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ORIGINAL PAPER

Conjugated push–pull salts derived from linear benzobisthiazole: preparation and optical properties

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Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

A series of novel monomethylated salts derived from linear benzobisthiazole was prepared. The push–pull attributes of these new compounds are represented by a quaternised azolium cycle as the acceptor part at one end of the structure and the dialkylamino- or diarylamino-substituted benzene ring as the donor part at the opposite end. Both moieties are connected by a conjugated linker consisting of one or two double bonds. Such dipolar structures are promising candidates for non-linear optical materials. The quantum-chemical indices describing linear and non-linear optical properties were obtained from semi-empirical calculations. The relationships between the chemical structure and non-linear optical properties of the cations studied were obtained. Effective conjugation was confirmed by measuring the optical properties in the UV-VIS region.

Keywords: heterocycles, thiazolium salts, conjugation, non-linear optics, condensation

Introduction

Organic heterocyclic compounds with a push–pull structure are noted for their wide range of applications as chromophores in non-linear optics (NLO), in the second harmonic generation (SHG) (Zhang et al., 2001), molecular probes (Fox, 1992), fluorescent markers (Lakowicz, 1994), organic light-emitting diodes (OLED) (Balaganesan et al., 2003), or photovoltaic cells (Loudet & Burgess, 2007). A typical push–pull organic chromophore consists of a polar A-π-D structure with a planar π-system end-capped with a strong electron donor (D) and a strong electron acceptor (A). These systems use the following conventional substituents: dialkylamino or diarylamino groups as donors and nitro, cyano, or carbonyl groups as acceptors. The special set of D-π-A molecules comprises heteroaromatic cations as the acceptor part; the heterocycles in most use are pyridinium, tetrazolium, acridinium, and benzothiazolium fragments. Conjugated benzothiazolium salts are known and in commercial use, mainly as cyanine dyes (Thioflavine T, Thiazole Orange, Basic Blue 41) (Mojzych & Henary, 2008). Some D-π-A benzothiazolium salts show antibacterial and anthelmintic effects (dithiazanine). The NLO properties of benzothiazolium salts, especially the unique two-photon absorption parameters, were demonstrated (Hrobáriková et al., 2010). In an effort to enhance NLO response, the benzothiazole part of the molecule was replaced with a more robust linear benzobisthiazole backbone which can occur in two isomers with axial or central symmetry. This structure renders it possible to prepare one- or two-armed condensation products. A further possibility for enhancing the acceptor capacity of the heterocyclic unit is alkylation of one or both of the heterocyclic nitrogen atoms. In this article, we focus on the synthesis and study of monomethylated salts derived from linear centrosymmetric benzobisthiazole and its one-armed condensation products with donor-substituted aromatic aldehydes. The electron donor part of the de-

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signed dipolar structures is represented by a dimethylaminophenyl fragment by default. Here, a variation in substituents renders it possible to modify other physicochemical properties of the target compounds, e.g. solubility in different solvents. In order to enlarge the second order hyperpolarisability we proposed exchanging the dialkylamino group for the diphenylamino group and, in addition, for *N*-carbazolyl residue with a stable conformation of the benzene rings. The planar aromatic structures are known for their poor solubility in common solvents. Designed compounds with additional hydroxyl or methoxy groups as well as the *N*-methylpiperazinyl group with non-planar conformation are characteristic of improved solubilities in solvents like methanol and dimethyl sulphoxide (DMSO). The connection between the donor and acceptor parts ensured by one or two double bonds originated in the condensation reactions.

Computational details

The restricted Hartree–Fock method was chosen for the quantum-chemical calculations. The optimised geometries for each compound in vacuo were calculated in the Turbomole V6.2 program (Turbomole, 2010), using the DFT method (Treutler & Ahlrichs, 1995) and the B3LYP exchange-correlation functional (Becke, 1993; Lee et al., 1988). On all atoms, the TZVP basis set (Schäfer et al., 1994) was employed. DFT total energy as well as orbital energies were obtained in this way.

The DFT geometry was used as input for calculation of all the required linear and non-linear quantities. The final characteristics (polarisability α, first and second hyperpolarisabilities β and γ were obtained using the semi-empirical PM3 method (Stewart, 1989a, 1989b, 1991). A finite-field method for calculation of the static first and second hyperpolarisability developed by Kurtz et al. (1990) was applied. This procedure, as well as the semi-empirical method used, is implemented in the AMPAC molecular modelling package (Semichem, 2004).

