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# Synthesis and characterization of a group of new medium responsive nonsymmetric viologens. Chromotropism and structural effects

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# 1. Introduction

Viologens are charged aromatic heterocyclic compounds which for many years attract the interest of chemical and materials scientists. They structurally are N,N'-disubstituted 4,4'-bipyridines. In most of the cases their importance is aligned with their strong electron withdrawing character. Besides their biological activity [1] they have been used as building redox active functional blocks of switchable interlocked molecules such as rotaxanes and catenanes [2-5], as well as molecular sensors of some compounds of biological importance such as NAD [6] and glucose. [7–9] Their reversible one-electron reduction leading in colorful relatively stable radical cations (blue or violet depending on the substituents) has been proposed for use in new hi-tech applications such as in electrochromic displays and rear view windows [10]. The phorophysics and photochemistry of viologens has also been investigated in the past [11], as well as their photochromic properties, with very interesting results. [12] The nonlinear optical properties and solvatochromism of molecules possessing N-monoquaternized 4,4'-bipyridine (the so-called monoquats) as ligands of complexes

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# ABSTRACT

A group of new non-symmetric viologens was synthesized and characterized spectrally using various techniques. These viologens contain active methylene moieties being capable to act as hydrogen bond donors (HBD) and interact in solution with various solvents, the latter acting as hydrogen bond acceptors (HBA). These specific solute-solvent interactions result in intense coloration of the resulting solutions. The chromotropic behavior of these compounds is triggered by basic solvents, and no significant change in color is observed in poorer HBA-solvents, such as several alcohols. The dependence of the color of the solutions on the polarity parameters of solvents (solvatochromism) was investigated. Solvent polarity parameters expressing both dipolarity/polarizability and basicity of solvents have been used. Finally the correlation of the chromotropic behavior of these compounds with their structure is examined, using both experimental data and Hammett equation.

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of transition metals like Ru<sup>II</sup> and Fe<sup>II</sup> have been recently reported. In these cases 4,4'-bipyridine exhibits important dual functionality: aromatic and electron withdrawing system [13–15]. Solvatochromism is an additional interesting aspect of the chromotropic behavior of viologens which to the best of our knowledge has not been intensely investigated. Recently we described the medium responsive character of a new N-(2,4-dinitrophenyl), N'- phenacyl viologen [16].

In this work a group of new non-symmetric N-aryl,N'-phenacetyl viologens has been synthesized and fully characterized. Their interesting chromotropic behavior strongly dependent on solvent polarity (solvatochromism) was thoroughly investigated. This unique behavior which was proved to be triggered by basic enough solvents, was connected to their structure using experimental data as well as empirical parameters (i.e. Hammett parameter).

# 2. Experimental section

## 2.1. Physical measurements

NMR spectra were obtained using a Varian Gemini 300 spectrometer (300 MHz <sup>1</sup>H, 75 MHz <sup>13</sup>C). Both <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded in [D<sub>6</sub>]DMSO or [D<sub>6</sub>]Me<sub>2</sub>CO at  $25 \pm 1$  °C. The <sup>1</sup>H NMR spectra were calibrated by using residual undeuterated solvent as an internal reference (4.79 ppm) and <sup>13</sup>C-NMR spectra were



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calibrated using the  $[D_6]DMSO$  signal at 39.52 ppm or the  $[D_6]$ Me<sub>2</sub>CO at 29.84 ppm [17]. Abbreviations used for multiplicity in the text: s = single; d = doublet; m = multiplet; arom = aromatic.UV-Visible spectra were recorded using a Varian CARY 1E UV–Visible spectrophotometer at  $25 \pm 1$  °C. The concentrations of the solutions used, were about 50 ppm and they were prepared right before each measurement. Electrosprav ionization (ESI) HRMS spectra were obtained on a Waters. Inc. O-TOF Premier Mass Spectrometer. The solvent used was MeOH. IR spectra were recorded on a Perkin-Elmer Spectrum 1 FTIR spectrophotometer in the solid state (without any preparation of the samples) using the attenuated total reflectance technique (ATR) in the region 600–4000 cm<sup>-1</sup>. Melting points were determined in open capillary tubes using a Gallenkamp HFB-595 melting point apparatus and are uncorrected. Finally elemental analyses were carried out using a Perkin-Elmer Elemental Analyzer 2400 CHN.

