Dyes and Pigments 95 (2012) 180–187

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Do stilbazolium betaine dyes exhibit inverted solvatochromism by changes in solvent dipolarity?

Javier Catalán

Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, 28049 Madrid, Spain

ARTICLE INFO

Article history:
Received 14 February 2012
Received in revised form
12 March 2012
Accepted 18 March 2012
Available online 18 April 2012

Keywords:
Inverted solvatochromism
Dipolarity
Stilbazolium betaine dyes

ABSTRACT

The thermochromic behavior of solutions of stilbazolium dyes in dipolar 1-chlorobutane toward a solvent dipolarity change was used for the first time to demonstrate that stilbazolium betaine dyes exhibit inverted solvatochromism, with a bathochromic band shift in the low-dipolarity solvent region and a hypsochromic band shift in the high-dipolarity solvent region. Interestingly, the hypsochromic band shifts of the stilbazolium betaine dyes studied here are twice more sensitive to the dipolarity of the medium than its bathochromic band shifts.

The solvatochromic behavior observed affords the following conclusions: (*a*) the solvated molecular forms of the chromophore involved in the hypsochromic band shifts are identical for absorption and emission in stilbazolium betaine dyes; (*b*) the absorbing form involved in the hypsochromic band shifts absorb at a longer wavelength ($\lambda_{max} = 696$ nm) than that involved in the bathochromic band shifts ($\lambda_{max} = 609$ nm) in the gas-phase spectrum, a fact which should be considered in developing structural models to account for this phenomenon.

1. Introduction

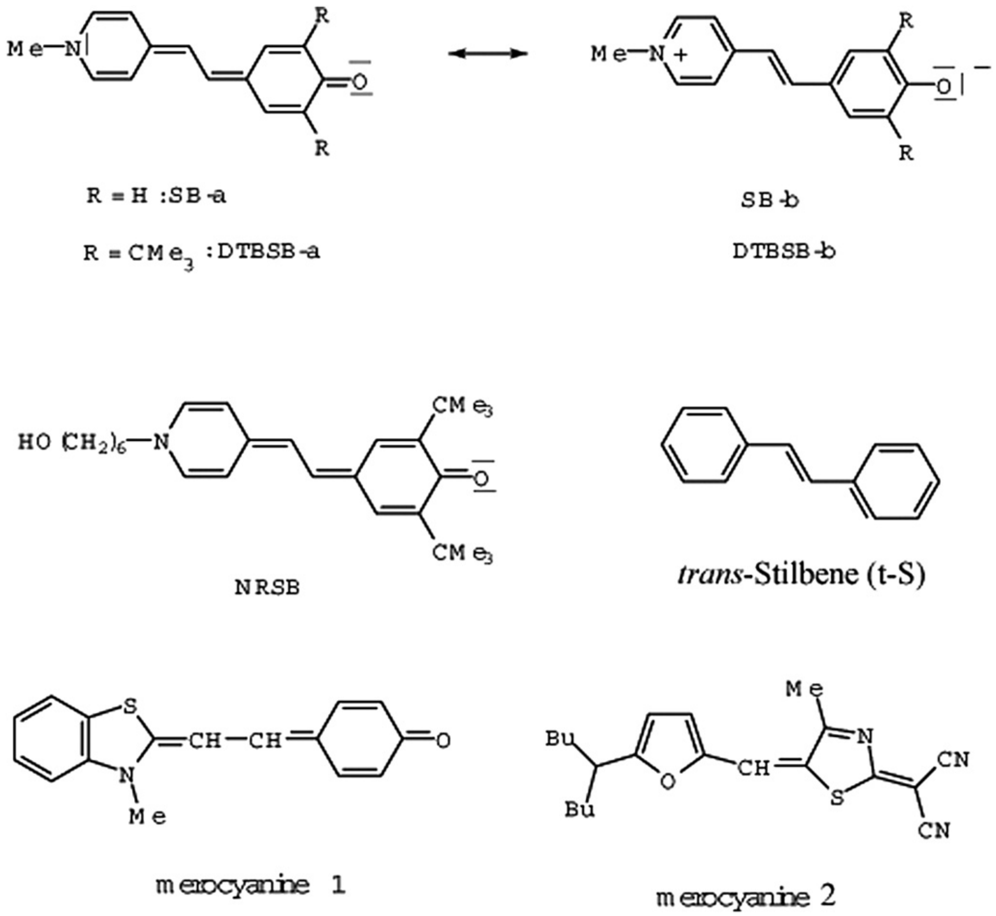
Stilbazolium betaine dyes are a group of functional dyes which are, because of their solvatochromism [1], high dipole moments [2], and high hyperpolarizability [3], especially suitable as organic materials for nonlinear optical [4] and photorefractive applications [5], also based on the noncentrosymmetric ordering of the dye molecules. In addition, these substances have also been used as chemical models for the storage of information and subsequent regeneration of information carriers in biological systems. Thus, Shulten and Tavan [6] used the stilbazolium betaine 4-[(1-methyl-4(1H)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one (SB-a,b in Scheme 1), to establish the role of the Schiff base of retinal in the light-driven proton pump, discovered by Oesterhelt and Stoeckenius [7] in the purple membrane of *Halobacterium halobium*. These substances are also believed to respond to a change in dipolarity of the medium with a bathochromic shift of their first electronic absorption band in the low-dipolarity solvent region and with a hypsochromic shift in the high-dipolarity solvent region [1]. Thus, the UV/Vis spectroscopic behavior of stilbazolium betaine dyes therefore depends on the properties of the surrounding, in a manner which requires further clarification.

In 1951, Brooker et al. [8] studied the extinction coefficient and wavelength of the first absorption band of such extremely dipolar merocyanine dyes as the stilbazolium betaine dye SB-a,b (Scheme 1) and found that this band produces a color shift from deep blue in anhydrous pyridine ($\lambda_{max} = 605$ nm, $\varepsilon_{max} = 15.3 \times 10^4$) to amber in pure water ($\lambda_{max} = 444$ nm, $\varepsilon_{max} = 5.4 \times 10^4$); they also found the largest band shift in going from pyridine to pure water ($\Delta\bar{\nu} = 6000$ cm^{-1} and $\Delta\varepsilon = 5.4 \times 10^4$) occurring when water was added in small portions (less than 4% by volume) to anhydrous pyridine. They ascribed this behavior of SB by adopting a more dipolar (zwitterionic) benzenoid structure (SB-b in Scheme 1) in high-polar media water and a less dipolar quinonoid structure (SB-a in Scheme 1) in low-polar media, e.g., pyridine. Kiprianov and Petrun'kin [9] had previously proposed a similar mechanism to account for the solvent-dependent UV/Vis spectral behavior of merocyanine 1 (see Scheme 1).

