SYNTHESIS AND STUDY OF NOVEL BENZOTHIAZOLE DERIVATIVES WITH POTENTIAL NONLINEAR OPTICAL PROPERTIES

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Dedicated to Professor Štefan Toma on the occasion of his 70th birthday.

The synthesis of new benzothiazole push-pull systems as candidates for NLO-phores is described. Spectral (UV/VIS and solvatochromic) and theoretical studies (electronic properties based on semiempirical AM1 and PM3 methods) of the prepared compounds were carried out. The structure and physico-chemical parameters affecting the push-pull character and intramolecular charge transfer (ICT) of the studied compounds have been investigated and compounds with enhanced hyperpolarizability β have been predicted. The benzothiazolium salts were found to be much more effective NLO-phores in comparison with the corresponding neutral benzothiazoles. The 4-NPh_2 group is the most effective donor. The extension of conjugated bridge improves the studied NLO characteristics. An additional acceptor group bonded to the heterocycle causes a red shift of λ_{max} but does not increase hyperpolarizability.

Keywords: Push-pull benzothiazoles; Alkenes; Dienes; NLO-phores; Intramolecular charge transfer; UV/VIS spectroscopy; Hyperpolarizability; Organic nonlinear optic materials.

In the recent decade, a considerable effort has been focused on the development of organic molecules with enhanced second order nonlinear optical (NLO) properties due to their potential applications in various areas such as optical modulation, frequency doubling and molecular switching[1]. Organic nonlinear optical materials have emerged as viable alternatives to conventional inorganic crystals in active photonic components[2]. These organic materials offer many possible advantages: (i) they show higher electronic susceptibility ($\chi^{(2)}$) through high molecular hyperpolarizability (β) and fast response time; (ii) they are easier to fabricate and cheaper to produce; (iii) they are compatible with the existing semiconductor technology;

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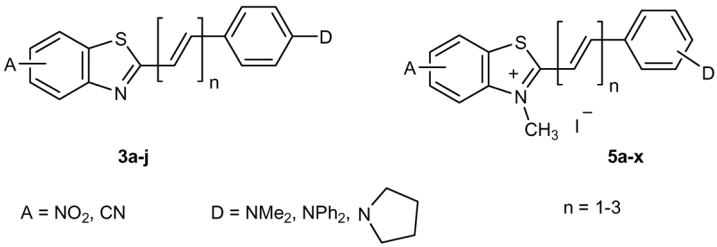
(iv) their structures can be tailored in many ways in order to finely tune NLO properties for required applications.

Dipolar push-pull organic chromophores probably constitute the largest class of compounds investigated for their NLO properties. Push-pull NLO-phores basically involve an electron donor and an electron-acceptor groups interacting through a π-conjugated spacer. Structure–property relationships based on the theoretical and experimental work have shown that high structure hyperpolarizabilities β generally arise from a combination of a strong electron-donor and -acceptor positioned at the opposite ends of a suitable conjugation path[3]. The nature of the conjugation path is of critical importance. While polyenes are superior in efficient charge transfer from donor to acceptor, their low chemical and thermal stabilities have shifted the interest toward aromatic and heteroaromatic compounds because of their higher molecular hyperpolarizabilities, improved optical transparency, and good thermal stability. Heteroaromatics are superior to those of the corresponding aromatic analogues. Chromophores containing heterocycles such as thiophene[4], thiazole[5], and benzothiazole[6] are among the most studied systems having an optimal donor–acceptor and conjugation bridge combination for a given chromophore.

In this paper we present synthesis, UV/VIS absorption, solvatochromic properties and theoretical study of a series of potential NLO-phores of the benzothiazole type **3** and **5**.



The studied compounds are dipolar push-pull chromophores containing a benzothiazole electron-acceptor group, alkenylene conjugation spacer with 1–3 double bonds and a donor in *para* position of the substituted phenyl group (structure **3**). The acceptor strength of benzothiazole heterocycle can be enhanced by methylation of the heterocyclic nitrogen to *N*-methyl in benzothiazolium salts (structure **5**). Another modification of the benzothiazole acceptor consists in introducing an additional acceptor into the benzothiazole skeleton (NO_2 or CN). The conventional dimethylamino or cyclic amino (e.g. pyrrolidin-1-yl) groups have been employed as

electron-donor substituents. Diphenylamino group was also chosen because this moiety brings high thermal stability and the obtained hyperpolarizability is often increased compared with dialkylamino group[7]. The positions *ortho* and *meta* for dimethylamino group were tested too.

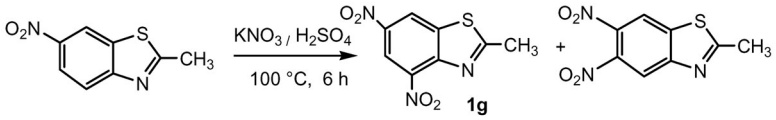
RESULTS AND DISCUSSION

Synthesis

The key step in the synthetic approach is the condensation of substituted 2-methylbenzothiazoles with suitable substituted aldehydes. The starting benzothiazole derivatives **1** have been prepared as follows:

2-Methylbenzothiazole-6-carbonitrile[8] (**1b**) was prepared from 2-methylbenzothiazol-5-amine by the Sandmeyer reaction. The synthesis of 2-methyl-4-nitrobenzothiazole[9] (**1c**) started from protected 2-methylbenzothiazol-5-amine, followed by nitration, deprotection and removal of amino group. 2-Methyl-5-nitrobenzothiazole[10] (**1d**) was prepared by cyclization of corresponding 2-bromobenzanilides, 2-methyl-6-nitrobenzothiazole[11] (**1e**) by nitration of 2-methylbenzothiazole. A similar route to **1c** was used also for the synthesis of 2-methyl-7-nitrobenzothiazole[11] (**1f**) starting from 2-methylbenzothiazol-6-amine.

A modified procedure was found for the synthesis of 2-methyl-4,6-dinitrobenzothiazole. The previously published synthesis used an eight-step reaction[12]. Our starting material was more accessible 2-methyl-6-nitrobenzothiazole. We studied its nitration and achieved a conversion of 85% at 100 °C after 6 h with two products: 2-methyl-4,6-dinitrobenzothiazole and 2-methyl-5,6-dinitrobenzothiazole in the 9:2 ratio (Scheme 1). Increased temperature led to undesirable oxidation products.

