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# Solvatochromic behavior of dyes with dimethylamino electron-donor and nitro electron-acceptor groups in their molecular structure

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Six dyes with *N*,*N*-dimethylaminophenyl and 4-nitrophenyl or 2,4-dinitrophenyl groups in their molecular structures were prepared and characterized. These compounds have different conjugated bridges (C=C, C=N, and N=N) connecting the electron-donor and the electron-acceptor groups. All compounds are solvatochromic, with reverse solvatochromism occurring. The solvatochromic band observed in each spectrum for the dyes is due to a  $\pi \rightarrow \pi^*$  transition, of an intramolecular charge transfer nature, which occurs from the electron-donor *N*,*N*-dimethylaminophenyl group to the electron-acceptor group in the molecules, which is reinforced by the structures of the compounds optimized by applying density functional theory, which exhibit high planarity. The reverse solvatochromism was explained considering two resonance structures. The benzenoid form is better stabilized in less polar solvents and characterizes the region displaying positive solvatochromism. The Catalán multiparametric approach was used to study the contribution of solvent acidity, basicity, dipolarity, and polarizability to the solvatochromism exhibited by the compounds. These compounds are good candidates for the investigation of the polarizability and, to a lesser extent, the dipolarity of the medium, with very little interference from specific interactions of the solvent through hydrogen bonding. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: dipolarity/polarizability; reverse solvatochromism; solvation; solvatochromic dyes; solvatochromism

## INTRODUCTION

It is well known that the choice of a particular solvent or a mixture of solvents is crucial in terms of the rate and course of chemical processes<sup>[1–5]</sup> as well as the success of the purification and separation of organic compounds in the laboratory, as in the case of recrystallization and chromatographic techniques. In addition, the medium can strongly influence the spectrometric data of compounds, such as the maximum absorption and emission bands of organic compounds.<sup>[1,2,5]</sup>These effects are usually explained in terms of the solvent polarity, which represents the overall solvating ability of the medium.<sup>[1,5]</sup> In order to investigate the polarity of the medium, many solvent polarity scales have been created, and several are based on the use of solvatochromic probes.<sup>[1,2,5,6]</sup> These compounds have bands in the visible region, and their position and/or intensity change when the polarity of the medium is altered.<sup>[1,5]</sup> One of the most popular solvent polarity scales is  $E_{T}(30)$ , which is based on the use of Reichardt's pyridinium N-phenolate betaine, 2,6diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (1), and its derivatives.<sup>[1,5,7–9]</sup> The negative solvatochromism exhibited by these probes is based on its solvent-dependent vis band, with a charge-transfer character (from the donor phenolate group to the pyridinium acceptor moiety in the molecule).

Many research groups have studied other probes inspired by the molecular structure of compound **1**. In general, the solvatochromic dyes exhibiting a pronounced negative solvatochromism have a pyridinium group as the electron acceptor and a phenolate as the electron-donor group.<sup>[10–22]</sup> Recently, our group studied the solvatochromism of nitro-substituted benzylideneaminophenolates,<sup>[23]</sup> which have phenolate donor groups and 4-nitro or 2,4-dinitrophenyl acceptor groups connected through a C=N conjugated bridge. The compounds studied exhibited a reversal in their solvatochromism: first a decrease in the molar transition energy ( $E_T$ ) values of the dyes occurred on changing from water to DMA, but for solvents with  $E_T(30)$  values below 42.9 kcal mol<sup>-1</sup> the  $E_T(dye)$  values increase until the least polar solvent studied (*n*-hexane). The concept of a reversal in the solvatochromism, observed for various solvatochromic cyanines and merocyanines,<sup>[15,24–29]</sup> has been studied over the past four decades<sup>[30]</sup> and interpreted in terms of: dye aggregation in low polarity solvents<sup>[12,27,31]</sup>; solvent-dependent cis-trans (E/Z) isomerization processes<sup>[32,33]</sup>; and, most commonly, on the basis of the different abilities of polar

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and non-polar solvents to stabilize the ground and excited states of the dye.

An aspect to be considered in the design of new dye systems involves the use of aminophenyl groups instead of phenolate groups as the donor moiety in the molecular structure of solvatochromic compounds. Although the literature reports some studies on solvatochromic dyes with amino donor groups in their molecular structures, they often have pyridinium centers as acceptor groups.<sup>[34–39]</sup> Whitten *et al.*<sup>[40,41]</sup> reported the synthesis of donor-acceptor-substituted azobenzenes with one nitro electron-acceptor group and one di-alkylamino electron-donor group in their molecular structures. These compounds exhibited a strong solvatochromic behavior. The solvatochromism of some nitrostyryl dyes has also been studied.<sup>[42-45]</sup> Effenberger and Würthner have synthesized the dye 5-dimethylamino-5'-nitro-2,2'-bithiophene and demonstrated its positive solvatochromism.<sup>[46]</sup> Beckert et al. have recently reported the negative solvatochromism of an anionic thiazole-based dye.<sup>[47]</sup>

Herein, we report the synthesis of the dyes **2–7** and their application as solvatochromic probes for the investigation of 24 solvents. The influence of an additional nitro group on the solvatochromic properties of the dyes was investigated. In addition, the importance of three conjugated bridges, C=C, C=N, and N=N, on the type and level of the solvatochromism of the dyes was studied. Multiparametric analysis of the experimental data was also carried out in order to verify the contribution of each parameter to the solvatochromism exhibited by the dyes.



### **EXPERIMENTAL**

#### Materials and methods

All solvents were HPLC grade, purified following the methodology described in the literature and stored on molecular sieves (Sigma-Aldrich). 4-Amino-N,N-dimethylaniline was synthesized in two steps,<sup>[48]</sup> first by nitrosation of N,N-dimethylaniline in the presence of sodium nitrite and concentrated HCl. The product obtained was reduced using granulated tin, concentrated HCl, and ethanol, under reflux conditions.