The extreme solvatochromism of SB observed between pyridine and water as solvent, $\Delta\bar{\nu} = 6000$ cm^{-1} [8], was studied in 1972 by Benson and Murrell [10] with a view to confirming whether the solvatochromic behavior of this merocyanine dye paralleled that observed for other merocyanines by Bayliss and McRae [11] in 1952, which was largely due to specific dye/solvent interactions. In these cases, the bulk dielectric effect of the solvent had only a small influence on the UV/Vis spectrum of the merocyanine dye.

E-mail address: javier.catalan@uam.es.

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2012.03.018



Scheme 1. Molecular structure of the merocyanine dyes considered in this work.

In 1984, Botrel et al. [12] optimized the molecular structure of SB in its electronic ground state by using the semi-empirical method CNDO/SCI with provision for solvation via the function $f(\varepsilon_r) = 1 - (1/\varepsilon_r^{1/2})$. They used the geometries thus obtained at variable $f(\varepsilon_r)$ values (0, 0.167, 0.333, 0.5, 0.667, 0.833, and 0.9) to estimate the energy of the first electronic excited state $(\pi \rightarrow \pi^*)^1$ and found that the transition energy increases slightly with decreasing $f(\varepsilon_r)$ at $f(\varepsilon_r) < 0.4$, but increases markedly with decreasing $f(\varepsilon_r)$ at $f(\varepsilon_r) > 0.4$. Based on these results, Botrel et al. predicted that raising the polarity of the medium, $f(\varepsilon_r)$, from 0 to 0.4 would cause a slight bathochromic band shift in the first electronic transition of SB, whereas further raising of $f(\varepsilon_r)$ would cause a substantial hypsochromic band shift. Twelve years later, Jacques [13], a member of the previous mentioned group, seemingly confirmed for the first time the presence of a so-called "inverted solvatochromism" in SB (see Fig. 3 in Ref. [13]). However, we believe that Jacques' conclusion cannot be entirely held since the Vis absorption maxima for SB were only measured in two of the eight solvents used to construct his figure; in fact, SB was insoluble in the other six solvents and the results were estimated from binary mixtures of solvents with strong differences in the spectral envelope, which make the results even more questionable.

Luzhkov and Warshel [14] used the QCFF/SOL method, which considers both permanent and induced dipole moments of the solvents, to examine the solvatochromism of SB and concluded that the zwitterionic form SB-b is the dominant species in both polar and nonpolar solvents. Subsequently, Niedbalska and Gruda [15] synthesized a series of SB derivatives which are more soluble than the parent compound, and ascribed the UV/Vis spectral behavior previously described by Jacques [13] to dye aggregation resulting from the poor solubility of this compound in low-polar solvents.

In 1992, our group [16] studied an SB derivative which is considerably better soluble than the parent substance [*viz.* the 2,6-di-*tert*-butylstilbazolium betaine (DTBSB-a,b, Scheme 1)] and we draw several valuable conclusions from its first solvent-dependent UV/Vis absorption band, namely: (*a*) the band for SB was structured only in a few of the solvents studied – normally the less polar ones–, whereas that for DTBSB was structureless only in water and formamide among the 28 solvents studied; (*b*) the structure of the first absorption band cannot be ascribed to dye aggregate formation since (i) DTBSB at concentrations over the range of $c = 10^{-7}$–10^{-4} M in ethyl acetate exhibits perfectly superimposable spectra (*i.e.* the spectral envelope for the band was retained), (ii) Gruda and Bolduc [17] found for the SB derivative NRSB (see Scheme 1) that it exhibits a structured first band in 1,4-dioxane, obeying the Lambert–Beer law at concentrations from $c = 0.25 \times 10^{-6}$ to 0.4×10^{-3} M for all peaks, and (iii) Tsukada et al. [18] found that the first peak and its shoulder at 518 nm for SB in trifluoromethane also obey the Lambert–Beer law; and (*c*) neither the transition energy of the first peak in the Vis absorption spectrum nor that of the emission maximum, or their combination via a modified version of the Lippert equation [19], allowed us to confirm whether DTBSB exhibits an inverted solvatochromism or not.

In 1994, theoretical calculations by Morley [20] showed that the zwitterionic form SB-b should absorb at a longer wavelength (587 nm) than the quinonoid form (470 nm), which contradicted previous theoretical data. In 1997, Morley et al. [21] revisited the solvatochromic mechanism proposed by Brooker et al. [8] on theoretical grounds, and so did Kiprianov and Petrun'kin [9] based on theoretical and experimental data. The latter authors concluded that “although this large solvatochromic shift was originally attributed to a distinct change in structure from the covalent quinone (SB-a) to the zwitterion (SB-b), our recent studies with more soluble merocyanine dyes have suggested that the molecule exists as a resonance hybrid which is weighted toward the zwitterion even in solvents of low dielectric constants”. Subsequent studies on the aromatic structure and solvatochromism of SB and its derivatives [22–27] have provided no solid experimental evidence confirming that SB exhibits inverted solvatochromism with increasing solvent dipolarity.

Worth mentioning are recent studies of Würthner et al. [2b], who reported evidence that the dipole moment of the electronic ground state of merocyanine 2 (Scheme 1) changes with the nature of the solvent – which supports the mechanism of Brooker – and the endeavor of Domínguez and Rezende [25] toward unifying the available knowledge about the solvatochromic behavior of merocyanines by studying 56 different dyes. The latter authors concluded that “The usual interpretation, based on structural changes of the ground states of these dyes caused by medium variations, is of little predictive value and cannot account for the fact that other compounds, which are also affected by the solvent, do not exhibit such a behavior, if the solvatochromic reversal of some of these betaine dyes is a true phenomenon and not an artifact. The resulting unified view reduces all types of solvatochromism to particular cases of a general inverted behavior. The only difference among a negative, an inverted, and a positive solvatochromism would then be the value of the medium polarity required by the betaine for its reversal to take place. Compounds exhibiting negative or positive solvatochromism would require «virtual» media of extremely high or low polarity, which cannot be experimentally accessed, for a reversal to take place”.