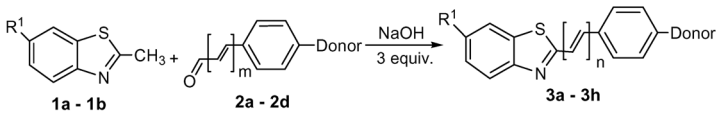


SCHEME 1

Aromatic aldehydes have been prepared using common protocols. Monoformylation of triphenylamine by the Vilsmeier reaction gave 4-(diphenylamino)benzaldehyde[13] (**2b**). 4-Pyrrolidin-1-yl-benzaldehyde[14] (**2c**) was prepared by sonochemical nucleophilic aromatic substitution of 4-fluorobenzaldehyde. (2*E*,4*E*)-5-[4-(Dimethylamino)phenyl]penta-2,4-dienal (**2e**) was prepared from commercially available 3-[4-(dimethyl-

amino)phenyl]propenal according to the procedure described in literature[15]. 3-(Dimethylamino)benzaldehyde[16] (**2f**) was prepared from ethyl 3-(dimethylamino)benzoate by partial reduction with the Red-Al–morpholine reagent. 2-(Dimethylamino)benzaldehyde[17] (**2g**) was prepared from 2-fluorobenzaldehyde by nucleophilic substitution with dimethylamine.

The neutral push-pull benzothiazoles have been synthesized by the condensation of 2-methyl- or 6-cyano-2-methylbenzothiazole with corresponding aldehydes (Scheme 2). The structures and yields of the prepared compounds are summarized in Table I.



	R^1
1a	H
1b	CN

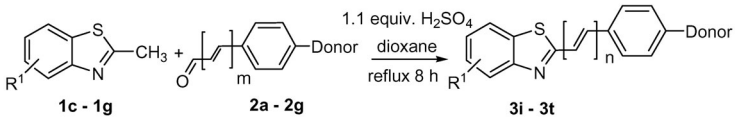
	m	Donor
2a	0	$N(CH_3)_2$
2b	0	NPh_2
2c	0	Pyrrolidin-1-yl
2d	1	$N(CH_3)_2$

SCHEME 2

TABLE I
Benzothiazoles prepared under basic catalysis

Compound	R^1	*n*	Donor	Yield, %
3a	H	1	H	95 (ref.[18], 98)
3b	H	1	$N(CH_3)_2$	86 (ref.[18], 71)
3c	H	1	NPh_2	98
3d	H	2	$N(CH_3)_2$	63
3e	CN	1	$N(CH_3)_2$	74
3f	CN	1	NPh_2	64
3g	CN	1	pyrrolidin-1-yl	72
3h	CN	2	$N(CH_3)_2$	53

Basic catalysis cannot be used for the condensation of nitrobenzothiazoles as they probably undergo destructive ring opening. Acid medium has been found to fulfil optimal conditions for this reaction (Scheme 3 and Table II).



	R^1
1c	4-NO_2
1d	5-NO_2
1e	6-NO_2
1f	7-NO_2
1g	4,6-$(NO_2)_2$

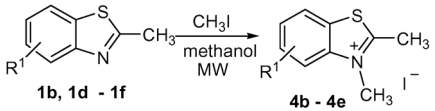
	m	Donor
2a	0	$N(CH_3)_2$
2b	0	NPh_2
2c	0	Pyrrolidin-1-yl
2d	1	$N(CH_3)_2$

SCHEME 3

TABLE II
Benzothiazoles prepared under acid catalysis

Compound	R^1	*n*	Donor	Yield, %
3i	4-NO_2	1	$N(CH_3)_2$	82
3j	5-NO_2	1	$N(CH_3)_2$	38
3k	6-NO_2	1	$N(CH_3)_2$	67
3l	7-NO_2	1	$N(CH_3)_2$	88
3m	4,6-$(NO_2)_2$	1	$N(CH_3)_2$	68
3n	5-NO_2	1	NPh_2	45
3o	6-NO_2	1	NPh_2	49
3p	4,6-$(NO_2)_2$	1	NPh_2	62
3q	6-NO_2	1	pyrrolidin-1-yl	45
3r	4,6-$(NO_2)_2$	1	pyrrolidin-1-yl	40
3s	6-NO_2	2	$N(CH_3)_2$	29
3t	4,6-$(NO_2)_2$	2	$N(CH_3)_2$	56

Various 2,3-dimethylbenzothiazolium iodides were prepared by quaternization of neutral 2-methylbenzothiazoles with methyl iodide under microwave condition. Scheme 4 and Table III present optimal conditions for the reaction. The methylation was unsuccessful in the case of 2-methyl-4-nitro- and 2-methyl-4,6-dinitrobenzothiazoles. 2,3-Dimethylbenzothiazolium iodide (**4a**) was prepared according to literature[15]. Methylation of 2-methylbenzothiazole with dimethyl sulfate yields the 2,3-dimethylbenzothiazolium hydrogen sulfate (**4f**). Its physico-chemical data were identical with the reported ones[19].



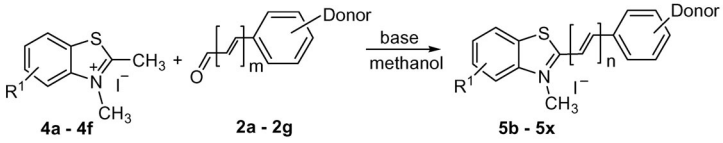
	R^1
4b	6-CN
4c	5-NO_2
4d	6-NO_2
4e	7-NO_2

SCHEME 4

TABLE III
2-Methylbenzothiazolium iodides

Compound	R^1	Temperature °C	MW power W	Pressure MPa	Yield %
4b	6-CN	115	60	1.4	81
4c	5-NO_2	117	60	1.9	68
4d	6-NO_2	118	60	1.8	86
4e	7-NO_2	115	70	1.9	73

2,3-Dimethylbenzothiazolium iodides condense more readily with aldehydes than corresponding neutral 2-methylbenzothiazoles due to the more acid hydrogens of the 2-methyl group. The reaction underwent under mild conditions (pyridine, piperidine catalysis or without catalysis). This method was used for all conjugated benzothiazolium derivatives (Scheme 5, Table IV).



