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Solvatochromism of New Substituted 4-[(E)-(4-

Nitrophenyl)diazenyl]phenolate Dyes

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ABSTRACT

Studies on the reverse solvatochromism of dyes in pure solvents are of interest to gain a better understanding of the nature of this phenomenon. In this paper, a series of nine compounds, exhibiting phenol and 4-nitrophenyl groups linked with an azo conjugated bridge, was synthesized and characterized. These compounds were deprotonated to generate solvatochromic phenolate dyes. The azo bridge makes the phenol more acidic, in comparison with the related compounds exhibiting a CH=CH or CH=N bridge in their molecular structure, indicating the electron withdrawing character of the azo bridge. The solvatochromism of the dyes was investigated in 29 solvents and their intense colors in solution were attributed to $\pi - \pi^*$ electronic transitions, with an intramolecular charge transfer from the phenolate towards the 4-nitroaryl group. The probes exhibited a reversal in their solvatochromism, in a similar fashion to the behavior verified with related dyes presenting CH=CH or CH=N as the conjugated bridge; however, the azo dyes are much less sensitive to solvent polarity changes. Multiparametric analysis showed that the azo dyes are very sensitive to the acidity of the medium, but still to a lesser degree than the corresponding imine and stilbene dyes, due to the electronegativity of the azo group. The reverse solvatochromism of the dyes is dictated by the electron-donor phenolate and by the electron-acceptor 4-nitroaryl groups, independently of the conjugated bridge, of the additional nitro group and of the nature of substituents in the 2,6-positions of the phenolate groups. Thus, the solvatochromic reversal verified represents a committed step involving the interaction of the nitro and phenolate groups in the probe with the molecules of structurally different solvents.

Keywords: solvatochromic dyes; reverse solvatochromism; solvatochromism; solute/solvent interactions; azo dyes; molecular dynamics

1. Introduction

Organic solvents are commonly used in many chemical procedures, such as in the preparation of solutions used as media in chemical reactions, and in different processes for the separation and purification of compounds. The medium influences the rate and position of equilibrium of many chemical processes and is responsible for important changes in the spectra for many chemical species.[1-4] This influence is commonly attributed to the polarity of the medium, a term that considers all specific and non-specific interactions involved in the overall solvation of a given solute by the solvent molecules.[1-6] To simplify our understanding of the complex phenomenon of solvation, the solvatochromic approach has been used in recent decades.[1-8] This strategy involves the use of solvatochromic dyes, which are probes that are sensitive to changes in the polarity of the medium. In other words, by varying the polarity of the solvent the position and/or maximum intensity of the absorption (or emission) band of the probe is modified. [2, 5-11] The most popular solvatochromic probe is (2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate) (1; Figure 1), known as Reichardt's dye.[12] This pyridinium N-phenolate betaine dye is well known for its very pronounced negative solvatochromic behavior, i.e., the vis solvatochromic band of the probe is hypsochromically shifted with an increase in the polarity of the solvent. This compound is the basis for the $E_{\rm T}(30)$ empirical solvent polarity scale, [2, 8, 9, 12, 13] defined by the expression: $E_{\rm T}(30) = 28590/\lambda_{\rm max}$, where $\lambda_{\rm max}$ is the maximum wavelength given in nm for the vis solvatochromic band for the dye in the solvent and $E_{\rm T}(30)$ represents the mole transition energy, in kcal mol⁻¹, for this electronic transition. Compound 2, Effenberger's dye, [14, 15] is a known example of a probe which exhibits

a positive solvatochromism, with the vis solvatochromic band of the probe undergoing a bathochromic shift when the polarity of the solvent is increased.

 NO_2

3



Figure 1. Molecular structure of compounds 1-3.

 0^{Θ}

1

Other classical example of a solvatochromic dye is Brooker's merocyanine (3).[16] Solvatochromic studies involving this dye have revealed an intriguing behavior: a reversal in the solvatochromism occurs in the region comprising low-polarity solvents. This phenomenon has been the subject of debate for the past sixty years, with many experimental and theoretical investigations, because a reversal of the solvatochromism occurs in solvents in which the dye is poorly soluble, with the possibility of self-aggregation in solution.[16-22]

Several theories have been proposed to explain the solvatochromic behavior of merocyanines and other related dyes. In these compounds a solvent-dependent internal charge transfer (CT) from an electron–donor to an electron–acceptor moieties (**D** and **A**) has been verified, which are eventually connected to an unsaturated conjugated bridge.

Based on the classical *cyanine–limit* model [23], the solvatochromism in merocyanines and related dyes can be described considering the contributions of a neutral (**N**) and a zwitterionic (**Z**) resonance structure to the resonance hybrid of the probe. The weight of the contribution of these resonance structures is influenced by the

type of **D**, **A**, and connector used, which is also responsible for changes in the **D**–**A** strength of the end groups (S_{D-A}) of the solvatochromic dye and consequently to changes in the transition energy of the solvatochromic band of the probe.[23, 24] According to this theory, two classes of compounds, I and II, can be identified.[24-26] Class I dyes have charged **D** and **A** groups in their ground state, being predominantly zwitterionic, while Class II dyes have neutral **D** and **A** moieties in their ground state. Pyridinium *N*-phenolate betaine **1** and compound **2** are examples of Class I and Class II dyes, respectively.

A more recent model, the *generalized reversal* model,[24] which complements the cyanine–limit model, describes all types of solvatochromic behavior in merocyanines (and related dyes) as particular cases of a general reversal behavior. It addresses how modifications in the molecular structure of the probe displace the position of the solvatochromic reversal along an extended solvent–polarity scale. According to this theory, experimental solvatochromic plots can be fitted to a hyperbolic function of a solvent–polarity parameter, allowing a direct comparison between experimental and theoretical results.[24]

Thus, investigations on the systems which exhibit a clear experimental inverted solvatochromism, in solvents of intermediate polarity, represent important contributions to an in-depth analysis of these theories. These probes should be easily soluble in such media, in order to inhibit the possibility of self-aggregation.[27-31]

In recent years we have investigated the solvatochromism of a family of dyes comprised of a charged phenolate electron–donor and neutral nitroaryl electron– acceptor moieties, which are connected through an unsaturated ethylene or methyleneimino bridge.[27-29, 31, 32] Two examples of these compounds are the 4– (4–nitrobenzylideneamino)phenolate **4b** and the 4-(4-nitrostyryl)phenolate **5b** (**Figure**

2), which are generated in solution by deprotonation of their corresponding phenols 4a and 5a. These dyes exhibit an experimentally well-defined reverse solvatochromism in solvents with medium polarity, such as DMSO ($E_{\rm T}(30) = 45.1$ kcal mol⁻¹; $E_{\rm T}^{\rm N} = 0.444$) and DMA ($E_{\rm T}(30) = 42.9$ kcal mol⁻¹; $E_{\rm T}^{\rm N} = 0.377$). Their solvatochromism has been investigated in many solvents of different polarity, from water to *n*-hexane, allowing the influence of various structural features on the reverse solvatochromism of merocyanines and other related solvatochromic dyes to be investigated. Thus, these compounds can be considered "hybrid cyanine" solvatochromic probes and are neither Class I nor Class II dyes, although they exhibit structural features from both classes of dyes.



Figure 2. Molecular structures of phenols 4a and 5a and "hybrid cyanine" dyes 4b and 5b.