This paper provides evidence for the existence of an inverted solvatochromism in case of stilbazolium betaine dyes by examining the SB derivative DTBSB, with two *tert*-butyl groups at positions 2 and 6 which shield the sensitive carbonyl group from hydrogen-bond donating (HBD) solvents and increase its solubility. This SB derivative was studied in 1-chlorobutane (ClB) as solvent, which possesses a negligible acidity and basicity, and exhibits considerable dipolarity changes as the solution temperature is lowered. It has a solvent dipolarity SdP value of 0.399 at 343 K and of 1.29 at 77 K – the SdP scale ranges from 0 for the gas phase to 1 for dimethyl sulfoxide [28,29]. Therefore, DTBSB dissolved in ClB is subject only to dipolar interactions the strength of which can be varied from $\mathrm{SdP} = 0.399$ to 1.29 simply by changing the solution temperature. This avoids errors arising from the use of a range of different solvents differing in dipole moment but not in acidity or basicity. One should bear in mind that, as noted by Bayliss and McRae [11] as well as by Benson and Murrell [10], the solvatochromism of merocyanines is largely the result of specific dye/solvent interactions or, in other words, that the bulk dielectric effect of the solvent has comparatively small influence on the UV/Vis spectrum of a merocyanine dye.

2. Experimental section

The 1-chlorobutane used was Chromasolv grade (99.8% purity, moisture content equal to or less than 0.001%). All other solvents (diethyl ether, ethyl acetate, DMSO, and MeOH) were of the highest available purity (Merck-Uvasol grade). DTBSB was prepared as described elsewhere [16]. Sample temperatures from 77 to 293 K were controlled by means of an Oxford DN1704 cryostat equipped with an ITC4 controller interfaced to the spectrophotometers. The cryostat was purged with dried nitrogen (99.99% pure). Sample temperatures from 343 to 293 K were controlled within ±0.1 °C with a Fisons Haake D8 GH thermostat. All UV/Vis absorption spectra were recorded at variable temperatures from 293 to 77 K, using Suprasil cells of 1 cm light path that were fixed to the cryostat and a cell holder thermostated at 343–293 K. UV–Vis spectra were recorded on a Cary-5 spectrophotometer.

Corrected fluorescence and fluorescence excitation spectra were obtained on a calibrated Aminco–Bowman AB2 spectrofluorimeter. The sensitivity factors for the emission channel, which include not only those depending on the detector, but also those related to the emission monochromator and optical arrangement – channel emission included – were obtained by using the FP-123 correction kit from SLM Instruments, Inc. This required mounting a standard lamp in a channel at a right angle from the emission channel on an OL 254 M spectra irradiance lamp from Optronic Laboratories, Inc. The lamp was operated at a constant voltage supplied by an SP-270 power source and its light output was driven into an integrating sphere with a pinhole leading to the fluorimeter emission channel. The conversion factors thus obtained allowed technical spectra to be converted into absolute spectra, which are instrument-independent.

Corrected excitation spectra were directly obtained on the AB2 spectrofluorimeter. A small fraction of the light intensity used for excitation was switched to a Hamamatsu S1336-8BQ photodiode by means of a beam splitter. Plotting the photodiode sensitivity as a function of wavelength allowed us to characterize changes in incident light intensity at each excitation wavelength. The ratio of emission intensity at the monitored wavelength to the corresponding excitation intensity at each excitation wavelength was used to construct absolute excitation spectra.

3. Results and discussion

We shall start our discussion by assigning the first UV/Vis absorption band of DTBSB to the monomeric structure of the compound and then examine the solvatochromic behavior of this band over the temperature range 343–77 K in ClB. Based on the thermochromic behavior of these absorption spectra and the corresponding emission spectra, we shall establish a possible mechanism for the solvatochromism of these merocyanine dyes. The photophysical behavior of a reference structure such as *trans*-stilbene (see Scheme 1) will be used wherever advisable to facilitate the discussion.

3.1. About the first electronic transition and molecular structure of DTBSB

Because DTBSB has a nearly planar molecular structure – in fact molecules of crystalline SB are planar [30] – , its first absorption band is due to a $\pi \rightarrow \pi^*$ transition; its envelope exhibits two peaks at *ca.* 620 and 575 nm, in addition to a shoulder at *ca.* 540 nm, as a result of the strong resonance arising from the presence of two benzene rings connected by an ethene chain which enables conjugation. Although SB can be considered as a derivative of *trans*-stilbene by replacement of its C–H groups at positions 4 and 4′ with an *N*-Me and a carbonyl group, respectively, the differences between the two molecular structures give rise to significant differences in their spectral behavior. Thus, the first electronic transition for SB is red-shifted by $\Delta\lambda = 300$ nm with respect to the corresponding transition of stilbene. In addition, stilbene is an apolar compound with a dipole moment of only 0.011 D [31], whereas stilbazolium betaines are highly dipolar (e.g., SB has a dipole moment of 26 D in DMF [2a]).

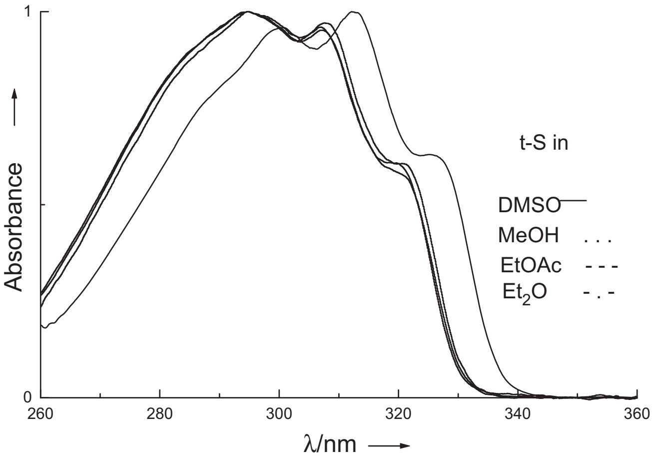


Fig. 1. Normalized UV-absorption band of *trans*-stilbene, measured in dimethyl sulfoxide (DMSO), methanol (MeOH), ethyl acetate (EtOAc), and diethyl ether (Et_2O).

