d	19.83	–0.48	–	–1.33	0.91	0.23	<0.0001	30

It can be seen that for **1a**–**d** the magnitude of the coefficients *a*, *b* and *s* from Equations (1) or (2) of the thiobarbiturates are generally lower than those of the barbiturates. This can be explained by the stronger electron-accepting ability of the thiocarbonyl group, which enhances the –M effect of the thiobarbiturate moiety. Thus, the overall dipolarity of the molecule is increased in the ground state and decreased in the excited state.[17b,23] As both these states are approaching the cyanine limit with ideal charge delocalization, the push–pull chromophore becomes less susceptible to solvent effects. This explanation is further supported by the lower UV/Vis absorption energy and the smaller solvatochromic range of about 3000 cm^{-1} for the thiobarbiturates, compared with more than 4000 cm^{-1} for the barbiturates.

Table 4. Values of the solvent-independent correlation coefficients *a*, *b*, *s* and *t* for the Catalán equation [Equation (2)], wavenumber of a reference system ($\tilde{\nu}_{max,0}$), correlation coefficient (*r*), standard deviation (*sd*), significance (*f*) and number of solvents (*n*) for compounds **1** and **2**.

	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*t*	*r*	*sd*	*f*	*n*
1a	21.41	–2.60	1.35	–2.70	–	0.96	0.24	<0.0001	22
1b	22.77	–2.55	–	–3.62	–	0.98	0.23	<0.0001	13
1c	20.44	–2.06	0.89	–2.57	–	0.95	0.22	<0.0001	23
1d	21.36	–1.61	–	–3.54	–	0.95	0.23	<0.0001	26
2a	22.92	–2.27	1.08	–	–3.74	0.92	0.23	<0.0001	27
2b	24.12	–2.23	–	–	–4.57	0.85	0.33	<0.0001	30
2c	22.37	–2.30	0.99	–	–4.69	0.92	0.25	<0.0001	30
2d	22.43	–2.03	–	–	–4.40	0.90	0.23	<0.0001	30

For **2a**–**d** the extent of the solvatochromic shift is almost the same, with $\Delta\tilde{\nu} \approx 2000$ cm^{-1}. Although the conjugated π system is quite long in these dyes, this solvatochromic range is rather small, clearly due to the lack of a strong electron donor. The solvent-independent correlation coefficients are not systematically different for the thio- and oxobarbiturates, but again the UV/Vis absorption energy is lower for the thiobarbiturates.

Specific Interactions

Specific solvent–solute interactions through hydrogen-bonding are expressed by the solvent acidity, *α* or SA, and the solvent basicity, *β* or SB. The respective correlation coefficients obtained for both solvent parameter sets (Tables 3 and 4) are in good agreement with each other, so both models are equally suitable for describing these kinds of interactions.

The influence of hydrogen-bonding on the UV/Vis absorption shift is essentially the same for both types of dyes, **1** as well as **2**. This shows that the barbiturate moiety plays the major role in this regard (Figure 4) and that the structure of the chromophoric π system is of less importance.

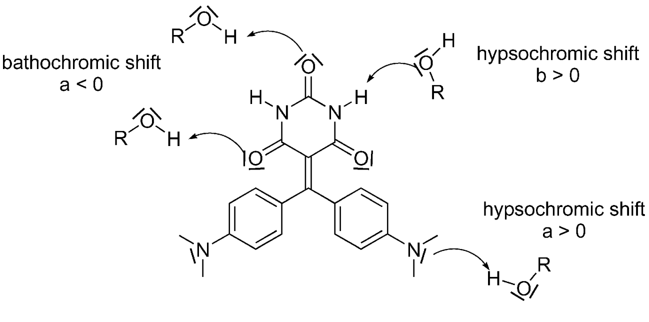


Figure 4. Possible hydrogen-bonding interactions between solute and solvent and their effect on the UV/Vis absorption, exemplified with dye **1a**.

As expected, the UV/Vis absorption maxima undergo a bathochromic shift with increasing solvent HBD capacity, as shown by the negative *a* terms. This can be explained by the interaction of HBD solvents with the barbiturate carbonyl moieties, which reduces their electron density and thus increases the push–pull character of the chromophore. On the other hand, interaction of the dimethylamino groups of **1** with HBD solvents, which would lead to a hypsochromic shift and positive *a* values, clearly is of minor importance. In contrast, the HBA properties of the solvents, represented by the *b* coefficient, play only a minor role. Because of the increase in electron-release due to hydrogen-bonding of the NH groups, the UV/Vis absorption maxima shift to slightly higher energies. For the *N*-alkylated derivatives the basicity term is negligible due to the lack of a suitable HBD moiety.