Experimental

Solvents were purified and dried using standard methods. Commercially unavailable substituted benzaldehydes were synthesised according to previously published methods: 4-diphenylaminobenzaldehyde (*IIIb*) from triphenylamine (Hrobáriková et al., 2010), 4-(4-methylpiperazin-1-yl)benzaldehyde (*IIId*) from 4-fluorobenzaldehyde (Magdolen et al., 2001), and 4-(bis-(2-hydroxyethyl)aminobenzaldehyde (*IIIe*) from the corresponding 4-bis-(2-acetoxyethyl) derivative (Le Bouder et al., 1998).

The reactions where the substrate was treated under ultrasound conditions were performed using a UUA Ultragen (20 kHz, 300 W) GENTECH ultrasonic submersible generator. For reactions performed under microwave irradiation, the Initiator^{TM} BIOTAGE (max. power 300 W) reactor was used. Melting points were measured on an Electrothermal IA-9200 Kofler apparatus and were not corrected. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Gemini 2000 spectrometer. IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer (Smart iTR diamond ATR). HRMS were recorded on a Shimadzu LC-IT-TOF MS instrument using both ESI positive and ESI negative modes. Electronic absorption spectra were obtained on a Jenway 6705 UV-VIS spectrophotometer. Chromatography was performed using Swambe Chemicals silica gel 60 A flash (230–400 mesh) or neutral aluminium oxide.

Preparation of 2,6-dimethylbenzo[1,2-d:4,5-d′] bisthiazole (I)

Triethylamine (3.58 mL, 25.7 mmol) was added dropwise to a stirred suspension of 2,5-diaminobenzene-1,4-dithiol dihydrochloride (3.0 g, 12.2 mmol) in dry 1,4-dioxane (100 mL) in a three-necked flask (equipped with thermometer, condenser, and dropping funnel) in an argon atmosphere below 35 ℃. Acetic anhydride (2.88 mL, 30.5 mol) was then added dropwise and the reaction mixture was heated to reflux for 3 h. After cooling to ambient temperature, the mixture was carefully neutralised with a 20 % aqueous NaOH solution. The precipitate was collected by filtration, then dried and purified by column chromatography on silica gel using hexane/ethyl acetate (φ_r = 1 : 1) as the eluent to give pure product (53 %) as a white solid; m.p. 229–230 ℃ (Mike et al. (2010) reported 232–233 ℃). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.36 (s, 2H, H_{Ar}), 2.88 (s, 6H, 2 × CH_3); ^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.58 (s, 2H, H_{Ar}), 2.83 (s, 6H, 2 × CH_3).

2,3,6-Trimethylbenzo[1,2-d:4,5-d′]bisthiazol-3-ium iodide (II)

Iodomethane (2.50 g, 17.6 mmol) was added to 2,6-dimethylbenzo[1,2-*d*:4,5-*d*′]bisthiazole (*I*) (0.775 g, 3.52 mmol) dissolved in methanol (20 mL) in the glass vessel from the microwave reactor and the reaction mixture was exposed to microwave irradiation at 115 ℃ for 50 min. After cooling to ambient temperature, the precipitated product was filtered and washed with diethyl ether. An additional portion was obtained by concentrating the filtrate at reduced pressure. The crude product contaminated by 5–10 mass % of diiodide was purified by crystallisation from ethanol to give 0.583 g (46 %) of white solid; m.p. 262–264 ℃ (Lochon et al. (1967) reported 264 ℃); ^{1}H NMR (300 MHz, DMSO-d_6), δ: 9.07 (s, 1H, H-4), 8.96 (s, 1H,

Table 1. Characterisation data of newly prepared benzobisthiazolium salts

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
			C	H	N	S	%	°C
IVa	$C_{20}H_{20}IN_3S_2$	493.43	48.68	4.09	8.52	13.00	70	279–281
			48.34	4.09	8.79	13.10		
IVb	$C_{30}H_{24}IN_3S_2$	617.57	58.35	3.92	6.80	10.38	76	228–230
			58.79	3.92	6.59	10.34		
IVc	$C_{30}H_{22}IN_3S_2$	615.55	58.54	3.60	6.83	10.42	52	194–196
			58.51	3.76	7.06	10.63		
IVd	$C_{23}H_{25}IN_4S_2$	548.51	50.36	4.59	10.21	11.69	78	238–241
			50.40	4.67	9.95	11.94		
IVe	$C_{22}H_{24}IN_3O_2S_2$	553.48	47.74	4.37	7.59	11.59	49	264–267
			47.54	4.24	7.35	10.95		
IVf	$C_{24}H_{28}IN_3O_2S_2$	581.53	49.57	4.85	7.23	11.03	47	215–218
			49.29	4.89	7.03	10.83		
V	$C_{22}H_{22}IN_3S_2$	519.46	50.87	4.27	8.09	12.35	89	277–280
			50.85	4.20	8.09	12.71		

