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SHORT COMMUNICATIONS

New Schiff Bases Derived from 2,5-Dihydroxybenzaldehyde and Amino-Substituted 2-Phenyl-1,3-benzothiazoles. Mesogenic Monomers for Liquid Crystalline Polyethers

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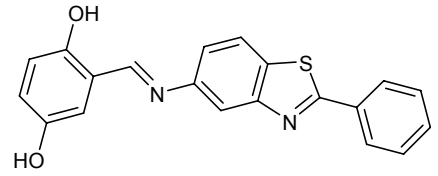
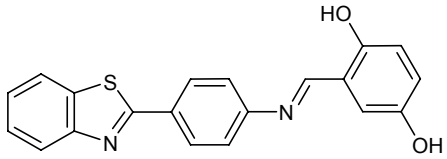
Condensation of 2,5-dihydroxybenzaldehyde (**I**) with amino-substituted 2-phenyl-1,3-benzothiazoles **II** and **III** in methanol in the presence of HCl gave new Schiff bases **IV** and **V** which can be used as mesogenic heteroaromatic monomers for the synthesis of potentially mesogenic rigid–flexible polyethers.



IV



V

4-(1,3-Benzothiazol-2-yl)aniline (**II**) was synthesized by condensation of 2-aminobenzenethiol with 4-aminobenzoic acid in 112% polyphosphoric acid at 145°C [1], and 2-phenyl-1,3-benzothiazol-5-amine (**III**) was obtained by condensation of 2,4-diaminobenzenethiol with benzoic acid under analogous conditions [1]. 2,4-Diaminobenzenethiol was prepared by reduction of 2,2′,4,4′-tetranitrodiphenyl disulfide [2] with tin(II) chloride in hydrochloric acid according to the procedure described in [3].

2-{(*E*)-[4-(1,3-Benzothiazol-2-yl)phenylimino]-methyl}benzene-1,4-diol (IV). A solution of 1.0 g (7.2 mmol) of 2,5-dihydroxybenzaldehyde (**I**) in 40 ml of methanol containing 0.02 ml of concentrated hydrochloric acid was added dropwise to a solution of 1.6 g (7.2 mmol) of compound **II** in 90 ml of methanol. The mixture was stirred for 5 h at 50°C, and the precipitate was filtered off, washed, and dried. Yield 1.58 g (63%), mp 237–240°C (from propan-2-ol), R_f 0.86. IR spectrum (KBr): ν 1621 cm^{-1} (CH=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.80 d (1H, CH, J = 8.0 Hz), 7.45 t (1H, CH, J = 7.8 Hz), 7.48 d (1H, H_{arom}, J = 8.8 Hz), 7.60–7.68 m (4H, H_{arom}), 7.85 d (1H, CH, J = 8.8 Hz), 7.89 s (1H, CH), 8.20 d (2H, CH, J = 7.0 Hz), 9.05 s (1H, HC=N), 10.48 s (1H, OH), 12.9 s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 117.4 (CH), 118.3 (C), 119.5 (CH), 120.2 (CH), 121.8 (CH), 121.9 (CH), 122.4 (CH), 122.9 (CH), 125.6 (CH), 126.3 (CH), 128.5 (CH), 128.8 (CH), 133.8 (C), 134.6 (C), 149.8 (C), 151.2 (C), 153.3 (COH), 153.7 (COH), 163.9 (CH=N), 166.7 (C). Found, %: C 69.66; H 4.20; N 8.38. $C_{20}H_{14}N_2O_2S$. Calculated, %: C 69.39; H 4.05; N 8.09.

2-{(*E*)-[(2-Phenyl-1,3-benzothiazol-5-yl)imino]-methyl}benzene-1,4-diol (V) was synthesized in a similar way from amine **III**. Yield 2.08 g (83%), mp 228–230°C (from propan-2-ol), R_f 0.84. IR spectrum (KBr): ν 1618 cm^{-1} (CH=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.98 d (1H, CH, J = 8.0 Hz), 7.43 t (1H, CH, J = 7.8 Hz), 7.49 d (1H, H_{arom}, J = 8.8 Hz), 7.62–7.68 m (4H, H_{arom}), 7.84 d (1H, CH, J = 8.8 Hz), 7.88 s (1H, CH), 8.20 d (2H, CH, J = 7.0 Hz), 9.03 s (1H, HC=N), 10.18 s (1H, OH), 13.01 s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 116.6

(CH), 117.4 (CH), 119.2 (C), 119.4 (CH), 120.2 (CH), 120.4 (CH), 125.6 (CH), 127.4 (CH), 129.4 (CH), 129.6 (CH), 132.2 (CH), 132.6 (CH), 133.3 (C), 142.5 (C), 145.7 (C), 149.2 (C), 151.2 (COH), 153.7 (COH), 160.2 (CH=N), 163.7 (C). Found, %: C 65.23; H 4.04; N 7.60. $C_{20}H_{14}N_2O_2S \cdot H_2O$. Calculated, %: C 65.93; H 4.39; N 7.69.

The ^{13}C NMR spectra were recorded on a Bruker CXP-100 spectrometer at 25 MHz using tetramethylsilane as internal reference. The ^{1}H NMR spectra were measured on a Bruker AC-400 spectrometer relative to TMS. The IR spectra were obtained on a Shimadzu FTIR-8400S instrument from samples pelleted with KBr. The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates using toluene–ethyl acetate (1 : 1) as eluent; spots were detected by UV irradiation. Compounds **IV** and **V** showed luminescence upon irradiation at λ 365 nm (Spectroline ENF-260C/FE). The elemental compositions were determined on a Leco CHNS(O)-932 analyzer.

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