To examine whether these hydrogen-bonding interactions are interfered with by steric effects, some bulky alcohols, namely *tert*-butyl alcohol and cyclohexanol, were tested. Comparison of their measured UV/Vis absorption maxima with those calculated with the correlation coefficients of Tables 3 or 4 yields a fairly good agreement (see the Supporting Information), so steric effects are negligible in this respect.

Non-Specific Interactions

Large differences occur when regarding non-specific interactions. These are expressed by Catalán's SP parameter (solvent polarizability) as well as by the π^* or SPP parameter (both of which represent a combination of the solvent dipolarity and polarizability).

As expected, the dipolar compounds **1a**–**d** show positive solvatochromism with regard to π^* or SPP (as indicated by the large negative *s* terms). This indicates a higher dipole moment of the electronically excited state compared with the ground state. Therefore the neutral resonance structure (**I** in Figure 5) clearly dominates over the zwitterionic ones (e.g., **II**) in the ground state, whereas in the excited state the reverse case is found. This behaviour is in fact typical for intramolecular charge-transfer (ICT) processes. Furthermore, with the Catalán model a markedly stronger dependence on the dipolarity/polarizability for the *N*,*N*-dialkylated dyes **1b** and **1d** relative to the NH derivatives **1a** and **1c** is indicated. The *s* values of the Kamlet–Taft model on the other hand do not depend significantly on the substitution pattern of the barbiturate moiety. The Catalán values are thus in better accord with the stronger electron-releasing effect of the alkyl groups, which leads to a less dipolar chromophore compared to the NH-substituted compounds **1a** and **1c**. The inclusion of Catalán's polarizability (SP) parameter does not lead to any improvement in the correlation quality. It can therefore be concluded that the solvent polarizability exerts only a small influence on the UV/Vis shifts of **1a**–**d**.

The retinal-type dyes **2a**–**d** show a somewhat different behaviour. Kamlet–Taft's π^* parameter suggests a moderate influence of the solvent's dipolarity/polarizability, yet this model yields only a mediocre correlation quality. When using Catalán's SPP parameter, the results are even worse

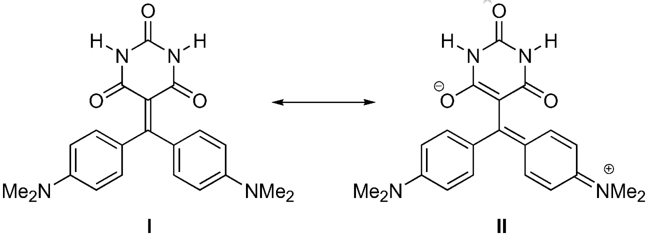


Figure 5. Possible resonance structures contributing to the ground- and excited-state structures of **1a**.

(see the Supporting Information). However, inclusion of the SP parameter instead of SPP leads to a substantial improvement in the correlation quality. Then a very strong bathochromic shift with increasing solvent polarizability (large negative *t* coefficients) can be stated, albeit this effect shows no marked trend with the substitution pattern. This is indicative of a π–π^* excitation in which the excited state is more polarizable than the ground state. To account for the dipolarity effects, some additional parameters were included in the analyses using the results in Table 4 as the starting point. Although none of these parameters led to any improvement for the barbiturates **2a** and **2b**, some improvement was achieved for **2c** and **2d**. The Kirkwood function,[1c,35] $K_m = (\varepsilon_r - 1)/(2\varepsilon_r + 1)$, was found to give the best results, leading to Equation (4) for **2d** (see the Supporting Information for all results). Thus, at least the excitation of the more polar thiobarbiturates seems to exhibit some charge-transfer character as well.

$$\tilde{\nu}_{max}\cdot[10^{-3}\ \mathrm{cm}^{-1}]\ (\mathbf{2d}) = 22.54 - 1.54\mathrm{SA} - 3.88\mathrm{SP} - 1.49K_m \qquad (4)$$
$$r = 0.94,\ sd = 0.19,\ f < 0.0001,\ n = 29$$

Interestingly, similar results are obtained when K_m is replaced by SPP, which leads to Equation (2). It should, however, also be noted that the error in this additional parameter, no matter which one is used, is rather high in comparison with SA, SB and SP. Thus, the conclusions drawn from these last correlation analyses should only be regarded as an approximation.