H-8), 4.22 (s, 3H, CH_3N^+), 3.20 (s, 3H, CH_3 at C6), 2.92 (s, 3H, CH_3 at C2).

General procedure for preparation of benzobisthiazol-3-ium salts IVa–IVf and V

The aldehyde *III* (0.525 mmol, 1.05 eq) was added to a suspension of 2,3,6-trimethylbenzo[1,2-*d*:4,5-*d*′]bisthiazol-3-ium iodide (*II*) (0.181 g, 0.5 mmol) in methanol (20 mL) in the glass vessel from the microwave reactor and the mixture was exposed to irradiation at 100 °C for 20 min. The course of the reaction was monitored by TLC. After cooling, the precipitated product was filtered, washed with a small portion of cold methanol, diethylether, and finally dried. In the case of *IVc*, the reaction time was prolonged to 5 h, the temperature increased to 115 °C, and two drops of pyridine were added to the reaction mixture. The yields and spectral characteristics of the salts obtained are summarised in Tables 1 and 2.

Preparation of 4-(carbazol-9-yl)benzaldehyde (IIIc)

Potassium carbonate (2.90 g, 21.0 mmol) was added to the solution of carbazole (3.34 g, 20.0 mmol) and 4-fluorobenzaldehyde (4.93 g, 40 mmol) in DMSO (30 mL). The reaction mixture was exposed to ultrasonic irradiation generated by an ultrasonic horn in an open flask for 30 min. The temperature of the reaction mixture attained 140 °C at the end of sonication. After cooling to 60 °C, the reaction mixture was poured into distilled water (400 mL), the precipitate was filtered, washed with water, and dried. The crude product was purified by crystallisation from cyclohexane (starting carbazole is insoluble) to give pure *IIIc* (3.18 g, 59 %); m.p. 153–155 °C (Zhang et al. (2001) reported 156–158 °C); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 10.12 (s, 1H, CHO), 8.15 (d, J = 7.5 Hz, 2H, H-1′, H-8′), 8.13 (d, J = 9.0 Hz, 2H, H-2, H-6), 7.80 (d, J = 9.0 Hz, 2H, H-3, H-5), 7.51 (d, J = 8.1 Hz, 2H, H-4′, H-5′), 7.44 (td, J = 7.0 Hz, J = 1.2 Hz, 2H, H-3′, H-6′), 7.33 (td, 2H, H-2′, H-7′).

Preparation of 4-(bis-(2-methoxyethyl)amino) benzaldehyde (IIIf)

Caesium carbonate (1.45 g, 4.5 mmol) was added to a solution of 4-fluorobenzaldehyde (1.22 g, 10.0 mmol) and bis(2-methoxyethyl)amine (1.33 g, 10.0 mmol) in DMSO (10 mL) in the glass vessel from the microwave reactor and the mixture was exposed to irradiation at 160 °C for 1 h. The cooled reaction mixture was poured into distilled water (200 mL) and extracted with diethyl ether (3 × 50 mL). The combined ether layers were washed with water and brine, dried with Na_2SO_4, and concentrated at reduced pressure to give the crude product (oil) which was purified by column chromatography on silica gel using hexane/ethyl acetate (φ_r = 2 : 1) as the eluent to give colourless oil (0.12 g, 5 %); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 9.73 (s, 1H, CHO), 7.71 (d, J = 9.0 Hz, 2H, H-2, H-6), 6.74 (d, J = 9.0 Hz, 2H, H-3, H-5), 3.65 (t, J = 5.3 Hz, 4H, 2 × CH_2O), 3.58 (t, J = 5.3 Hz, 4H, 2 × CH_2N), 3.35 (s, 6H, 2 × CH_3O).