	R^1
4a	H
4b	6-CN
4c	5-NO_2
4d	6-NO_2
4e	7-NO_2
4f (HSO_4^-)	H

	m	Donor
2a	0	4-$N(CH_3)_2$
2b	0	4-NPh_2
2c	0	4-pyrrolidin-1-yl
2d	1	4-$N(CH_3)_2$
2e	2	4-$N(CH_3)_2$
2f	0	3-$N(CH_3)_2$
2g	0	2-$N(CH_3)_2$

SCHEME 5

TABLE IV
Catalyst, reaction time and yields of products **5b**–**5x**

Compound	R^1	*n*	Donor	Catalyst	Reaction time, h	Yield, %
5b	H	1	4-$N(CH_3)_2$	pyridine	5	82
5c (HSO_4^-)	H	1	4-$N(CH_3)_2$	pyridine	4	70
5d	5-NO_2	1	4-$N(CH_3)_2$	–	6	88
5e	5-NO_2	1	3-$N(CH_3)_2$	–	8	84
5f	5-NO_2	1	2-$N(CH_3)_2$	–	7	72
5g	6-NO_2	1	4-$N(CH_3)_2$	–	8	84
5h	6-NO_2	1	3-$N(CH_3)_2$	piperidine	8	65
5i	6-(NO_2)	1	2-$N(CH_3)_2$	–	8	72
5j	7-NO_2	1	4-$N(CH_3)_2$	pyridine	6	68
5k	H	1	4-NPh_2	piperidine	8	76
5l	H	1	4-NPh_2	piperidine	8	76
5m	5-NO_2	1	4-NPh_2	piperidine	7	70
5n	6-NO_2	1	4-NPh_2	pyridine	10	77
5o	7-NO_2	1	4-NPh_2	–	7	71
5p	6-CN	1	4-NPh_2	piperidine	4	75
5q	H	1	4-pyrrolidinyl	–	8	66
5r	6-NO_2	1	4-pyrrolidinyl	–	6	64
5s	H	2	4-$N(CH_3)_2$	pyridine	9	78
5t	5-NO_2	2	4-$N(CH_3)_2$	pyridine	5	98
5u	6-NO_2	2	4-$N(CH_3)_2$	pyridine	5	83
5v	7-NO_2	2	4-$N(CH_3)_2$	–	6	80
5w	6-CN	2	4-$N(CH_3)_2$		3	83
5x	H	3	4-$N(CH_3)_2$	pyridine	12	77

Spectral and Theoretical Study

The intense low-energy band dominates in the visible region of the absorption spectra of both neutral compounds and salts. This band can be attributed to $\pi(NMe_2) \rightarrow \pi^*$ (benzothiazole) or π^*(benzothiazolium) charge-transfer excitation, respectively.

Neutral Benzothiazoles

The experimental values of absorption UV/VIS spectra characteristics λ_{max} and molar absorption coefficient ε measured in chloroform as well as representative theoretical electric properties of neutral benzothiazoles are presented in Table V. Chloroform was chosen as solvent because of poor solubility of the dinitro derivatives in methanol. The negligible value of dipole moment as well as the low λ_{max} of the unsubstituted benzothiazole derivative **3a** indicate that this compound has no push-pull character. The high ΔE and minimal β confirm the fact.

The push-pull systems with effective conjugation resulting in D→A charge transfer are characterized by a bathochromic shift of λ_{max}, a decreased value of ΔE and increased values of dipole moment μ and, in particular, hyperpolarizability β. All these facts were observed when donor group was introduced in the *para* position of the benzene ring.

Another enhancement of the push-pull character is caused by the additional acceptor group bound to the benzothiazole moiety. The effect of the NO_2 group is more distinct than that of the CN group. The most effective charge transfer is observed when acceptor group is in position 6- of benzothiazole (compounds **3k**, **3o**, **3s**). This intramolecular charge transfer (ICT)

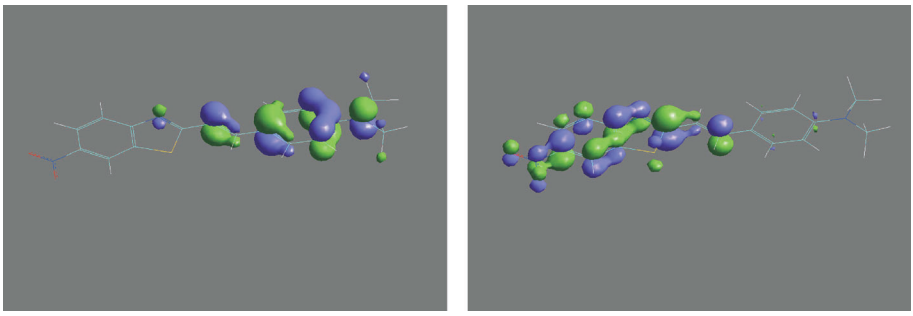
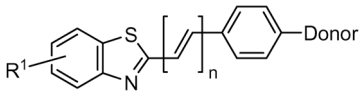


FIG. 1
Plot of calculated charge densities in frontier orbitals of benzothiazole derivative **3k**

represents “the most linear direction” from donor to acceptor, which is also confirmed by a high value of the molar absorption coefficient. The localization of orbital density in the donor part of HOMO orbital and in the acceptor part of the LUMO orbital is evidence of the fact (Fig. 1).

TABLE V

Long-wave band positions in the UV/VIS absorption spectra, molar absorption coefficients ε in chloroform, calculated values of dipole moments μ, first hyperpolarizabilities β and HOMO-LUMO energy differences Δ*E* of benzothiazoles



Compound	λ_{max} nm	ε l mol^{-1} cm^{-1}	μ D	β × 10^{-30} esu	Δ*E* eV
3a	341	61 000	0.178	2.360	7.747
3b	395	45 000	2.214	44.477	7.017
3c	406	24 000	0.755	49.684	6.669
3d	424	46 300	3.106	86.892	6.676
3e	428	26 400	6.524	76.327	6.711
3f	434	32 400	5.096	104.914	6.369
3g	440	26 300	6.579	80.785	6.719
3h	450	31 900	6.711	113.922	6.537
3i	446	23 100	6.018	39.953	6.579
3j	416	25 000	8.190	63.008	6.727
3k	454	50 200	8.777	95.290	6.494
3l	446	16 100	6.187	52.914	6.669
3m	514	14 000	10.394	139.010	6.042
3n	428	34 300	7.030	82.836	6.379
3o	458	54 200	7.420	135.137	6.150
3p	516	33 700	9.108	205.076	5.735
3q	466	49 400	8.834	100.942	6.503
3r	534	15 200	10.355	143.085	6.088
3s	471	59 800	8.988	143.553	6.318
3t	536	23 100	10.277	206.609	5.887

A much more extensive bathochromic shift of long-wave band over 500 nm can be observed in the derivatives with two NO_2 groups in positions 4 and 6 (compounds **3m**, **3p**, **3r**). The bathochromic shift is accompanied by decreasing ΔE and increasing hyperpolarizability β. Two double bonds in the conjugated spacer produce in all cases a bathochromic shift of ca. 20 nm in comparison with the corresponding compounds with one double bond (**3b**, **3d**; **3k**, **3s**; **3m**, **3t**; **3e**, **3h** pairs). ΔE and β are also changed in favour of the more effective charge transfer. In addition to the NMe_2 donor group, other amino donors have been also tested. While the pyrrolidine donor shows only a small effect, the NPh_2 donor improves the ICT significantly, resulting in the decreased ΔE and increased hyperpolarizability β.