Inverted Solvatochromism?

An occasionally described effect when dealing with polyene dyes is inverted solvatochromism,[18–20,36] that is, the change from positive to negative solvatochromism with increasing solvent polarity. This phenomenon is ascribed to a solvent-induced change in the ground-state structure from a less dipolar polyene-like structure (non-polar solvents) to a strongly dipolar betaine-like structure (polar solvents), the maximum wavelength being at the cyanine limit.

Although at first sight the measured UV/Vis absorption wavelengths of **2a**–**d** also follow the same trend in polar solvents (e.g., alcohols, acetonitrile), our investigations indicate a pronounced positive solvatochromism of these compounds even in polar solvents. This contrasting behaviour may only partially be attributed to the lack of a strong electron-donating moiety. Regarding the good correlation with

Catalán's SP parameter, it seems more reasonable to consider the solvent polarizability as a major influence on the solvatochromic behaviour instead of the frequently used dipolarity-based solvent parameters. In particular, when rather weak donor–acceptor systems are investigated, these considerations should be taken into account.

Conclusions

By using different solvatochromic dyes it can be shown that the Kamlet–Taft equation works as well as the Catalán equation when the highly dipolar barbiturate dyes **1a**–**d** are considered. A possible contribution of the solvent polarizability already is comprised in the π* parameter so that further differentiation does not improve the correlation quality. With regard to weakly dipolar but highly polarizable chromophores like **2a**–**d**, reasonable results are only obtained by including Catalán's SP parameter due to the unequal contribution of the solvent dipolarity and polarizability.

Specific interactions through hydrogen-bonding, expressed by solvent acidity and basicity, are essentially the same for both kinds of dyes and are described equally well by both solvent polarity scales. Thus, they can be attributed mainly to the barbiturate moiety and are hardly influenced by the nature of the chromophoric system. On the other hand, non-specific interactions depend mainly on the dipolarity and polarizability of the chromophoric system and are only slightly affected by the substitution pattern of the barbiturate moiety.

Experimental Section

General: Solvents were dried and distilled according to standard procedures prior to use. Bis[*p*-(dimethylamino)phenyl]methylium tetrafluoroborate was prepared according to known procedures.[30] All other compounds were commercially available and used as received. NMR spectra were recorded with a Varian Inova-400 or a Bruker Avance 250 spectrometer using the solvent residue signal as the internal standard. The signal designations are given as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br. = broad. Owing to the generally low solubility of **2a**–**d**, no evaluable ^{13}C NMR spectra of these compounds could be obtained. IR spectra were recorded in diffuse reflection with a BioRad FT-IR-Spektrometer FTS 165. Elemental analyses were obtained by using a Vario EL from Elementaranalysensysteme GmbH (Hanau). Mass spectra were obtained with a Hewlett–Packard HP 5988a mass spectrometer. The UV/Vis spectra of freshly prepared solutions ($c \approx 1\times10^{-5}$ to 1×10^{-4} mol L^{-1}) were measured with an MCS 400 diode-array spectrometer from Carl Zeiss Jena with a resolution of 1 nm. Multiple-regression analyses were performed with the statistical program Origin 5.0.[37]

Typical Procedures

5-{Bis[*p*-(dimethylamino)phenyl]methyl}barbituric Acid (3a): A suspension of barbituric acid (0.39 g, 3.1 mmol) in water (100 mL) was treated with KOH (0.16 g, 2.9 mmol) dissolved in water (25 mL). After stirring for 30 min, bis[*p*-(dimethylamino)phenyl]methylium tetrafluoroborate (1.00 g, 2.9 mmol) was added, and the mixture was stirred at room temperature for 96 h. The solid was vacuum-filtered, washed with water and acetone and dried in vacuo. Owing to its limited stability, the product was used immediately in the following reaction without further purification. Light-blue solid (0.33 g, 30%). M.p. 158–160 °C (decomp.). ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 2.87 (s, 12 H), 4.21 (d, J = 3.9 Hz, 1 H), 4.72 (d, J = 3.9 Hz, 1 H), 6.71 (d, J = 8.4 Hz, 4 H), 7.08 (d, J = 8.4 Hz, 4 H), 11.08 (br. s, 2 H) ppm. ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 40.0, 52.4, 53.3, 112.6, 129.2, 137.3, 150.5, 163.8, 169.8 ppm. IR (KBr): $\tilde{\nu}$ = 3354, 3045, 1694, 1586, 1366, 822 cm^{-1}. ESI-MS: *m*/*z* (%) = 253.19 (100) [CH(C$_6$H$_4$NMe$_2$)$_2$]$^+$, 381.23 (23) [M + H]$^+$.