Because of their high dipolarity, stilbazolium betaines can only be dissolved if the strong dipole/dipole interactions in the crystal lattice are overcome by the dipole/solvent interactions in dipolar solvents. Such interactions produce solvatochromic molecular structures with a reduced vibrational structure of the transitions involved. Also, as noted by Bayliss and McRae [32], if this is not enough, examining the influence of the polarity of the medium on the solvatochromism of these dyes is further complicated by the presence of a strong H-bond accepting carbonyl group in the stilbazolium betaine dyes which establishes strong specific hydrogen-bond interactions, ultimately masking the dipolar interactions.

As shown in a previous paper [16], the peak intensity of the first absorption band of DTBSB changes from solvent to solvent. Thus, this band is virtually structureless in MeOH, only the first peak and a shoulder are structured in DMSO, the second peak is significantly stronger than the first in diethyl ether, and both are virtually identical in ethyl acetate. By contrast, the apolar analog *trans*-stilbene exhibits an identical vibrational structure of its first absorption band in the four solvents mentioned (see Fig. 1). This suggests that the absorption band of DTBSB should correspond to transitions from the same molecular structure. For example, Morley et al. [33] used theoretical and experimental evidence for merocyanine structures of reduced planarity by assigning the first peak in the absorption band, at 620 nm, to a twisted conformer, and the second, at 575 nm, to the planar form. Also, they assigned the shoulder at 470 nm to dimers or tetramers, an assignation that can be better understood by reading Ref. [33,34].

Whether the peaks in the first absorption band for stilbazolium betaines are due to the same molecular structure can be confirmed by comparing their excitation and emission spectra with their absorption spectra. Fig. 2a–d shows the normalized Vis spectra of DTBSB dissolved in MeOH, DMSO, ethyl acetate, and diethyl ether, respectively. The absorption, excitation, and emission spectra measured in these four solvents with such disparate solvation power are so similar that they can only be due to an identical molecular form.

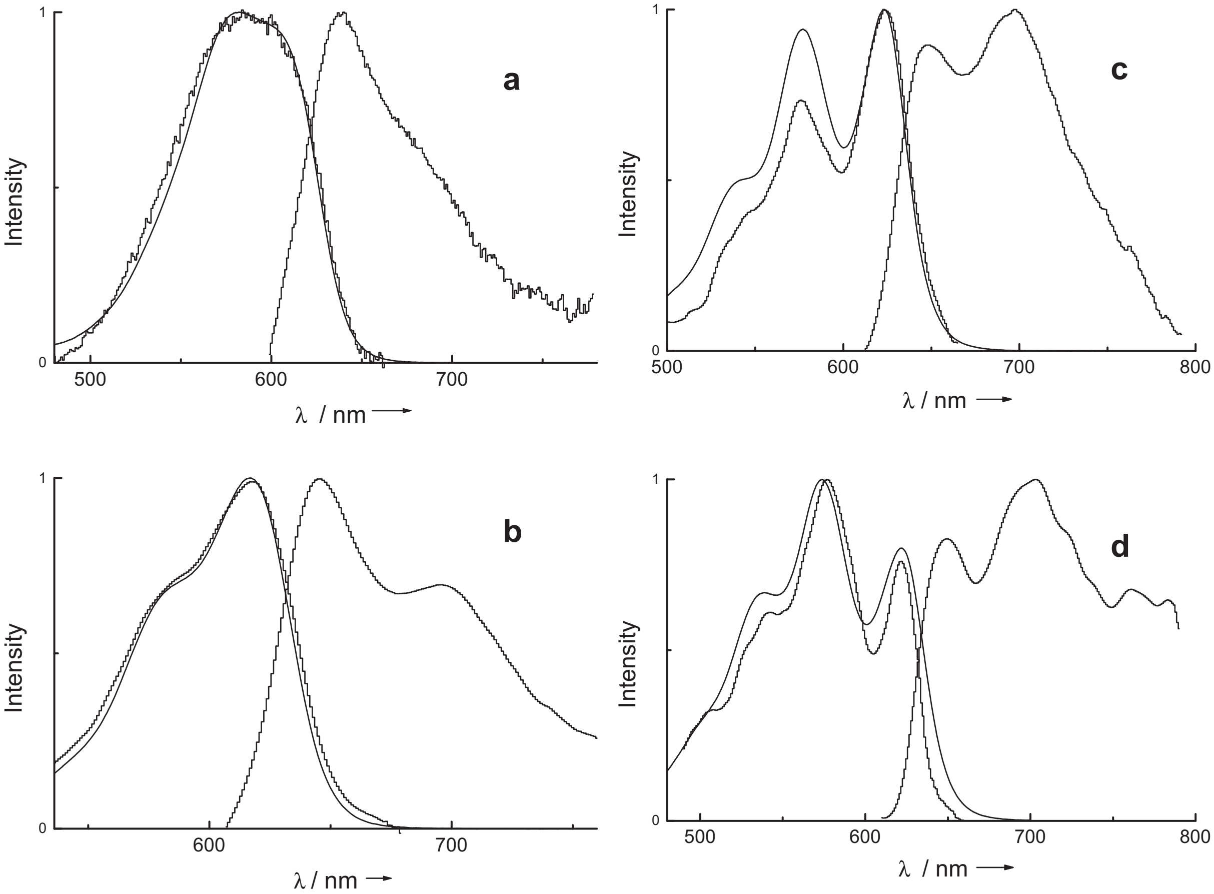


Fig. 2. UV-absorption band (solid), fluorescence excitation spectrum (- - -), and fluorescence band (. . .) normalized at the maximum of DTBSB, dissolved in a) MeOH, b) DMSO, c) EtOAc, and d) Et_2O.

These results should not be taken as proof that the DTBSB molecule has a planar, rigid structure undergoing none of the above-described changes with temperature as observed with *trans*-stilbene [35]. As shown above, one way of confirming the loss of planarity in the molecular conformation of *trans*-stilbene with temperature [31] is by checking whether it obeys the Mulliken–Rieke rule [36], *i.e.* whether the experimental dipole strength for the electronic transition is in fact temperature-independent or, in other words, whether the absorption strength for the transition is preserved after a change in the sample distribution among the vibrational levels of the molecular structure in equilibrium. Fig. 3 shows the area under the first absorption band of a DTBSB solution in ClB, corrected for the volume changes with temperature computed from the ClB density values reported by Smyth and Rogers [37]. As with *trans*-stilbene in 2-methylbutane, the data of Fig. 3 indicate that DTBSB violates the Mulliken–Rieke rule from 343 to 203 K [36]. In fact, the area under its first absorption band increases with decreasing temperature and this can be ascribed to DTBSB, like *trans*-stilbene, tending to a more planar structure as the temperature is lowered. It should be noted that the first absorption band of DTBSB in ClB at temperatures from 343 to 203 K invariably exhibits the above-described structural features (*i.e.* two peaks and a shoulder), which precludes assignation of the peaks to a twisted conformer or aggregation phenomena. Only the decrease in band area observed below 203 K is due to aggregation, which produces new absorption bands.

