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# Synthesis of new pyrazinomethylviologens and the substituent effect of the nitrogen ylid on their absorption spectra

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Dicyanopyrazinylviologens (4-5) can be prepared by the reaction of 2-bromomethyl-3-phenyl-5,6-dicyanopyrazine with some bipyridines. Their absorption spectra and electronic properties are correlated with their chemical structures.

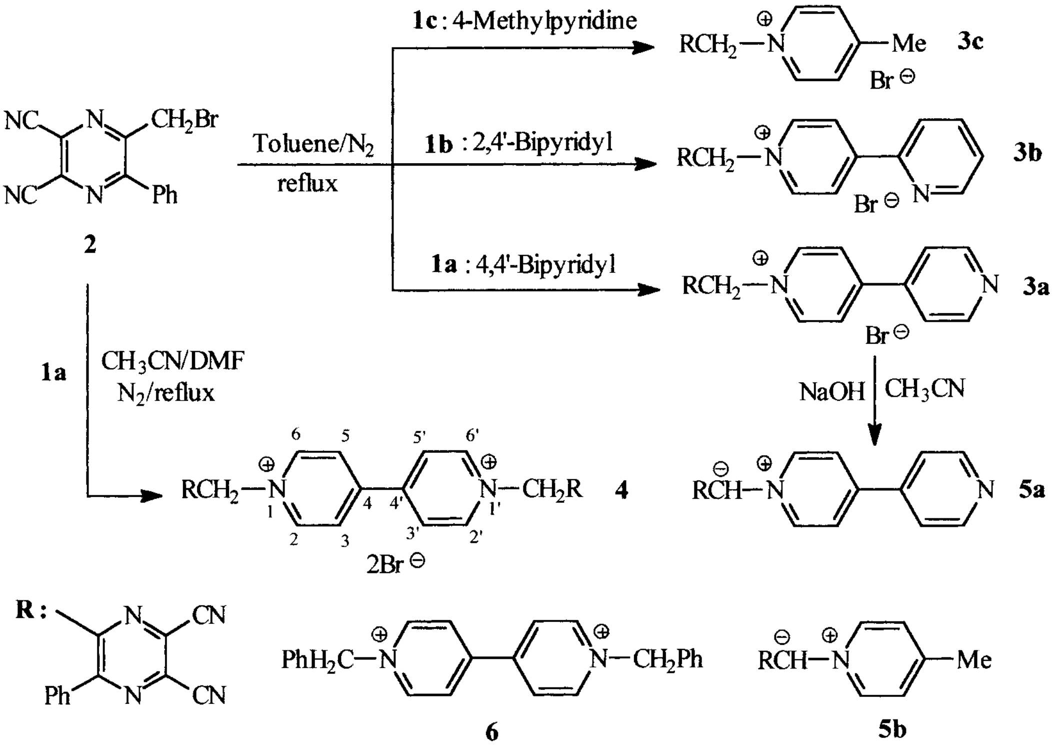
**Keywords:** azomethine ylids, bipyridines, dyes, electrochromism, pyrazines, viologens

Cyanopyrazines derived from hydrogen cyanide have been evaluated as new chromophores. New functional dyes based on dicyanopyrazines were synthesised, and their spectral and solid state properties revealed them as candidates for electroluminescence (EL)[1] and non linear optical (NLO) materials.[2,3] In this paper, we report the influence of a C–N ylid substituent on the absorption spectra and electronic properties of some viologens having 2,3-dicyano-5-phenylpyrazine groups.

Treatment of 4,4′-bipyridyl **1a** with 0.5 equiv of **2** in toluene under dry nitrogen afforded the mono-substituted product 1-(5,6-dicyano-3-phenylpyrazin-2-yl)methyl-4,4′-bipyridinium bromide **3a** because of the insolubility of **3a** in toluene (Scheme 1). The reaction of 4,4′-bipyridyl with 0.5 equiv. of **2** in a mixture of acetonitrile and DMF (7/3 v/v) under reflux gave the bis-quaternary product 1,1′-bis-(5,6-dicyano-3-phenylpyrazin-2-yl)methyl-4,4′-bipyridinium dibromide (**4**).