5-{Bis[*p*-(dimethylamino)phenyl]methylene}barbituric Acid (1a): A suspension of **3a** (0.20 g, 0.5 mmol) in water (50 mL) was treated with *p*-chloranil (0.12 g, 0.5 mmol) and stirred at room temperature for 144 h. The solid was vacuum-filtered, washed with water and suspended in dichloromethane. The mixture was filtered and the filtrate was concentrated and dried in vacuo. Remaining impurities were finally removed by sublimation in vacuo at 200 °C. Dark-green solid (0.11 g, 57%). M.p. 211 °C. ^{1}H NMR (250 MHz, [D$_6$]-DMSO): δ = 3.07 (s, 12 H), 6.68 (d, J = 9.0 Hz, 4 H), 7.09 (d, J = 9.0 Hz, 4 H), 10.31 (br. s, 2 H) ppm. ^{13}C NMR (63 MHz, [D$_6$]-DMSO): δ = 39.6, 105.4, 110.4, 128.3, 136.2, 150.6, 153.6, 163.4, 175.7 ppm. IR (KBr): $\tilde{\nu}$ = 3184, 3083, 1698, 1652, 1586, 1362, 826 cm^{-1}. ESI-MS: *m*/*z* (%) = 379.11 (100) [M + H]$^+$.

(2*Z*,4*Z*,6*Z*,8*Z*)-5-[3,7-Dimethyl-9-(2,6,6-trimethylcyclohex-1-enyl)-nona-2,4,6,8-tetraenylidene]barbituric Acid (2a): This compound has to be prepared and stored under strict exclusion of light. Barbituric acid (0.262 g, 2.05 mmol) was dissolved in ethanol (20 mL) at 45 °C. After addition of a solution of all-(*E*)-retinal (0.567 g, 2.00 mmol) in ethanol (20 mL), stirring was continued at 45 °C for 1 h. The mixture was cooled to room temperature and concentrated in air overnight. The resulting solid was filtered, washed with hot water and dried in vacuo. Violet solid (0.742 g, 94%). M.p. >210 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.05 (s, 6 H), 1.50 (m, no integration possible due to signal overlap), 1.63 (m, 2 H), 1.75 (d, J = 0.6 Hz, 3 H), 2.05 (m, 5 H), 2.31 (d, J = 0.6 Hz, 3 H), 6.26 (m, 2 H), 6.45 (d, J = 15.8 Hz, 1 H), 6.65 (d, J = 14.8 Hz, 1 H), 7.30 (dd, J = 14.8, J = 11.8 Hz, no integration possible due to signal overlap), 7.96 (d, J = 13.3 Hz, 1 H), 8.02 (br. s, 1 H), 8.18 (br. s, 1 H), 8.53 (d, J = 13.3 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3213, 3078, 2926, 2862, 2733, 1736, 1676, 1657, 1574, 1516, 1418, 1373, 1339, 1304, 1234, 1184, 961, 812, 790 cm^{-1}. C$_{24}$H$_{30}$N$_2$O$_3$ (394.51): calcd. C 73.07, H 7.66, N 7.10; found C 73.46, H 7.67, N 6.88.

Supporting Information (see also the footnote on the first page of this article): Characterization data for all new compounds, UV/Vis absorption maxima of **1a**–**d** and **2a**–**d** in various solvents, multiple-regression data of the solvatochromic studies.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged. We also thank the BASF AG, Ludwigshafen, for kindly providing all-(*E*)-retinal and Prof. M. Antonietti (Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Golm) for hosting A. B. during her diploma thesis.

---

[1] a) C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358; b) P. Suppan, N. Ghoneim, *Solvatochromism*, The Royal Society of Chemistry, London, **1997**; c) C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed., Wiley-VCH, Weinheim, **2003**.

