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Syntheses of 1,2-Bis[5-(2'-Benzoxazolyl)-Pyrrole-2-yl] Ethene

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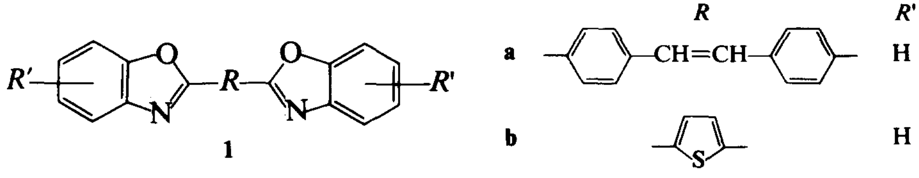
ABSTRACT

Condensation of 1,2-bis(5-ethoxycarbonyl-pyrrolyl)ethene with 2-aminophenol gives new bis(benzoxazol-2-yl) fluorescent compounds which contain a bispyrrolylethene fragment. Their properties were compared with those of 1,2-bis[5-(2'-benzoxazolyl)]stilbene.

1 INTRODUCTION

4,4'-Bis[5-(2'-benzoxazolyl)]stilbene **1a** has been used for many years as a brightening agent. Although numerous investigations have focused on substituent patterns for *R'* and *R* in this type of compound,[1] few have been concerned with the replacement of the phenyl ring by a pyrrole ring in compounds of type **1a**.



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In the synthesis of a bis[5-(2'-benzoxazol-2-yl)]stilbene **1a** analogue, we found that 1,2-bis[5-(2'-benzoxazolyl)-pyrrole-5-yl]ethene could be prepared by condensing 1,2-bis(5-ethoxycarbonyl-pyrrolyl)ethene **3** with 2-aminophenol. The synthetic route and the properties of the compounds are discussed.

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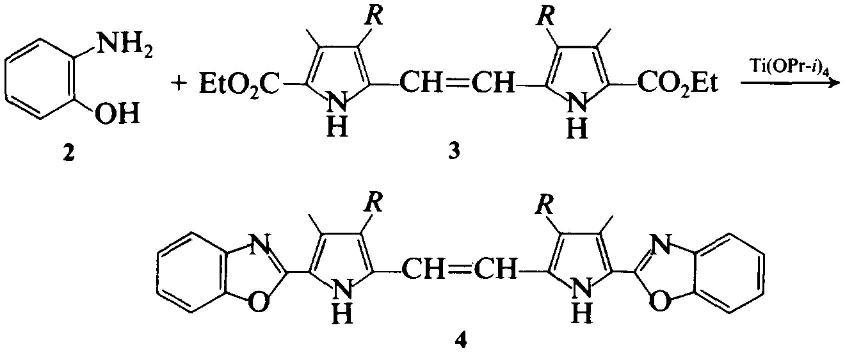
2 RESULTS AND DISCUSSIONS

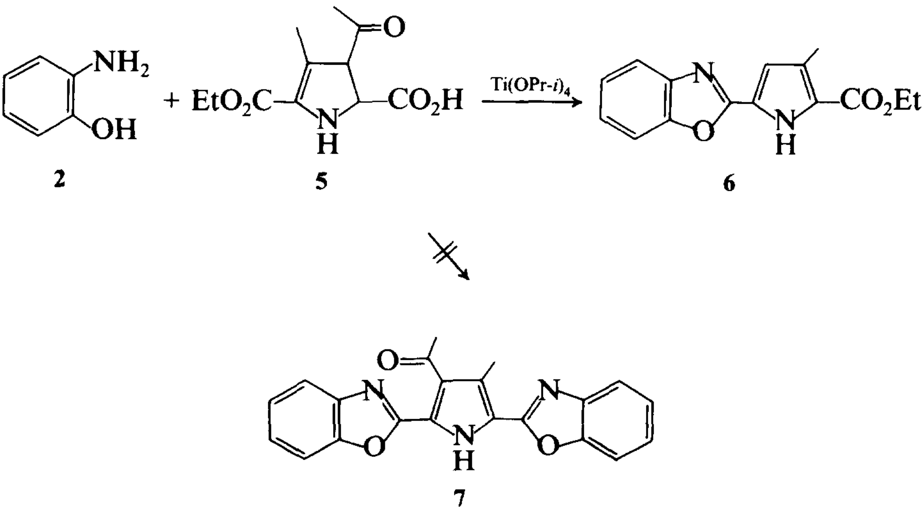
Bis(benzoxazol-2-yl) derivatives **1** are usually prepared by treatment of dicarboxylic acids (e.g. stilbene-4,4'-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid, thiophenedicarboxylic acid, etc) with 2 moles of an appropriately substituted 2-aminophenol, followed by ring closure.[1]