3.2. Thermochromism of the first $\pi \leftrightarrow \pi^*$ transition of DTBSB in ClB

The Vis absorption spectra for DTBSB, dissolved in ClB and measured at decreasing temperatures from 343 to 77 K, reveal the presence of three distinct behaviors of the first band: Lowering the temperature caused a hyperchromic effect and a bathochromic band shift over the range 343–233 K (Fig. 4a); no band shift from 223 to 163 K (Fig. 4b); and a hypochromic effect and hypsochromic band shift from 153 to 77 K (Fig. 4c). Since, as recently shown by our group [29], lowering the temperature of ClB significantly increases its dipolarity (SdP), this solvent is optimal to check whether DTBSB exhibits the phenomenon known as "inverted solvatochromism" since our measurements would not be affected by specific interactions of the chromophore with the medium. Fig. 5 shows the wavenumbers for the first peak in the band – which can be assigned to the 0–0 component of the transition – as a function of the dipolarity (SdP) of the medium. Undoubtedly, this figure provides the first experimental evidence of a bathochromic band shift in the first electronic transition of a chromophore with an increase in dipolarity (in particular, from SdP = 0.4 to 0.7, which was accomplished by lowering the solution temperature from 343 to 243 K). The shift is fitted by Eq. (1), with $n = 11$ and $r = 0.989$.

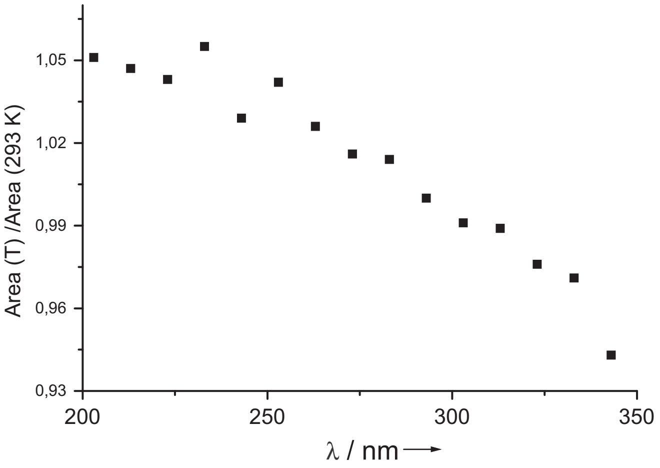


Fig. 3. Areas of the Vis spectra of DTBSB shown in Fig. 4, at 343–203 K, divided by the respective area at 293 K. These areas are divided by the corresponding value of the density from the ClB to these temperatures.

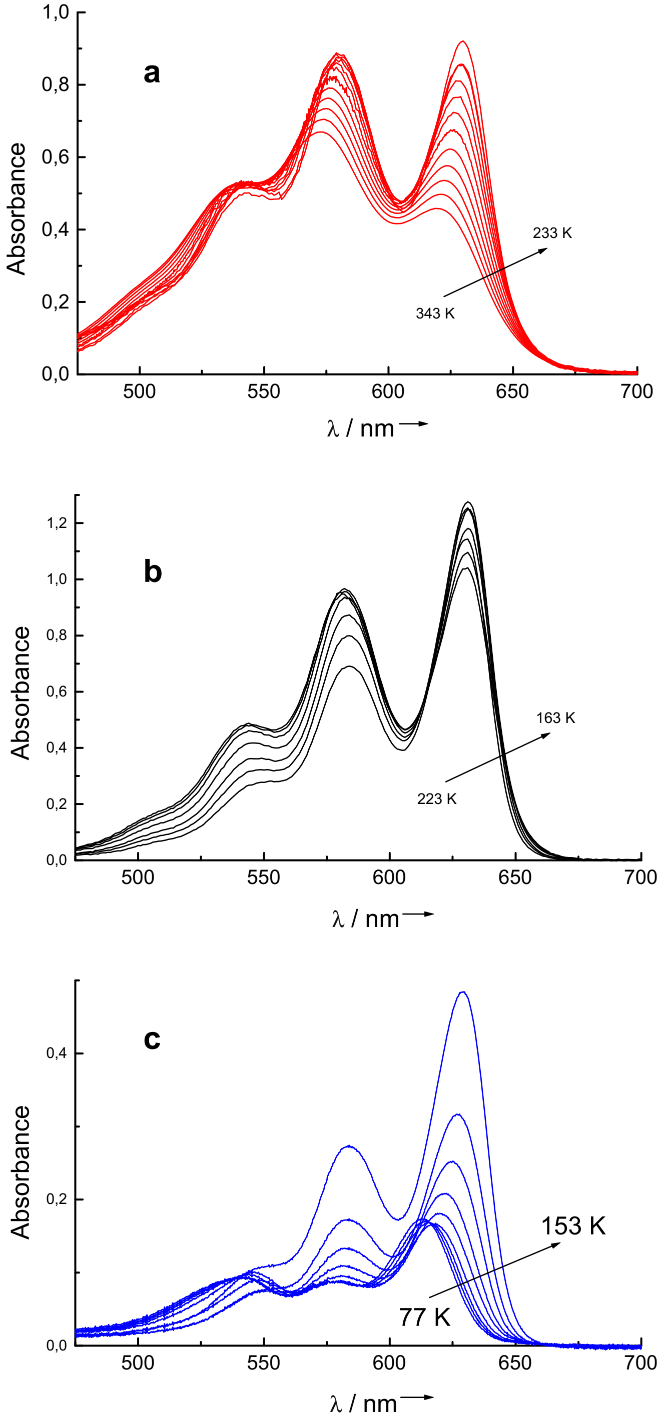


Fig. 4. Vis absorption bands of DTBSB, dissolved in ClB and measured (a) from 343 to 233 K, (b) from 223 to 163 K, and (c) from 153 to 77 K.