In the study reported herein, compounds **6a-14a** (**Figure 3**) were synthesized and characterized. These compounds were deprotonated to generate solvatochromic dyes **6b-14b**, and their solvatochromism was investigated in 29 solvents. The behavior verified was compared with that exhibited by the families of related dyes represented by dyes **4b** and **5b**, to verify the influence of the conjugated bridge (CH=CH, CH=N and N=N) on the solvatochromism of the dyes.



		6a,b	7a,b	8a,b	9a,b	10a,b	11a,b	12a,b	13a,b	14a,b
-	R ¹	Н	Н	Н	Η	Н	NO ₂	NO ₂	NO ₂	NO ₂
	R ²	Н	CH ₃	Cl	Br	Ph	Н	CH ₃	Cl	Br
Figure 3. Molecular structure of compounds 6a,b–14a,b .										

2. Experimental

2.1. Materials and methods

I

All reagents used in the synthesis of the compounds were analytically pure and were purchased from commercial sources (Sigma–Aldrich and Vetec). They were employed without any further purification. All solvents were HPLC grade and were purified following a methodology described in the literature.[33, 34] Deionized water was used in all measurements, and it was boiled and bubbled with nitrogen and kept in a nitrogen atmosphere to avoid the presence of carbon dioxide. The aqueous Britton-Robinson buffer was prepared through the mixing of 1.2 g of boric acid, 1.2 mL of glacial acetic acid, 1.1 mL of phosphoric acid and 497.7 mL of deionized water.[35]

The melting points were determined through DSC analysis using a Perkin Elmer Jade-DSC and a Shimadzu DSC-50. The IR spectra were obtained with KBr pellets on a FT Varian 3100 spectrometer. The NMR spectra were recorded in DMSO- d_6 or acetone- d_6 using 200–MHz Bruker AC–200F and 400–MHz Bruker Avance 400 spectrometers. Chemical shifts were recorded in ppm with the solvent resonance as the internal standard and data are reported as follows: chemical shift, multiplicity (s =

singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a Bruker OTOF–Q II 10243 electrospray ionization-quadrupole time-of-flight mass spectrometer (HR ESI-MS QTOF). UV–vis spectra were obtained with an Agilent Technologies Cary 60 spectrometer. The pK_a values were determined using a benchtop pH meter Kasvi K39-1014B and the pH measurements were recorded at 25.0 °C.

2.2. Synthesis of the compounds 6a-9a and 11a-14a

Compounds **6a-9a** and **11a-14a** were synthesized according to a methodology adapted from Keil *et al.*[36] In an Erlenmeyer flask, 0.4 mmol of the corresponding amine (4-nitroaniline or 2,4-dinitroaniline), 7.2 mL of glacial acetic acid and 720 μ L of concentrated HCl were mixed in an ice bath (0 °C). In parallel, in another Erlenmeyer flask, also in an ice bath, 0.4 mmol of the corresponding phenol and 5 mL of dry methanol were mixed. An aqueous solution of NaNO₂ (0.4 mol L⁻¹, 1 mL) was then added to a solution of the amine. The reaction mixture was stirred for 30 min and then poured into the mixture containing the phenol. In the next step, 50 mL of deionized water was added to the resulting reaction solution to precipitate the product that was collected by filtration. Compounds **6a-9a** and **11a-14a** were recrystallized from a water:ethanol mixture (1:1 v/v).

4-[(*E*)-(4-Nitrophenyl)diazenyl]phenol (**6a**). Brown solid (yield: 40%). M.p.: 212.49 °C. IR (KBr, \bar{v}_{max} /cm⁻¹): 3406 (OH); 1603 and 1584 (aromatic C=C); 1505 and 1336 (NO₂); 1458 (N=N); 1138 (C-O). ¹H NMR (200 MHz, DMSO-*d*₆) δ /ppm: 10.59 (*s*, 1H); 8.41 (*d*, 2H, *J* = 9.0 Hz); 8.00 (*d*, 2H, *J* = 9.0 Hz); 7.89 (*d*, 2H, *J* = 8.8 Hz); 6.99 (*d*, 2H, *J* = 8.8 Hz). ¹³C NMR (50 MHz, DMSO-*d*₆) δ /ppm: 162.31; 155.51; 147.71; 145.36;

125.75; 124.95; 122.94; 116.19. HRMS m/z: 242.0556 [M-H]⁻, calculated for $C_{12}H_8N_3O_3^-$, 242.0560.

2,6-Dimethyl-4-[(*E*)-(4-nitrophenyl)diazenyl]phenol (**7a**). Orange solid (yield: 82%). M.p.: 188.04 °C. IR (KBr, \bar{v}_{max} /cm⁻¹): 3512 (OH); 1591 (aromatic C=C); 1519 and 1340 (NO₂); 1474 (N=N); 1340 (CH₃); 1119 (C-O). ¹H NMR (200 MHz, DMSO-*d*₆) δ /ppm: 9.43 (*s*, 1H); 8.40 (*d*, 2H, *J* = 9.0 Hz); 7.99 (*d*, 2H, *J* = 9.0 Hz); 7.63 (*s*, 2H); 2.26 (*s*, 6H). ¹³C NMR (50 MHz, DMSO-*d*₆) δ /ppm: 158.44; 147.60; 145.01; 128.09; 124.98; 124.15; 122.80; 16.54. HRMS *m*/*z*: 270.08726 [M-H]⁻, calculated for C₁₄H₁₂N₃O₃⁻, 270.08732.

2,6-Dichloro-4-[(*E*)-(4-nitrophenyl)diazenyl]phenol (**8a**). Orange solid (yield: 55%). M.p.: 199.15 °C. IR (KBr, \bar{v}_{max} /cm⁻¹): 3416 (OH); 1603 and 1584 (aromatic C=C); 1523 and 1342 (NO₂); 1454 (N=N); 1136 (C-O); 801 (C-Cl). ¹H NMR (200 MHz, DMSO-*d*₆) δ /ppm: 8.32 (*d*, 2H, *J* = 8.6 Hz); 7.87 (*d*, 2H, *J* = 8.6 Hz); 7.83 (*s*, 2H). ¹³C NMR (50 MHz, acetone-*d*₆) δ /ppm: 156.69; 154.21; 150.39; 146.81; 126.22; 125.22; 124.86; 124.18. HRMS *m*/*z*: 309.9785 [M-H]⁻, calculated for C₁₂H₆Cl₂N₃O₃⁻, 309.9781.

2,6-Dibromo-4-[(*E*)-(4-nitrophenyl)diazenyl]phenol (**9a**). Dark yellow solid (yield: 40%). M.p.: 198.31 °C. IR (KBr, \bar{v}_{max} /cm⁻¹): 3418 (OH); 1607 and 1582 (aromatic C=C); 1521 and 1344 (NO₂); 1466 (N=N); 1136 (C-O); 740 (C-Br). ¹H NMR (200 MHz, DMSO-*d*₆) δ /ppm: 8.44 (*d*, 2H, *J* = 8.8 Hz); 8.17 (*s*, 2H); 8.04 (*d*, 2H, *J* = 8.8 Hz). ¹³C NMR (50 MHz, DMSO-*d*₆) δ /ppm: 155.66; 154.49; 148.15; 145.18; 127.64; 125.05; 123.10. HRMS *m*/*z*: 399.8751 [M-H]⁻, calculated for C₁₂H₆Br₂N₃O₃⁻, 399.8750.

