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SYNTHESIS OF A NEW CONJUGATED 2,2'-(1,4-PHENYLENEDIVINYLENE)BISQUINOXALINE AND A SERIES OF STYRYL DERIVATIVES OF QUINOXALINE AND QUINOLINE AS PROMISING ELECTRO- AND PHOTOLUMINESCENT MATERIALS

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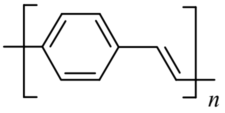
A new poly(p-phenylenedivinylene) oligomer 2,2'-(1,4-phenylenedivinylene)bisquinoxaline, a promising candidate in organic electroluminescent devices, was synthesised via a Knoevenagel condensation reaction of 2-methylquinoxaline with 1,4-benzenedicarbaldehyde. The same synthetic strategy was applied to obtain substituted styryl dyes, derivatives of quinoxaline, whereas styryl derivatives of quinoline were prepared by "Anil Synthesis". The considered dyes are of interest as fluorescence emitting materials.

Keywords: "Anil Synthesis", Knoevenagel condensation, luminophores, poly(*p*-phenylenedivinylene) oligomer.

Organic compounds used as electroluminescent materials can be divided into two major classes, the first one is based on low molecular weight compounds like fluorescent dyes and metal chelates, and the second one involves polymeric materials [1]. The nitrogen/oxygen-containing π-electron deficient heterocycles such as oxadiazoles, triazoles, triazines, pyridines, pyrimidines, quinolines, and quinoxalines are potential candidates for ETL (electron-transporting layer) materials [2]. Polyquinoxalines (PQxs), for example, combine advantageous features such as high electron affinity, good thermal stability, and good processability with sufficiently low refractive indices [3]. Due to their chemical structure PQxs have been utilized as electron



PPV

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transporting materials in OLEDs (organic light emitting diodes) [4, 5]. Another fundamental work concerning the evolution of OLEDs was published by Friend et al. [6]. They used a highly fluorescent conjugated polymer: poly(*p*-phenylenevinylene) (PPV) as the active material in a single-layer OLED.

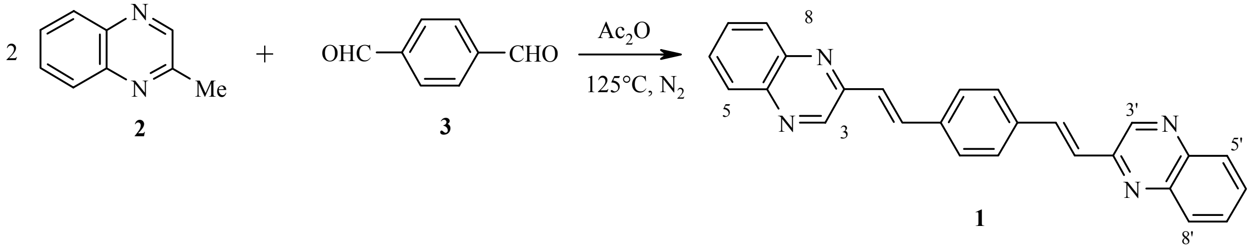
Although PPV itself is insoluble and difficult to process, Friend et al. [6] found a way to build up PPV-OLEDs *via* the thermoconversion of a processable precursor polymer. Today growing attention is paid to modification of conjugated molecules by changing their central cores in order to investigate the structural influence on the LED properties [7]. In this context Liang and coworkers have tested PPV oligomers containing 8-substituted quinolines [8, 9].