Benzothiazolium Iodides

Table VI presents analogous physico-chemical characteristics for the *N*-methylbenzothiazolium iodides (experimental spectral data) and *N*-methylbenzothiazolium cations (calculated properties).

Quaternization of heterocyclic nitrogen produces a huge bathochromic shift of the long-wave band of *N*-methylbenzothiazolium salts in comparison with neutral benzothiazoles (ca. 120 nm). This absorption is caused by the $\pi \rightarrow \pi^*$ transition accompanied by the important ICT from the substituted amino donor group to the benzothiazolium ring. This charge-transfer effect is much larger than in the neutral benzothiazoles. The values of absorption maxima exceed 500 nm in all compounds except for the unsubstituted derivative **5a** and the salts with the donor group in *ortho* or *meta* position of the phenyl ring (compounds **5f**, **5e**, **5i**, **5h**). The push-pull character of these compounds is lower.

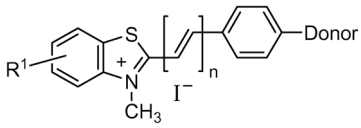
The values of calculated theoretical indices μ, β and ΔE also express an important push-pull charge transfer. Mainly the hyperpolarizabilities β and the HOMO-LUMO ΔE values of benzothiazolium cations changed much compared with the corresponding neutral benzothiazoles. An additional acceptor group bound to the benzothiazolium ring (NO_2 or CN) enhances the acceptor capacity of benzothiazolium ring resulting in the bathochromic shift of the long-wave band, enhanced dipole moment and hyperpolarizability.

The length of the conjugated bridge is also an important factor for the push-pull character and ICT. The compounds with two double bonds in combination with NO_2 or CN group show the long-wave absorption band red-shifted to 600 nm. The hyperpolarizability β is more influenced by the number of double bonds than by the presence of an additional electron-

acceptor group. The compound **5x** with three double bonds exhibits the highest calculated static hyperpolarizability β. The exchange of the electron-donor NMe_2 for NPh_2 group causes a significant increase in the β value (compound **5l**). The exchange of anion I^- for HSO_4^- (compounds **5b** and

TABLE VI

Position and intensities of long-wave band in the UV/VIS absorption spectra in methanol, calculated values of dipole moments μ, hyperpolarizabilities β and HOMO-LUMO energy differences Δ*E* of benzothiazolium cations



Compound	λ_{max} nm	ε l mol^{-1} cm^{-1}	μ D	β × 10^{-30} esu	Δ*E* eV
5a	374	6 900	4.346	60.377	6.477
5b	520	67 800	2.402	98.478	5.408
5c	522	71 500	2.402	98.478	5.408
5d	548	58 800	10.748	190.811	5.397
5e	384	24 300	3.834	128.609	4.809
5f	464	8 700	5.095	109.464	5.624
5g	562	32 700	12.396	183.25	5.360
5h	392	23 800	6.583	80.301	4.735
5i	476	9 100	7.927	66.379	5.546
5j	558	51 700	9.121	95.580	5.364
5k	554	64 000	7.309	183.73	5.369
5l	508	20 200	11.030	345.090	5.201
5m	542	29 600	1.876	263.793	5.224
5n	552	23 600	5.483	147.389	5.193
5o	548	39 800	9.028	170.488	5.185
5p	542	39 000	5.169	212.866	5.184
5q	534	72 100	3.809	177.958	5.416
5r	572	27 300	10.826	172.417	5.384
5s	562	54 400	4.125	370.09	4.978
5t	610	68 000	10.324	340.309	5.026
5u	628	15 700	11.974	317.301	5.010
5v	622	60 000	8.337	140.527	4.984
5w	616	55 300	6.089	321.534	4.972
5x	580	46 300	7.326	744.769	4.593

5c) had no influence on the measured spectral characteristics. Based on these conclusions, hyperpolarizability β has been predicted for the cation with unsubstituted *N*-methylbenzothiazolium acceptor, conjugated hexatrienyl bridge and 4-(diphenylamino)phenyl donor. The calculated static hyperpolarizability of this compound is 950×10^{-30} esu.

Solvatochromism

UV/VIS absorption measurements of selected structurel types of neutral benzothiazoles as well as benzothiazolium iodides have been carried out in chloroform (dielectric permittivity ε = 4.8) and methanol (ε = 33). Table VII summarizes the values of long-wave absorption bands λ_{max} in both solvents and their differences. A hypsochromic shift in more polar methanol can be observed in all studied compounds. The difference $\Delta\lambda_{max}$ is much larger in benzothiazolium salts compared with neutral benzothiazoles (**3n**–**5d**, **3l**–**5j**). This difference increases with the number of double bonds in the

TABLE VII
Solvatochromic data λ_{max} for the long-wave ICT band of selected neutral and ionic chromophores in methanol and chloroform and their difference $\Delta\lambda_{max}$

Compound	Salt	λ_{max}, nm (methanol)	λ_{max}, nm ($CHCl_3$)	$\Delta\lambda_{max}$, nm
5b	+	520	550	30
5s	+	562	612	50
5x	+	580	636	56
3n	–	422	428	4
5d	+	548	574	26
3k	–	446	456	8
3s	–	460	471	11
3o	–	444	458	14
5g	+	562	596	34
3l	–	440	446	2
5j	+	558	586	28
3e	–	427	428	1
3f	–	429	434	5
5k	+	554	582	28
5p	+	542	592	50

conjugated bridge (**5b**, **5s**, **5x**) and when NMe_2 is exchanged for NPh_2 (**5k**, **5p**). Analogous negative solvatochromism was observed also in a study of similar compounds[20].