UV–vis measurements were performed with an HP 8452A spectrophotometer equipped with thermostated cell compartments at ±0.1 °C, using 1-cm square quartz cuvettes. The NMR spectra were recorded on a Varian AS-400 spectrometer. Chemical shifts were recorded in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, and *dd* = double doublet), integration, and coupling constants (Hz). Infrared (IR) spectra were obtained on a Shimadzu model Prestige-21 spectrophotometer, with KBr pellets. High-resolution mass spectra were obtained with an electrospray ionization-quadrupole time-of-flight mass spectrometer (HR ESI-MS QTOF).

#### Synthesis

#### N,N-Dimethyl-4-[(E)-2-(4-nitrophenyl)vinyl]aniline (2)

4-Nitrotoluene (1.00 g; 7.20 mmol), 4-dimethylaminobenzaldehyde (0.99 g; 6.60 mmol), and pyrrolidine (1.20 mL; 14.5 mmol) were mixed in a roundbottomed flask, and the mixture was refluxed for 24 h. After this period a red solid was obtained. Diethyl ether (10 mL) was added to the flask, and the solid was filtered and washed with water, yielding 0.48 g (27%) of the product; m.p. obtained: 251.8 °C (m.p. lit.<sup>[49]</sup>: 255 °C). IR (KBr,  $\overline{\nu}_{max}/cm^{-1}$ ): 1442 (C—N); 1504 (N=O); 1365, 1223 (N=O); 1365 (C—H); 1524 (C=C). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ /ppm: 8.17 (*d*, 2H, *J* = 8.6 Hz), 7.75 (*d*, 2H, *J* = 8.4 Hz), 7.50 (*d*, 2H, *J* = 8.6 Hz), 7.41 (*d*, 1H, *J* = 16.4 Hz), 7.11 (*d*, 1H, *J* = 16.4 Hz), 6.73 (*d*, 2H, *J* = 8.4 Hz), 2.95 (*s*, 6H). HRMS (ESI, TOF): *m/z* calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup> 269.1285, found 269.1283.

#### 4-[(E)-2-(2,4-Dinitrophenyl)vinyl]-N,N-dimethylaniline (3)

2,4-Dinitrotoluene (0.55 g; 3.00 mmol), 4-dimethylaminobenzaldehyde (0.67 g; 4.49 mmol), and pyrrolidine (0.25 g; 3.50 mmol) were stirred in a round-bottomed flask, and the mixture was refluxed in an oil bath (90 °C) for 30 min. The solid product formed was filtered, washed with iced water, and recrystallized from ethanol, yielding 0.14 g (14.9%) of a dark red product; m.p. obtained: 176 °C (m.p. lit.<sup>[50]</sup>: 181 °C). IR (KBr,  $\bar{\nu}_{max}/cm^{-1}$ ): 1444 (C—N); 1367, 1270 (N=O); 1331 (C—H); 1523 (C=C). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ /ppm: 8.67 (s, 1H, *J* = 2.3 Hz); 8.38 (*dd*, 1H, *J* = 9.0 and 2.3 Hz), 8.21 (*d*, 1H, *J* = 9.0 Hz), 7.56 (*d*, 1H, *J* = 16.0 Hz), 7.49 (*d*, 2H, *J* = 8.6 Hz), 7.21 (*d*, 1H, *J* = 16.0 Hz), 6.73 (*d*, 2H, *J* = 8.6 Hz), 2.98 (s, 6H). HRMS (ESI, TOF): *m*/z calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub>O<sub>4</sub> [M + H]<sup>+</sup> 314.1135, found 314.1132.

#### *N*,*N*-Dimethyl-4-[(1*E*)-(4-nitrobenzylidene)amine]aniline (4)<sup>[51]</sup>

4-Amino-*N*,*N*-dimethylaniline (0.21 g; 1.46 mmol) and 4-nitrobenzaldehyde (0.23 g; 1.46 mmol) were dissolved in methanol (3 mL) in a closed round-bottomed flask. One drop of glacial acetic acid was added, and the reaction mixture was stirred for 3 h. The dark solid formed was filtered and washed with cold methanol, yielding 0.14 g (35.8%); m.p. obtained: 224 °C (m.p. lit.<sup>[51]</sup>: 228 °C). IR (KBr,  $\bar{\nu}_{max}/cm^{-1}$ ): 1595 (C=N); 1444 (C–N); 1514, 1367 (N=O); 1341 (C—H); 1514 (C=C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.58 (*s*, 1H), 8.27 (*d*, 2H, *J*=9.2 Hz); 8.00 (*d*, 2H, *J*=9.2 Hz); 7.33 (*d*, 2H, J=9.2 Hz); 7.33 (*d*, 2H,



**Figure 1**. Dyes **2–7** in: a) *n*-hexane, b) diethyl ether, c) propan-2-ol, and d) DMSO



Figure 2. UV-vis spectra for dyes 2-7 in *n*-hexane (—), diethyl ether (—), propan-2-ol (—), and DMSO (—)

J = 9.2 Hz), 6.74 (d, 2H, J = 9.2 Hz), 3.01 (s, 6H). HRMS (ESI, TOF): m/z calcd. for  $C_{15}H_{16}N_3O_2$  [M + H]<sup>+</sup> 270.1237, found 270.1245.

#### 4-[(E)-(2,4-Dinitrobenzylidene)amine]-N,N-dimethylaniline (5)

2,4-Dinitrobenzaldehyde (0.15 g; 0.76 mmol) and 4-amino-*N*,*N*-dimethylaniline (0.11 g; 0.76 mmol) were mixed with absolute ethanol (5 mL), propan-2-ol (5 mL), and one drop of glacial acetic acid. The reactants were dissolved under magnetic stirring at room temperature, and the reaction mixture was stirred for 4 h. The resulting dark solid was filtered and recrystallized from propan-2-ol, yielding 0.05 g (21.0%) of a dark red product; m.p. obtained: 206 °C (m.p. lit.<sup>[52]</sup>: 211 °C). IR (KBr,  $\bar{\nu}_{max}/cm^{-1}$ ): 1604 (C=N); 1517 (C=C); 1345 (N=O); 1160 (C—N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 9.04 (*s*, 1H); 8.84 (*d*, 1H, *J*=2.3 Hz); 8.63 (*d*, 1H, *J*=8.6 Hz); 8.44 (*dd*, 1H, *J*=8.6 and 2.3 Hz); 7.38 (*d*, 2H, *J*=9.0 Hz); 6.73 (*d*, 2H, *J*=9.0 Hz); 3.04 (*s*, 6H). HRMS (ESI, TOF): *m/z* calcd. for C<sub>15</sub>H<sub>15</sub>N<sub>4</sub>O<sub>4</sub> [M+H]<sup>+</sup> 315.1088, found 315.1087.