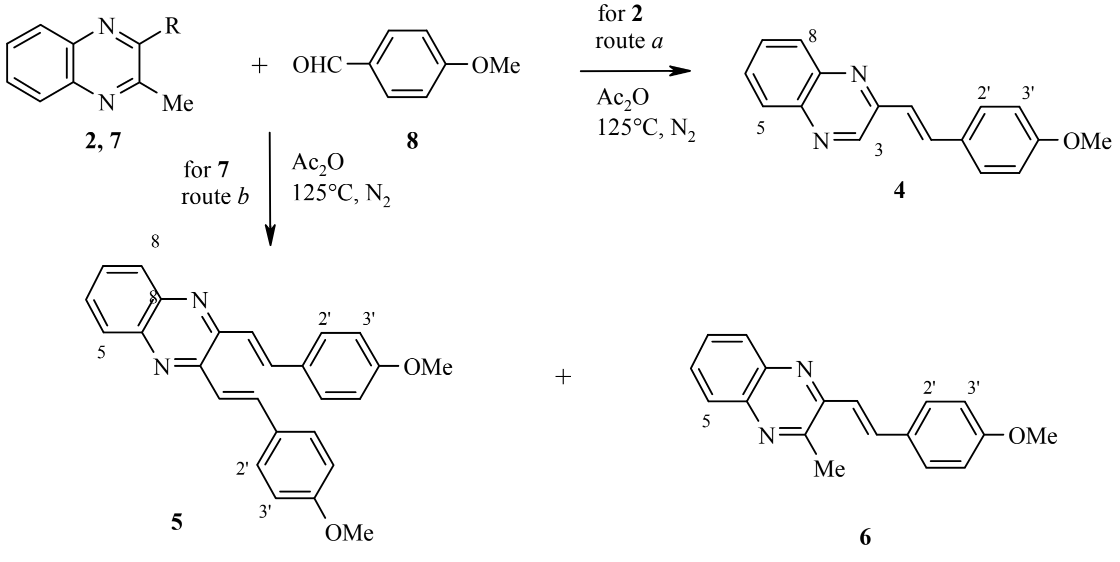
In recent years, the technical importance of stilbenyl and styryl heterocycles has rapidly increased as a result of the wide application of products, especially those serving as fluorescent whitening agents [10, 11].

Styrylpyridinium salts, for example, have interesting physical properties enabling their use in nonlinear optics and in physiology/biochemistry areas [12], whereas styrylquinolinium methyl sulfate is useful in photography as an optical sensitizer [13].

In the present work we have performed a one-pot synthesis of a new PPV oligomer: 2,2'-(1,4-phenylenedivinylene)bisquinoxaline (**1**) from 2-methylquinoxaline (**2**) serving as a starting material. The reason for using quinoxaline as a building block is that polyquinoxalines are excellent electroluminescent and electron-transporting materials [4, 5]. We have also examined the synthesis and properties of styryl derivatives of quinoxaline and quinoline.

It is well known that the methyl group in position 2 of the quinoline and quinoxaline ring can be activated by the presence of a nitrogen atom, and then it undergoes condensation with an aldehyde catalyzed by an acid or base [14, 15]; in our experiments we chose the acid catalyst. The reaction of 2-methylquinoxaline (**2**) with 1,4-benzenedicarbaldehyde (**3**) in acetic anhydride affords the condensation product **1**.





2 R = H, **7** R = Me

Compound **1** was fully characterized by ^{1}H NMR spectroscopy and elemental analysis. In the ^{1}H NMR spectrum it exhibits two doublets at 6.97 and 7.11 ppm with a three-bond coupling constant $^3J_{H,H} = 16.4$ Hz arising from *trans* carbon–carbon double bonds, indicating the presence of *trans*-configuration in the vinylene units.

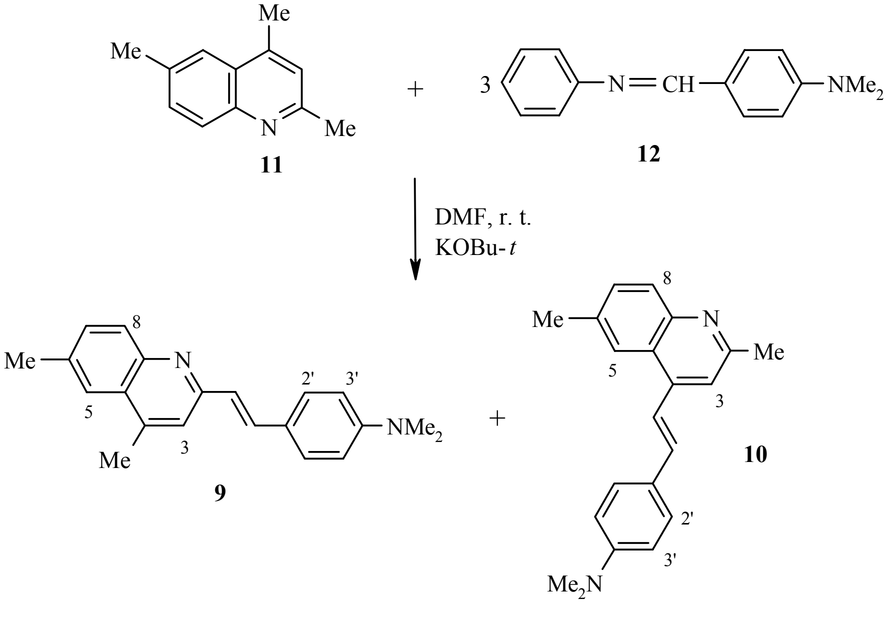
For the synthesis of styrylquinoxalines **4–6** the same synthetic strategy (Knoevenagel condensation) as for PPV oligomer was used. The styrylquinoxalines **4–6** were prepared by condensation of 2-methyl-quinoxaline **2** (route *a*) and 2,3-dimethylquinoxaline (**7**) (route *b*) with 4-methoxybenzaldehyde (**8**).