4-[(*E*)-(2,4-Dinitrophenyl)diazenyl]phenol (**11a**). Red solid (yield: 55%). M.p.: 191.79 °C. IR (KBr, \bar{v}_{max} /cm⁻¹): 3471 (OH); 1603 and 1584 (aromatic C=C); 1519 and 1342 (NO₂); 1460 (N=N); 1142 (C-O). ¹H NMR (200 MHz, DMSO-*d*₆) δ /ppm: 10.87 (*s*, 1H); 8.92 (*d*, 1H, *J*₁ = 2.3 Hz); 8.61 (*dd*, 1H, *J*₁ = 2.3 Hz and *J*₂ = 8.8 Hz); 7.90 (*t*, 3H, *J*₂ = 8.8 Hz and *J*₃ = 8.8 Hz); 7.01 (*d*, 2H, *J*₃ = 8.8 Hz). ¹³C NMR (100 MHz, DMSO-*d*₆) δ /ppm: 163.54; 147.58; 146.98; 146.28; 145.60; 128.27; 126.67; 129.13; 119.98; 116.55. HRMS *m*/*z*: 287.0415 [M-H]⁻, calculated for C₁₂H₇N₄O₅⁻, 287.0411.

2,6-Dimethyl-4-[(*E*)-(2,4-dinitrophenyl)diazenyl]phenol (**12a**). Yellow solid (yield: 45%). M.p.: 224.71 °C. IR (KBr, \bar{v}_{max}/cm^{-1}): 3286 (OH); 1611 and 1595 (aromatic C=C); 1511 and 1348 (NO₂); 1325 (CH₃); 1427 (N=N); 1136 (C-O). ¹H NMR (200 MHz, DMSO-*d*₆) δ /ppm: 8.90 (*d*, 1H, *J*₁ = 2.4 Hz); 8.60 (*dd*, 1H, *J*₁ = 2.4 Hz and *J*₂ = 9.0 Hz); 7.87 (*d*, 1H, *J*₂ = 9.0 Hz); 7.57 (*s*, 2H); 2.24 (*s*, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ /ppm: 147.57; 146.43; 145.42; 145.13; 128.31; 126.24; 125.07; 120.21; 120.04; 16.63. HRMS *m*/*z*: 315.0723 [M-H]⁻, calculated for C₁₄H₁₁N₄O₅, 315.0724.

2,6-Dichloro-4-[(*E*)-(2,4-dinitrophenyl)diazenyl]phenol (**13a**). Brown solid (yield: 43%). M.p.: 177.31 °C. IR (KBr, \bar{v}_{max}/cm^{-1}): 3404 (OH); 1599 and 1562 (aromatic C=C); 1527 and 1348 (NO₂); 1325 (CH₃); 1474 (N=N); 1148 (C-O); 799 (C-Cl). ¹H NMR (200 MHz, DMSO- d_6) δ /ppm: 8.81 (d, 1H, J_1 = 2.3 Hz); 8.52 (dd, 1H, J_1 = 2.3 Hz and J_2 = 8.9 Hz); 8.44 (d, 1H, J_1 = 2.4 Hz); 8.19 (dd, 1H, J_1 = 2.4 Hz and J_2 = 8.9 Hz); 8.01 (s, 2H); 7.96 (s, 2Hz); 7.80 (d, 1H, J_2 = 8.9 Hz); 7.77 (d, 1H, J_2 = 8.9 Hz). ¹³C NMR (50 MHz, CDCl₃ and acetone- d_6) δ /ppm: 143.87; 143.64; 129.83; 129.29; 128.04; 127.66; 127.16; 125.89; 124.42; 124.11; 123.84; 123.49; 122.68; 122.62; 122.42;

119.94; 119.04; 118.15; 117.19. HRMS m/z: 354.9729 [M-H]⁻, calculated for C₁₂H₅Cl₂N₄O₅⁻, 354.9632.

2,6-Dibromo-4-[(*E*)-(2,4-dinitrophenyl)diazenyl]phenol (**14a**). Orange solid (yield: 52%). M.p.: 210.70 °C. IR (KBr, \bar{v}_{max} /cm⁻¹): 3390 (OH); 1597 (aromatic C=C); 1527 and 1344 (NO₂); 1462 (N=N); 1142 (C-O); 728 (C-Br). ¹H NMR (200 MHz, DMSO-*d*₆) δ /ppm: 8.94 (*d*, 1H, *J*₁ = 2.4 Hz); 8.63 (*dd*, 1H, *J*₁ = 2.4 Hz and *J*₂ = 8.8 Hz); 8.10 (*s*, 2H); 7.87 (*d*, 1H. *J*₂ = 8.8 Hz). ¹³C NMR (50 MHz, DMSO-*d*₆) δ /ppm: 149.78; 135.11; 129.29; 128.68; 128.33; 123.36; 120.24; 119.83; 119.75; 113.55. HRMS *m*/*z*: 444.8604 [M-H]⁻, calculated for C₁₂H₅Cl₂N₄O₅⁻, 444.8601.

2.2. Synthesis of compound 10a

Compound **10a** was synthesized according to a methodology adapted from Rajagopal and Buncel.[37] In an Erlenmeyer flask, 0.4 mmol of 4-nitroaniline and 4 mL of 4 mol L⁻¹ HCl were mixed in an ice bath (0 °C). Simultaneously, in another Erlenmeyer flask, also in an ice bath (0 °C), 0.4 mmol of 2,6-diphenylphenol, 10 mL of dry ethanol, 0.3 mmol of sodium tetraborate (borax) and 5 mL of an aqueous NaOH solution (1.7 mol L⁻¹) were mixed. An aqueous NaNO₂ solution (0.15 mol L⁻¹; 2 mL) was then added to the solution of the amine and the reaction mixture was stirred for 1 min and then poured into the mixture containing the phenol. The medium was acidified until pH 6 and the solid product formed was collected by filtration. Compound **10a** was purified by silica gel column chromatography using an *n*-hexane:ethyl acetate mixture (9:1 v/v) as the eluent.

2,6-Diphenyl-4-[(*E*)-(4-nitrophenyl)diazenyl]phenol (**10a**): Red-orange solid (yield: 20%). M.p.: 187.98 °C. IR (KBr, \bar{v}_{max}/cm^{-1}): 3520 (OH); 1588 (aromatic C=C); 1519

and 1331 (NO₂); 1462 (N=N); 1138 (C-O). ¹H NMR (200 MHz, acetone- d_6) δ /ppm: 8.45 (d, 2H, J = 9.1 Hz); 8.12 (d, 2H, J = 9.1 Hz); 7.95 (s, 2H); 7.69 (m, 3H); 7.53 (m, 3H); 7.46 (m, 6H). ¹³C NMR (50 MHz, acetone- d_6) δ /ppm: 138.87; 131.36; 130.99; 130.56; 129.79; 129.36; 129.22; 128.51; 126.65; 126.24; 124.61. HRMS m/z: 394.1187 [M-H]⁻, calculated for C₂₄H₁₆N₃O₃, 394.1186.