[2] P. Müller, *Pure Appl. Chem.* **1994**, *66*, 1151.

[3] C. Chiappe, D. Pieraccini, *J. Phys. Org. Chem.* **2005**, *18*, 275–297.

[4] A. Oehlke, K. Hofmann, S. Spange, *New J. Chem.* **2006**, *30*, 533–536.

[5] a) S. Spange, A. Reuter, E. Vilsmeier, *Colloid Polym. Sci.* **1996**, *274*, 59–69; b) S. Spange, A. Reuter, *Langmuir* **1999**, *15*, 141–150; c) S. Spange, A. Reuter, D. Lubda, *Langmuir* **1999**, *15*, 2103–2111; d) S. Spange, Y. Zimmermann, A. Gräser, *Chem. Mater.* **1999**, *11*, 3245–3251; e) S. Spange, E. Vilsmeier, Y. Zimmermann, *J. Phys. Chem. B* **2000**, *104*, 6417–6428.

[6] a) R. S. Helburn, S. C. Rutan, J. Pompano, D. Mitchern, W. T. Patterson, *Anal. Chem.* **1994**, *66*, 610–618; b) S. C. Rutan, J. M. Harris, *J. Chromatogr. A* **1993**, *656*, 197–215.

[7] R. W. Sinkeldam, Y. Tor, *Org. Biomol. Chem.* **2007**, *5*, 2523–2528.

[8] F. Jara, C. Mascayano, M. C. Rezende, C. Tirapegui, A. Urzua, *J. Inclusion Phenom. Macrocycl. Chem.* **2006**, *54*, 95–99.

[9] S. Spange, C. Schmidt, H. R. Kricheldorf, *Langmuir* **2001**, *17*, 856–865.

[10] L. P. Novaki, O. A. El Seoud, *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 648–655.

[11] a) R. W. Taft, M. J. Kamlet, *J. Chem. Soc. Perkin Trans. 2* **1979**, 1723–1727; b) M. J. Kamlet, T. H. Hall, J. Bodkin, R. W. Taft, *J. Org. Chem.* **1979**, *44*, 2599–2604; c) M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877–2887.

[12] δ has only three values: 1.0 for aromatic, 0.5 for polyhalogenated and 0.0 for aliphatic solvents.

[13] a) J. Catalán, V. López, P. Pérez, R. Martín-Villamil, J.-G. Rodriguez, *Liebigs Ann.* **1995**, 241–252; b) J. Catalán, V. López, P. Pérez, *Liebigs Ann.* **1995**, 793–795; c) J. Catalán, C. Díaz, V. López, P. Pérez, J.-L. G. DePaz, J.-G. Rodriguez, *Liebigs Ann.* **1996**, 1785–1794; d) J. Catalán, C. Díaz, *Liebigs Ann./Recueil* **1997**, 1941–1949; e) J. Catalán, C. Díaz, *Eur. J. Org. Chem.* **1999**, 885–891.

[14] J. Catalán, H. Hopf, *Eur. J. Org. Chem.* **2004**, 4694–4702.

[15] G. Sun, Y.-Q. Qiu, H. Z. Sun, Z.-M. Su, J.-D. Feng, Y. L. Zhu, *Chin. J. Chem.* **2004**, *22*, 425–429.

[16] X. Zhou, A.-M. Ren, J. K. Feng, X. J. Liu, C. C. Shu, *Chin. J. Chem.* **2004**, *22*, 38–46.

[17] a) R. Andreu, M. A. Cerdan, J. Orduna, *ARKIVOC* **2004**, 32–41; b) R. Andreu, M. J. Blesa, L. Carrasquer, J. Garín, J. Orduna, B. Villacampa, R. Alcalá, J. Casado, M. C. Ruiz Delgado, J. T. López Navarrete, M. Allain, *J. Am. Chem. Soc.* **2005**, *127*, 8835–8845.

[18] G. Bourhill, J.-L. Brédas, L.-T. Cheng, S. R. Marder, F. Meyers, J. W. Perry, B. G. Tiemann, *J. Am. Chem. Soc.* **1994**, *116*, 2619–2620.