## 2.2. Synthetic procedures and characterization details

Synthetic procedures and characterization of compounds **1**, **3a–d** and **5a–e** are included in the Supplementary data file.

# 2.2.1. General synthetic procedure (**6a**-**d**)

A total of 1.20 mmol of the product  $5(\mathbf{a}-\mathbf{d})$  were dissolved in H<sub>2</sub>O by sonication and mild heating (at about ~50 °C). To the resulting solution 5 mL of a 4 M NH<sub>4</sub>PF<sub>6</sub> aqueous solution was added. Immediately a beige or pale-yellow solid was formed (**6a**-**d**). The solid was washed thoroughly with water in order to remove the NH<sup>+</sup><sub>4</sub> salts, and then with EtOH and finally with Et<sub>2</sub>O. The as formed products are cleaned as follows. The hexa-fluorophosphate viologen salt **6(a**-**d)** was dissolved in MeCN and a solution of tetraethylammonium bromide (Et<sub>4</sub>NBr) in MeCN (containing approximately 10 times the equimolar quantity of Et<sub>4</sub>NBr in the minimum volume of MeCN) was added. The resulting bromide salt was filtered and washed with MeCN and Et<sub>2</sub>O. Finally the bromide salt was transformed to the desired product **6a**-**d** by ion exchange using NH<sub>4</sub>PF<sub>6</sub> as described before [16].

2.2.1.1. *Viologen* **6a** (4-*MePh*). Beige powder, 629 mg (0.864 mmol) 72% mp = 228–230 °C. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>] AcMe): 9.69 (d, J = 6.0 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.30 (d, J = 5.7 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.99 (m, 4H: arom.), 8.14 (d, J = 7.5 Hz, 2H: arom.), 7.88 (m, 3H: PhAc.), 7.71 (t, J = 7.2 Hz, 2H: PhAc), 7.63 (d, J = 8.1 Hz, 2H: PhAc), 6.57 (s, 2H, >CH<sub>2</sub>), 2.50 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C-NMR (75 MHz, [D<sub>6</sub>]AcMe): 190.25, 149.17, 149.40, 147.26, 145.67, 141.87, 139.90, 134.90, 133.39, 130.61, 129.23, 128.27, 126.67, 126.61, 124.48, 66.38 (>CH<sub>2</sub>), 20.73 (Me). HRMS-ESI (*m*/*z*): [M-2PF<sub>6</sub>], 100%, calc. for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O, 366.1732; found, 366.1727; IR (ATR):  $\nu$ (C=O): 1739, 1641, 1541, 1438, 1369 cm<sup>-1</sup>.

2.2.1.2. Viologen **6b** (4-*FP*h). Beige powder, 591 mg (0.828 mmol) 69%, mp = 225–226 °C. <sup>1</sup>H NMR (300 MHz, [D6]AcMe): 9.71 (d, J = 6.0 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.42 (d, J = 6.3 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.07 (d, J = 6.6 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.03 (d, J = 6.3 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.17 (m, 4H,arom.), 7.81 (t, J = 7.5 Hz, 1H: PhAc) 7.70 (m, 4H: arom.), 6.77 (s, 2H, >CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, [D<sub>6</sub>]AcMe): 190.52, 151.91, 151.57, 148.58, 147.12, 140.11, 137.30, 135.82, 134.55, 130.10, 129.23, 128.33, 127.97, 118.52, 118.20, 67.71 (>CH<sub>2</sub>). HRMS-ESI (m/z): [M-2PF<sub>6</sub>], 100%, calc. for C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>OF, 370.1481; found, 370.1489; IR (ATR):  $\nu$ (C=O): 1739, 1504, 1367 cm<sup>-1</sup>.