In our studies of the synthesis of the fluorescent compounds **4** (Scheme 1), it was found that 1,2-bis(ethoxycarbonyl-pyrrolyl)ethene **3** could be condensed directly with 2-aminophenol to form the goal compounds. Compared with typical methods, in which the dicarboxylic acid and not the dicarboxylate ester is used, this procedure was more convenient and



(R = **a** Et, **b** CO_2Et)

Scheme 1



Scheme 2

effective, because the dicarboxylic acids of **3** were less stable than the esters under the reaction conditions used.

Attempts to synthesize **7**, which is a homologue of 2,5-bis(5-benzoxazolyl-2-yl)thiophene **1b**, did not succeed by condensing 2,5-pyrroledicarboxylic acid **5** with 2-aminophenol, as the product obtained was **6**. In this reaction, the acetyl group was lost at the high temperature used, and the reaction occurred at only one side of the system, the other side remaining unchanged.

3 EXPERIMENTAL

3.1 General

^{1}H NMR and ^{13}C NMR were recorded on a Bruker-500 MHz with TMS as the internal standard. UV/Vis spectra were recorded on a HP-8451A instrument, and IR spectra on a Perkin-Elmer 983G spectrophotometer. Mass spectra were measured on a Finnigan MS-90 instrument, and melting points were determined with a micro-melting point apparatus. The fluorescence spectra were measured on a Hitachi-8501 Model spectrofluorimeter; fluorescence quantum yields were determined by three or four independent measurements using 9,10-anthracene as standard (ϕ_f (298 K) = 0·27 in ethanol).[2] Elemental analyses were run on a Carlo Erba 1102 apparatus. Silica gel G_{254} was used for column chromatography.

3.2 General procedure for preparation of compounds 4

A mixture of 1,2-bis(ethoxycarbonyl-pyrrolyl)ethene **3** (4·2 mmole),[3,4] 2-aminophenol (0·96 g, 8·82 mmole, 2·1 mole equiv.), naphthalene (20 g) and Ti(OPr-*i*)$_4$ (0·2 g, 0·7 mmole, 0·17 mole equiv.) was heated to reflux for 7 h under an argon atmosphere. After cooling to room temperature, the mixture was extracted with methylene chloride (50 ml), then the solid residue was removed by filtering. The solution was passed through a flash chromatographic column (silica G_{254}, ϕ 5·5 × 7 cm) using petroleum ether (60–90°C): methylene chloride (v : v from 9 : 1 to 1 : 9). The fluorescent compounds were crystallized from methylene chloride: petroleum ether (30–60°C).

3.3 1,2-Bis[3-ethyl-4-methyl-5-(2'benzoxazoyl)-1*H*-pyrrol-2-yl]ethene [4a; $C_{30}H_{28}N_4O_2$]

This compound was prepared as above; yield 52%, m.p. > 300°C. ^{1}H NMR (CDCl$_3$, δ, 400 MHz): 1·23 (t, J = 7·5 Hz, 2 CH$_2$CH$_3$), 2·50 (s, 2

CH_3), 2·70 (q, J = 7·5 Hz, 2 CH_2CH_3), 5·27 (s, —CH=CH—), 7·21–7·69 (m, phenyl), 11·80 (br s, 2 NH) ppm. ^1H NMR (DMSO-d_6, δ, 400 MHz): 1·20 (t, J = 7·5 Hz, 2 CH_2CH_3), 2·56 (s, 2 CH_3), 2·69 (q, J = 7·5 Hz, 2 CH_2CH_3), 5·75 (s, —CH=CH), 7·40–7·70 (m, phenyl), 11·78 (br s, 2 NH) ppm. IR (KBr), ν = 3434, 3184, 2925, 1616, 1582, 1538, 1479 cm^{-1}. MS (EI, 70 eV): *m/e* (%) = 476 (M^+, 100), 475 (2·2), 432 (3·9), 431 (10·1), 238 (5·0), 28 (42·9). For $C_{30}H_{28}N_4O_2$ *m/e* (M^+) calc. 476·2210, found 476·2209; $C_{30}H_{28}N_4O_2$ (476·2), calc. C 75·63, H 5·88, N 11·76, found C 75·84, H 6·00, N 11·53. UV/Vis ($CHCl_3$): λ_{max} = 260 (25 400), 325 (13 700), 440 (42 800), 469 (36 500) nm (ε); UV/Vis (DMSO): λ_{max} = 270 (44 400), 440 (59 400), 469 (52 000) nm (ε). ϕ_f = 0·39 at 520 nm in ethanol.