#### N,N-Dimethyl-4-[(E)-(4-nitrophenyl)diazenyl]aniline (6)<sup>[53]</sup>

4-Nitroaniline (1.38 g; 10 mmol) was placed in a mixture of acetic acid (50 mL) and concentrated sulfuric acid (20 mL). The reaction mixture was placed in an ice bath at 0–5 °C. Subsequently, a solution of sodium nitrite (0.70 g; 10 mmol) in water (2.5 mL) was added dropwise under magnetic stirring. After a period of 30 min the resulting diazonium salt

solution was poured into another solution of *N*,*N*-dimethylaniline (1.25 mL; 10 mmol) in methanol (50 mL). The final orange solution was alkalinized using KOH pellets, and the precipitate obtained was filtered and washed with methanol, yielding 0.81 g (30.2%) of a dark red solid; m.p. obtained: 220 °C (m.p. litt<sup>[53]</sup>; 225–228 °C). IR (KBr,  $\bar{\nu}_{max}/cm^{-1}$ ): 1423 (N=N); 1602 (N=O); 1511 (N—H); 1333 (C—H); 1587 (C=C); 1136 (C—N). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ /ppm: 8.35 (*d*, 2H, *J* = 8.6 Hz); 7.93 (*d*, 2H, *J* = 8.6 Hz); 7.85 (*d*, 2H, *J* = 8.6 Hz); 6.86 (*d*, 2H, *J* = 8.6 Hz); 3.10 (*s*, 6H). HRMS (ESI, TOF): *m*/z calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub> [M+H]<sup>+</sup> 271.1190, found 271.1194.

#### 4-[(E)-2,4-Dinitrophenyl)diazenyl)-N,Ndimethylaniline (7)<sup>[53]</sup>

2,4-Dinitroaniline (1.83 g; 10 mmol) was dissolved in a mixture of glacial acetic acid (50 mL) and concentrated sulfuric acid (20 mL). The reaction mixture was placed in an ice bath at 0-5 °C. A solution of sodium nitrite (0.70 g; 10.1 mmol) in water (2.5 mL) was added dropwise under magnetic stirring, and after 30 min the resulting solution of the diazonium salt was mixed with another solution of N,N-dimethylaniline (1.25 mL; 9.8 mmol) in methanol (50 mL). The resulting red solution was diluted with 200 mL of water, yielding a dark precipitate, which was filtered and washed with methanol. The yield was 1.30 g (41.2%); m.p. obtained: 206.7 °C (m.p. lit.<sup>[53]</sup>: 211 °C). IR (KBr,  $\overline{v}_{max}/cm^{-1}$ ): 1423 (N=N); 1594 (N=O); 1364 (C-N); 1332 (C—H); 1521 (C=C). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ /ppm: 8.83 (*d*, 1H, J = 1.9 Hz), 8.48 (dd, 1H, J = 9.0 Hz, J = 1.9 Hz), 7.88 (d, 1H, J = 9.0 Hz), 7.76 (d, 2H, J = 9.0 Hz), 6.87 (d, 2H, J = 9.0 Hz), 3.31 (s, 6H). HRMS (ESI, TOF): m/z calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub> [M + H]<sup>+</sup> 316.1040, found 316.1045.

#### UV-vis measurements

The following procedure was typical for all measurements performed. A  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> stock solution of compounds **2–7** was prepared in anhydrous trichloromethane. From this stock solution 5 µL was transferred to 5-mL volumetric flasks. After evaporation of the trichloromethane the compounds were dissolved in the pure solvent, yielding a solution with a final dye concentration of  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>. The UV–vis spectra were recorded at 25 °C using a 1-cm square cuvette. The maxima of the UV–vis spectra ( $\lambda_{max}$ ) were calculated from the first derivative of the absorption spectrum. The  $\lambda_{max}$  values thus obtained were transformed into  $E_{\rm T}$ (dye) values, according to the expression  $E_{\rm T}$ (dye) = 28591/ $\lambda_{max}$ .<sup>[1,5]</sup>

#### **Computational details**

All theoretical calculations were made at the DFT level of theory using the hybrid functional B3LYP and the basis set 6-31 + G(d,p) with the aid of the GAUSSIAN09 package.<sup>[54]</sup> The geometries were optimized in the gas-phase and re-optimized in the presence of the polarized/continuum solvent model (SCRF-PCM)<sup>[55]</sup> in *n*-hexane ( $\varepsilon = 1.88$ ), tetrahydrofuran ( $\varepsilon = 7.43$ ), dichloromethane ( $\varepsilon = 8.93$ ), acetone ( $\varepsilon = 20.49$ ), dimethylsulfoxide ( $\varepsilon = 46.83$ ), ethanol ( $\varepsilon = 24.85$ ), and methanol ( $\varepsilon = 32.61$ ). All optimized geometries correspond to a minimum on the potential energy surface, since no imaginary values were obtained in the Hessian matrix. The spectra were



**Figure 3**. Optimized molecular geometry of compounds **2–7** obtained in gas phase at B3LYP/ 6-31 + G(d,p) level of theory



Figure 4. HOMO and LUMO of compound 2 in gas phase obtained at B3LYP/6-31 + G(d,p) TD level of theory

calculated at the same level of theory and the solvent model using the time depending (TD) method.