2.2.1.3. *Viologen* **6c** (4-*ClPh*). Beige powder, 584 mg (0.780 mmol) 65%, mp =  $232-234 \degree C$ . <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]AcMe): 9.65 (d, *J* = 6.6 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.41 (d, *J* = 6.0 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.02 (m, 4H: C<sub>5</sub>H<sub>4</sub>N), 8.18 (d, *J* = 7.8 Hz, 2H: Ph), 8.00 (d, *J* = 8.7 Hz, 2H, Ph), 7.81

(t, *J* = 7.2 Hz, 1H, PhAc), 7.70 (m, 2H: arom.), 7.35 (d, *J* = 8.7 Hz, 2H: arom.), 6.76 (s, 2H: >CH<sub>2</sub>).<sup>13</sup>C-NMR (75 MHz, [D<sub>6</sub>]AcMe): 190.32, 163.30, 151.68, 151.13, 148.56, 146.69, 135.85, 135.39, 134.56, 130.12, 129.24, 128.27, 127.93, 126.95, 116.51, 66.51 (>CH<sub>2</sub>). Elemental analysis calcd for C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>OCIP<sub>2</sub>F<sub>12</sub>: C 42.59, H 2.83, N 4.14, found: C 42.82, H 2.34, N 4.23, IR (ATR):  $\nu$ (C=O): 1739, 1513, 1367 cm<sup>-1</sup>.

2.2.1.4. *Viologen* **6d** (4-*CNPh*). Beige powder, 536 mg (0.744 mmol) 62%, mp = 207–208 °C. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]AcMe): 9.76 (d, J = 6.6 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.31 (d, J = 5.1 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.00 (m, 4H: arom.), 8.37 (d, J = 8.4 Hz, 2H: Ph), 8.22 (d, J = 8.1 Hz, 2H: Ph), 7.84 (pt, J = 7.2 Hz, 1H: PhAc), 7.71 (pd, 2H: Ph), 6.58 (s, 2H, >CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, [D<sub>6</sub>] AcMe): 191.42, 150.98, 150.26, 149.87, 148.63, 147.21, 147.34, 139.90, 137.09, 136.62, 134.72, 131.31, 129.97, 127.42, 126.94, 65.41 (>CH<sub>2</sub>). HRMS-ESI (m/z): [M-2PF<sub>6</sub>], 100%, calc. for C<sub>25</sub>H<sub>19</sub>N<sub>3</sub>O, 377.1528; found, 377.1524; IR (ATR):  $\nu$ (C=O): 1739, 1602, 1500, 1367 cm<sup>-1</sup>.

Viologen **6e** (2,4-dinitrophenyl): This compound was synthesized according to an already published procedure [16].

## 3. Calculations

The Van der Waals radii of the cationic parts of the viologens **6a–d** studied, were calculated using the <sup>3</sup>V: Voss Volume Voxalator, available on-line. The results for each compound are listed in Table S1 (Supplementary data). The difference of dipole moments in ground and excited state were determined graphically using the Lippert–Mataga equation according to literature [18,19]. All correlations and linear regression analyses were performed using the program QtiPlot.

