Synthesis and spectral properties of new quinoxalines with electron donor groups

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Three new 6,7-bis(3-methylbutyloxy)-2,3-(2-phenylethenyl)quinoxalines with groups of different electron-donating ability on the phenyl rings were prepared. The substituent effects on the absorption spectra of these fluorescent dyes in solution were studied.

Keywords: halochromism, UV absorption spectra, quinoxalines

Fluorescent heterocyclic compounds are of interest as functional materials in the fields of emitters for electroluminescence devices,[1a] molecular probes for biochemical research,[1b] and in traditional textile and polymer areas.[2] Heterocyclic fluorophores are useful materials in the search for new biologically active compounds and diagnostic methods.[3]

Our research group has been interested in the chemistry of nitrogen-containing heterocyclic molecules for many years. We have studied new fluorescent chromophores based on the pyrazine nucleus. New fluorescent compounds such as styrylpyrazines,[4] pyrazinophthalocyanines[5] and pyrazino-heterocycles[6] have been reported. As part of this study, we have designed and synthesised some new 6,7-bis (3-methylbutyloxy)quinoxaline derivatives with different electron-donating abilities. The chromophoric systems of these compounds, and the substituent effects on their absorption spectra in solution, were studied

The preparation of 1,2-bis-(3-methylbutyloxy)-4,5-diaminobenzene (**1**) has been described in the literature.[7] Treatment of 1,4-dibromobutane-2,3-dione with **1** in the presence of a catalytic amount of *p*-toluenesulfonic acid in methanol afforded 2,3-bis-(bromomethyl)-6,7-bis-(3-methylbutyloxy)quinoxaline (**2**) in 55% yield. Reaction of **2** with excess of triethylphosphite produced [3-(diethoxy-phosphorylmethyl)-6,7-bis-(3-methylbutyloxy)quinoxalin-2-ylmethyl]-phosphonic acid diethyl ester (**3**). This crude product was used in the next step without purification. Reaction of **3** with two equivalents of arylaldehydes in the presence of 2.1 equivalents of sodium hydride in tetrahydrofuran gave the styryl derivatives **4** in moderate yield. (Scheme 1)

The formation of **4** was supported by ^{1}H NMR spectroscopy and elemental analysis. For example, the ^{1}H NMR spectra of **4c** showed the ethylene protons as doublets at 7.72 and 7.45 ppm with J = 15.6 Hz revealing a *trans*-configuration. The chemical shifts of the phenyl protons were at 7.57 and 6.74 ppm, while those of the quinoxaline protons and the protons of the NMe_2 group were singlets at 7.27 and 3.02 ppm, respectively.

The absorption and fluorescence maxima of **4** in chloroform were observed in the regions 420–444 nm and 470–567 nm, respectively (Table 1).

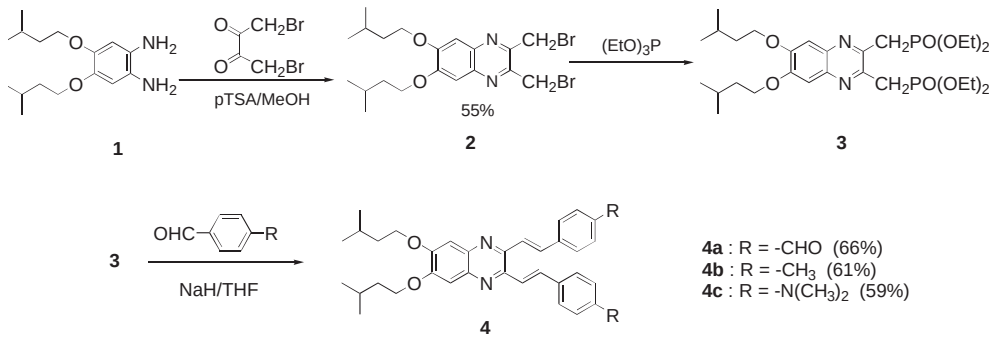
In acidic medium the absorption spectra of **4** were dramatically changed. Thus, the original yellow solution of **4b** became orange on addition of *p*-toluenesulfonic acid, returning to the original yellow by addition of triethylamine. The colour change is considered to be due to the protonation of the nitrogen atom in the quinoxaline ring. It has been reported that protonation of nitrogen of heteroaromatic poly(arylene) systems in acidic media sometimes leads to a bathochromic shift of the absorption peak.[8,9]