2.3. UV-vis measurements

The following procedure was typical for all measurements performed. A 7.0×10^{-3} mol L⁻¹ stock solution of each compound was prepared in acetone. From this stock solution, 3-12 µL were transferred to twenty-nine 5 mL volumetric flasks. After evaporation of the acetone, the probe was dissolved in the pure solvent, resulting in a solution presenting a final dye concentration of 1.0×10^{-5} to 4.0×10^{-5} mol L⁻¹. In order to generate the deprotonated compounds, 5 µL of an aqueous tetra-n-butylammonium hydroxide solution (0.1 mol L^{-1}) was added to each flask. The addition of this very small amount of water did not change the position of the UV-vis band of the dye. The bulky tetra-n-butylammonium ion has no influence on the UV-vis spectrum of the anionic dye. The UV-vis spectra were recorded at 25.0 °C, using a 1-cm square cuvette. The maxima of the UV-vis spectra were calculated from the first derivative of the absorption spectrum, with a precision of ± 0.5 nm, and the reproducibility of the λ_{max} values was verified through the determination of five spectra for each dye in each pure solvent. The λ_{max} values thus obtained were transformed into $E_T(dye)$ values, according to the expression $E_{\rm T}({\rm dye}) = 28590/\lambda_{\rm max}$, [2, 3, 9] given in kcal mol⁻¹ with a precision of ± 0.1 kcal mol⁻¹.

2.4. Determination of pK_a

Stock solutions of compounds **6a-14a** were prepared in acetone with a concentration of 7.0×10^{-3} mol L⁻¹. The aqueous Britton-Robinson buffer was placed in a beaker in the amount appropriate to perform the study and the pH meter electrode was then immersed in it. Aliquots of an aqueous NaOH solution (0.1 mol L⁻¹) were added under magnetic stirring, in order to adjust the pH. When the desired pH was reached, 1.5 mL of the solution was transferred to a cuvette, 9 µL of the stock solution of the dye was added to give a concentration of 4.0×10^{-5} mol L⁻¹ and the UV-vis spectrum was then collected. This procedure was carried out for all compounds at different pH values and the absorbances were collected at the λ_{max} values corresponding to the deprotonated species. Plots of pH as a function of absorbance were constructed (**Figure S47**) and the p*K*_a values were determined from a sigmoidal fit of the curve using the Boltzmann equation.

3. Calculation Methods

The multiparametric analysis was performed from non-linear regressions using ORIGIN 8.5 software. Optimizations were carried out using the ORCA quantum chemistry package, version 4.1.1,[38] at the ω B97X-D3/ma-def2-TZVP/SMD [39-44] level of theory, with both water and *n*-hexane as implicit solvents. Resolution of identity was used throughout the calculations.[45, 46] Vibrationally-resolved spectra were obtained using the ESD module of ORCA.[47] Molecular dynamics simulations were performed using the GROMACS package,[48] with the OPLS–AA force field [49] and the SPC/E model [50] for water. Simulation boxes containing the solvents (water, DMF and *n*-hexane) were thermalized at the NVT ensemble (298 K, $\tau = 0.1$ ps) for 500 ps and equilibrated at the NPT ensemble (1 bar, $\tau = 0.5$ ps) for 2 ns. Atomic charges for

compounds **4b-6b** were obtained with the Ante RED software,[51] with the GAMESS package [52] at the HF/6-31G** level of theory.[53, 54] Relevant molecular mechanics (MM) parameters are described in the Supporting Information (**Tables S6** and **S7**).

4. Results and discussion

The synthesis of compounds **6a-14a** was performed in two steps according to procedures adapted from the literature [36, 37], as shown in **Scheme 1**. Firstly, the nitroanilines were reacted with sodium nitrite in acidic medium, in an ice bath, to form the corresponding diazonium salts. The coupling reaction products were obtained with the addition of the corresponding phenols in dried methanol (compounds **6a-9a** and **11a-14a**) or in a basic ethanolic borax solution (compound **10a**). Compounds **6a-9a** and **11a-14a** were recrystallized from a water:ethanol mixture (1:1 v/v) and compound **10a** was purified by silica gel column chromatography using a *n*-hexane:ethyl acetate mixture (9:1 v/v) as the eluent. The products of the reactions were obtained in yields of 20-82%. Compounds **6a-14a** were characterized using IR, ¹H NMR, ¹³C NMR, HRMS, and DSC techniques.



Scheme 1. Preparation of compounds 6a-14a.

Table 1 gives the pK_a values for compounds **6a–14a** at 25.0 °C. Electron withdrawing groups in the phenol moiety reduce the pK_a while methyl and phenyl groups reduce the acidity of the compounds. The data also show that, in general, the presence of a second nitro group in the molecule reduces the pK_a value. However, for compounds **7a** and **12a** the presence of an additional nitro group leads to **12a** 1.1 pK_a unit less acidic than **7a**. These compounds are more acidic than 2,6-dimethylphenol ($pK_a = 10.59$ [55]), which is expected from the electron withdrawing substituents in the *para* position of **7a** and **12a**. Thus, the fact that compound **12a** is less acidic than **7a**.

Dye ^a	pK ^{ab}
ба	8.01 ± 0.01
7a	8.83 ± 0.01
8a	5.63 ± 0.04
9 a	5.68 ± 0.03
10a	11.43 ± 0.03
11a	7.63 ± 0.03
12a	9.90 ± 0.01
13a	5.28 ± 0.02
14a	5.25 ± 0.03
	Dye ^a 6a 7a 8a 9a 10a 11a 12a 13a 14a

Table 1. The p K_a values for compounds **6a–14a** at 25.0 °C.

 ^{a}c (dye) = 4×10⁻⁵ mol L⁻¹.

^b Calculated by spectrophotometric method using aqueous Britton-Robinson buffer.

Buncel and Rajagopal verified that the azo bridge represents a powerful acceptor group in merocyanine dyes.[56] The influence of the conjugated bridge on the acidity of the nitrophenols can be observed by comparing the pK_a of **6a** (8.01± 0.01), with those of the iso- π -electronic compounds **4a** (10.57±0.01)[57] and **5a** (10.79 ±

0.02).[58] These results demonstrate that the 4-(nitrophenyl)diazenyl group makes the phenol more than 2.5 p K_a units more acidic, which illustrates the electron withdrawing character of the azo bridge.

4.1. Solvatochromism of probes 6b-14b

Figure 4A shows the solutions of dye 9b in four selected solvents, while Figure 4B provides the corresponding UV-vis spectra, confirming that the compound is solvatochromic. In methanol, the absorption band for this dye has a maximum at 486 nm, which is displaced to $\lambda_{max} = 519$ nm in toluene, while in dimethoxyethane and acetophenone the band maximum is shifted to 550 and 571 nm, respectively. The other azo dyes studied exhibited a similar behavior (Figures S48 and S49), their intense colors being a result of π - π * electronic transitions, with an intramolecular CT from the electron-donor phenolate towards the 4-nitrophenyl (or 2,4-dinitrophenyl) electronacceptor group.



Figure 4. (A) Solutions and (B) UV-vis spectra of dye 9b in (a) methanol, (b) toluene,(c) dimethoxyethane, and (d) acetophenone.