$$\tilde{\nu} = (-754.4 \pm 37.2)\mathrm{SdP} + (16\,410 \pm 21) \qquad (1)$$

On the other hand, raising SdP from 0.7 to 0.98 (*i.e.* lowering the temperature further from 233 to 163 K) causes nearly no change in

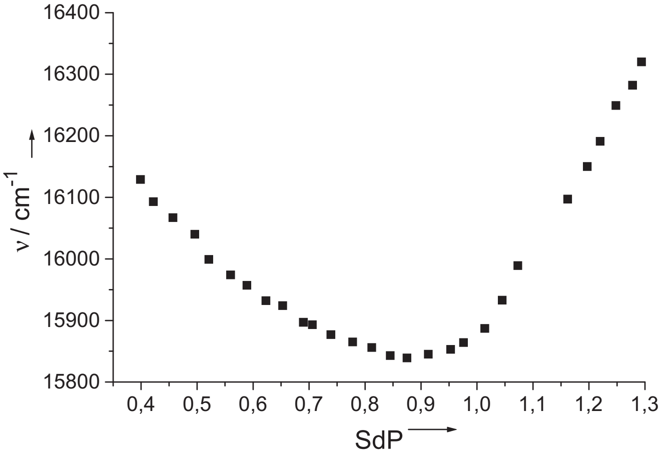


Fig. 5. Wavenumbers for the maxima of the first Vis absorption band of DTBSB, dissolved in ClB and measured at temperatures over the range 343–77 K vs the corresponding solvent dipolarity parameter SdP.

the first transition of the dye. Finally, raising SdP above 1.0 causes a hypsochromic band shift that is fitted by Eq. (2), with $n = 9$ and $r = 0.998$.

$$\tilde{\nu} = (1508 \pm 36)\mathrm{SdP} + (14\,358 \pm 42) \tag{2}$$

Eqs. (1) and (2) expose two significant solvatochromic facts. First, in a highly polar medium, the chromophore exhibits a hypsochromic band shift that is twice more sensitive to the solvent dipolarity (with a slope of +1508) than it is its bathochromic band shift found in a low-dipolarity medium (with a slope of −754). Second, the decrease in the dipole moment upon electronic excitation associated to the hypsochromic band shift must be twice as large as that for the bathochromic band shift. Varma and Groenen [2a] found that the dipole moment of SB decreases from 26.0 D in its electronic ground state to 22.4 D in its first excited state, corresponding to a reduction of $\Delta\mu = 3.6$ D. Therefore, if the slopes of Eqs. (1) and (2) also hold for SB, then its bathochromic band shift found in the region of low solvent dipolarity should involve a increase of the dipole moment of only $\Delta\mu = 1.8$ D.

Although examining this solvatochromic phenomenon in terms of corresponding emission measurements would be, without doubt, interesting, however a study of this type is hindered by the extremely low fluorescence of these compounds. For example, DTBSB has only $\Phi_f < 0.01$ at room temperature. However, as for *trans*-stilbene, the Φ_f value of which increases strongly with decreasing temperature (from 0.06 at room temperature to 0.75 at −183 °C) because of the increased solvent viscosity [38], DTBSB should also exhibit a significant increase in Φ_f as the temperature is lowered. As can be seen in Fig. 6, Φ_f increases substantially in going from 298 to 173 K and its Vis emission spectra contain two similarly strong peaks which exhibit no substantial band shift with decreasing temperature (*i.e.* with increasing dipolarity of the medium). Fig. 7 shows the fluorescence spectra of DTBSB obtained at still lower temperatures from 163 to 77 K; as can be clearly seen, Φ_f continues to increase as the temperature was lowered and, more important, the emission bands were shifted to increasingly shorter wavelengths.

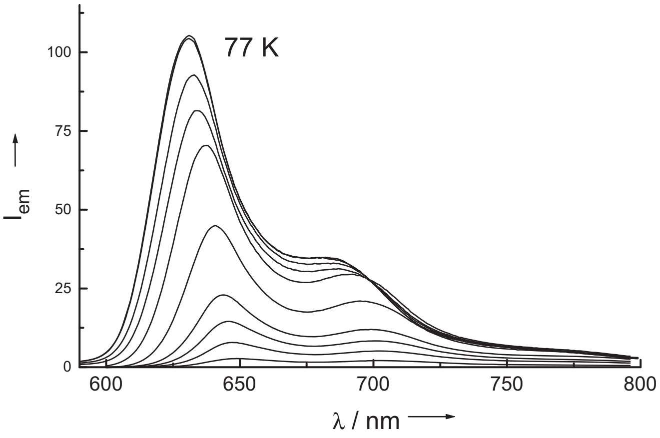


Fig. 7. Fluorescence spectra of DTBSB ($\lambda_{\mathrm{exc}} = 570$ nm), dissolved in ClB and measured at temperatures over the range 163–77 K.

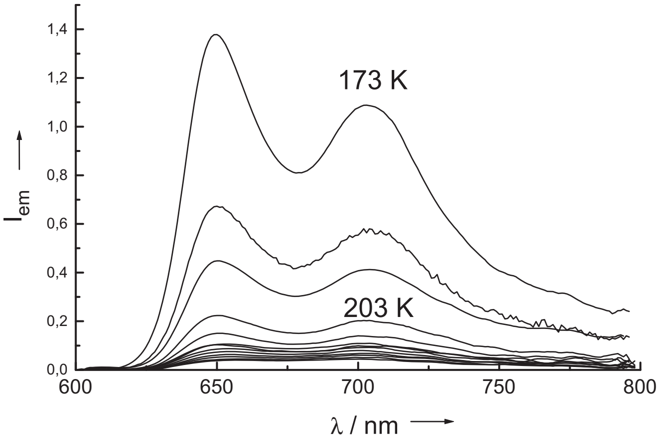


Fig. 6. Fluorescence spectra of DTBSB ($\lambda_{\mathrm{exc}} = 570$ nm), dissolved in ClB and measured at temperatures over the range 293–173 K.

Fig. 8 shows the wavenumbers of the first peak in the fluorescent band of DTBSB – which should be assigned to the 0–0 component – as a function of the dipolarity (SdP) of the medium. As can be seen, the compound exhibits a hypsochromic band shift at high SdP values and, especially, no bathochromic band shift at low SdP values. The hypsochromic band shift above SdP = 1.0 can be fitted by Eq. (3), with $n = 9$ and $r = 0.989$.