Theory and Methods

The restricted Hartree–Fock theory at the semiempirical level has been chosen for the quantum-chemical calculations. The optimal geometries of the compounds under study were obtained by complete geometry optimization employing the AM1 method. This geometry was used as input for the single SCF calculation by the PM3 method. The final characteristics (dipole moment μ, hyperpolarizability β as well as HOMO-LUMO gap ΔE) were obtained in this way. A finite-field method for the calculation of static first hyperpolarizability developed by Kurtz was used. This procedure as well as the semiempirical methods used are implemented in the AMPAC molecular modeling package[21].

Conclusion

Two series of benzothiazole chromophores containing a conjugated alkenyl bridge, benzothiazole or *N*-methylbenzothiazolium electron-acceptor and electron-donating phenyl ring have been synthesized and characterized.

Benzothiazolium salts show a more effective push-pull character than corresponding neutral benzothiazoles. The better ICT results in a high red shift of long-wave ICT bands and larger hyperpolarizabilities β on replacing benzothiazole with an *N*-methylbenzothiazolium moiety. Extension of the conjugated bridge improves the studied NLO characteristics. An additional acceptor group bonded to the heterocycle causes a red shift of λ_{max} but does not increase the hyperpolarizability. 4-Diphenylaminophenyl has been found the most effective electron-donating group.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian Gemini spectrometer (VNMRJ 1.1 D) at 300 MHz in $CDCl_3$ or DMSO-d_6 with tetramethylsilane as internal standard. Chemical shifts are given in ppm (δ-scale), coupling constant (*J*) in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ or DMSO-d_6; determined in the APT and 2D experiment gHSQC, gHMBC. The numbering of carbon atoms used in assigning NMR data is presented in Fig. 2.

Elemental analyses were determined on a Carlo-Erba instrument. The UV/VIS spectra (in nm) were measured using a Hewlett–Packard Diode array spectrophotometer 8452A in

methanol and chloroform. Microwave reactions were conducted using a microwave synthesizer Initiator™ Biotage with power range 0–300 W and pressure range 0–2.0 MPa in glass microwave vials sealed with septum.

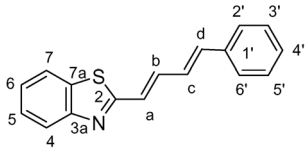


FIG. 2
Numbering of carbon atoms used in assigning NMR data

2-Methyl-4,6-dinitrobenzothiazole (**1g**)

A mixture of 2-methyl-6-nitrobenzothiazole (3.88 g, 0.02 mol), KNO_3 (8.08 g 0.08 mol) and H_2SO_4 (30 ml, d = 1.836) was heated at 100 °C for 6 h. After cooling the mixture was poured into 100 ml of ice water, then extracted with chloroform (2 × 50 ml), washed with 10% solution of $NaHCO_3$ (2 × 50 ml) and with water (2 × 50 ml). The organic layer was dried with anhydrous sodium sulfate. After removing solvent, the residue containing mainly 4,6- and a minor amount of 5,6-dinitro isomer was crystallized twice from ethanol. The yield of isolated 2-methyl-4,6-dinitrobenzothiazole (**1g**) was 2.49 g (52%). M.p. 186.0–187.5 °C; ref.[12] gives m.p. 150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 9.04 d, 1 H, J(7,5) = 2.4 (H-7); 9.02 d, 1 H, J(5,7) = 2.4 (H-5); 3.06 s, 3 H (CH_3). 2-Methyl-4,5-dinitrobenzothiazole isomer was not isolated. ^{1}H NMR (300 MHz, $CDCl_3$): 8.46 s, 1 H (H-7); 8.42 s, 1 H (H-4); 2.97 s, 3 H (CH_3).

Reaction of 2-Methylbenzothiazole (**1a**) or 2-Methylbenzothiazole-6-carbonitrile (**1b**) with Aromatic Aldehydes. General Procedure

2-Methylbenzothiazole (**1a**; 1.49 g, 10 mmol) or 2-methylbenzothiazole-6-carbonitrile (**1b**; 1.94 g, 10 mmol) and corresponding aldehydes **2a**–**2d** (10 mmol) were added to a solution of NaOH (1.2 g, 30 mmol) in methanol (25 ml). The reaction mixture was refluxed for 6–12 h and the resulting precipitate was collected and purified by column chromatography (silica gel, hexanes–ethyl acetate 4:1) or was recrystallized from methanol. Yields of isolated products **3a**–**3h** are summarized in Table I.

2-((E)-Styryl)benzothiazole (**3a**). M.p. 110.5–112 °C (methanol); ref.[18] gives m.p. 111–112 °C.

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}benzothiazole (**3b**). M.p. 204–206 °C (methanol); ref.[22] gives m.p. 201–202 °C (ethanol).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}benzothiazole (**3c**). M.p. 154–156 °C. For $C_{27}H_{20}N_2S$ (404.5) calculated: 80.17% C, 4.98% H, 6.92% N, 7.93% S; found: 80.05% C, 4.96% H, 7.98% N, 7.92% S. ^{1}H NMR (300 MHz, $CDCl_3$): 7.96 dd, 1 H, J(7,6) = 8.0, J(7,5) = 0.6 (H-7); 7.84 dd, 1 H, J(4,5) = 8.1, J(4,6) = 0.6 (H-4); 7.43 d, 2 H, J = 8.7 (H-2′, H-6′); 7.29 d, 1 H, J(*trans*) = 15.3 (H-b); 7.48–7.42 m, 1 H (H-5); 7.37–7.31 m, 1 H (H-6); 7.32–7.24 m, 4 H (H-Ar); 7.15–7.03 m, 6 H (H-Ar); 7.14 d, 2 H, J = 8.6 (H-3′, H-5′); 7.06 d, 1 H, J(*trans*) = 15.3 (H-a). ^{13}C NMR (75 MHz, $CDCl_3$): 167.51 (C-2); 153.91 (C-3a); 149.08 (C-4′); 147.04 (2 × C); 137.31 (C-7a); 134 20 (CH-b); 129.35 (4 × CH); 128.65 (2 × CH); 128.41 (C-2′, C-6′); 126.23 (C-5); 125.07 (4 × CH); 124.95 (C-6); 123.76 (C-7); 122.67 (C-1′); 122.23 (C-3′, C-5′); 121.42

(C-4); 119.77 (C-a). UV/VIS (methanol), λ_{max} (ε): 208 (52 000), 262 (12 400), 300 (21 700), 408 (36 400). UV/VIS ($CHCl_3$), λ_{max} (ε): 302 (25 000), 406 (24 000).