UV-visible spectra of synthesised novel quinoxalines in chloroform/methanol (10 / 1) were measured while varying the mole ratio of quinoxaline : *p*-toluenesulfonic acid (pTSA). Both quinoxaline derivatives showed bathochromic shifts with increase of the proportion of pTSA. The UV-visible spectra of **4a** showed the maximum shift of the absorption band at the mole ratio 1:32 but the absorption band of **4c** shifted dramatically from 1:0 to 1:3 and remained unchanged above 1:7. These observations are a result of the various electron-donating abilities of the substituents. In the case of **4c**, we suppose that the quinoxaline nitrogen atoms in the 1,4-positions are easily saturated with electrons and so protonated by less PTC than those of **4a**, and that subsequently the electron density of protonated nitrogen decreased and the electron-withdrawing ability of quinoxaline increased. This was verified by the shift in

Table 1 Visible and fluorescence spectra of quinoxalines **4**

Compd	λ_{max} [a] (nm)	λ_{max} [b] (nm)	F_{max} [c] (nm)	F_{max} [d] (nm)
4a	420	480	470	574
4b	422	494	474	560
4c	444	600	567	602

[a]In $CHCl_3/CH_3OH$ (10/1), [b]In acid solution, [c]Fluorescence maximum excited at λ_{max} [a]value, [d]Fluorescence maximum excited at λ_{max} [b]value.



Scheme 1 Reaction route to the quinoxalines

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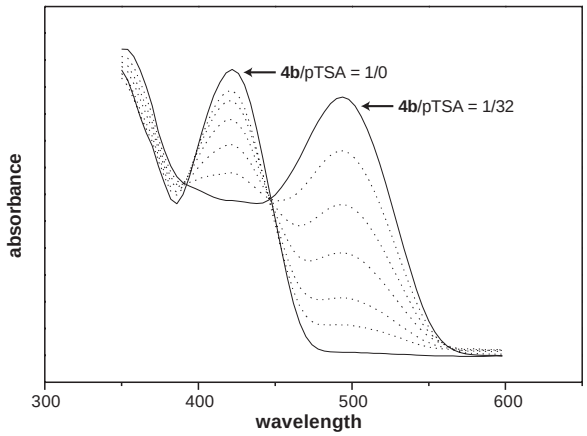

Fig. 1 The effect of *p*-toluenesufonic acid (pTSA) on the absorption spectra of **4b** in $CHCl_3$ / CH_3OH (10 / 1).

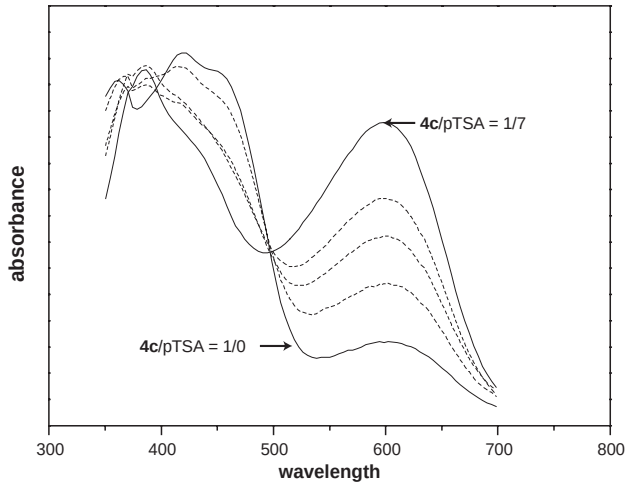

Fig. 2 The effect of *p*-toluenesufonic acid (pTSA) on the absorption spectra of **4c** in $CHCl_3$ / CH_3OH (10 / 1).

the proton signal of the quinoxaline ring (H5/8) from 7.27ppm to 7.32ppm in the ^{1}H NMR when trifluoroacetic acid was added.

In conclusion, it is expected that quinoxaline derivatives with different electron-donor groups will have different sensitivity and absorption spectra under acidic conditions.

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Experimental

Melting points were obtained with a capillary melting point apparatus. ^{1}H NMR spectra were recorded on a Bruker DRX-300 FT-NMR Spectrometer using TMS as internal standard. Elemental analyses were performed on a CE, EA 1110. The visible and fluorescence spectra were measured on Unicam 8700 and Shimadzu RF-5301PC spectrophotometers.