#### Calculations

All constants were calculated through the fitting of least-squares regression curves using the program  $ORIGIN^{\circ}$  6.1.

## **RESULTS AND DISCUSSION**

Figure 1 shows the colors of the solutions of compounds **2–7** in solvents of different polarity, and it can be observed that all compounds are solvatochromic. For instance, solutions of compound **7** are yellow in *n*-hexane, orange in diethyl ether, red in propan-2-ol, and purple in DMSO.

The solvatochromic behavior could be quantified through the variations observed in the  $\lambda_{max}$  values obtained from the solvatochromic band of each dye in solution. Figure 2 shows the UV-vis spectra for the probes 2-7 in selected solvents. By way of example, it can be observed for compound 3 that in diethyl ether its solvatochromic band occurs at  $\lambda_{max} = 475$  nm. In *n*-hexane, the solvatochromic band shifts to 466 nm, while in DMSO the shift is to 496 nm. The solvatochromic band observed in each spectrum for the dyes is due to a  $\pi \rightarrow \pi^*$  transition, of an intramolecular charge transfer nature, which occurs from the electron-donor N,Ndimethylaminophenyl group to the electronacceptor group, 4-nitrophenyl (compounds 2, 4, and 6) or 2,4-dinitrophenyl (compounds 3, 5, and 7), in the molecules, which is reinforced by the structures of 2-7 optimized by applying density functional theory, DFT, which exhibit high planarity (Fig. 3). According to Fig. 4, the HOMO density in compound 2 is mainly located in the N,Ndimethylaminophenyl donor group, while the

LUMO is mainly located in the nitro acceptor groups, indicating the donor and acceptor moieties. A similar scenario was verified for compounds **3–7** (see Figs. S22–S26).

The spectrophotometric studies were performed for the six dyes in 24 solvents of different polarity, the  $\lambda_{max}$  values being obtained from the UV-vis spectra. The measurements could not be taken in water since the compounds are not sufficiently soluble in this solvent. Table 1 shows the  $[E_T(dye)]$  values for each solvent and also the corresponding  $E_T(30)$  values. These data were used to make plots of  $E_T(dye)$  as a function of  $E_T(30)$  for each dye (Fig. 5). The presence of two regions, one in less polar solvents and the other in more polar solvents, is evident in all plots. More specifically, starting with less polar solvents, the  $E_T$  values for the dyes decreased until solvents of intermediate polarities, after which the  $E_T$  values increased with an increase in the polarity of the medium, with a reversal in the solvatochromism occurring.

<b>Table 1.</b> $E_{\rm T}(30)$ and $E_{\rm T}({\rm dye})$ values for compounds <b>2–7</b> in 24 solvents											
Solvent	<i>E</i> <sub>T</sub> (30) <sup>a</sup>	$E_{\rm T}(2)^{\rm b}$	$E_{\rm T}({\bf 3})^{\rm b}$	$E_{\rm T}({\bf 4})^{\rm b}$	$E_{\rm T}({\bf 5})^{\rm b}$	$E_{\rm T}({\bf 6})^{\rm b}$	$E_{\mathrm{T}}(7)^{\mathrm{b}}$				
Methanol	55.4	66.5	60.0	63.2	58.1	59.9	55.5				
Ethanol	51.9	66.2	59.5	63.5	57.6	60.2	55.4				
Diethyl ether	34.5	67.2	60.2	64.1	58.1	62.4	57.3				
1-Butanol	49.7	65.9	58.9	63.2	56.5	59.0	55.7				
Propan-2-ol	48.4	66.0	59.5	63.3	56.8	60.3	55.6				
1-Octanol	48.1	65.7	58.9	62.2	55.9	60.0	55.2				
1-Decanol	47.7	65.9	58.6	63.0	56.0	60.2	55.7				
2-Butanol	47.1	66.0	59.5	63.3	56.5	60.3	55.6				
Acetonitrile	45.6	65.6	60.0	63.3	57.7	59.3	54.6				
DMSO	45.1	62.8	57.6	61.4	56.6	56.5	53.0				
2-Methylpropan-2-ol	43.3	66.6	59.5	63.0	57.0	60.9	56.0				
DMF	43.2	63.9	58.1	61.5	56.7	57.6	53.6				
DMA	42.9	63.8	58.1	62.2	56.9	57.6	53.5				
Acetone	42.2	65.6	59.3	63.8	58.1	59.0	55.7				
1,2-Dichloroethane	41.3	64.5	58.0	62.2	55.6	58.3	54.0				
Dichloromethane	40.7	64.5	58.1	62.0	55.4	59.2	54.3				
Acetophenone	40.6	63.0	57.4	60.1	54.5	57.0	52.8				
Trichloromethane	39.1	65.1	58.3	62.6	55.2	58.8	54.6				
Ethyl acetate	38.1	66.5	59.7	63.7	57.9	59.9	56.1				
1-Pentanol	49.1	65.9	59.2	63.0	56.7	59.8	55.4				
THF	37.4	65.7	59.5	62.3	57.4	60.2	55.6				
Toluene	33.9	66.0	58.8	63.5	56.4	61.1	56.3				
<i>n</i> -Hexane	31.0	70.1	61.3	65.6	58.4	64.2	59.9				
Cyclohexane	30.9	69.0	61.5	65.0	57.7	63.0	58.8				
<sup>a</sup> Values obtained from Re <sup>b</sup> In kcal mol <sup>-1</sup> .	ichardt, 1994.										