The structures of resulting compounds were confirmed by ^{1}H NMR spectroscopy and elemental analysis. The spin-spin coupling constants for the olefinic protons of compounds **4–6** (15.6–16.3 Hz) indicate the presence of *trans*-double bond.

The variously substituted N,N-dimethylaminostyrylquinoline derivatives **9** and **10** were obtained by "Anil Synthesis" [16]. In this procedure 2,4,6-trimethylquinoline (**11**) (prepared by the reaction of *p*-toluidine with acetylacetone) and Schiff's base **12** in the ratio 1 equivalent per one reacting methyl group of **11** were stirred at room temperature for 1.5 h.

Products **9** and **10** were isolated by separation of the reaction mixture by column and TLC preparative chromatography. Their structures were confirmed by ^{1}H NMR and elemental analysis results.

All considered products exhibited intense luminescence in $CHCl_3$ and DMF solution under UV excitation (365 nm). The color of luminescence is pale blue for compounds **1**, **4–6** and yellow-green for compounds **9** and **10**. This strong fluorescence suggests that these materials are suitable candidates for fabricating a light-emitting devices. Further research on their emissive applications is in progress.



EXPERIMENTAL

Melting points were determined on a Boetius apparatus. The TLC was performed on 60F 254 silica gel precoated DC aluminium sheets (Merck). ^{1}H NMR spectra were recorded on a 200 MHz Bruker spectrometer using TMS as an internal standard. Mass spectra were measured on a AMD-604 instrument at 70 eV. The results of elemental analyses agreed favorably with the calculated data.

2,2'-(1,4-Phenylenedivinylene)bisquinoxaline (1). A mixture of 2-methylquinoxaline **2** (1.44 g, 10 mmol), 1,4-benzenedicarbaldehyde (**3**) (0.67 g, 5 mmol), and acetic anhydride (10 ml) was stirred and heated at 125°C for 40 h under N_2. The reaction mixture was then poured into ice water (ca 100 ml) and stirred overnight. The dark-brown solid obtained was filtered off, washed with water, and dried to give compound **1** (1.44 g, 75%) as an orange powder from DMF. Mp 268–270°C. ^1H NMR (DMSO-d_6), δ, ppm (*J*, Hz): 9.25 (2H, s, H-3,3'); 8.11 (2H, d, *J* = 8.6, H-5, 5'); 7.93–7.75 (6H, m, H-6, 6', 7,7', 8,8'); 7.60 (4H, s, H Ar); 7.11 (d, *J* = 16.4, 2H *trans*-olefinic); 6.97 (d, *J* = 16.4, 2H *trans*-olefinic). Mass spectrum, *m/z* (*I*, %): 386 $[M^+]$ (100), 257 $[M^+–C_8H_5N_2]$ (25). Found, %: C 80.64; H 4.74; N 14.31. $C_{26}H_{18}N_4$. Calculated, %: C 80.81; H 4.69; N 14.49.