Results and discussion

The condensation reaction between 2,5-diaminobenzene-1,4-dithiol and acetic anhydride was chosen for synthesis of the linear benzobisthiazole skeleton. The older method (Finzi & Grandolini, 1959), originally employed for synthesis of isomeric 2,6-dimethylbenzo[1,2-*d*:5,4-*d*′]bisthiazole, was improved

Table 2. Spectral data of newly prepared compounds

Compound	Spectral data[a]
IVa	IR, $\tilde{\nu}$/cm^{-1}: 3065, 2913, 1600, 1568, 1435, 1381, 1263, 1160 ^{1}H NMR (DMSO-d_6), δ: 2.90 (s, 3H, CH_3), 3.13 (s, 6H, $(CH_3)_2N$), 4.24 (s, 3H, CH_3N^+), 6.87 (d, 2H, J = 9.1 Hz, H_{Ar}), 7.66 (d, 1H, J = 15.2 Hz, CH═), 7.94 (d, 2H, J = 9.1 Hz, H_{Ar}), 8.11 (d, 1H, J = 15.2 Hz, CH═), 8.84 (s, 2H, H_{Ar}) ^{13}C NMR (DMSO-d_6), δ: 20.1 (CH_3), 35.6 (CH_3), 48.5 (CH_3), 106.1 (CH), 109.0 (CH), 111.9 (2 × CH), 116.3 (CH), 121.4 (C), 125.1 (C), 133.0 (2 × CH), 136.5 (C), 139.3 (C), 150.5 (CH), 151.6 (C), 153.5 (C), 170.6 (C), 171.5 (C)
IVb	IR, $\tilde{\nu}$/cm^{-1}: 3032, 1568, 1505, 1483, 1428, 1326, 1260, 1166 ^{1}H NMR (DMSO-d_6), δ: 2.91 (s, 3H, CH_3), 4.30 (s, 3H, CH_3N^+), 6.92 (d, 2H, J = 8.9 Hz, H_{Ar}), 7.20–7.28 (m, 6H, H_{Ar}), 7.45 (t, 4H, J = 7.6 Hz, H_{Ar}), 7.80 (d, 1H, J = 15.5 Hz, CH═), 7.93 (d, 2H, J = 8.9 Hz, H_{Ar}), 8.17 (d, 1H, J = 15.5 Hz, CH═), 8.91 (s, 1H, H_{Ar}), 8.95 (s, 1H, H_{Ar}) ^{13}C NMR (DMSO-d_6), δ: 20.2 (CH_3), 36.1 (CH_3), 109.8 (CH), 110.0 (CH), 116.5 (CH), 118.8 (2 × CH), 125.5 (2 × CH), 125.6 (C), 126.0 (C), 126.1 (4 × CH), 130.0 (4 × CH), 131.9 (2 × CH), 136.9 (C), 139.2 (C), 145.3 (2 × C), 149.0 (C), 151.5 (CH), 152.0 (C), 171.2 (C), 172.0 (C)
IVc	IR, $\tilde{\nu}$/cm^{-1}: 3046, 1515, 1444, 1398, 1353, 1333, 1265, 1165 ^{1}H NMR (DMSO-d_6), δ: 2.94 (s, 3H, CH_3), 4.45 (s, 3H, CH_3N^+), 7.29 (d, 2H, J = 8.6 Hz, H_{Ar}), 7.33–7.38 (m, 2H, H_{Ar}), 7.47–7.52 (m, 2H, H_{Ar}), 7.55 (d, 2H, J = 7.7 Hz, H_{Ar}), 8.21 (d, 1H, J = 15.7 Hz, CH═), 8.29 (d, 2H, J = 7.7 Hz, H_{Ar}), 8.40 (d, 2H, J = 8.6 Hz, H_{Ar}), 8.43 (d, 1H, J = 15.7 Hz, CH═), 9.02 (s, 1H, H_{Ar}), 9.08 (s, 1H, H_{Ar}) ^{13}C NMR (DMSO-d_6), δ: 20.3 (CH_3), 36.7 (CH_3), 109.8 (2 × CH), 110.4 (CH), 114.6 (CH), 116.7 (CH), 120.6 (4 × CH), 123.1 (2 × CH), 126.1 (C), 126.4 (2 × CH), 126.7 (2 × CH), 132.7 (2 × CH), 132.7 (C), 137.3 (C), 139.3 (C), 139.4 (2 × C), 140.2 (C), 147.8 (C), 152.3 (CH), 171.8 (C), 172.3 (C)