Experiments were performed, according to a previously described methodology[59], to discard the possibility of *cis–trans* isomerization as a source of the observed spectral changes. No significant changes in the form and position of the solvatochromic bands were verified (**Figure S50**). In addition, the possibility of dye aggregation within the range of absorbance readings collected was also discarded as a cause of the observed solvatochromic reversal. Plots of the absorbance reading as a function of the dye concentration in ethyl acetate and methanol, two solvents of widely different polarities, were all linear (**Figures S51-S59**).

Compounds 6b-14b are salts, which can form, in principle, ion pairs in solution, especially in low polarity solvents, which would influence the absorption spectra. Although studies performed previously with related dyes have demonstrated that the possibility of the formation of ion pairs can be discarded, [27] some experiments to verify this were conducted. Thus, the influence of the addition of increasing amounts of tetra-*n*-butylammonium iodide on the UV-vis absorption spectrum of dye 13b in toluene was investigated. The addition of this salt at a concentration of up to 1.9×10^{-3} mol L⁻¹ did not cause a shift or changes in the form of the solvatochromic band of the probe (Figure S60). In another experiment, compound 6a in toluene was deprotonated to form dye 6b through the addition of KOH (Figure S61). The UV-vis spectrum was obtained and the solvatochromic band of **6b** had a λ_{max} value of 424 nm, which is much lower than the value obtained when tetra-*n*-butylammonium hydroxide is used (λ_{max} = 516 nm), due to the electrostatic interaction of K^+ with the phenolate moiety of the dye. It was verified that the addition of 18-crown-6, which is highly selective for K^+ , leads to the spectrum obtained being exactly the same as that measured in the presence of tetra*n*-butylammonium hydroxide. Thus, the experiments allow us to conclude that the

presence of the tetra-*n*-butylammonium cation does not influence the solvatochromism of the dyes.

The UV-vis spectra for each probe in the 29 solvents were used to obtain the maximum wavelength (λ_{max}) values for the solvatochromic bands, which were required for the calculation of the corresponding transition energies $E_{\rm T} = 28590/\lambda_{\rm max}$, in kcal mol⁻¹ (**Table 2**).

Solvent	$E_{\mathrm{T}}(30)^{\mathrm{a}}$	$E_{\mathrm{T}}(\mathbf{6b})^{\mathrm{b}}$	$E_{\mathrm{T}}(7\mathrm{b})^{\mathrm{b}}$	$E_{\mathrm{T}}(\mathrm{8b})^{\mathrm{b}}$	$E_{\mathrm{T}}(9\mathrm{b})^{\mathrm{b}}$	$E_{\mathrm{T}}(10\mathrm{b})^{\mathrm{b}}$	$E_{\mathrm{T}}(11\mathrm{b})^{\mathrm{b}}$	$E_{\mathrm{T}}(12\mathrm{b})^{\mathrm{b}}$	$E_{\mathrm{T}}(13\mathrm{b})^{\mathrm{b}}$	$E_{\mathrm{T}}(14\mathrm{b})^{\mathrm{b}}$
Cyclohexane	30.9	58.1	52.5	58.0	57.5	51.7	51.8	47.1	52.4	52.0
<i>n</i> -Hexane	31.0	58.3	52.9	58.1	58.2	52.0	52.1	47.3	52.9	52.4
Toluene	33.9	55.4	49.7	56.3	55.1	49.4	50.2	46.3	51.8	50.4
Ethyl ether	34.5	53.3	49.7	54.6	53.7	48.4	48.5	46.9	50.6	49.5
THF	37.4	49.3	45.6	52.1	51.3	45.8	47.1	46.3	50.7	47.5
Ethyl acetate	38.1	50.2	46.5	53.1	52.6	46.9	47.5	47.3	48.5	48.7
Dimethoxyethane	38.2	49.9	45.8	52.3	52.0	46.3	47.2	46.4	48.7	48.1
Trichloromethane	39.1	52.3	47.0	54.1	53.1	47.6	47.5	45.9	49.1	48.6
Acetophenone	40.6	49.4	45.2	51.4	50.1	44.8	46.4	45.4	47.0	46.9
Dichloromethane	40.7	50.7	46.4	53.5	51.9	46.6	47.2	45.7	47.9	47.8
1,2-Dichloroethane	41.3	50.4	46.3	53.0	51.8	46.3	46.9	45.7	47.9	47.5
Acetone	42.2	49.5	46.1	52.1	51.5	46.1	47.5	46.6	48.4	48.5
DMA	42.9	47.4	45.3	50.5	50.6	45.2	47.0	46.0	47.8	48.1
DMF	43.2	47.7	45.5	51.3	51.1	45.5	47.1	46.1	48.2	48.2
2-Methylpropan-2-ol	43.3	51.5	47.7	53.6	53.8	48.0	48.1	46.0	49.5	49.0
DMSO	45.1	47.8	45.2	51.1	51.1	45.5	46.9	45.7	48.0	48.1
Acetonitrile	45.6	50.6	46.8	53.3	52.9	47.2	48.0	46.8	49.3	49.1
Butan-2-ol	47.1	52.8	49.0	54.0	53.9	48.6	48.4	46.0	50.3	49.4
Decan-1-ol	47.7	55.5	50.2	55.6	55.4	49.6	50.1	46.4	51.2	50.4
Octan-1-ol	48.1	54.5	49.7	55.4	55.5	49.7	50.2	46.4	51.2	50.4
Propan-2-ol	48.4	53.8	46.5	54.7	54.8	49.1	49.1	46.4	50.1	50.0
Pentan-1-ol	49.1	55.2	50.1	55.5	56.0	49.8	49.7	46.6	51.0	50.6
Butan-1-ol	49.7	55.6	50.4	55.8	55.7	49.9	50.0	46.7	51.2	50.9
Benzyl alcohol	50.4	55.5	49.7	55.4	55.5	49.5	49.9	46.0	51.6	50.5
Propan-1-ol	50.7	55.6	50.3	56.1	56.4	50.2	50.4	46.8	50.7	51.2
Ethanol	51.9	56.9	51.3	56.7	56.7	50.9	51.2	47.3	52.7	52.0
Methanol	55.4	59.2	53.5	58.9	58.8	52.8	54.0	48.5	54.4	54.3
Ethane-1,2-diol	56.3	58.4	53.2	58.9	58.8	52.4	53.2	47.9	54.5	54.7
Water	63.1	59.7	55.3	60.4	61.0	55.1	55.7	49.6	56.8	57.0

Table 2. $E_{\rm T}(30)$ and $E_{\rm T}(dye)$ values for compounds **6b-14b** in 29 solvents.

^a Values obtained from ref. [2].

^b In kcal mol⁻¹.

Figure 5 shows a plot of the $E_{\rm T}$ values as a function of the $E_{\rm T}(30)$ solvent polarity values for dye **10b**, these being similar to those obtained for the other probes

(Figure S62). In all cases, an inverted behavior was verified, as previously described for analogous dyes.[27-29, 31] As a typical example, for dye 10b, the solvatochromic band has a maximum at 519 nm $[E_T(10b) = 52.0 \text{ kcal mol}^{-1}]$ in *n*-hexane (the least polar solvent studied), while in acetophenone $\lambda_{\text{max}} = 638 \text{ nm} [E_T(10b) = 44.8 \text{ kcal mol}^{-1}]$. This reduction in the $E_T(10b)$ value follows an increase in the medium polarity, leading to a bathochromic shift of $\Delta \lambda_{\text{max}} = +119 \text{ nm}$, characteristic of a positive solvatochromism. A reversal in the solvatochromism starts to occur in the region of the plot obtained with acetophenone as the solvent. A further increase in the solvent polarity leads to an increase in the $E_T(10b)$ value, a negative solvatochromism being verified. The vis band of 10b in water has a maximum at 550 nm $[E_T(10b) = 55.1 \text{ kcal mol}^{-1}]$, which, compared with the same dye in acetophenone, corresponds to $\Delta \lambda_{\text{max}} = -88 \text{ nm}$.