# 4. Results and discussion

## 4.1. Synthesis and characterization of the viologens

For the synthesis of the solvatochromic non-symmetric viologens the synthetic procedure depicted in Scheme 1 was followed. The compounds 3a-d (monoquats) were synthesized through Zincke reactions between suitable substituted anilines (2a-d) and the precursor compound 1, as described before [20]. These monoquats further reacted with phenacetyliodide (4) in refluxing EtOH to spontaneously result in microcrystalline precipitates of viologens with mixed anions ( $Cl^-$  and  $I^-$ , compounds **5a**-**e**). These compounds (5a-d) were transformed to the desired hexafluorophosphate corresponding salts (soluble in various organic solvents) by ion exchange to give compounds 6a - e in high yields. The compounds 5,6e have been reported in an earlier publication of our group [16] and their intense solvatochromic behavior and HBD activity has been discussed (see also synthetic details in Supplementary data file). The compounds 5,6a-d were characterized using NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopy, UV-Vis and FTIR spectrophotometry as well as ESI-HRMS (Figs. S3-S6 of Supplementary data file). As mentioned compounds 5a-d were isolated as microcrystalline solids. Representative scanning electron microphotographies and powder-XRD pattern of the compound 5a, are depicted in Figs. S1 and S2 of Supplementary data file, respectively. Attempts to grow bigger crystals suitable for single-crystal XRD in order to solve their structure failed. Nevertheless these compounds were also proved to be solvatochromic as well. It is though of great interest to examine the unique chromotropic character of compounds **5a**–**d** separately since it is known that iodide salts of N-substituted pyridinium (especially those with electron withdrawing moieties at position 4) behave as solvatochromic compounds as well, Kosower's salt being one of the most popular solvatochromic analogue [21]. Besides



Scheme 1. Synthetic procedure followed for the synthesis of the solvatochromic viologens 6a-d.

their red-brown color in the solid state reflects this behavior. In this work we focus on the solvatochromism of the hexafluorophosphate salts.

It was also attempted to synthesize compounds **6a**–**d** via Zincke reactions of the product **5e**, using the arylamines **2a**–**d** respectively. Unfortunately these reactions did not yield in the formation of the desired viologens **6a**–**d**. This fact was attributed to the "acidic" character of the product **5e**, described also before. [16] Thus upon addition of a substituted aniline, the solution in any case turned dark and the resulting product was not the desired product **6a**–**d**.

#### 4.2. UV–Vis spectrophotometry

Compounds **6a**–**d** show an intense solvatochromic behavior. It is noteworthy though, that they express this behavior upon solvation in solvents which can rather act as Lewis bases, or more specifically as HBA-bases. In Fig. 1 the visible spectra of the compound **6d** are depicted, in five solvents capable of acting as HBA-bases: dimethyl-acetamide (DMAC), formamide (FA), Nmethyl-formamide (NMF), hexamethylphosphoramide (HMPA), and pyridine (PY). Nevertheless it was observed that the solvation of the pale-yellow to beige colored solids **6a**–**d**, in solvents acting as better HBD-acids rather than HBA-bases like several alcohols, e.g. MeOH and EtOH resulted in yellow colored solutions, whereas when these compounds were dissolved in HBA-solvents (like the aforementioned) they yielded in blue-purple solutions strongly depending on the polarity of solvents.

Compounds **6a–d**, present two main features in their UV–Vis spectra. One high absorbance sharp Gaussian type band attributed to the  $\pi$ – $\pi$ \* excitations, appearing at about 230 nm of the viologen aromatic system, which is generally not intensely affected by solvent polarity, temperature, or substituents. The molecular extinction coefficient of this band is high, reaching values of about 7500 M<sup>-1</sup> cm<sup>-1</sup>. The second band is a low energy visible band, assigned as a charge transfer band (CT) from the carbene of the

methylene of the phenacetyl moiety (formed in basic solutions) to the strong electron withdrawing quaternized nitrogen atom of the viologen, through the aromatic system of the 4,4'-bipyridyl bridge. This band is strongly affected by solvent polarity and substituents of different nature attached to 4,4'-bipyridyl (see structure of compounds **5,6a–d** of Scheme 1). The latter appears at about 450–550 nm, and presents a molecular extinction coefficient of about 850  $M^{-1}$  cm<sup>-1</sup>. What is interesting with this band is that it only exists in solvents presenting basic character, whereas in solvents of low or negligible HBA-basicity there is no visible contribution in the electronic absorption spectra of the studied compounds. This is a strong indication that proton donation or even deprotonation can occur only in basic solvents, as expected. Thus in