IVd	IR, $\tilde{\nu}$/cm^{-1}: 3061, 1575, 1518, 1436, 1233, 1184, 1140 ^{1}H NMR (DMSO-d_6), δ: 2.25 (s, 3H, CH_3N), 2.46 (s, 4H, 2 × CH_2), 2.90 (s, 3H, CH_3), 3.48 (s, 4H, 2 × CH_2), 4.27 (s, 3H, CH_3N^+), 7.10 (d, 2H, J = 9.1 Hz, H_{Ar}), 7.74 (d, 1H, J = 15.4 Hz, CH═), 7.95 (d, 2H, J = 9.1 Hz, H_{Ar}), 8.12 (d, 1H, J = 15.4 Hz, CH═), 8.88 (s, 1H, H_{Ar}), 8.89 (s, 1H, H_{Ar}) ^{13}C NMR (DMSO-d_6), δ: 20.2 (CH_3), 35.9 (CH_3), 45.4 (CH_3), 46.0 (2 × CH_2), 54.0 (2 × CH_2), 107.7 (CH), 109.3 (CH), 113.6 (2 × CH), 116.4 (CH), 123.0 (C), 125.3 (C), 132.6 (2 × CH), 136.7 (C), 139.2 (C), 149.3 (CH), 151.7 (C), 153.6 (C), 170.8 (C), 171.8 (C)
IVe	IR, $\tilde{\nu}$/cm^{-1}: 1567, 1517, 1489, 1436, 1395, 1336, 1257, 1165 ^{1}H NMR (DMSO-d_6), δ: 2.90 (s, 3H, CH_3), 3.62 (bs, 8H, 2 × NCH_2CH_2O), 4.23 (s, 3H, CH_3N^+), 4.87 (bs, 2H, OH), 6.91 (d, 2H, J = 8.9 Hz, H_{Ar}), 7.61 (d, 1H, J = 15.1 Hz, CH═), 7.89 (d, 2H, J = 8.9 Hz, H_{Ar}), 8.07 (d, 1H, J = 15.1 Hz, CH═), 8.83 (s, 2H, H_{Ar}) ^{13}C NMR (DMSO-d_6), δ: 20.2 (CH_3), 35.7 (CH_3), 53.1 (2 × CH_2), 58.2 (2 × CH_2), 105.9 (CH), 109.1 (CH), 112.1 (2 × CH), 116.3 (CH), 121.4 (C), 125.1 (C), 133.1 (2 × CH), 136.6 (C), 139.3 (C), 150.4 (C), 151.6 (CH), 152.7 (C), 170.6 (C), 171.4 (C)
IVf	IR, $\tilde{\nu}$/cm^{-1}: 2873, 1568, 1515, 1397, 1338, 1261, 1168, 1100 ^{1}H NMR (DMSO-d_6), δ: 2.90 (s, 3H, CH_3), 3.28 (s, 6H, 2 × OCH_3), 3.55 (t, 4H, J = 5.7 Hz, 2 × NCH_2), 3.71 (t, 4H, J = 5.7 Hz, 2 × OCH_2), 4.24 (s, 3H, CH_3N^+), 6.92 (d, 2H, J = 9.2 Hz, H_{Ar}), 7.64 (d, 1H, J = 15.2 Hz, CH═), 7.90 (d, 2H, J = 9.2 Hz, H_{Ar}), 8.09 (d, 1H, J = 15.2 Hz, CH═), 8.84 (s, 1H, H_{Ar}), 8.85 (s, 1H, H_{Ar}) ^{13}C NMR (DMSO-d_6), δ: 20.7 (CH_3), 36.2 (CH_3), 50.5 (2 × CH_3), 58.8 (2 × CH_2), 70.1 (2 × CH_2), 106.9 (CH), 109.6 (CH), 112.7 (2 × CH), 116.8 (CH), 122.2 (C), 125.7 (C), 133.5 (C), 137.1 (2 × CH), 139.9 (C), 150.9 (C), 152.2 (CH), 152.9 (C), 171.2 (C), 172.1 (C)
V	IR, $\tilde{\nu}$/cm^{-1}: 2908, 1545, 1478, 1372, 1350, 1149, 1067, 996 ^{1}H NMR (DMSO-d_6), δ: 2.90 (s, 3H, CH_3), 3.05 (s, 6H, $(CH_3)_2N$), 4.17 (s, 3H, CH_3N^+), 6.80 (d, 2H, J = 9.0 Hz, H_{Ar}), 7.21 (dd, 1H, J = 11.0 Hz, J = 14.4 Hz, CH═), 7.33 (d, 1H, J = 15.0 Hz, CH═), 7.50 (d, 1H, J = 15.0 Hz, CH═), 7.56 (d, 2H, J = 9.0 Hz, H_{Ar}), 8.03 (dd, 1H, J = 11.0 Hz, J = 14.4 Hz, CH═), 8.86 (s, 1H, H_{Ar}), 8.89 (s, 1H, H_{Ar}) ^{13}C NMR (DMSO-d_6), δ: 20.7 (CH_3), 36.1 (CH_3), 49.0 (2 × CH_3), 109.8 (CH), 112.5 (CH), 112.6 (2 × CH), 116.9 (CH), 122.7 (CH), 123.3 (C), 126.0 (C), 131.2 (2 × CH), 137.4 (C), 139.8 (C), 149.2 (C), 152.2 (CH), 152.3 (CH), 152.8 (C), 171.3 (C), 171.4 (C)