The methylene protons of compounds **3** and **4** are quite acidic because they are located between the dicyanopyrazine and the pyridinium groups. Compounds **3a** and **3c**, for example, were readily deprotonated by an excess of sodium hydroxide in acetonitrile to give the ylids **5a** and **5b** in 37% and 28% yields, respectively.

The absorption spectra of dyes **3** and **4** in acetonitrile were measured at the cathode after electrocolouration in the presence of tetrabutylammonium perchlorate as electrolyte. Their absorption spectra are relatively narrow, and produced



**Scheme 1**

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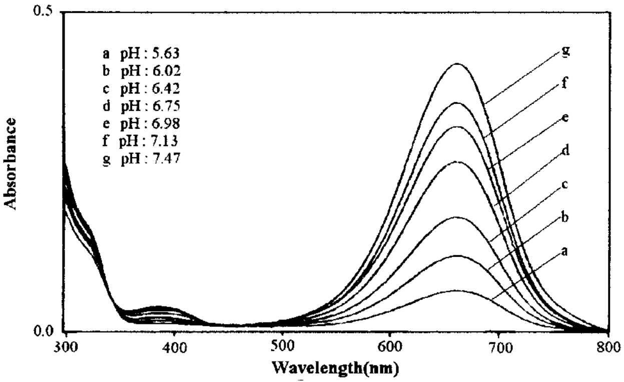

**Fig. 3** Spectral changes of **4** on varying the pH of the buffer solution.

hypsochromic shifts of 40–90 nm compared with those of 1,1′-dibenzyl-4,4′-bipyridinium dibromide **6**, which shows a very broad absorption band. In the case of the dye **4** a bathochromic shift of 70 nm over the band of **6** is observed. The absorbance increases significantly depending on the applied voltage and time. In the case of dyes **3a** and **3b**, which are violet, the absorption maximum was observed at around 570 nm. Dye **3c** absorbs at 495 nm and its colour is red. In the case of **4**, the predominant peak appears at 668 nm and the colour is blue. The $\lambda_{max}$ of dye **3** produced a bathochromic shift depending on the order of the enlargement of $\pi$-conjugation from **3c** to **4**. Reversible spectra changes were also observed on the anode, leading to discoloration.

We had assumed at an earlier stage of this work that the coloured species ($\lambda_{max}$ = 665 nm) formed by applying the cathodic voltage to **4** were the corresponding radical cations, like the viologen radical cations of **6**. But the absorption spectra of dyes **3a** and **3c** at the cathode show the same pattern to those in the DMSO solution of **5a** and **5b**. An aqueous solution showed a drastic pH change in the cathodic and anodic compartments. Applying the cathodic voltage turned the medium basic, while the anode compartment become acidic. Although the electrical reduction and oxidation of dye may readily occur in the solution and be followed by a colour change, the effect of applied potential to these compounds may be the result of an acid–base reaction, different from that of benzyl viologen **6** which produced the cation radical in the same conditions.

The same absorption spectral changes were also observed when pyridine as a base was added to an acetonitrile solution of dyes **3** and **4**. The intensity of $\lambda_{max}$ increased with increasing base concentration, as shown in Fig. 3.

These ylids show an intense absorption band in the visible region and are isolated as stable colored solids. These compounds have considerable stability even in solution (lifetime $\tau_{1/2}$ = *ca* 4h for **4**). It is very interesting that these species are stable ylids, in which a negative carbon is strongly stabilised by the dicyanopyrazine ring and besides the positive charge on the pyridine nitrogen seems to be strengthened by an electron withdrawing group substituted at the 4-position and useful electrostatically to stabilize the carbanion, as a field effect.

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Techniques used: $^1$H NMR spectroscopy, mass spectrometry, UV-VIS, elemental analysis

Table 1: Reactions of Bipyridyl **1** with **2**

Table 2: Scale of acidity (25°C)

Schemes: 2

References: 8

Fig. 1: Visible spectral changes of **3a** (A), **3c** (B) and **4** (C) in $CH_3CN$ by the electro-reduction.

Fig. 2: The effects of pyridine on the absorption spectra of **3a** (A), **3c** (B) and **4** (C) in $CH_3CN$ ($2 \times 10^{-5}$ mol/l).

Fig. 3: Spectral change of **4** on varying the pH of the buffer solution.

Fig. 4: Relationship between $pK_a$ and $\lambda_{max}$ in buffer solutions of **3** and **4**.

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