Fig. 1. Normalized visible spectra of 6d (p-CN) in different solvents at 298 K.

cases of solutions of **6a**–**d** in MeOH and other alcohols acting as poorer bases, the color observed is pale yellow or beige (Figs. S7 and S8 of Supplementary data file). The aforementioned visible band does not exist either in the solid state. This fact reflects the strong solute-solvent interaction (solute being compounds **6a**–**d**) which is pronounced in basic media, giving rise to solvatochromism. The proposed limiting resonance structures of compound **6d**, and the corresponding structures in ground and excited states are depicted in Scheme 2.

## 4.3. Solvent effects

Solvent polarity has a significant effect on the visible spectra of the viologens studied in this work. As shown in Fig. 1 and Table 1, bathochromic shifts of the CT bands of the viologens **6a–d**, are induced upon decreasing solvent polarity (following the sequence FA, NMF, HMPA, DMAC, PY). This behavior corresponds to negative solvatochromism. As shown in Fig. 2 (see also Figs. S9–S12 of Supplementary data file), the measured CT absorption maxima wavenumbers are correlated very well with the polarity function  $f(\varepsilon) + g(n)$ , describing both solvent polarity (dipolarity through the term  $f(\varepsilon)$  and polarizability through the term g(n), see Eqs. (ES1) and (ES2) of Supplementary data file). This is attributed to the fact that the excited state in all cases is less polar than the ground state, thus the excited state (e.g. Scheme 2) is stabilized by solvents of lower polarity (i.e. pyridine) and this corresponds to a classical negative solvatochromic behavior.

The results of the correlations between the CT maxima absorption energies ( $I_{CT}$ ) and the polarity function  $f(\varepsilon) + g(n)$ , are listed in Table 2. From the graphically obtained slopes of the family of these linear equations it is possible to determine the term  $\|\Delta \mu\|^2 / \alpha^3$  with energy dimensions, where  $\alpha$  is the Van der Waals radius of the solvatochromic compound (**6a**–**d**), and  $\|\Delta \mu\|$  is the difference  $\|\mu_{ex}\| - \|\mu_g\|$  (where  $\|\mu_{ex}\|$  is the norm of the vector of the dipole moment of the excited state and  $\|\mu_{g}\|$  that of the ground state). By calculating the Van der Waals radii of 6a-d (see Section 3), the  $\|\Delta \mu\|$  were determined for each compound, and they are listed in Table 2 as well. As expected the difference  $\|\Delta \mu\|$  was higher for the case of **6d** which is the compound possessing the most electron withdrawing moiety (p-CN) amongst 6a-d, as it is analyzed thoroughly in next paragraph. Increasing the electron withdrawing character of the aryl substituent, an increase of the dipole moment difference between the ground and excited state is observed, implying a more intense susceptibility on the solvent polarity for compound 6d, possessing the electron deficient group p-CN-phenyl.

What is interesting is that successful correlations were obtained as well, between the CT maxima absorption energies  $(I_{CT})$  and the solvent normalized donor numbers (DN<sup>N</sup>) or the Kamlet-Taft  $\beta$  parameters, both expressing the donicity of the solvent (Lewis basicity and HBA-basicity respectively). The results of these correlations are depicted in Figs. S13 and S14 of Supplementary data file. This observations have the meaning that the solvatochromic phenomena in all cases are controlled by both dipolarity/polarizability (expressed by the function  $f(\varepsilon) + g(n)$ ) and by the basicity of solvents (expressed by the parameter  $DN^N$  or  $\beta$ ). Basic enough solvents are needed to interact strongly with the "active methylenes" of **6a**–**d** and thus generate a betaine of the type of Scheme 2, which is stabilized by the solvent with lower dipolarity/polarizability. This fact is also reflected by the negative slopes of the correlations  $J_{CT} \propto DN^N$  (or  $\beta$ ) and the positive slopes of the correlations  $J_{CT} \propto [f(\varepsilon) + g(n)]$ . Thus increasing solvent basicity induces bathochromic shifts on the CT absorption band of **6a-d**, whereas increasing of solvent dipolarity/polarizability induces hypsochromic shifts on the CT absorption band of 6a-d.