a) Aromatic (aryl) protones are indicated by subscript Ar.

when stable dihydrochloride of the starting diaminodithiol was used instead of disodium diaminodithiolate that needed to be prepared afresh. The other old method claimed as leading to linear benzobistizole, in fact provides angular 2,7-dimethylbenzo[1,2-*d*:4,3-*d*′]bisthiazole (Kiprianov et al., 1956). Recently, another condensation reaction of 2,5-diaminobenzene-1,4-dithiol leading to linear benzothiazoles appeared, using orthoesters and indium triflate as a catalyst (Mike et al., 2010). In our case, acetic anhydride is sufficiently effective and the reaction could be performed simply with a high yield. Two methyl groups in the prepared benzobisthiazole derivative are sufficiently acidic to undergo a Knoevenagel-type reaction with aromatic aldehydes. Carrying out this reaction solely with one methyl group is problematic. When the benzobisthiazole skeleton is quaternised at

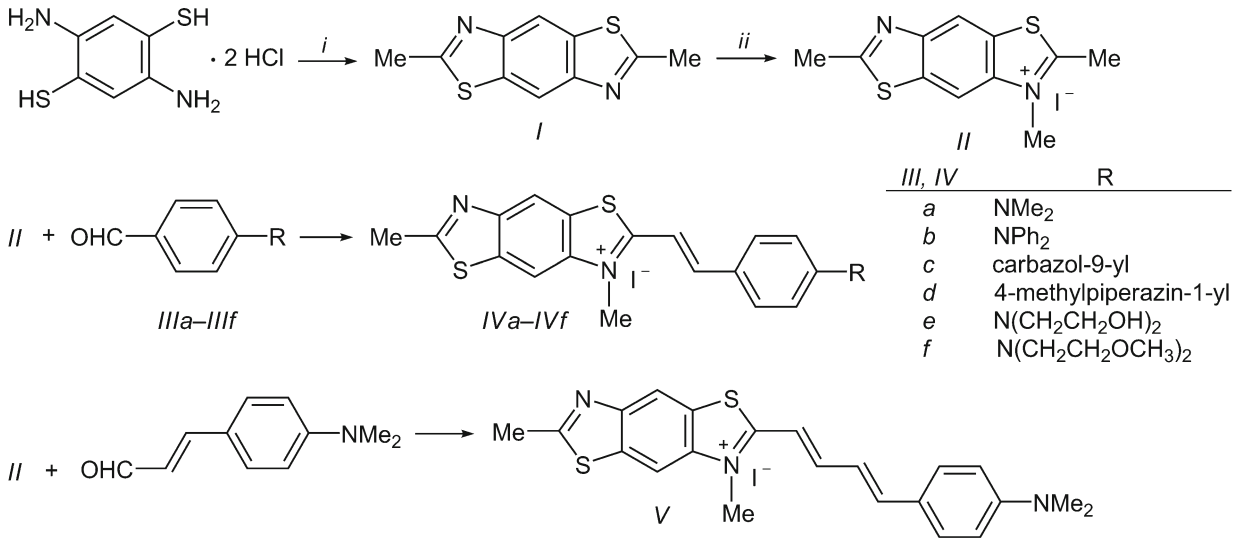

Fig. 1. Synthesis of 2-substituted 3,6-dimethylbenzo[1,2-*d*:4,5-*d*′]bisthiazol-3-ium iodides (*IV* and *V*). Reaction conditions: *i*) Ac_2O; *ii*) MeI, microwave irradiation.