2-{(E,E)-4-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}benzothiazole (**3d**). M.p. 191.5–193 °C; ref.[23] gives m.p. 173–175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.96–7.93 m, 1 H (H-7); 7.83–7.80 m, 1 H (H-4); 7.46–7.27 m, 3 H (H-b, H-5, H-6); 7.39 d, 2 H, *J* = 9.1 (H-2′, H-6′); 7.37 d, 1 H, *J* = 14.4 (H-d); 6.85 d, 1 H, *J* = 14.4 (H-a); 6.81–6.80 m, 1 H (H-c); 6.69 d, 2 H, *J* = 9.0 (H-3′, H-5′); 3.01 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 167.58 (C-2); 154.07 (C-3a); 150.75 (C-4′); 139.52 (CH-c); 134.28 (C-7a); 128.39 (2 × CH-2′, 6′); 126.14 (CH-5); 124.87 (CH-6); 124.68 (CH-b); 123.06 (CH-a); 122.73 (CH-d); 122.58 (C-7); 121.35 (CH-4); 112.18 (2 × CH-3′, 5′); 40.28 ($N(CH_3)_2$). UV/VIS (methanol), λ_{max} (ε): 206 (30 600), 246 (13 500), 316 (12 500), 422 (48 600). UV/VIS ($CHCl_3$), λ_{max} (ε): 316 (10 700), 424 (46 300).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}benzothiazole-6-carbonitrile (**3e**). M.p., ^{1}H and ^{13}C NMR, and UV/VIS ($CHCl_3$) data are consistent with ref.[24]. UV/VIS (methanol), λ_{max} (ε): 427 (17 000).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}benzothiazole-6-carbonitrile (**3f**). M.p. 202–204 °C. For $C_{28}H_{19}N_3S$ (429.5) calculated: 78.29% C, 4.46% H, 9.78% N, 7.46% S; found: 77.93% C, 4.46% H, 9.54% N, 7.23% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.16 d, 1 H, *J*(7,5) = 1.6 (H-7); 8.00 d, 1 H, *J*(4,5) = 8.6 (H-4); 7.69 dd, 1 H, *J*(5,4) = 8.6, *J*(5,7) = 1.6 (H-5); 7.55 d, 1 H, *J*(*trans*) = 16.2 (H-b); 7.44 d, 2 H, *J* = 8,6 (H-2′, H-6′); 7.34–7.28 m, 4 H (H-Ar); 7.25 d, 1 H, *J*(*trans*) = 16.2 (H-a); 7.16–7.08 m, 6 H (H-Ar); 7.04 d, 2 H, *J* = 8.6 (H-3′, H-6′). ^{13}C NMR (75 MHz, $CDCl_3$): 171.82 (C-2); 156.66 (C-3a); 150.00 (C-4′); 147.02 (2 × C); 139.91 (CH-b); 134.97 (C-7a); 129.76 (CH); 129.74 (CH); 129.08 (CH); 127.97 (C-1′); 126.25 (CH); 125.68 (CH); 124.35 (CH); 123.35 (CH); 121.93 (CH); 119.10 (CN); 118.75 (CH-a); 108.28 (CH-6). UV/VIS ($CHCl_3$), λ_{max} (ε): 434 (32 400). UV/VIS (methanol), λ_{max} (ε): 429 (38 300).

2-[(E)-2-(4-Pyrrolidin-1-ylphenyl)vinyl]benzothiazole-6-carbonitrile (**3g**). M.p. 235.5–238 °C. For $C_{20}H_{17}N_3S$ (331.4) calculated: 72.48% C, 5.17% H, 12.68% N; found: 71.92% C, 5.13% H, 12.36% N. ^{1}H NMR (300 MHz, $CDCl_3$): 8.12 d, 1 H, *J*(7,5) = 1.6 (H-7); 7.95 d, 1 H, *J*(4,5) = 8.2 (H-4); 7.67 dd, 1 H, *J*(5,4) = 8.2, *J*(5,7) = 1.6 (H-5); 7.54 d, 1 H, *J*(*trans*) = 15.9 (H-b); 7.48 d, 2 H, *J* = 8.8 (H-2′, H-6′); 7.16 d, 1 H, *J*(*trans*) = 15.9 (H-a); 6.57 d, 2 H, *J* = 8.8 (H-3′, H-5′); 3.37 t, 4 H, *J* = 6.6 ($N(CH_2)_2$); 2.05 m, 4 H (CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 172.79 (C-2); 156.67 (C-3a); 149.23 (C-4′); 141.11 (CH-b); 134.62 (C-7a); 129.65 (C-2′, C-6′); 129.46 (CH-7); 125.85 (CH-5); 122.66 (CH-4); 122.00 (C-1′); 119.08 (CN); 115.31 (CH-a); 111.87 (C-3′, C-5′); 107.47 (C-6); 47.59 (2 × CH_2); 25.47 (2 × CH_2). UV/VIS ($CHCl_3$), λ_{max} (ε): 440 (26 300).

2-{(E,E)-4-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}benzothiazole-6-carbonitrile (**3h**). M.p. 233–235 °C. For $C_{20}H_{17}N_3S$ (331.4) calculated: 72.48% C, 5.17% H, 12.68% N; found: 72.13% C, 5.12% H, 12.46% N. ^{1}H NMR (300 MHz, $CDCl_3$): 8.12 d, 1 H, *J*(7,5) = 1.5 (H-7); 7.96 d, 1 H, *J*(4,5) = 8.4 (H-4); 7.67 dd, 1 H, *J*(5,4) = 8.4, *J*(5,7) = 1.5 (H-5); 7.41 dd, 1 H, *J*(*trans*) = 15.4, *J* = 9.5 (H-b); 7.40 d, 2 H, *J* = 8.8 (H-2′, H-6′); 6.92–6.77 m, 3 H (H-d, H-a, H-c); 6.69 d, 2 H, *J* = 8.8 (H-3′, H-5′); 3.02 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 171.82 (C-2); 156.78 (C-3a); 151.21 (C-4′); 141.90 (CH-b); 140.73 (CH-c); 134.98 (C-7a); 129.67 (2 × CH-2′, 6′); 128.95 (CH-7); 126.11 (CH-5); 124.38 (C-1′); 123.13 (CH-a); 122.62 (CH-d); 121.63 (C-4); 119.16 (CN); 112.18 (2 × CH-3′, 5′); 107.96 (C-6); 40.40 ($N(CH_3)_2$). UV/VIS ($CHCl_3$), λ_{max} (ε): 450 (31 900).