Interestingly there are several analogies of the as formed betaines and some pentacyanoferrate complexes with N-arylsubstituted monoquats already published by our group in the past [20]. As shown in Scheme S1 of Supplementary data file, in both cases, upon excitation with visible light charge transfer from the electron donating moiety (in one case Fe<sup>II</sup>(CN)<sub>5</sub> and PhCO-HC in the other) to the quaternary electron withdrawing nitrogen atom, connected with the arvl substituent, occurs. The colors of the solutions obtained in both cases were blue-purple indicating that the charge transfer in both cases demands relatively low energy (visible light). The main difference is that the betaine "solvatochromically active" form of the viologens studied here, is formed in solution. In the solid state the viologens are stable and their colors as already mentioned are beige or pale yellow. Whereas in the case of the corresponding pentacyanoferrate complexes, the color of the substances is blue even in the solid state. The behavior of the viologens **6a**–**d**, is a special case of chromotropism, triggered only by solvents presenting HBA-basicity.

#### 4.4. Structural effects

The electron donating or withdrawing nature of the aryl substituent, readily affects the UV–Vis spectra (mainly the visible CT band) of **6a–d**. The plots of the experimentally obtained CT maxima absorption wavelengths in all solvents, versus the Hammett constants are depicted in Fig. 3. In all cases of solvents, negative slopes were determined for the equations of the type  $\tilde{v}_x = \tilde{v}_o + \rho \sigma_x$  (where  $\tilde{v}_x$  is the maximum CT absorption wavelength for



Scheme 2. Limiting resonance structures and ground and excited states of compound 6d. S: symbolizes an HBA-solvent.

	( 21)	•			, i			
Solvent	$\tilde{v}_{CT}$ 6a (10 <sup>3</sup> cm <sup>-1</sup> )	$\tilde{\upsilon}_{CT} \; \textbf{6b} \; (10^3 \: cm^{-1})$	$\tilde{v}_{CT}$ 6c (10 <sup>3</sup> cm <sup>-1</sup> )	$\tilde{\upsilon}_{CT} \; \textbf{6d} \; (10^3 \: cm^{-1})$	ε (–) [21,22]	n (–) [21,22]	$DN^{N}(-)[23]$	β (−) [25]
DMAC	21.692	21.692	21.692	21.598	37.8	1.4384	0.72 <sup>a</sup> [23,24]	0.69
FA	22.523	22.422	22.573	21.786	109.5	1.4475	0.64	0.48
HMPA	21.368	21.413	21.368	21.322	29.3	1.4588	1.00	1.00
NMF	22.222	22.124	22.222	21.834	182.4	1.4319	0.70	0.80
Pv	20.747	20.833	20.833	20.161	12.9	1.5102	0.85	0.64

Wavenumbers ( $\bar{v}_{CT}$ ) of the CT Vis absorption maxima of **6a–d**, measured in five solvents of different polarity and polarity parameters of these solvents.

<sup>a</sup> The relationship between the donor numbers and the parameter  $\beta$ , has been discussed in detail in the past [26–28].

a compound (**6a**–**d**) having the aryl substituent x,  $\tilde{v}_o$  the maximum CT absorption wavelength when x = H,  $\sigma_x$  is the Hammett substituent constant and  $\rho$  is the susceptibility of the CT absorption maxima wavenumbers of a compound **6a**–**d** on the substituent changes). The results of the corresponding correlations are listed in Table 3. These negative slopes in all cases reflect the tense of electron withdrawing substituents to decrease the energy needed to cause the excitation of the viologen betaines, possibly by efficiently decreasing the energy of excited state (depicted in Scheme 2). The substituent *p*-CN, in all solvents, is the one which causes the highest stabilization than the less electron withdrawing substituents *p*-CI and *p*-F, and by far the electron donating *p*-Me substituent.