In the case of compound **7**, the  $\lambda_{max}$  for the solvatochromic band in *n*-hexane occurs at 477 nm  $[E_T(\mathbf{7}) = 59.9 \text{ kcal mol}^{-1}]$ , while in acetophenone the  $\lambda_{\text{max}}$  occurs at 541 nm  $[E_{\text{T}}(\mathbf{7}) = 52.8 \text{ kcal mol}^{-1}]$ . Therefore, an increase in the polarity of the solvent shifts the solvatochromic band of the dye to larger  $\lambda_{max}$  values (bathochromic shift), with  $\Delta \lambda_{max} = +64$  nm. In the region of  $E_{\rm T}(7)$  value corresponding to acetophenone, at 52.8 kcal mol<sup>-1</sup>, a reversal in the solvatochromism occurs. From this region onward, a gradual increase in the polarity of the medium causes a hypsochromic shift in the solvatochromic band, which characterizes negative solvatochromism. For the solvatochromic band in methanol  $\lambda_{\text{max}} = 515 \text{ nm} (E_{\text{T}}(\text{dye}) = 55.5 \text{ kcal mol}^{-1})$ , which in comparison with  $\lambda_{max} = 541 \text{ nm}$  in acetophenone provides  $\Delta \lambda_{max} = -26 \text{ nm}$ , characterizing the hypsochromic shift. The plots of  $E_{T}(30)$  vs  $E_{T}(dye)$  for compounds 4 and 5 show that the positive solvatochromism begins with the dyes in *n*-hexane [4:  $E_{\rm T}(4) = 65.6 \, \rm kcal \, mol^{-1}$ ; 5:  $E_{\rm T}(\mathbf{5}) = 58.4 \, \rm kcal \, mol^{-1}$ ], and continues until polarities approaching that of acetophenone [4:  $E_T(4) = 60.1 \text{ kcal mol}^{-1}$ ; 5:  $E_{T}(\mathbf{5}) = 58.4 \text{ kcal mol}^{-1}$ ], and from this region the negative solvatochromism occurs with an increase in the solvent polarity, values obtained in methanol being  $E_{T}(\mathbf{4}) = 63.2 \text{ kcal mol}^{-1}$  and  $E_{\rm T}(\mathbf{5}) = 58.1 \, \rm kcal \, mol^{-1}$ . For compounds **2** and **6**, the positive solvatochromism starts with the dye in *n*-hexane [2:  $E_T(2)$ = 70.1 kcal mol<sup>-1</sup>; **6**:  $E_T(6) = 64.2$  kcal mol<sup>-1</sup>], and the region characterizing the reversal in the solvatochromism occurs for solvents with polarities close to that of DMSO [**6**:  $E_T$ (**6**) = 56.5 kcal mol<sup>-1</sup>; **1**:  $E_{\rm T}(2) = 62.8 \, \rm kcal \, mol^{-1}$ ]. The most polar solvent studied using the dyes was methanol [6:  $E_{T}(6) = 57.0 \text{ kcal mol}^{-1}$ ; 2:  $E_{T}(2) =$ 66.5 kcal mol<sup>-1</sup>]. For compound **3**, the positive solvatochromism starts in cyclohexane  $[E_T(\mathbf{3}) = 61.5 \text{ kcal mol}^{-1}]$  and continues until acetophenone  $[E_T(\mathbf{3}) = 57.4 \text{ kcal mol}^{-1}]$ , after which a reversal in the solvatochromism occurs, with negative solvatochromism being observed until methanol  $[E_T(\mathbf{3}) = 60.0 \text{ kcal mol}^{-1}]$ .

Table 2 lists the  $\lambda_{max}$  values for the dyes in the most polar, least polar, and intermediate polarity solvents, as well as the  $\Delta\lambda_{max}$  values that characterize the bathochromic and hypsochromic shifts for each system. The data show that the azo (N=N) conjugated bridge, in general, leads to the dye exhibiting greater variations in the wavelengths and consequently a more accentuated solvatochromism. Except for the azocompounds, the dyes with only one nitro group exhibit a more extensive solvatochromism, suggesting that a greater planarity of the systems is an important factor regarding the contribution of the mesomeric effect in the studied systems. Another aspect to be observed involves the suggestion that the charge transfer is strongest in the systems with only one nitro group.

With the application of the B3LYP/6-31 + G(d,p) SCRF = PCM TD level of theory to the previously optimized structures of dyes **2–7**, on comparing HOMO and LUMO molecular orbitals, it was verified that the transition is strongly dependent on the surrounding solvent. Table 3 shows the calculated  $E_T$  values in kcal mol<sup>-1</sup> for the dyes in the gas phase and in seven different solvents. Although PCM calculations do not provide good results for solvents with medium to high polarity<sup>[56]</sup> and TD-DFT calculations tend to overestimate the internal charge-transfer transition-energy of solvatochromic dyes,<sup>[57]</sup> the results are good. The data show a reversal in the solvatochromism for all dyes, as shown in Fig. 6 for compound **7**, this being a representative example of the results obtained for compounds **2–6**.



**Figure 5**.  $E_T(30)$  values as a function of  $E_T(dye)$  for dyes **2–7** 

All compounds studied have the features expected according to their molecular structure. The reverse solvatochromism of the compounds studied can be explained on the basis of Scheme 1, considering two resonance structures, the benzenoid and dipolar forms. The benzenoid form is better stabilized in less polar solvents and characterizes the region displaying positive solvatochromism, while the dipolar form is better stabilized in more polar solvents, in the region of negative solvatochromism. Thus, the reversal in the solvatochromism, from positive to negative, is probably a result of the fact that with the increase in the polarity of the medium the weight of the contribution of the dipolar form to the resonance hybrid of the dye is gradually increased.

Therefore, the solvatochromism of the dyes studied herein can be summarized by the diagram for compound 2 in Fig. 7, which can be applied to the other dyes investigated. According to this proposal, the resonance forms with a greater contribution are strongly dependent on the solvent. In non-polar solvents, such as nhexane, the resonance form with the greatest contribution is the benzenoid form. With a gradual increase in the polarity of the medium the solvent is less able to solvate the ground state of the dye, but in compensation it effectively stabilizes the excited state, due to the fact that the latter is more polar. This explains the positive solvatochromism observed for dye 2 in solvents with polarity between *n*-hexane and DMSO. Above a certain polarity of the medium, the dipolar resonance form provides the largest contribution for the resonance hybrid. In this case, since the excited state is now less polar, negative solvatochromism occurs with an increase in the polarity of the medium.