Figure 5. $E_{\rm T}(30)$ value as a function of $E_{\rm T}({\rm dye})$ for dye **10b**.

Table 3 summarizes the inverted behavior of dyes **6b-14b**, in the form of a list of their maximum λ_{max} variations in the least polar, intermediate polarity, and most polar solvents, as well as the $\Delta\lambda_{max}$ values for each dye, considering the regions of positive and negative solvatochromic effects.

A comparison of dyes **6b-14b** with the standard stilbene probe **5b** (**Table S1** and **Figure S63**) could be made with the aid of Eqn. (1), where m measures the average shift of the solvatochromic λ_{max} value for a given dye with respect to dye **5b** and n compares the solvatochromic sensitivity of the dye to polarity changes with that of **5b**.

$$E_{\rm T}(\rm dye) = m + n E_{\rm T}(\mathbf{5b}) \tag{1}$$

Table 3. Values of λ_{max} for compounds **6b–14b** 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 (H ₂ O) λ_{max} (nm)	Intermediate polarity solvent λ_{max} (nm)	Least polar solvent (<i>n</i> -hexane) λ_{max} (nm)	$\Delta \lambda_{\max}^{a}$ (nm)	$\Delta \lambda_{\max}^{b}$ (nm)
6b	479	602 (DMA)	490	+112	-123
7b	517	633 (Acetophenone)	540	+93	-116
8b	474	566 (DMA)	492	+74	-92
9b	469	571 (Acetophenone)	491	+80	-102
10b	550	638 (Acetophenone)	519	+119	-88
11b	513	616 (Acetophenone)	548	+68	-103
12b	577	630 (Acetophenone)	604	+26	-53
13b	503	608 (Acetophenone)	540	+68	-105
14b	502	610 (Acetophenone)	546	+64	-108

^a $\Delta \lambda_{\max} = \lambda_{\max}$ (intermediate solvent) $-\lambda_{\max}$ (*n*-hexane).

^b $\Delta \lambda_{\text{max}} = \lambda_{\text{max}} (\text{H}_2\text{O}) - \lambda_{\text{max}} (\text{intermediate solvent}).$

Table 4 summarizes these values for dyes **6b-14b**. The linear correlations are better for the 4-nitrophenyl in comparison with the 2,4-dinitrophenyl derivatives. Positive values of m were obtained for all dyes, which indicates that the solvatochromic band of the probe is hypsochromically shifted in comparison with the vis band of the standard probe

5b. The presence of substituents on the phenolate moiety makes the m values more positive and the same occurs if the second nitro group is present in the molecular structure of the dye. The inspection of the n values shows that all azo dyes studied herein are much less sensitive to solvent polarity changes in comparison to the standard dye **5b**. The differences verified for the m and n values in comparison with structurally related dyes,[29, 31] but with other different conjugated bridges (CH=CH and CH=N), suggest that the azo bridge has plays an important role in the solvatochromism of these systems, making them less solvatochromic, as suggested by Fabian and Hartmann.[60]

Table 4. Values for the slope n and intercept m on linear plots of $E_T(dye)$ as a function of $E_T(5b)$ values, for compounds **6b–14b**.

Dye	m	V n	r ²
6b	9.77 ± 2.51	0.74 ± 0.04	0.91
7b	15.95 ± 2.76	0.55 ± 0.04	0.83
8b	24.29 ± 1.67	0.51 ± 0.02	0.92
9b	22.26 ± 2.53	0.54 ± 0.04	0.85
10b	19.02 ± 2.34	0.50 ± 0.04	0.85
11b	22.93 ± 2.43	0.44 ± 0.04	0.80
12b	38.65 ± 1.47	0.13 ± 0.02	0.50
13b	25.13 ± 2.49	0.43 ± 0.04	0.78
14b	24.70 ± 2.70	0.43 ± 0.04	0.75

4.2. Multiparametric studies on the solvatochromism of 6b-14b

The experimental $E_{\rm T}$ (dye) values for compounds **6b-14b** in pure solvents were analyzed using the Kamlet-Abboud-Taft (KAT) [61, 62] and Catalán [63] multiparameter equations. The KAT approach uses Eqn. (2), where α , β , and π^* are parameters that represent the solvent hydrogen-bond donor (HBD) acidity, hydrogen-

bond acceptor (HBA) basicity, and solvent dipolarity/polarizability, respectively, while δ is a polarizability correction term for the solvent. The Catalán approach [63] requires the use of Eqn. (3), where specific solvent parameters *SA* and *SB* represent the solvent HBD acidity and HBA basicity, respectively, while *SP* and *SdP* are the nonspecific solvent parameters polarizability and dipolarity, respectively. In these equations, $E_{\rm T}({\rm dye})_0$ represents the $E_{\rm T}({\rm dye})$ value related to an inert solvent.

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

$$E_{\rm T}(\rm dye) = E_{\rm T}(\rm dye)_0 + aSA + bSB + cSP + dSdP$$
(3)

Tables 5, S2, S3 and **S4** show the contributions of the solvent properties to the $E_{\rm T}$ (dye) values determined for dyes **6b-14b**, obtained from the multiple square correlation analysis with the use of Eqns. (2) and (3). Similarly to the analysis performed with related systems that exhibit reverse solvatochromism,[27-29, 31], the application of Eqn. (3) to compounds **6b-14b** provided more coherent results in comparison with those obtained from the KAT analysis: (a) the *r* values are > 0.93 for all compounds; (b) the contribution of the HBA basicity of the solvent is small (small b coefficients); (c) in general, the most important contribution was that of the HBD acidity of the solvent; and (d) the coefficients related to the solvent parameters polarizability and dipolarity represent important contributions to the solvatochromic behavior of the systems studied. For all dyes, with the exception of dye **6b**, the contribution of the polarizability term is more important than that of the dipolarity term.

Table 6 shows data from the Catalán multiparametric analysis for dyes 1, 2, 4b, 5b, and 6b to allow a comparison of the results for these compounds. Reichardt's dye (1) is very sensitive to the acidity of the medium and quite sensitive to the dipolarity of the medium. Effenberger's dye (2) shows almost no sensitivity to the

acidity and basicity of the medium, but is sensitive to the polarizability of the medium and also, although to a lesser extent, to the dipolarity of the medium. It is important to observe that all coefficients are positive for dye **1**, which exhibits a well-known negative solvatochromism, while both the polarizability and dipolarity coefficients are negative for dye **2**, which represents a classical example of a positively solvatochromic probe. Regarding this aspect, as a common feature for the series of dyes **4b**, **5b**, and **6b**, a positive sign is verified for the acidity coefficient, while the other three coefficients are negative. This common trend is related to the reverse solvatochromic behavior exhibited by these dyes, reflecting the strong interaction with hydrogen-bond donating solvents in the negative solvatochromism region and mainly the non-specific interactions with the less polar solvents in the positive solvatochromism region. The data show that although dyes **4b-6b** are very sensitive to the acidity, the azophenolate **6b** is the least sensitive, which could reflect the previously discussed action of the azo groups as electron acceptors, reducing the electronic availability of the oxygen phenolate moiety.