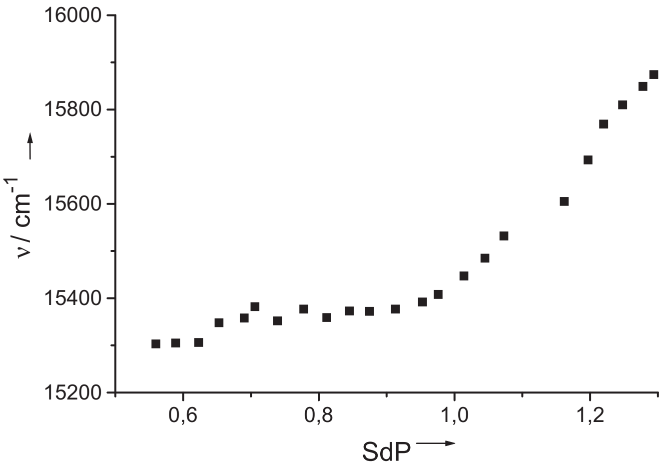


Fig. 8. Wavenumbers for the maxima of the emission band of DTBSB, dissolved in ClB and measured at temperatures over the range 343–77 K vs the corresponding solvent dipolarity parameter SdP.

$$\tilde{\nu} = (1550 \pm 88)\text{SdP} + (13\,861 \pm 103) \quad (3)$$

Eqs. (2) and (3) are so similar that one can assume that the absorption and emission data of DTBSB correspond to the same transition process.

3.3. *About the molecular structures involved in the solvatochromism of stilbazolium betaines*

If the absorption and emission data for stilbazolium betaines correspond to the same process, then the solvated molecular structures involved in the absorption and emission processes must also be the same, and the corrected emission spectrum, obtained by dividing each point by its corresponding frequency, and the excitation or absorption spectrum divided by the cube of the frequency at each point, should be mutual mirror images. This mirror symmetry and its implications are described in detail on pp. 85 and 86 of Ref. [39]. Fig. 9 shows the spectra obtained at 113 K. As can be seen, their mirror symmetry is close enough to assume that the absorbing molecular structure is the same as the emitting structure in both photophysical processes. One should bear in mind that the hypsochromic behavior of stilbazolium betaines is usually assigned to their zwitterionic forms.

As can be seen in Figs. 6 and 7, the envelopes of the fluorescence spectra of DTBSB were significantly different: the two peaks of Fig. 6 are fairly similar in intensity, whereas those in Fig. 7 are not – the first is invariably stronger than the second. Therefore, DTBSB obviously exists with two different molecular structures: (i) one at low solvent dipolarity values that gives two peaks and a shoulder in its absorption and excitation spectra – and, based on the independent term in Eq. (1), would have its 0–0 component in the gas phase at *ca.* 609 nm if it could be measured; and (ii) the other form at $\text{SdP} > 1$ the absorption and emission spectra of which are governed by its 0–0 component – which, based on the independent term in Eq. (2), would fall at 696 nm in the gas phase if it could be measured. If, based on data from Ref. [6,9], we estimated that the two *tert*-butyl groups in DTBSB cause a red-shifted of its first band by $\Delta\tilde{\nu} = 1100\ \text{cm}^{-1}$ with respect to unsubstituted SB, then the corresponding values for the 0–0 component in the gas phase should be 571 and 647 nm, respectively. Eqs. (1) and (2) clearly indicate that the electronic transition behind the hypsochromic behavior in the gas phase should be red-shifted from the bathochromic process. The estimations for the quinonoid and zwitterionic molecular structures of unsubstituted SB differ markedly from author to author. Thus, the quinonoid and zwitterionic form should absorb at 470 and 587 nm, respectively, according to Morley [20]; at 451.04 and 545.96 nm, respectively, according to Alberti and Echave [40]; at 446 and 378 nm according to Baraldi et al. [22]; and at 498 and 440 nm according to Murugan et al. [26].

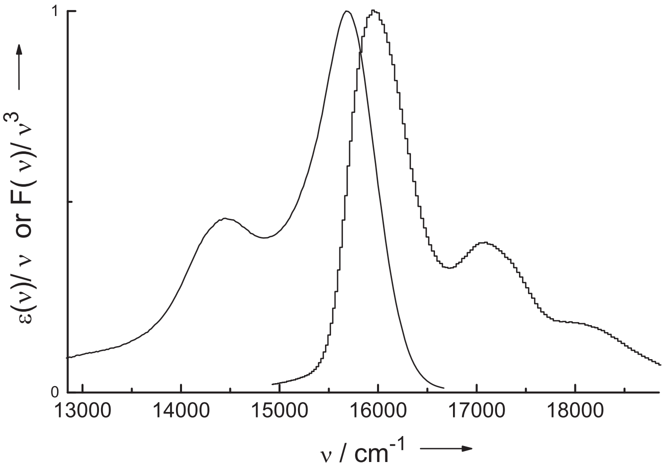


Fig. 9. Mirror symmetry relation for DTBSB, dissolved in ClB at 113 K. Modified absorption band $\varepsilon(\tilde{\nu})/\tilde{\nu}$ (solid); and modified fluorescence band $F(\tilde{\nu})/\tilde{\nu}^3$ (. . .).

Interestingly, femtosecond spectroscopy tests have revealed that the electronic excited state of SB can also give minima well apart from its Franck–Condon structures [41].

4. Conclusions

The thermochromic behavior of solutions of stilbazolium dyes in dipolar 1-chlorobutane, the dipolarity of which increases markedly with decreasing temperature without changing its acidity or basicity, allows for the first time confirm the phenomenon known as “inverted solvatochromism” beyond doubt for a stilbazolium betaine dye, which exhibits a bathochromic band shift at low solvent dipolarity (SdP) values, and a hypsochromic band shift at high SdP values, as the solution temperature is lowered. Also, the hypsochromic band shift is twice more sensitive to the dipolarity of the medium than is the bathochromic band shift.

If the molecular structures behind these solvatochromic effects could be examined in the absence of solvent, the UV–Vis absorption spectrum for the structure causing the hypsochromic band shift would invariably fall at a longer wavelength than that for the structure involved in the bathochromic band shift. This inference should, therefore, be considered in any structural model developed to account for this phenomenon.

As shown by their mirror symmetry, the molecular structure behind the first absorption band for a stilbazolium betaine dye is identical with that producing its fluorescence emission.