Studies on the influence of the dye concentration on the absorbance values were carried out to verify that there is no aggregation of the compounds in the con-

centration range in which the absorbance values were collected. The studies were performed with the dyes in two solvents of very different polarity, methanol, and ethyl acetate. For all compounds studied the plots of the absorbance values ( $\lambda_{max}$ ) as a function of the dye concentration were linear, indicating the absence of solute–solute aggregation under the experimental

**Table 2.** Values of  $\lambda_{max}$  for compounds **2–7** in the most polar, least polar, and intermediate polarity solvents, as well as the  $\Delta \lambda_{max}$  values obtained considering the regions of positive and negative solvatochromism

Dye	Most polar solvent (methanol)	st polar solvent (methanol) Intermediate solvent		$\Delta \lambda_{max}^{a}$ (nm)	$\Delta \lambda_{\max}^{b}$ (nm)				
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)						
2	430	455 (DMSO)	408 ( <i>n</i> -hexane)	+47	-25				
3	476	498 (acetophenone)	465 (cyclohexane)	+33	-22				
4	452	475 (acetophenone)	435 ( <i>n</i> -hexane)	+40	-23				
5	492	524 (acetophenone)	489 ( <i>n</i> -hexane)	+35	-32				
6	477	506 (DMSO)	445 ( <i>n</i> -hexane)	+61	-29				
7	515	541 (acetophenone)	477 ( <i>n</i> -hexane)	+64	-26				
<sup>a</sup> $\Delta\lambda_{max} = \lambda_{max}$ (intermediate solvent) – $\lambda_{max}$ (least polar solvent) <sup>b</sup> $\Delta\lambda_{max} = \lambda_{max}$ (methanol) – $\lambda_{max}$ (intermediate solvent)									

**Table 3.**  $E_T$  values (in kcal mol<sup>-1</sup>) for dyes **2–7** calculated applying B3LYP/6-31 + G(d,p) SCRF = PCM TD level of theory to previously optimized structures

Medium	2	3	4	5	6	7
Gas phase	59.6	53.7	55.0	51.0	56.3	55.3
<i>n</i> -Hexane	53.5	49.2	50.3	46.8	55.5	53.9
Tetrahydrofuran	49.3	46.2	46.8	44.1	52.4	50.9
Dichloromethane	49.0	45.9	46.5	43.9	52.1	50.6
Acetone	48.5	45.4	46.1	43.7	51.7	50.4
DMSO	47.8	45.0	45.6	43.2	51.1	49.8
Ethanol	48.3	45.3	45.9	43.6	51.6	50.2
Methanol	48.4	45.3	46.0	43.7	51.7	50.3



**Figure 6**. Variation in the calculated  $E_T$  values for compound **7** in media with different  $E_T$ (30) values

conditions of the studies performed. Therefore, the reverse solvatochromism could not be attributed to the aggregation phenomenon, but may be the result of the differential solvation of the medium on the resonance structures of the dyes. This differential solvation of the two forms, dipolar and benzenoid, changes the extent of the contribution of different species and is responsible for the reverse solvatochromism observed experimentally.

The values for the molar absorptivity of the dyes were obtained in methanol and ethyl acetate (see supplementary data). Azocompound 7 had the highest molar absorptivity value, due to the fact that the azo (N=N) bridge is a strong electronacceptor group,<sup>[58]</sup> increasing the rigidity of the conjugated system, which leads to high light absorption, as well as a great variety of colors in solution. Comparing data in methanol, compound 4 had the lowest molar absorptivity value, since the C=N bridge is not as effective as electron-acceptor group compared with the azo bridge. Apart from the conjugate bridge, the compounds with two nitro groups (compounds 3, 5, and 7) had the highest absorptivity values, because the presence of these groups enhances the mesomeric effect, leading to more resonance contributors. For compounds 3 and 5 in ethyl acetate, the molar absorptivity values were lower than those for dyes 2 and 4. These data reinforce the previous proposal that in less polar solvents the contribution of the benzenoid resonance



**Scheme 1**. Benzenoid and dipolar forms of the compounds

structure is very important, suggesting less interaction through resonance structure between electron-donor and electron-acceptor groups due to steric hindrance caused by nitro groups at *ortho* position.

#### Interpretation of the solvatochromism using the multiparametric approaches of Kamlet–Abboud–Taft and Catalán

Two different approaches to the analyses of the experimental  $E_{\rm T}$ (dye) values in pure solvents for compounds **2–7** were carried out with the use of Kamlet–Abboud–Taft<sup>[59–64]</sup> and Catalán<sup>[63–68]</sup> multiparameter approaches. These strategies consider a linear correlation between the measured spectroscopic parameter,  $E_{\rm T}$ (dye), and several solvent parameters, as shown in Equation (1):

$$E_{T}(dye) = E_{T}(dye)_{0} + aA + bB + cC + ...$$
 (1)

where  $E_{\rm T}({\rm dye})_0$  represents the  $E_{\rm T}({\rm dye})$  value relating to an inert solvent, and a, b, and c are coefficients that reflect the importance of the solvent parameters *A*, *B*, and *C*, respectively, in terms of  $E_{\rm T}({\rm dye})$ . The Kamlet–Abboud–Taft strategy<sup>[59,60]</sup> requires the use of Equation (2),

$$E_{\rm T}(\rm dye) = E_{\rm T}(\rm dye)_0 + a\alpha + b\beta + s(\pi^* + d\delta)$$
(2)

where  $\alpha$ ,  $\beta$ , and  $\pi^*$  are parameters that represent the solvent hydrogen-bond donor (HBD) acidity, hydrogen-bond acceptor (HBA) basicity, and solvent dipolarity/polarizability, respectively, while  $\delta$  is a polarizability correction term of the solvent. Another multiparametric polarity scale was developed by Catalán *et al.*,<sup>[68]</sup> employing Equation (3),

$$E_{T}(dye) = E_{T}(dye)_{0} + aSA + bSB + cSP + dSdP$$
(3)

where SA (solvent HBD acidity) and SB (solvent HBA basicity) are specific and SP (solvent polarizability) and SdP (solvent dipolarity) are nonspecific solvent parameters.