Table 5. Correlation coefficients a, b, c, and d obtained from the Catalán multiparametric (Eqn. 2) analysis through the treatment of $E_{\rm T}(dye)$ values for compounds **6b–14b** in various solvents.

Dye	$E_{\mathrm{T}}(\mathrm{dye})_{\mathrm{0}}$	a	b	c	d	N^{a}	r ^b	S.D. ^c
6b	62.25	12.93	-1.73	-6.77	-8.62	29	0.96	1.16
7b	57.40	10.27	-1.47	-8.26	-5.87	29	0.96	0.80
8b	62.11	9.04	-2.16	-6.38	-5.29	29	0.97	0.66
9b	62.35	10.25	-1.43	-7.90	-5.40	29	0.97	0.75
10b	56.40	9.42	-1.49	-7.73	-4.94	29	0.97	0.60
11b	55.30	8.71	-1.78	-6.07	-3.71	29	0.96	0.74
12b	50.91	2.57	-1.12	-5.79	-0.19	29	0.93	0.33

13b	55.98	8.77	-1.54	-5.52	-3.87	29	0.95	0.77		
14b	55.95	8.66	-1.79	-6.77	-2.79	29	0.96	0.71		

^a Number of solvents.

^b Linear correlation.

^c Standard deviation.

Table 6. Correlation coefficients a, b, c, and d obtained from the Catalán multiparametric analysis through the treatment of $E_{\rm T}$ (dye) values for different dyes in various solvents.

Dye	$E_{\mathrm{T}}(\mathrm{dye})_{0}$	a	b	с	d	$m{N}^{ m a}$	R ^b	S.D. ^c
$1^{d,e}$	29.47	22.64	4.96	2.12	9.20	29	0.98	1.62
2 ^e	70.09	0.01	0.06	-14.66	-7.32	18	0.99	0.32
4b ^e	69.14	14.42	-3.77	-12.52	-6.41	23	0.90	2.22
5b ^f	71.46	15.48	-3.33	-10.54	-9.79	28	0.95	1.60
6b	62.25	12.93	-1.73	-6.77	-8.62	29	0.96	1.16

^a Number of solvents.

^b Linear correlation.

^c Standard deviation.

^d Using $E_{\rm T}(30)$ values from **Table 1**.

^eCalculated by the authors with data from the literature.[26]

^fFrom the literature.[28, 29]

4.3. Theoretical Calculations

Table 7 shows the calculated absorption wavelengths for compounds **4b-6b**. In all cases the values are blue-shifted in water when compared with *n*-hexane. For dye **6b**, the calculated values are around 60 nm lower than the experimental values, although the differences are in agreement with the empirical results. The calculated results for **6b** show a difference of 9 nm between *n*-hexane and water, while the experimental difference was 11 nm. This difference is smaller than those observed for dyes **4b** and **5b**, which are considerably more solvatochromic. The excitations associated with the values in **Table 7** can be seen in **Table 8**. In all cases, the most significant transitions

are associated with polarizations among the highest occupied molecular orbitals of the phenolate moiety during excitation. Figure 6 shows the calculated spectra for 6b in *n*-hexane and water, along with the most significant transition.

Table 7. Experimental and calculated	λ_{\max} v	values f	for 4b -	-6b	in water	and <i>n</i> -hexane.
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Dye	H ₂ O	<i>n</i> -hexane	$\Delta \lambda_{\max}$ (nm)	H ₂ O	<i>n</i> -hexane	$\Delta \lambda_{\max}$ (nm)
	$\lambda_{\max}^{\text{theor}}(\mathbf{nm})$	$\lambda_{\max}^{\text{theor}}(\mathbf{nm})$		λ_{\max}^{exp} (nm)	λ_{\max}^{exp} (nm)	
4b	401.3	498.2	-96.9	430.6 ^a	486.2 ^a	-55.6
5b	390.5	467.1	-76.6	428.0 ^b	450.2 ^b	-22.2
6b	416.9	425.7	-8.8	479.0	490.0	-11.0
	3 - 0 0					

^a Data from ref. 26.

^b Data from ref. 27.



Figure 6. Calculated spectra for **6b** in water and *n*-hexane. The most significant transitions (HOMO-2 and HOMO-1 to HOMO, respectively) are shown in the insert.

Table 8. Most prominent states associated with transitions of Table 7. Density cut-offs

are 0.03 a.u. The strongest delocalization for each structure is shown in bold text.

Dye	Most	polar solvent (H ₂	0)	Least polar solvent (<i>n</i> -hexane)				
-	Donor	Acceptor	ΔE (eV) / %	Donor	Acceptor	ΔE (eV) / %		
4 b	HOMO-3 (60a)	HOMO (63a)	8.18 (< 1%)	HOMO-3 (60a)	HOMO (63a)	7.81 (1%)		
	HOMO-3 (60a)	LUMO (64a)	9.90 (<1%)	HOMO-3 (60a)	LUMO (64a)	9.57 (< 1%)		
	HOMO-2 (61a)	HOMO (63a)	7.89 (<1%)	HOMO-2 (61a)	HOMO (63a)	6.85 (<1%)		
	HOMO-2 (61a)	LUMO (64a)	9.61 (<1%)	HOMO-2 (61a)	LUMO (64a)	8.61 (<1%)		
	HOMO-1 (62a)	HOMO (63a)	5.98 (72%)	HOMO-1 (62a)	HOMO (63a)	5.11 (83%)		
	HOMO-1 (62a)	LUMO (64a)	7.70 (16%)	HOMO-1 (62a)	LUMO (64a)	6.87 (9%)		
5b	HOMO-3 (60a)	HOMO (63a)	8.16 (8%)	HOMO-3 (60a)	HOMO (63a)	7.89 (5%)		
	HOMO-3 (60a)	LUMO (64a)	9.92 (1%)	HOMO-3 (60a)	LUMO (64a)	9.67 (<1%)		
	HOMO-2 (61a)	HOMO (63a)	8.04 (< 1%)	HOMO-2 (61a)	HOMO (63a)	7.06 (<1%)		
	HOMO-2 (61a)	LUMO (64a)	9.81 (<1%)	HOMO-2 (61a)	LUMO (64a)	8.84 (<1%)		
	HOMO-1 (62a)	HOMO (63a)	6.01 (77%)	HOMO-1 (62a)	HOMO (63a)	5.29 (83%)		
	HOMO-1 (62a)	LUMO (64a)	7.78 (10%)	HOMO-1 (62a)	LUMO (64a)	7.07 (6%)		
6b	HOMO-3 (60a)	HOMO (63a)	8.10 (3%)	HOMO-3 (60a)	HOMO (63a)	7.67 (19%)		
	HOMO-3 (60a)	LUMO (64a)	9.37 (2%)	HOMO-3 (60a)	LUMO (64a)	9.01 (9%)		
	HOMO-2 (61a)	HOMO (63a)	7.88 (47%)	HOMO-2 (61a)	HOMO (63a)	7.50 (11%)		
	HOMO-2 (61a)	LUMO (64a)	9.14 (30%)	HOMO-2 (61a)	LUMO (64a)	8.84 (6%)		

HOMO-1 (62a)	HOMO (63a)	6.20 (7%)	HOMO-1 (62a)	HOMO (63a)	5.76 (43%)
HOMO-1 (62a)	LUMO (64a)	7.47 (2%)	HOMO-1 (62a)	LUMO (64a)	7.09 (6%)

In order to investigate the solvation pattern of the dyes, molecular dynamics simulations of compounds **4b-6b** were performed with water, DMF and *n*-hexane as solvents. These dyes and solvents were chosen as prototypes to analyze different solvation behaviors that can arise depending on the bridging group and on the solvent polarity. Radial distribution functions (RDFs) were calculated from equilibrated trajectories obtained via molecular dynamics simulations. The analysis was focused on bridging atoms (nitrogen or carbon of CH=CH, CH=N and N=N bridges) and on the phenolate and nitro substituents of the donor and acceptor groups, respectively.