3.4 1,2-Bis[3-ethoxycarbonyl-4-methyl-5-(2'-benzoxazoyl)-1*H*-pyrrol-2-yl]-ethene [4b; $C_{32}H_{28}N_4O_6$]

This compound was prepared as above; yield 48%, m.p. 240–242°C. ^1H NMR ($CDCl_3$, δ, 400 MHz): 1·35 (t, J = 7·5 Hz, 2 OCH_2CH_3), 2·70 (s, 2 CH_3), 4·30 (q, J = 7·5 Hz, 2 OCH_2CH_3), 7·50 (m, phenyl), 7·80 (s, —CH=CH—), 11·03 (br s, 2 NH) ppm. ^1H NMR (DMSO-d_6, δ, 400 MHz): 1·37 (t, J = 7·65 Hz, 2 OCH_2CH_3), 2·73 (s, 2 CH_3), 2·78 (q, J = 7·65 Hz, 2 OCH_2CH_3), 7·64 (m, phenyl), 8·03 (s, —CH=CH—), 11·78 (br s, 2 NH) ppm. IR (KBr), ν = 3410, 2990, 1690, 1620, 1590, 1460 cm^{-1}. MS (EI, 70 eV): *m/e* (%) = 564 (M^+, 100), 474 (15·4), 418 (3·9), 282 (15·0), 28 (42·9). For $C_{32}H_{28}N_4O_2$ *m/e* (M^+) calc. 564·2009, found 564·2012. $C_{32}H_{28}N_4O_6$ (564·2), calc. C 68·08, H 4·59, N 9·92, found C 68·20, H 4·80, N 9·80. UV/Vis ($CHCl_3$): λ_{max} = 260 (25 400), 318 (36 800), 408 (42 300) nm (ε); UV/Vis (DMSO): λ_{max} = 265 (24 300), 320 (35 000), 400 (25 200) nm (ε). ϕ_f = 0·41 at 490 nm in ethanol.

3.5 Ethyl-5-(2'-benzoxazolyl)-3-methyl-1*H*-pyrrole-2-carboxylate [6; $C_{15}H_{14}N_2O_3$]

A mixture of the pyrrole compound **5** (1·66 g, 6·94 mmole),[5] 2-aminophenol (1·74 g, 6 mmole, 2·3 mole equiv.), biphenyl (10 g), and Ti(OPr-*i*)$_4$ (0·2 g, 0·7 mmole, 0·1 mole equiv.) was heated to reflux for 10 h under an argon atmosphere. After cooling to room temperature, the mixture was purified as above, yielding the title compound (0·62 g, 33%), m.p. 166–168°C. ^1H NMR ($CDCl_3$, δ, 80 MHz): 1·40 (t, J = 7·65 Hz, OCH_2CH_3), 2·35 (s, CH_3), 4·35 (q, J = 7·65 Hz, OCH_2CH_3), 7·24–7·75 (m, 5H, 4 × phenyl-H, pyrrolyl-H), 10·50 (br s, NH) ppm. IR (KBr), ν = 3296, 3000, 1688, 1620, 1590, 1300 cm^{-1}. MS (EI, 70 eV): *m/e* (%) = 270 (5·2, M^+), 197 (100), 152 (33·3), 118 (25·3). $C_{15}H_{14}N_2O_3$ (270·2), calc. C 66·67, N 10·37, H 5·19, found C 66·85, N 10·50, H 5·30. UV/Vis ($CHCl_3$): λ_{max} = 249 (8 640), 328 (29 000), 344 (18 900) nm (ε); UV/Vis (DMSO): λ_{max} = 326 (28 000), 341 (17 000) nm (ε). ϕ_f = 0·57 at 390 nm in ethanol.

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REFERENCES

1. Zweidler, R. & Hefti, H., In Encyclopedia of Chemical Technology, 3rd edn. ed. Kirk-Othmer. John Wiley & Sons, 1978, Vol. 4, p. 213.
2. Demas, J. N., *J. Phy. Chem.*, **75** (1971) 991.
3. Chen, Q.-Q., Yan, F., Ma, J.-S. & Jin, S., *Chinese Chem. Lett.*, **4** (1993) 567.
4. Chen, Q.-Q., Falk, H. & Micura, R., *Monats. Chem.*, **126** (1995) 473.
5. Chen, Q.-Q., *Doctoral dissertation*, Peking University, 1993.