Reaction of Nitro Derivatives of 2-Methylbenzothiazole with Aromatic Aldehydes. General Procedure

A nitro derivative of 2-methylbenzothiazoles **1c**–**1f** (0.39 g, 2 mmol) or 2-methyl-4,6-dinitrobenzothiazole (**1g**; 0.48 g, 2 mmol), corresponding aldehydes **2a**–**2d** (2 mmol) and sulfuric acid (0.22 g, 2.2 mmol) was refluxed in dry dioxane (10 ml) for 8 h. Unreacted starting benzothiazole was dissolved in dioxane. The precipitated material in protonized form was filtered off, diluted with chloroform (30 ml) and organic solution was washed with 10% aqueous sodium carbonate (3 × 20 ml) and water (3 × 30 ml). The organic layer was dried with anhydrous sodium sulfate and solvent was removed. The unreacted aldehyde was removed from the mixture by distillation under vacuum in the Kugelrohr apparatus. The crude products **3i**–**3t** were recrystallized from methanol. The results are given in Table II.

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-4-nitrobenzothiazole (**3i**). M.p. 184 °C. For $C_{17}H_{15}N_3O_2S$ (325.4) calculated: 62.75% C, 4.65% H, 12.91% N, 9.85% S; found: 62.51% C, 4.61% H, 12.62% N, 9.84% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.15 dd, 1 H, *J*(5,6) = 8.1, *J*(5,7) = 1.2 (H-5); 8.06 dd, 1 H, *J*(7,6) = 8.1, *J*(7,5) = 1.2 (H-7); 7.54 d, 1 H, *J*(*trans*) = 15.6 (H-b); 7.50 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.50 t, 1 H, *J* = 8.1 (H-6); 7.33 d, 1 H, *J*(*trans*) = 15.6 (H-a); 6.71 d, 2 H, *J* = 8.7 (H-3′, H-5′); 3.05 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 172.87 (C-2); 151.86 (C-4′); 146.94 (C-3a); 141.95 (C-4); 141.59 (CH-b); 137.74 (C-7a); 129.75 (C-2′, C-6′); 126.91 (CH-6); 123.85 (CH-7); 122.91 (C-1′); 122.87 (CH-5); 116.93 (CH-a); 112.21 (C-3′, C-5′); 40.37 ($N(CH_3)_2$). UV/VIS ($CHCl_3$), λ_{max} (ε): 446 (23 100). UV/VIS (methanol), λ_{max} (ε): 440 (15 700).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-5-nitrobenzothiazole (**3j**). M.p. 225–228 °C. For $C_{17}H_{15}N_3O_2S$ (325.4) calculated: 62.75% C, 4.65% H, 12.91% N, 9.85% S; found: 62.80% C, 4.55% H, 12.82% N, 9.63% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.74 d, 1 H, *J*(4,6) = 1.8 (H-4); 8.19 dd, 1 H, *J*(6,7) = 9.0, *J*(6,4) = 1.8 (H-6); 7.92 d, 1 H, *J*(7,6) = 8.7 (H-7); 7.52 d, 1 H, *J*(*trans*) = 16.2 (H-b); 7.49 d, 2 H, *J* = 8.7 (H-2′, H-6′); 7.19 d, 1 H, *J*(*trans*) = 16.2 (H-a); 6.72 d, 2 H, *J* = 8.7 (H-3′, H-5′); 3.05 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 171.57 (C-2); 154.04 (C-3a); 151.62 (C-4′); 146.86 (C-5); 140.98 (C-7a); 140.57 (C-b); 129.40 (C-2′, C-6′); 122.61 (C-1′); 121.56 (C-6); 119.11 (C-7); 117.44 (C-4); 116.02 (C-a); 112.00 (C-3′, C-5′); 40.17 ($N(CH_3)_2$). UV/VIS ($CHCl_3$), λ_{max} (ε): 270 (13 300), 416 (16 600). UV/VIS (methanol), λ_{max} (ε): 204 (22 500), 232 (20 100), 314 (13 800), 416 (27 900).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-6-nitrobenzothiazole (**3k**). M.p. 252–253 °C. For $C_{17}H_{15}N_3O_2S$ (325.4) calculated: 62.75% C, 4.65% H, 12.91% N, 9.85% S; found: 62.48% C, 4.65% H, 12.67% N, 9.73% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.74 d, 1 H, *J*(7,5) = 2.4 (H-7); 8.31 dd, 1 H, *J*(5,4) = 9.0, *J*(5,7) = 2.4 (H-5); 7.96 d, 1 H, *J*(4,5) = 9.0 (H-4); 7.56 d, 1 H, *J*(*trans*) = 16.2 (H-b); 7.50 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.19 d, 1 H, *J*(*trans*) = 16.2 (H-a); 6.72 d, 2 H, *J* = 9.0 (H-3′, H-5′); 3.06 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 173.87 (C-2); 158.11 (C-3a); 151.75 (C-4′); 144.36 (C-6); 141.23 (CH-b); 134.47 (C-7a); 129.58 (CH-2′, 6′); 122.56 (C-1′); 122.08 (CH-4); 121.89 (CH-5); 117.84 (CH-7); 116.02 (CH-a); 111.99 (CH-3′, 5′); 40.15 ($N(CH_3)_2$). UV/VIS ($CHCl_3$), λ_{max} (ε): 264 (5 000), 320 (7 700), 456 (31 200). UV/VIS (methanol), λ_{max} (ε): 206 (9 800), 262 (5 000), 308 (5 000), 446 (9 700).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-7-nitrobenzothiazole (**3l**). M.p. 173–175 °C. For $C_{17}H_{15}N_3O_2S$ (325.4) calculated: 62.75% C, 4.65% H, 12.91% N, 9.85% S; found: 62.55% C, 4.57% H, 12.60% N, 9.65% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.14 dd, 1 H, *J*(6,5) = 8.1, *J*(6,4) = 0.9 (H-6); 8.06 dd, 1 H, *J*(4,5) = 8.1, *J*(4,6) = 0.9 (H-4); 7.54 d, 1 H, *J*(*trans*) = 15.3 (H-b); 7.50 d, 2 H, *J* = 8.7 (H-2′, H-6′); 7.40 t, 1 H, *J* = 8.1 (H-5); 7.33 d, 1 H, *J*(*trans*) = 15.3 (H-a);