[19] M. Blanchard-Desce, V. Alain, P. V. Bedworth, S. R. Marder, A. Fort, C. Runser, M. Barzoukas, S. Lebus, R. Wortmann, *Chem. Eur. J.* **1997**, *3*, 1091–1104.

[20] A. V. Kulinich, N. A. Derevyanko, A. A. Ishchenko, *Russ. J. Gen. Chem. (Engl. Trans.)* **2006**, *76*, 1441–1457.

[21] a) M. C. Rezende, P. Campodonico, E. Abuin, J. Kossanyi, *Spectrochim. Acta Part A* **2001**, *57*, 1183–1190; b) M. C. Rezende, P. Flores, J. Guerrero, L. Villarroel, *Spectrochim. Acta Part A* **2004**, *60*, 1637–1640.

[22] S. Nakatsuji, T. Yahiro, K. Nakashima, S. Akiyama, H. Nakazumi, *Chem. Express* **1989**, *4*, 601–604.

[23] G. U. Bublitz, R. Ortiz, S. R. Marder, S. G. Boxer, *J. Am. Chem. Soc.* **1997**, *119*, 3365–3376.

[24] a) S. Horie, M. Nagata, J. Nakano, H. Sato, DE-3150266, **1982**, *Chem. Abstr.* **1983**, *99*, 131329; b) K. Inai, N. Go, H. Miyazaki, T. Miyaji, JP-03012660, **1991**, *Chem. Abstr.* **1991**, *115*, 146585.

[25] See selected publications: a) P. E. Blatz, J. H. Mohler, H. V. Navangul, *Biochemistry* **1972**, *11*, 848–855; b) T. Baasov, M. Sheves, *J. Am. Chem. Soc.* **1985**, *107*, 7524–7533; c) Y. Kawabe, H. Ikeda, T. Sakai, K. Kawasaki, *J. Mater. Chem.* **1992**, *2*, 1025–1031.

[26] See selected publications: a) N. Acton, A. Brossi, D. L. Newton, M. B. Sporn, *J. Med. Chem.* **1980**, *23*, 805–809; b) C. C. Willhite, M. I. Dawson, K. J. Williams, *Toxicol. Appl. Pharmacol.* **1984**, *74*, 397–410; c) E. P. Jaeger, P. C. Jurs, T. R. Stouch, *Eur. J. Med. Chem.* **1993**, *28*, 275–290.

[27] a) A. M. Asiri, *Molecules* **2000**, *5*, M170; b) A. M. Asiri, *Molecules* **2000**, *57*, 1183–1190; c) A. M. Asiri, *Appl. Orgonomet. Chem.* **2001**, *15*, 905–915.

[28] M. A. Whiteley, *J. Chem. Soc. Trans.* **1907**, *91*, 1330–1350.

[29] S. Naya, K. Yoda, M. Nitta, *Tetrahedron* **2005**, *61*, 8616–8624.

[30] a) T. Bug, H. Mayr, *J. Am. Chem. Soc.* **2003**, *125*, 12980–12986; b) H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512.

[31] k is the second-order rate constant for an electrophile–nucleophile recombination in $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, E is the electrophilicity parameter, N is the nucleophilicity parameter, and s is a nucleophile-specific slope parameter ($s \approx 1$ can be assumed for such qualitative considerations).

[32] K.-D. Nolte, S. Dähne, *J. Prakt. Chem.* **1976**, *318*, 643–657.

[33] See, for example: a) Z. He, D. Gosztola, Y. Deng, G. Gao, M. R. Wasielewski, L. D. Kispert, *J. Phys. Chem. B* **2000**, *104*, 6668–6673; b) D. Laage, P. Plaza, M. Blanchard-Desce, M. M. Martin, *Photochem. Photobiol. Sci.* **2002**, *1*, 526–535.

[34] Y. Marcus, *Chem. Soc. Rev.* **1993**, *22*, 409–416.

[35] J. G. Kirkwood, *J. Chem. Phys.* **1934**, *2*, 351–361.

[36] a) B. W. Domagalska, K. A. Wilk, S. Wysocki, *Phys. Chem. Chem. Phys.* **2003**, *5*, 696–702; b) B. W. Domagalska, K. A. Wilk, R. Zielinski, *J. Photochem. Photobiol. A: Chem.* **2006**, *184*, 193–203.

[37] *Origin 5.0*, MicroCal Software Inc., Northampton, MA, USA, **1997**.

Received: April 7, 2008