2-(*p*-Methoxystyryl)quinoxaline (4). A mixture of 2-methylquinoxaline **2** (1.44 g, 10 mmol), *p*-methoxybenzaldehyde **8** (1.36 g, 10 mmol), and acetic anhydride (15 ml) was stirred and heated at 125°C for 40 h under N_2. It was poured into ice water (100 ml) and stirred for 2 h. After extraction with dichloromethane (3×30 ml) the organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was then evaporated and the residue was purified by column chromatography using hexane–ethyl acetate (5:4) as an eluent to give compound **4** (1.52 g, 58%) as bright-red needles. Mp 118–119°C. ^1H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 9.03 (s, H-3); 8.15 (d, *J* = 8.6, H-5); 7.92–7.77 (3H, m, H-6,7,8); 7.45 (d, *J* = 8.8, 2H-2'); 7.13 (d, *J* = 16.3, 1H *trans*-olefinic); 6.98 (d, *J* = 16.3, 1H *trans*-olefinic); 6.91 (d, *J* = 8.8, 2H-3'); 3.82 (s, OCH_3). Mass spectrum, *m/z* (*I*, %): 262 $[M^+]$ (86.5), 231 $[M^+–OCH_3]$ (18). Found, %: C 77.59; H 5.43; N 10.41. $C_{17}H_{14}N_2O$. Calculated, %: C 77.84; H 5.38; N 10.68.

2,3-Di(*p*-methoxystyryl)quinoxaline (5) and 2-(*p*-methoxystyryl)-3-methylquinoxaline (6). A mixture of compound **7** (1.58 g, 10 mmol), compound **8** (2.72 g, 20 mmol), and acetic anhydride (20 ml) was stirred and heated at 125°C for 40 h under N_2. It was poured into ice water (100 ml) and stirred overnight. After extraction with dichloromethane (3×30 ml) the organic layer was washed with water and dried over anhydrous Na_2SO_4. Evaporation of the solvent left an oil, which was separated by column chromatography using dichloromethane as an eluent to give compound **5** (1.3 g, 31.4%) as bright-orange crystals (from trichloromethane–ethanol, 1:1) and compound **6** (0.95 g, 34.4%) as yellow plates (from trichloromethane–ethanol, 1:1).

Compound 5. Mp 130°C. ^1H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 7.87 (2H, d, *J* = 8.6, H-5, 8); 7.72 (2H, dd, *J* = 8.6, *J* = 6.9, H-6,7); 7.28 (d, *J* = 8.6, 4H-2'); 7.10 (d, *J* = 16.0, 2H *trans*-olefinic); 7.05 (d, *J* = 16.0, 2H *trans*-olefinic); 6.93 (d, *J* = 8.6, 4H-3'); 3.85 (s, $2OCH_3$). Mass spectrum, *m/z* (*I*, %): 153 $[M^+–2C_6H_4OCH_3–C_2H_3]$ (100). Found, %: C 78.95; H 5.71; N 7.04. $C_{26}H_{22}N_2O_2$. Calculated, %: C 79.16; H 5.62; N 7.10.

Compound 6. Mp 138°C. ^1HNMR ($CDCl_3$), δ, ppm (*J*, Hz): 7.87-7.77 (3H, m, H-5,7,8); 7.56 (dd, *J* = 8.6, *J* = 6.8, H-6); 7.43 (d, *J* = 8.6, 2H-2'); 7.09 (d, *J* =15.6, 1H *trans*-olefinic); 6.95–6.90 (3H, m, 2H-3' and 1H olefinic); 3.83 (s, OCH_3); 2.65 (s, CH_3). Mass spectrum, *m/z* (*I*, %): 276 $[M]^+$ (7), 277 $[M^++1]$ (100). Found, %: C 78.03; H 5.97; N 10.03. $C_{18}H_{16}N_2O$. Calculated, %: C 78.23; H 5.83; N 10.13.

4,6-Dimethyl-2-(*p*-N,N-dimethylaminostyryl)quinoline (9) and 2,6-Dimethyl-4-(*p*-N,N-dimethylaminostyryl)quinoline (10). A mixture of 2,4,6-trimethylquinoline **11** (1.71 g, 10 mmol) and (*p*-N,N-dimethylaminobenzylidene)aniline **12** (6.72 g, 30 mmol) in anhydrous DMF (70 ml) was stirred while potassium *tert*-butoxide (3.36 g, 30 mmol) was slowly added. After addition, the color of the mixture was changed from yellow to brown and tthe emperature increased to 30°C. After 1.5-h stirring followed by cooling the reaction mixture was poured into water and acidified with 10% HCl. The orange precipitate was filtered off, dried, and separated by column chromatography using dichloromethane–acetone (5:1) as an eluent. The main fraction of noncrystalline material, 1.98 g showing two spots in TLC, was separated by preparative TLC chromatography using dichloromethane–methanol (9:1) as an eluent. Two products were obtained: **9** (1.12 g, 37,3%) as red crystals (benzene) and **10** (0.60 g, 20%) as violet crystals (ethanol).