It was also observed that as the polarity of the solvent increases, the susceptibilities expressed by the obtained regression values of  $\rho$  (slopes of Hammett equations, Table 3 and Fig. 3), tend to linearly increase, as shown in Fig. S16 of Supplementary data file. The physical meaning of this observation is that in more polar solvents the substituent effects are more pronounced, or in other words, the contribution of the substituent electron donating or withdrawing



Fig. 2. Plot of the experimentally obtained wavenumbers of the CT absorption maxima versus the calculated ones for **6a-d** in all five solvents used.

## Table 2

Results of the linear regression analysis between the wavenumbers of the CT absorption maxima of **6a**–**d** and the solvent polarity function  $[f(\varepsilon) + g(n)]$ .

Compound	$\alpha_{\rm LM}~(10^{-19}~{ m Joule})^{\rm a}$	$\tilde{v}_{o} \ (10^{-19} \text{ Joule})^{a}$	R <sup>b</sup>	$\ \Delta\mu\ $ (D)
<b>6a</b> : <i>p</i> -Me	$2.566 \pm 0.568$	$2.410\pm0.422$	0.93	10.986
<b>6b</b> : <i>p</i> -F	$\textbf{2.247} \pm \textbf{0.494}$	$2.643\pm0.367$	0.94	10.201
6c: p-Cl	$\textbf{2.460} \pm \textbf{0.633}$	$\textbf{2.494} \pm \textbf{0.470}$	0.91	10.619
<b>6d</b> : <i>p</i> -CN	$2.676\pm0.195$	$\textbf{2.253} \pm \textbf{0.145}$	0.99	11.535

<sup>a</sup> Slope and intercept of the family of equations:  $\tilde{v} = \tilde{v}_o + \alpha_{LM}[f(\epsilon) + g(n)]$ . <sup>b</sup> Correlation coefficient. character becomes higher in solvents of high dipolarity/polarizability, i.e. in the cases of higher energy difference between the ground and excited states of **6a**–**d**.

There is also an interesting correlation between the <sup>13</sup>C-NMR shifts of the compounds **6a**–**d**, and their CT maxima absorption wavelengths. As shown in Fig. 4, hypsochromic UV-Vis shifts keep up with the increasing low-field <sup>13</sup>C chemical shifts attributed to the resonance of the methylene carbon nuclei (measured in deuterated acetone) which follow the sequence: p-CN < p-Me < p-Cl < p-F. This general tense reflects the importance of the structure on the observed solvatochromic behavior. The deshielding of the carbon nuclei of the methylenes of compounds 6a-d in NMR, is a strong indication of the electron withdrawing character of the cationic part of the viologens, and of the HBD-acidic character of the compound. The compounds demonstrating the most acidic character are those which present the highest energy gap between the ground and excited state, since the ground state in these cases is more polar because of the intense charge separation. Thus in those cases the wavenumber of the CT visible maxima is higher. A linear plot is obtained for HMPA, whereas for the other four solvents parabolic plots were obtained. This can be attributed to the fact that HMPA is the best HBA-base of the examined group of solvents (HMPA, FA, NMF, DMAC PY). For a strong base like HMPA small



**Fig. 3.** Correlation plots between Hammett's substituent constants,  $\sigma_{x_i}$  and the wavenumbers of **6a-d**, measured in different solvents at room temperature.

Table 3

Results of the linear regression analysis between the wavenumbers of the CT absorption maxima of **6a**–**d** and the Hammett's substituent constants,  $\sigma_x$ .