*6,7-Bis-(3-methylbutyloxy)-2,3-bis(bromomethyl)quinoxaline (**2**)*

The reaction mixture of 1,4-dibromobutane-2,3-dione (18g, 70 mmol), an equivalent amount of 1,2-bis-(3-methylbutyloxy)-4,5-diaminobenzene, and a catalytic amount of *p*-toluenesulfonic acid in methanol (50 ml) were refluxed for 2hr under nitrogen atmosphere. After the reaction was completed, the reaction mixture was cooled to room temperature and the precipitate was filtered off. The crude product was purified by flash chromatography (silica gel, EtOAc : hexane = 1:4) to give **2** in 55% yield as a white solid, m.p. 66–67 °C. ^{1}H NMR (300MHz, $CDCl_3$) δ 0.99 (d, 12H, J 6.0, CH_3). 1.81 (m, 6H, CH and CH_2), 4.18(t, 4H, J 6.3, OCH_2), 4.88 (s, 4H, CH_2Br), 7.30 (s, 2H, ArH); Anal. Calcd. for $C_{20}H_{28}Br_2N_2O_2$: C, 49.20; H, 5.78; N, 5.74. Found: C, 49.35; H, 5.88; N, 5.70 %.

*Distyrylquinoxalines **4**, typical procedure*

A mixture of **2** (24.4g, 50 mmol) and triethyl phosphite (41.5g, 250 mmol) was refluxed for 16 hr. After cooling, the excess of triethylphosphite was removed in vacuo to leave a brown residue. This crude product **3** was used in the next step without purification.

To a mixture of N,N-dimethylaminobenzaldehyde (0.957g, 4 mmol) and sodium hydride (0.083g, 4.2 mmol) in tetrahydrofuran (THF, 10ml) was added the bis-phosphonate ester (**3**) (1.205g, 2 mmol) in THF (20ml), and the mixture was refluxed for 2 h. Concentration of the mixture under reduced pressure afforded a crude product which was purified by flash chromatography (silica gel, EtOAc : hexane = 1 : 3) to provide the *bis-(4-dimethylaminostyryl) compound* **4c** (0.7g, 59%) as a yellow solid, m.p. 137–138 °C from methanol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (d, 12H, *J* 6.3, CH_3). 1.83–1.91 (m, 6H, CH and CH_2), 3.02 (s, 12H, NCH_3), 4.21 (t, 4H, *J* 6.3, OCH_2), 6.74 (d, 4H, *J* 7.8, ArH), 7.27 (s, 2H, quinoxaline), 7.45 (d, 2H, *J* = 15.6Hz, ethylene), 7.57 (d, 4H, *J* 7.8, ArH), 7.72 (d, 2H, *J* = 15.6Hz, ethylene); Anal. Calcd. for $C_{38}H_{48}N_4O_2$: C, 76.99; H, 8.16; N, 9.45. Found: C, 76.56; H, 8.20; N, 9.28 %.

Dialdehyde **4a**: the product formed as a yellow solid, m.p. 197-198 °C, from methanol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02ppm (d, 12H, CH_3), 1.82-1.90ppm (m, 6H, CH and CH_2), 4.14ppm (t, 4H, OCH_2), 7.32ppm (s, 2H, quinoxaline), 7.76 (d, 2H, *J* = 15.6Hz, ethylene), 7.81 (d, 4H, *J* = 6.9Hz, ArH), 7.93 (d, 4H, *J* = 6.9Hz, ArH), 7.96 (d, 2H, *J* = 15.6Hz, ethylene), 9.98ppm (s, 2H, CHO). Anal. Calcd. for $C_{36}H_{38}N_2O_4$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.99; H, 6.95; N, 4.85 %.

Bis-(4-methylstyryl) compound **4b.** The product was recrystallised form methanol as a yellow solid, m.p. 159–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02ppm (d, 12H, CH_3), 1.82-1.86ppm (m, 6H, CH and CH_2), 2.4ppm (s, 6H, CH_3), 4.22ppm (t, 4H, OCH_2), 7.22 (d, 4H, *J* = 7.8Hz, ArH), 7.30ppm (s, 2H, quinoxaline), 7.56 (d, 4H, *J* = 7.8Hz, ArH), 7.58 (d, 2H, *J* = 15.6Hz, ethylene), 7.84ppm (d, 2H, *J* = 15.6Hz, ethylene). Anal. Calcd. for $C_{36}H_{42}N_2O_2$: C, 80.86; H, 7.92; N, 5.24. Found: C, 81.02; H, 7.99; N, 5.19 %.

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