one nitrogen atom, the acidic character of the adjacent methyl is increased, and the subsequent condensation results in only one product. The requisite methylation was performed with various reagents (dimethyl sulphate, trimethyloxonium tetrafluoroborate) and the best results were achieved using iodomethane under microwave conditions. The reaction was appropriately selective and efficient in 5–7 molar excess of iodomethane. The second nitrogen atom in some portion of the starting material was also methylated but the yield of a double salt did not exceed 10 % and was easily removed by crystallisation. Methylation under thermal conditions without irradiation required a substantially longer reaction time and the yield was poorer. Microwave conditions were also used in the final step. Irradiation at 100 °C for 20 min led to completion of the reaction in the case of most benzaldehydes with dialkylamino or diarylamino groups. Both the temperature and the reaction time needed to be increased when the aldehyde with the carbazole fragment was used. The relatively harsh conditions needed for reaction of this substituted benzaldehyde are due to the reluctance of elimination in the second step of the condensation because of the weaker push–pull character of the resultant product in comparison with other target compounds. All the final compounds were prepared as solely *E* isomers and they did not show any *E*/*Z* isomerisation on standing for several months. The complete synthesis is shown in Fig. 1 and the data characterising the new products are summarised in Tables 1 and 2.

The aromatic aldehydes that were not commercially available were synthesised mostly via nucleophilic substitution (Fig. 2) from 4-fluorobenzaldehyde according to the published procedure (Magdolen et al., 2001). Some modifications were made in the cases

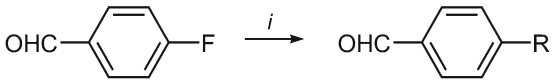

Fig. 2. Preparation of 4-substituted benzaldehydes *IIIc* and *IIIf* via nucleophilic substitution. Reaction conditions: *i*) carbazole or bis(2-methoxyethyl)amine, potassium carbonate or caesium carbonate, DMSO, 140–160 °C.

of carbazolyl and bis(2-methoxyethyl)amino derivatives.

As described by Magdolen et al. (2001), the reaction under ultrasound conditions showed low conversion of carbazole, so both the reaction time and the relative amount of 4-fluorobenzaldehyde were increased until the yield of 4-(carbazol-9-yl)benzaldehyde (*IIIc*) was sufficient. These improvements did not affect the substitution with bis(2-methoxyethyl)amine, which emerged as being notably unreactive. Only a low yield was achieved under quite harsh conditions – irradiation in the microwave reactor at 160 °C for 1 h. These conditions caused a remarkable decomposition of the starting material to the complex mixture; although we isolated the crude product containing the desired compound and 4-fluorobenzaldehyde in about the same amount, after chromatographic purification only a low-percentage yield was achieved.

The experimental UV-VIS absorption spectra of the compounds studied measured in CH_3OH are presented in Fig. 3. Table 3 summarises the UV-VIS experimental data as well as the results of quantum-chemical calculations.

The quantum-chemical calculations verified the planar geometry of the central unit including conjugated linkers in each of the compounds under study.

An intensive absorption band in the region of 450–600 nm caused by the π–π^* transition due to intra-

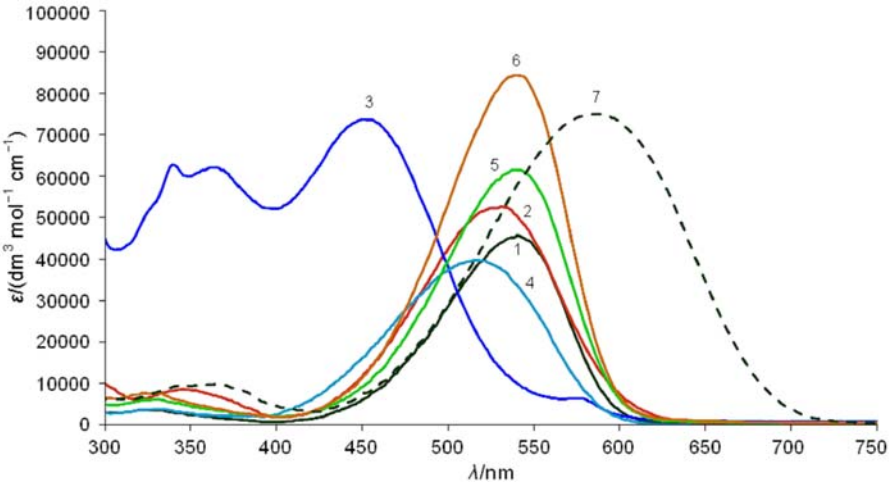

Fig. 3. UV-VIS absorption spectra of studied compounds (1 – *IVa*, 2 – *IVb*, 3 – *IVc*, 4 – *IVd*, 5 – *IVe*, 6 – *IVf*, 7 – *V*) measured in methanol.