Solvent	$\tilde{v}_{o} \ (10^3 \ cm^{-1})^{a}$	$ ho (10^3  { m cm^{-1}})^{ m a}$	R <sup>b</sup>
FA	$\textbf{22.499} \pm \textbf{0.139}$	$-0.889 \pm 0.385$	0.85
NMF	$22.189 \pm 0.066$	$-0.455 \pm 0.184$	0.87
DMAC	$21.692 \pm 0.016$	$-0.118\pm0.040$	0.89
HMPA	$21.382 \pm 0.020$	$-0.074 \pm 0.054$	0.70
Ру	$20.792 \pm 0.133$	$-0.764 \pm 0.370$	0.83

<sup>a</sup> Intercepts and slopes of the linear Hammett equations:  $\tilde{v} = \tilde{v}_0 + \rho \sigma_x$ .

<sup>b</sup> Correlation coefficient.

Table 1



**Fig. 4.** Correlation plots between the wavenumbers of **6a**–**d**, measured in different solvents at room temperature, and the <sup>13</sup>C chemical shifts of the methylenes of **6a**–**d** measured in [D6]ACMe.

changes in HBD-acidity amongst **6a**–**d** (reflected by downfield chemical shifts as mentioned) do not demonstrate an important role on the absorption maxima of the formed betaines. Thus linear dependence between  $\delta_{C-13}$  and  $\nu_{max}$  in this case is observed, as depicted in Fig. 4.

Additionally the difference in the dipole moments between the ground and excited states  $(\|\mu_{ex}\| - \|\mu_{g}\| = \|\Delta\mu\|)$  of the compounds **6a**–**d**, determined using the Lippert–Mataga model as described, are in good agreement with the NMR results. A successful correlation between the calculated  $\|\Delta \mu\|$  values and the <sup>13</sup>C-NMR shifts of the compounds attributed to the methylene carbon nuclei of **6a-d**, was observed as shown in Fig. 5. The negative slope corresponds to the increasing difference between the ground and excited states of **6a**–**d**, as the HBD-acidity of these viologens decreases, following the sequence p-CN < p-Me < p-Cl < p-F. The dependence of  $||\Delta \mu||$  on the Hammett constants  $\sigma_x$ , reveals different slopes ( $\rho$  values) for electron donor and electron acceptor substituents as shown in Fig. S15b of Supplementary data file. The deviation of linearity of the Hammett equation has been observed before. [29] The slope  $\rho$  corresponds to the susceptibility of the  $\|\Delta \mu\|$  on the electron withdrawing or donating character of the aromatic substituent of the viologen betaines, formed in mildbasic conditions. It is clear that the electron accepting ability of the



**Fig. 5.** The dependence of the calculated differences in ground and excited state dipole moments (absolute values) of **6a–d** on the <sup>13</sup>C chemical shifts of the methylenes of **6a–d** measured in [D6]AcMe.

aryl substituents of **6a–d**, do not control the observed phenomenon. The main impact is the HBD-acidity of **6a–d** (namely the HBD-acidity of the methylenes of **6a–d**). Thus linear correlations of  $\|\Delta\mu\|$  with the <sup>13</sup>C-NMR shifts are obtained, in contrast to the correlations of  $\|\Delta\mu\|$  with the Hammet parameter. This observation is aligned with our findings regarding the correlation  $\delta_{C-13} = f(\sigma_x)$ (Fig. S15a, of Supplementary data file).

# 5. Concluding remarks

A group of new solvatochromic viologens was synthesized. Their chromotropic behavior was induced only by solvents showing significant HBA-basic character. The impact of solvent dipolarity and polarizability as well as solvent basicity was proved to play an important role on the solvatochromic behavior of the studied non-symmetric viologens. Structural effects were also investigated and it was proved that the <sup>13</sup>C shifts of the methylenes of compounds **6a**–**d**, correlate well with the dipolarity of these compounds in their ground and exited states.

## Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.dyepig. 2012.06.013.

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