All three dyes yielded very similar RDFs around the phenolate oxygen (**Figure 7A**) and nitro oxygens (**Figure 7C**) with water as the solvent. In the phenolate moiety, a first solvation shell centered at 1.9 Å with three water molecules and a second more diffuse shell centered at 3.3 Å with 16-17 water molecules were verified (**Figure 8**). The nitro oxygen of **4b-6b** also formed hydrogen bonds with the solvent, as shown by the RDFs of **Figure 7C**, giving rise to a broader solvation shell centered at 2.9 Å with seven water molecules. The solvation shell around the nitro moiety is less intense compared to the donor group. A solvation shell consisting of 21 molecules is observed for the bridging groups of compounds **4b-6b**. However, different patterns were observed depending on the bridging moiety. A broad and unique shell centered at ~2.5 Å was observed for the ethylene bridge of **4b**. In comparison, two well-defined solvation shells were verified at ~2 Å and 3 Å with 2 and 19 water molecules, respectively, for compounds **5b** and **6b**. This difference in the behavior observed for the solvation pattern is due to the presence of nitrogen atoms in the bridging group, and it

may be associated with the differences in the solvatochromism observed for compounds4b-6b as the bridging atoms are varied.

A similar pattern for the solvation around the phenolate and nitro groups was observed with DMF as the solvent for the three dyes, as evidenced in **Figures 7B** and **7D**. All compounds showed a diffuse first solvation layer at 4.4 Å with 4-6 solvent molecules for the phenolate group and the peak centered at 4.4-4.6 Å with four DMF molecules for the nitro moiety. As expected, interactions of **4b-6b** with DMF are specific, but less intense compared to water. Differences in the solvation structure of the bridging moieties are also observed for DMF. **Figure 7F** demonstrates a more compact solvation structure for the azo group of **6b** compared to the CH=CH group of **4b**, as observed from the peak centered at ~ 6 Å for **4b** with 12 molecules and the peak centered at ~ 5.4 Å with 9 molecules for **6b**. Similarly to the case where water was used as the solvent, the behavior of compound **5b** was intermediate, between those of **4b** and **6b**, because of the CH=N group, with two peaks at 4.5 Å and 6 Å and with nine molecules in the solvation shell.

The solvation patterns of the three dyes in n-hexane are very similar (see **Figure S66**). The hydrogens of the solvent interact more strongly with the electronegative atoms of the probes, but the interactions are, as expected, much weaker than those in the intense and strongly packed first solvation shell verified with water. Similar results have been obtained recently in a study on a related family of imine solvatochromic dyes.[30]



Figure 7. Radial distribution functions (RDFs) for the solvation of (A)-(B) phenolate oxygen, (C)-(D) nitro oxygen, and (E)-(F) bridging atom of **4b-6b** in water (left) and DMF (right). Atom types (HW) and (OW) denote the hydrogen and oxygen atoms of water, respectively, (OH) the oxygen of the phenolate group, (ON) the oxygen of the acceptor nitro group, (CM) the sp^2 carbon of the CH=CH bridge and (NC) the nitrogen of the azo and methyleneimino moieties, while (N) and (O) represent heteroatoms of DMF.



Figure 8. Snapshots of the molecular dynamics simulation emphasizing the two solvation shells of water molecules around **4b-6b**. The water molecules highlighted are within 6 Å from the oxygen of the dyes.

5. Conclusions

A family of 4-[(E)-(4-nitrophenyl)diazenyl]phenols was synthesized and characterized. These compounds are more acidic in water in comparison with related compounds presenting CH=N or CH=CH in their conjugated bridge, due to the electron withdrawing effect of the azo group in the compounds.

All compounds in their deprotonated form yielded solvatochromic dyes which exhibited a reversal in their solvatochromism. The azo dyes are much less sensitive to solvent polarity changes in comparison to similar dyes exhibiting CH=N or CH=CH as the conjugated bridge. The use of Catalán multiparametric analysis showed that the azo dyes are very sensitive to the acidity of the medium, but to a lesser extent than their corresponding imine and stilbene dyes. Experimental data were explained considering the influence of the azo group, which is sufficiently electronegative to reduce the electronic availability of the phenolate moiety of the dye.

The fact that the family of compounds **4b-6b** correlates linearly with the standard dye **5b** means that these compounds can be considered as interesting models to investigate reverse solvatochromism and to reinforce the generalized reversal model, currently used to explain the solvatochromism of merocyanine and merocyanine-like dyes. Compounds **4b-6b** could be considered Class III dyes and used as simple standards to classify and compare experimentally verified reverse solvatochromism in other dyes, similarly to the use of dyes **1** and **2** as Class I and II standard dyes in negative and positive solvatochromic studies, respectively.

The results suggest that the reverse solvatochromism of compounds **4b-6b** is dictated by the electron-donor phenolate and by the electron-acceptor 4-nitroaryl groups, independently of the conjugated bridge, of the additional nitro group and of the nature of the substituents in the 2,6-positions of the phenolate groups. An analysis of the

solvatochromic behavior of the three series of dyes studied shows that the systems interact efficiently with polar hydrogen-bond donating solvents (mainly using the phenolate moiety) and dipolarity-polarizability effects are observed in solvents presenting lower polarity. Thus, the reversal in the solvatochromism verified for these dyes represents a committed step involving the interaction of the nitro and phenolate groups in the probe with the molecules of structurally different solvents.

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Supporting Information

IR, HRMS, ¹H and ¹³C NMR data for compounds **6a-14a**; experiments conducted to verify that aggregation of the compounds does not occur; UV-vis spectra for **6b-14b** at 25 and 50 °C; 'polarity' parameters for the pure solvents; tables containing the correlation coefficients obtained from the multiparametric analysis; pK_a determination curves for **6b-14b**; experiments to verify the lack of influence of the tetra-*n*-butylammonium ion on the UV-vis spectrum for **6b**; relevant molecular mechanics parameters. This material is available free of charge via the Internet at http://

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
 The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

Nine 4-[(*E*)-(4-nitrophenyl)diazenyl]phenolate dyes synthesized and characterized Intense color in solution: intramolecular charge transfer $\Box \Box \Box^*$ electronic transitions All dyes exhibit a reversal in their solvatochromism

Very sensitive to acidity of the medium, due to the electronegativity of azo group Solvatochromism of the dyes dictated by phenolate and 4-nitroaryl groups