The contributions of the solvent properties to the  $E_{T}(dye)$  values obtained for dyes **2–7** were ascertained with the use of Equations (2) and (3). The results of the multiple square correlation analysis are shown in Tables 4 and 5 for the Kamlet–Abboud–Taft and Catalán approaches, respectively. Some general trends can be observed through a comparison of the correlation data given in the tables. A notable aspect is related to the analysis of the coefficients associated with the acidity and basicity of the medium. Considering the molecular structure of dyes **2–7** they would be expected to be sensitive to the acidity of the medium, exhibiting very low sensitivity to the basicity of the medium. This is because acidic hydrogens, which could interact through hydrogen bonding with the basic groups of HBA solvents, are not present in the molecular structure of these compounds. On the



Figure 7. Reverse solvatochromism exhibited by dye 2

other hand, all compounds have basic dimethylamino groups, which are potentially able to interact through hydrogen bonding with HBD solvents. An inspection of the coefficients in Table 4 reveals that the contribution of the b coefficients, related to the sensitivity of the dye to the basicity of the medium, is larger than the contribution of the a coefficients, related to the sensitivity of the dye to the medium acidity. On the other hand, the results obtained using the Catalán approach offered a more coherent picture, since the sensitivity of the dyes with respect to the basicity of the medium was negligible, while the contribution of the coefficient related to the sensitivity of the dyes to the solvent acidity was more important. Figure 8 shows a comparison between the measured and calculated transition energy values, using the multiparametric strategies studied, for compound 2. It can be verified that the Catalán strategy is more appropriate for describing the system.

The inclusion of another term in the multiparametric equations, log P, which is a parameter associated with the lipophilicity of the medium, yielded Equations (4) and (5) for the Kamlet-Abboud-Taft and Catalán approaches, respectively.<sup>[20,69]</sup> The use of this term in the Kamlet-Abboud-Taft analysis [Equation (4)] generally led to an improvement in the correlations (see Supporting Information), except for

ment of $E_{\rm T}$ (dye) values for compounds <b>2–7</b> in various solvents										
Dye	Constant	а	b	S	Ν	F	R	S.D.		
2	69.07	0.57	-0.87	-5.28	24	$< 1.4 \times 10^{-8}$	0.92	0.66		
3	60.99	-0.10	-0.15	-3.13	24	$< 5.3 \times 10^{-5}$	0.81	0.64		
4	65.10	0.32	-0.68	-3.25	24	$< 5.6 \times 10^{-5}$	0.81	0.71		
5	57.27	-0.80	1.02	-2.07	24	<0.12	0.49	0.96		
6	63.51	0.26	-0.79	-5.90	24	$< 1.9 \times 10^{-8}$	0.92	0.74		
7	59.93	-0.12	-0.53	-5.52	24	$< 8.5 \times 10^{-9}$	0.93	0.65		
<sup>a</sup> Equation	<sup>a</sup> Equation (2) was used (see text).									

**Table 4.** Correlation coefficients a, b, and s obtained from the Kamlet–Abboud–Taft multiparametric analysis <sup>a</sup> through the treat-

**Table 5.** Correlation coefficients a, b, c, and d obtained from the Catalán multiparametric analysis <sup>a</sup> through the treatment of  $E_{\rm T}$ (dye) values for compounds 2-7 in various solvents

	Constant	а	b	с	d	Ν	F	R	S.D.
2	79.11	0.12	-0.88	-15.22	-3.41	24	$< 4.1 \times 10^{-15}$	0.98	0.27
3	68.89	-0.51	-0.69	-12.06	-1.27	24	$< 3.2 \times 10^{-9}$	0.94	0.36
4	73.15	-0.32	-0.92	-12.20	-1.67	24	$< 2.3 \times 10^{-8}$	0.93	0.44
5	66.27	-1.79	-0.42	-13.10	0.35	24	$< 4.8 \times 10^{-5}$	0.84	0.60
6	72.99	-0.66	-0.50	-14.33	-4.27	24	$< 5.8 \times 10^{-12}$	0.97	0.44
7	67.71	-0.84	-0.58	-13.28	-3.86	24	$< 1.9 \times 10^{-13}$	0.98	0.34
<sup>a</sup> Equation (3) was used (see text).									



**Figure 8**. Relationship between calculated and measured  $E_T$  for dye **2** considering Kamlet–Abboud–Taft and Catalán strategies

compounds **6** and **7**, but the inconsistencies observed with the use of Equation (2) remained. No improvements were obtained with the use of Equation (5), the only exception being in the case of dye **5** (from R = 0.84 to 0.91). Thus, the results offered by the Catalán approach suggest that the contribution of the lipophilic methyl groups to the solvatochromism of the compounds can be neglected.

$$E_{T}(dye) = E_{T}(dye)_{0} + a\alpha + b\beta + s(\pi^{*} + d\delta) + p(logP)$$
 (4)

$$E_{T}(dye) = E_{T}(dye)_{0} + aSA + bSB + cSP + dSdP + p(logP)$$
(5)

Another important aspect to be analyzed through a comparison of the data shown in Table 5 concerns the

fact that for all dyes studied the most important contribution from the solvent is associated with the polarizability of the medium. Considering the data in Table 5, the c/a ratio for the polarizability and acidity coefficients shows that, for probe **2**, c/a = 15.22/0.120 = 127, while a comparison between the contribution of polarizability and dipolarity terms shows c/d = 15.22/3.41 = 4.46. The highest c/d ratios were obtained for dyes **3** and **5**, 9.49 and 37.4, respectively. This observation, which is valid for all other dyes studied, confirms the importance of the contribution of the polarizability term to the solvatochromism reported for these probes.