Compound 9. Mp 158–160°C. ^1H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 7.82 (d, *J* = 15.8, 1H *trans*-olefinic); 7.74 (s, H-5); 7.51 (d, *J* = 8.5, H-8); 7.41 (s, H-3); 7.25 (d, *J* = 8.5, H-7); 7.10–7.03 (3H, m, 2H-2', and 1H olefinic); 6.60 (d, *J* = 8.7, 2H-3'); 2.90 (s, $N(CH_3)_2$); 2.73 (s, CH_3); 2.35 (s, CH_3). Mass spectrum, *m/z* (*I*, %): 303 $[M^++1]$ (22.6). Found, %: C 83.17; H 7.49; N 9.09. $C_{21}H_{22}N_2$. Calculated, %: C 83.40; H 7.33; N 9.26.

Compound 10. Mp 209–210°C. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 7.76 (s, H-5); 7.55 (d, *J* = 15.6, 1H *trans*-olefinic); 7.48 (d, *J* = 8.5, H-8); 7.30 (s, H-3); 7.23 (d, *J* = 8,45, H-7); 7.18 (d, *J* = 15.6, 1H *trans*-olefinic); 7.03 (d, *J* = 8.5, 2H-2'); 6.74 (d, *J* = 8.5, 2H-3'); 2.99 (s, $N(CH_3)_2$); 2.67 (s, CH_3); 2.42 (s, CH_3). Mass spectrum, *m/z* (*I*, %): 302 [M^+] (12), 303 [M^++1] (100), 172 [$M^+ - C_6H_4N(CH_3)_2$] (15). Found, %: C 83.37; H 7.21; N 9.05. $C_{21}H_{22}N_2$. Calculated, %: C 83.40; H 7.33; N 9.26.

REFERENCES

1. J. Salbeck, *Ber. Bunsenges. Phys. Chem.*, **100**, 1667 (1996).
2. M. Thelakkat, H.-W. Schmidt, *Polym. Adv. Technol.*, **9**, 429 (1998).
3. V. Mitschke, P. Bäuerle, *J. Mater. Chem.*, **10**, 1471 (2000).
4. T. Fukuda, T. Kanbara, T. Yamamoto, K. Ishikava, H. Takezoe, A. Fakuda, *Appl. Phys. Lett.*, **68**, 2346 (1996).
5. D. O'Brien, A. Bleyer, D. D. C. Bradley, S. Meng, *Synth. Methods*, **76**, 105 (1996).
6. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature*, **347**, 539 (1990).
7. A. J. Attias, P. Hapiot, V. Wintgens, P. Volat, *Chem. Mater.*, **12**, 461 (2000).
8. F. Liang, Z. Xie, L. Wang, X. Jing, F. Wang, *Tetrahedron Lett.*, **43**, 3427 (2002).
9. F. Liang, J. Chen, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, *J. Mater. Chem.*, **13**, 1392 (2003).
10. H. Gold, *The Chemistry of Synthetic Dyes*, Academic Press, New York, 1971, Vol. 5, p. 535.
11. R. Anliker, G. Müller, *Environmental Quality and Safety*, Suppl. Vol. IV, Thieme, Stuttgart, 1975.
12. T. K. Das, N. Periasamy, G. Krishnamoorthy, *Biophys. J.*, **64**, 1122 (1993).
13. T. Lesiak, K. Marzec, J. Nowakowski, Pol. Pat. PL 164,792 (1994); *Chem. Abstr.*, **125**, 221601y (1996).
14. F. Cherioux, P. Audebert, *Chem. Mater.*, **10**, 1984 (1998).
15. A. J. Attias, C. Cavalli, B. Bloch, N. Guillou, C. Noël, *Chem. Mater.*, **11**, 2057 (1999).
16. A. E. Siegrist, *Helv. Chim. Acta,* **50**, 906 (1967).