Stilbazolium betaine dyes, such as DTBSB, can clearly undergo two electronic transitions with the dipole moment increasing (bathochromic process) or decreasing (hypsochromic process) upon electronic excitation, depending on the solvent dipolarity, *i.e.* this chromophore can exhibit “inverted solvatochromism”.

References

[1] Reichardt C, Welton T. Solvents and solvent effects in organic chemistry. 4th, updated and enlarged ed. Weinheim, Germany: Wiley-VCH Verlag; 2011. Chapter 6, p. 359.
[2] (a) Varma CAGO, Groenen EJJ. Recl Trav Chim Pays-Bas 1972;91:296;
(b) Würthner F, Archetti G, Schmidt R, Kuball HG. Angew Chem 2008;120:4605;
(c) Würthner F, Archetti G, Schmidt R, Kuball HG. Angew Chem Int Ed 2008;47:4529.
[3] (a) Albert IDL, Marks TJ, Ratner MA. J Phys Chem 1996;100:9714;
(b) Levine BF, Bethea CG, Wasserman E, Leenders L. J Chem Phys 1978;68:5042;
(c) Dulcic A, Flytzanis C. Opt Commun 1978;25:402;
(d) Gilling IIR, Kolinsky PV, Cade NA, Earls JD, Peterson IR. Opt Commun 1985;55:289.
[4] (a) Zyss J, editor. Molecular nonlinear optics: materials, physics, devices. Boston, MA: Academic Press; 1994;
(b) Nalwa HS, Miyata S, editors. Nonlinear optics of organic molecules and polymers. Boca Raton, FL: CRC Press; 1997;
(c) Prasad PN, Williams DJ. Introduction to nonlinear optical effects in molecules and polymers. New York: Wiley; 1991;
(d) Wolff JJ, Wortmann R. Adv Phys Org Chem 1999;32:121;
(e) Marks TJ, Ratner MA. Angew Chem 1995;107:167;
(f) Marks TJ, Ratner MA. Angew Chem Int Ed Engl 1995;34:155;
(g) Ma H, Jen AK. Adv Mater 2001;13:1201;
(h) Würthmer F, Yao S, Dabaerdemaeker T, Wortmann R. J Am Chem Soc 2002;124:9431.
[5] (a) Moerner WE, Silence SM. Chem Rev 1994;94:127;
(b) Zhang Y, Burzynski R, Ghosal S, Casstevens MK. Adv Mater 1996;8:111;
(c) Zilker S. Chem Phys Chem 2000;1:72;
(d) Würthner F, Wortmann R, Meerholz K. Chem Phys Chem 2001;3:17.
[6] (a) Schulten K, Tavan P. Nature 1978;85:272;
(b) Schulten K, Tavan P. Chem Phys Lett 1984;110:191.
[7] Oesterhelt D, Stoeckenius W. Proc Natl Acad Sci USA 1973;70:2853.

[8] Brooker LGS, Keyes GH, Heseltine DW. J Am Chem Soc 1951;73:5350.
[9] Kiprianov AI, Petrun'kin VE. Zh Obshch Khim (J Gen Chem USSR) 1940;10:613.
[10] Benson HG, Murrell JN. J Chem Soc Faraday Trans 2 1972;68:137.
[11] Bayliss NG, McRae EG. J Am Chem Soc 1952;74:5803.
[12] Botrel A, Le Beuze A, Jacques P, Strub H. J Chem Soc Faraday Trans 2 1984;80:1235.
[13] Jacques P. J Phys Chem 1986;90:5535.
[14] Luzhkov V, Warshel A. J Am Chem Soc 1991;113:4491.
[15] Niedbalska M, Gruda I. Can J Chem 1990;68:691.
[16] Catalán J, Mena E, Meutermans W, Elguero J. J Phys Chem 1992;96:3615.
[17] Gruda I, Bolduc F. J Org Chem 1984;49:3300.
[18] Tsukada I, Mineo Y, Itoh K. J Phys Chem 1989;93:7989.
[19] Balter A, Nowak W, Pawelkiewicz W, Kowalczyk A. Chem Phys Lett 1988;143:565.
[20] Morley JO. J Mol Struct (Theochem) 1994;304:191.
[21] Morley JO, Morley RM, Docherty R, Charlton MH. J Am Chem Soc 1997;119:10192.
[22] Baraldi I, Brancolini G, Momicchioli F, Ponterini G, Vanossi D. Chem Phys 2003;288:309.
[23] Cavalli V, da Silva DC, Machado C, Machado VG, Soldi V. J Fluorescence 2006;16:77.
[24] Martins CT, Lima MS, Bastos EL, El Seoud OA. Eur J Org Chem; 2008:1165.
[25] Domínguez M, Rezende MC. J Phys Org Chem 2010;23:156.
[26] Murugan NA, Kongsted J, Rinkevicius Z, Aidas K, Ågren H. J Phys Chem B 2010;114:13349.
[27] Murugan NA, Kongsted J, Rinkevicius Z, Agren H. Phys Chem Chem Phys 2011;13:1290.
[28] Catalán J. J Phys Chem B 2009;113:5951.
[29] Catalán J, de Paz JL, Reichardt C. J Phys Chem A 2010;114:6226.
[30] DeRidder DJA, Heijdenrijk D, Schenk H, Dommisre RA, Lemiere GL, Lepoivre JA. Acta Cryst Pt C 1990;C46:2197.
[31] Catalán J. Chem Phys Lett 2005;416:165.
[32] Bayliss NS, McRae EG. J Phys Chem 1954;58:1002.
[33] Morley JO, Morley RM, Fitton AL. J Am Chem Soc 1998;120:11479.
[34] West W, Pearce S. J Phys Chem 1965;69:1894.
[35] Catalán J. Chem Phys Lett 2006;421:134.
[36] Mulliken RS, Rieke CA. Phys Soc Lond Prog Phys 1941;8:231.
[37] Smyth CP, Rogers HE. J Am Chem Soc 1930;52:2227.
[38] Gegion D, Mustak KA, Fischer E. J Am Chem Soc 1968;90:3907.
[39] Birks JB. Photophysics of aromatic molecules. New York: Wiley-Interscience; 1970.
[40] Alberti SF, Echave J. Chem Phys 1997;223:183.
[41] Burda C, Abdel-Kader MH, Link S, El-Sayed MA. J Am Chem Soc 2000;112:6720.