



Synthesis and characterization of a group of new medium responsive non-symmetric viologens. Chromotropism and structural effects

Raffaello Papadakis^{a,b,*}, Ioanna Deligkiozi^b, Athanase Tsolomitis^b

^aAix-Marseille Université, iSm2/Biosciences, UMR CNRS 7313, 13397, Marseille, France

^bSchool of Chemical Engineering, National Technical University of Athens (NTUA), Laboratory of Organic Chemistry, 15780 Athens, Greece

ARTICLE INFO

Article history:

Received 24 April 2012

Received in revised form

14 June 2012

Accepted 21 June 2012

Available online 28 June 2012

Keywords:

Viologens

Betaines

Solvatochromism

Substituent effects

Chromotropism

Dipole moments

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.

© 2012 Elsevier Ltd. All rights reserved.

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 photophysics 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

of transition metals like Ru^{II} and Fe^{II} 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'-phenacyl 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 ¹H, 75 MHz ¹³C). Both ¹H and ¹³C-NMR spectra were recorded in [D₆]DMSO or [D₆]Me₂CO at 25 ± 1 °C. The ¹H NMR spectra were calibrated by using residual undeuterated solvent as an internal reference (4.79 ppm) and ¹³C-NMR spectra were

* Corresponding author. School of Chemical Engineering, National Technical University of Athens (NTUA), Laboratory of Organic Chemistry, 15780 Athens, Greece. Tel.: +30 2107723081; fax: +30 2107723072.

E-mail address: rafpapadakis@gmail.com (R. Papadakis).

calibrated using the $[D_6]$ DMSO signal at 39.52 ppm or the $[D_6]$ Me₂CO 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 ± 1 °C. The concentrations of the solutions used, were about 50 ppm and they were prepared right before each measurement. Electrospray ionization (ESI) HRMS spectra were obtained on a Waters, Inc. Q-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⁻¹. 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(a–d)** were dissolved in H₂O by sonication and mild heating (at about ~50 °C). To the resulting solution 5 mL of a 4 M NH₄PF₆ 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 NH₄⁺ salts, and then with EtOH and finally with Et₂O. The as formed products are cleaned as follows. The hexafluorophosphate viologen salt **6(a–d)** was dissolved in MeCN and a solution of tetraethylammonium bromide (Et₄NBr) in MeCN (containing approximately 10 times the equimolar quantity of Et₄NBr in the minimum volume of MeCN) was added. The resulting bromide salt was filtered and washed with MeCN and Et₂O. Finally the bromide salt was transformed to the desired product **6a–d** by ion exchange using NH₄PF₆ as described before [16].

2.2.1.1. Viologen 6a (4-MePh). Beige powder, 629 mg (0.864 mmol) 72% mp = 228–230 °C. ¹H NMR (300 MHz, [D₆] AcMe): 9.69 (d, *J* = 6.0 Hz, 2H: C₅H₄N), 9.30 (d, *J* = 5.7 Hz, 2H: C₅H₄N), 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, >CH₂), 2.50 (s, 3H, CH₃). ¹³C-NMR (75 MHz, [D₆] 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 (>CH₂), 20.73 (Me). HRMS-ESI (*m/z*): [M-2PF₆]⁻, 100%, calc. for C₂₅H₂₂N₂O, 366.1732; found, 366.1727; IR (ATR): ν(C=O): 1739, 1641, 1541, 1438, 1369 cm⁻¹.

2.2.1.2. Viologen 6b (4-FPh). Beige powder, 591 mg (0.828 mmol) 69%, mp = 225–226 °C. ¹H NMR (300 MHz, [D₆] AcMe): 9.71 (d, *J* = 6.0 Hz, 2H: C₅H₄N), 9.42 (d, *J* = 6.3 Hz, 2H: C₅H₄N), 9.07 (d, *J* = 6.6 Hz, 2H: C₅H₄N), 9.03 (d, *J* = 6.3 Hz, 2H: C₅H₄N), 8.17 (m, 4H, arom.), 7.81 (t, *J* = 7.5 Hz, 1H: PhAc) 7.70 (m, 4H: arom.), 6.77 (s, 2H, >CH₂). ¹³C-NMR (75 MHz, [D₆] 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 (>CH₂). HRMS-ESI (*m/z*): [M-2PF₆]⁻, 100%, calc. for C₂₄H₁₉N₂O₂F, 370.1481; found, 370.1489; IR (ATR): ν(C=O): 1739, 1504, 1367 cm⁻¹.

2.2.1.3. Viologen 6c (4-ClPh). Beige powder, 584 mg (0.780 mmol) 65%, mp = 232–234 °C. ¹H NMR (300 MHz, [D₆] AcMe): 9.65 (d, *J* = 6.6 Hz, 2H: C₅H₄N), 9.41 (d, *J* = 6.0 Hz, 2H: C₅H₄N), 9.02 (m, 4H: C₅H₄N), 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: >CH₂). ¹³C-NMR (75 MHz, [D₆] 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 (>CH₂). Elemental analysis calcd for C₂₄H₁₉N₂OClP₂F₁₂: C 42.59, H 2.83, N 4.14, found: C 42.82, H 2.34, N 4.23, IR (ATR): ν(C=O): 1739, 1513, 1367 cm⁻¹.

2.2.1.4. Viologen 6d (4-CNPh). Beige powder, 536 mg (0.744 mmol) 62%, mp = 207–208 °C. ¹H NMR (300 MHz, [D₆] AcMe): 9.76 (d, *J* = 6.6 Hz, 2H: C₅H₄N), 9.31 (d, *J* = 5.1 Hz, 2H: C₅H₄N), 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, >CH₂). ¹³C-NMR (75 MHz, [D₆] 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 (>CH₂). HRMS-ESI (*m/z*): [M-2PF₆]⁻, 100%, calc. for C₂₅H₁₉N₃O, 377.1528; found, 377.1524; IR (ATR): ν(C=O): 1739, 1602, 1500, 1367 cm⁻¹.

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 ³V: 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 phenacetyl iodide (**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 (¹H and ¹³C) 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

Download English Version:

<https://daneshyari.com/en/article/176828>

Download Persian Version:

<https://daneshyari.com/article/176828>

[Daneshyari.com](https://daneshyari.com)