Table 3. Position and intensities of the long-wave band in the UV-VIS absorption spectra measured in methanol, calculated values of energies of frontier orbitals (DFT), linear polarisabilities α, first and second order hyperpolarisabilities β and γ (PM3) of studied benzobisthiazol-3-ium cations, respectively

Parameter	Compound						
	IVa	*IVb*	*IVc*	*IVd*	*IVe*	*IVf*	*V*
λ_{max}/nm	540	531	450	516	539	541	588
ε/(dm^3 mol^{-1} cm^{-1})	45600	52600	73600	39700	61500	84300	74900
HOMO/eV	–8.22	–7.93	–7.86	–7.92	–8.22	–8.19	–7.85
LUMO/eV	–5.59	–5.53	–5.93	–5.52	–5.59	–5.58	–5.55
$\alpha \cdot 10^{32}$/C	4.2029	5.7707	5.4705	4.7033	4.5031	4.7366	5.7373
$\beta \cdot 10^{38}$/C	6.4044	9.2064	22.182h0	3.2022	0.9006	5.5372	11.4746
$\gamma \cdot 10^{44}$/C	9.3064	22.9159	84.7920	11.0743	2.1682	2.4350	22.8158

molecular charge transfer is characteristic of the prepared push–pull salts. All of the salts with dialkyl or diarylamino substituents, in which free rotation around the N—C_{Ar} single bond is possible, absorb at negligibly different λ_{max} near 535 nm. A distinct bathochromic shift of 50 nm is observed when the conjugation is extended with one more double bond in compound *V*; this is in accordance with the lower value of the calculated HOMO–LUMO energy gap (ΔE_{IVa} = 2.63 eV; ΔE_V = 2.31 eV). Compound *IVc* exhibits a different UV-VIS spectrum. The most intensive transition is shifted to 450 nm, probably owing to the twisting of the carbazole residue as was also confirmed by the quantum-chemical calculations (in the DFT optimised structure the carbazole moiety is turned through about 42° from the remaining planar part of the molecule). The values of linear polarisability α corroborate the more extensive conjugation in compound *V* compared with *IVa* and the donating preference of NPh_2 and carbazole substituents compared with $N(CH_3)_2$. It is known that third-order polarisability increases significantly when the energy associated with the transition from the ground to the first excited state (HOMO–LUMO gap) decreases (Armstrong et al., 1962). This could explain the unexpectedly high value of γ for compound *IVc* with the carbazole substituent (ΔE_{IVc} = 1.92 eV).

The number of double bonds in the conjugated bridge enhances the values of β and γ. Out of the donor substituents studied, the diphenylamino- and carbazole groups increased the hyperpolarisabilities β and γ. These findings will determine the direction of subsequent research aimed at predicting structures with possible applications in non-linear optics.

Conclusions

Dipolar conjugated salts based on the linear benzobisthiazol-3-ium building block were synthesised in a three-step sequence starting from 2,5-diaminobenzene-1,4-dithiol. Electron-donating fragments represented by the dialkylamino, diarylamino, or *N*-heterocyclic substituted benzene rings were introduced into the molecule via a Knoevenagel-type condensation with substituted benzaldehydes. Microwave irradiation was used to accelerate the reac-

tions in both the condensation and quaternisation steps. Intensive absorption in the visible region due to intra-molecular charge transfer is characteristic of all the prepared final salts. The farthest wavelength of the absorption maximum for the long-wave band was observed for compound *V* with two double bonds in the conjugated bridge in accordance with the difference between HOMO–LUMO orbitals. The values of the first and second hyperpolarisabilities were calculated for the synthesised salts. Remarkably high values were achieved for compounds with diphenylamino and *N*-carbazolyl substituted benzene fragments. These calculations predict the newly prepared structures as being promising NLO materials.

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