Table 6 shows the influence of each parameter using the Catalán multiparametric analysis [Equation (3)] on the fitting of the data for dyes 2 and 3 (see Supporting Information for the other dyes). The use of the equation with the suppression of the polarizability term to fit the data led to a decrease in the R value from 0.98 to 0.78 for dye 2, while the influence of the acidity and basicity parameters on this relationship was negligible. The suppression of the dipolarity term resulted in a decrease in the R value (0.82). However, the most important effect was observed with the suppression of the combined dipolarity and polarizability terms in Equation (3), with a decrease in the R value from 0.98 to 0.19 for dye 2. It was also verified that suppressing both the acidity and basicity terms in Equation (3) resulted in an R value of 0.97, which is practically the same as the value obtained when all solvent terms were used. Similar results were obtained for dye  $\mathbf{3}$ , with a reduction in the R value from 0.94 to 0.58 and 0.89 with the suppression of polarizability and dipolarity terms in Equation (3), respectively, and to 0.13 with the removal of both polarizability and dipolarity terms. For all other dyes the suppression of the acidity and the basicity terms did not significantly alter the R values. For instance, for dyes 6 and 7, the R values remained almost the same with the suppression of the acidity and basicity terms (see Supporting Information). On the other hand, the suppression of the polarizability and dipolarity terms resulted in a reduction in the R value from 0.97 to 0.82

Table 6.	Influence of each	parameter in Catalá	n multiparametric	analysis <sup>a</sup> on	the fitting of	data for dyes 2 and 3	i i
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	Constant	а	b	с	d	Ν	F	R	S.D.
2	79.11	0.12	-0.88	-15.22	-3.41	24	$< 4.1 \times 10^{-15}$	0.98	0.27
	79.15	-	-0.86	-15.28	-3.40	24	$< 2.2 \times 10^{-16}$	0.98	0.27
	78.20	-0.26	-	-14.24	-3.70	24	$< 1.0 \times 10^{-13}$	0.97	0.36
	78.06	-	-	-1.06	-3.73	24	$< 7.1 \times 10^{-15}$	0.97	0.36
	68.49	1.20	0.13	-	-4.58	24	$< 2.2 \times 10^{-4}$	0.78	1.08
	80.47	-0.38	-1.99	-19.40	-	24	$< 2.8 \times 10^{-5}$	0.82	0.97
	77.66	-	-	-16.98	-	24	$< 3.5 \times 10^{-5}$	0.74	1.11
	66.19	0.89	-1.08	-	-	24	<0.68	0.19	1.67
3	68.89	-0.51	-0.69	-12.06	-1.27	24	$< 3.2 \times 10^{-9}$	0.94	0.36
	68.71	-	-0.78	-11.82	-1.30	24	$< 7.1 \times 10^{-10}$	0.94	0.36
	68.18	-0.82	-	-11.29	-1.51	24	$< 5.3 \times 10^{-9}$	0.93	0.40
	67.72	-	-	-10.72	-1.61	24	$< 2.1 \times 10^{-9}$	0.92	0.42
	60.48	0.34	0.10	-	-2.20	24	$< 3.4 \times 10^{-2}$	0.58	0.90
	69.40	-0.70	-1.11	-13.62	-	24	$< 3.4 \times 10^{-7}$	0.89	0.50
	67.55	-	-	-11.98	-	24	$< 1.1 \times 10^{-6}$	0.81	0.61
	59.37	0.18	-0.47	-	-	24	<0.83	0.13	1.08
<sup>a</sup> Equat	ion (3) was used	(see text).							



**Figure 9**. Relationship between calculated and measured  $E_T$  for dyes **3** and **7** considering Catalán strategy [Equation (3)] using (**A**) all parameters, (**B**) without *SP* parameter, (**C**) without *SdP* parameter, and (**D**) without both *SP* and *SdP* parameters

and 0.75, respectively, for dye **6** and from 0.98 to 0.97 and 0.77, respectively, for dye **7**. The simultaneous removal of the two terms lowered the correlation coefficients, to R = 0.16 for dye **6** and to R = 0.19 for dye **7**.

Figure 9 shows plots of the experimentally obtained  $E_{\rm T}$  (dye) values as a function of the  $E_{\rm T}$ (dye) value calculated for dyes **2** and **3**, using the data from Table 5. The plots verify the contribution of the polarizability and, to a lesser extent, the dipolarity to the solvatochromism of the dyes studied. In addition, it is clear from the plots that the suppression of both the polarizability and dipolarity contributions weakened considerably the correlation between the experimental and calculated data. The results suggest that dyes **2–7** are good candidates for use as probes to measure, with high efficiency, the dipolarity/polarizability of the solvents, with negligible ability to report the influence of the acidity and basicity of the medium.

## CONCLUSIONS

Compounds 2-7 are solvatochromic and can be used as probes in the investigation of the physico-chemical properties of the solvents. The conjugated bridge influences the solvatochromic properties of the dyes, compounds 6 and 7, with the azo bridge, having a more pronounced solvatochromism. The data suggest that the reverse solvatochromism observed for all compounds studied is due to the differential solvation of the medium on the resonance structures of the compounds. This differential solvation of the two forms, dipolar and benzenoid, changes the extent of the contribution of each species and is responsible for the type of solvatochromism observed.

The multiparametric approaches applied to the data obtained for the six compounds revealed that the Catalán equation provided a better fit with the experimental data and that the use of log P improved only slightly the relationships. In addition, this study showed that for these dyes the ability to probe the basicity of the medium is negligible, which was expected based on the analysis of their molecular structure. However, the multiparametric analysis revealed that the contribution of the acidity parameter to the overall solvatochromism of the dyes studied is small, which is somewhat surprising considering that all compounds have a dimethylamino group in their molecular structure, which is, in principle, able to interact, as a HBA group, with the medium. Therefore, the data suggest that the electronic density of the amino group is delocalized due to the presence of the electron withdrawing nitro groups in the acceptor moiety of the molecules. Finally, the multiparametric analysis of the data showed that the main factor contributing to the solvatochromism exhibited by compounds 2-7 is the

polarizability parameter and, to a lesser extent, the dipolarity parameter, which makes these compounds good candidates for the investigation of these types of physical properties of the medium, the interference of specific interactions of the solvent through hydrogen bonding being negligible.

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