6.71 d, 2 H, *J* = 8.7 (H-3′, H-5′); 3.05 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 172.62 (C-2); 151.63 (C-3a); 146.70 (C-4′); 141.72 (C-7); 141.34 (CH-b); 137.51 (C-7a); 129.51 (CH-2′, 6′); 126.67 (CH-4); 123.61 (CH-5); 122.67 (C-1′); 122.62 (CH-6); 116.69 (CH-a); 111.97 (CH-3′, 5′); 40.13 ($N(CH_3)_2$). UV/VIS ($CHCl_3$), λ_{max} (ε): 256 (15 4000), 320 (10 800), 446 (16 100). UV/VIS (methanol), λ_{max} (ε): 204 (20 100), 258 (9 000), 318 (7 000), 440 (13 400).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-4,6-dinitrobenzothiazole (**3m**). M.p. 252.5–254.5 °C. For $C_{17}H_{14}N_4O_4S$ (370.4) calculated: 55.13% C, 3.81% H, 15.13% N, 8.66% S; found: 54.90% C, 3.94% H, 15.44% N, 8.52% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.99 d, 1 H, *J*(5,7) = 2.4 (H-5); 8.93 d, 1 H, *J*(7,5) = 2.4 (H-7); 7.68 d, 1 H, *J*(*trans*) = 15.9 (H-b); 7.51 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.30 d, 1 H, *J*(*trans*) = 15.9 (H-a); 6.70 d, 2 H, *J* = 9.0 (H-3′, H-5′); 3.08 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 178.01 (C-2); 152.47 (C-3a); 150.32 (C-4′); 144.60 (CH-b); 142.62 (C-6); 138.90 (C-7a); 138.41 (C-4); 130.59 (C-2′, C-6′); 122.23 (C-1′); 121.59 (CH-7); 118.80 (CH-5); 115.67 (CH-a); 112.13 (C-3′, C-5′); 40.31 ($N(CH_3)_2$). UV/VIS ($CHCl_3$), λ_{max} (ε): 272 (16 600), 330 (14 400), 514 (14 400).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}-5-nitrobenzothiazole (**3n**). M.p.162–164.5 °C. For $C_{27}H_{19}N_3O_2S$ (449.5) calculated: 72.14% C, 4.26% H, 9.35% N, 7.13% S; found: 72.20% C, 4.25% H, 9.45% N, 7.04% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.78 d, 1 H, *J*(4,6) = 2.1 (H-4); 8.23 dd, 1 H, *J*(6,7) = 9.0, *J*(6,4) = 2.1 (H-6); 7.95 d, 1 H, *J*(7,6) = 9.0 (H-7); 7.53 d, 1 H, *J*(*trans*) = 15.9 (H-b); 7.45 d, 2 H, *J* = 8.4 (H-2′, H-6′); 7.34–7.23 m, 4 H (H-Ar); 7.19–7.09 m, 6 H (H-Ar); 7.16 d, 1 H, *J*(*trans*) = 15.9 (H-a); 7.05 d, 2 H, *J* = 8.7 (H-3′, H-5′). ^{13}C NMR (75 MHz, $CDCl_3$): 169.85 (C-2); 152.84 (C-3a); 148.70 (C-4′); 145.86 (2 × CH); 145.78 (C-5); 139.95 (C-7a); 138.48 (C-b); 128.48 (4 × CH); 127.79 (C-2′, C-6′); 126.70 (C-1′); 125.27 (2 × CH); 124.40 (4 × CH); 123.07 (C-7); 120.69 (C-3′, C-5′); 118.38 (C-6); 117.48 (C-4); 116.73 (C-a). UV/VIS ($CHCl_3$), λ_{max} (ε): 242 (18 600), 300 (30 600), 428 (34 300). UV/VIS (methanol), λ_{max} (ε): 208 (29 400), 296 (16 000), 422 (17 400).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}-6-nitro-benzothiazole (**3o**). M.p. 183–185 °C; ref.[25] gives m.p. 184–186 °C (ethanol).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}-4,6-dinitrobenzothiazole (**3p**). M.p. 227–229 °C. For $C_{27}H_{18}N_4O_4S$ (494.5) calculated: 65.58% C, 3.67% H, 11.33% N, 6.48% S; found: 65.28% C, 3.55% H, 11.21% N, 6.33% S. ^{1}H NMR (300 MHz, $CDCl_3$): 9.02 d, 1 H, *J*(5,7) = 2.1 (H-5); 8.97 d, 1 H, *J*(7,5) = 2.1 (H-7); 7.71 d, 1 H, *J*(*trans*) = 15.9 (H-b); 7.48 d, 2 H, *J* = 8.7 (H-2′, H-6′); 7.44 d, 1 H, *J*(*trans*) = 15.9 (H-a); 7.36–7.31 m, 4 H (H-Ar); 7.18–7.12 m, 6 H (H-Ar); 7.04 d, 2 H, *J* = 8.7 (H-3′, H-5′). ^{13}C NMR (75 MHz, $CDCl_3$): 177.36 (C-2); 150.90 (C-3a); 150.32 (C-4′); 146.64 (2 × C); 143.42 (CH-b); 143.01 (C-6); 140.77 (C-4); 138.43 (C-7a); 129.84 (4 × CH); 126.98 (C-1′); 126.51 (2 × CH); 126.05 (4 × CH); 124.84 (C-2′, C-6′); 121.85 (CH-7); 121.13 (C-3′, C-5′); 118.80 (CH-5); 118.04 (CH-a). UV/VIS ($CHCl_3$), λ_{max} (ε): 276 (18 800), 302 (20 000), 348 (19 400), 516 (33 700).

2-[(E)-6-Nitro-2-(4-pyrrolidin-1-ylphenyl)vinyl]benzothiazole (**3q**). M.p. 268–271 °C. For $C_{19}H_{17}N_3O_2S$ (351.4) calculated: 64.94% C, 4.88% H, 11.96% N, 9.12% S; found: 64.59% C, 4.86% H, 11.72% N, 9.14% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.73 d, 1 H, *J*(7,5) = 2.2 (H-7); 8.30 dd, 1 H, *J*(5,4) = 9.4, *J*(5,7) = 2.2 (H-5); 7.95 d, 1 H, *J*(4,5) = 9.4 (H-4); 7.57 d, 1 H, *J*(*trans*) = 15.9 (H-b); 7.49 d, 2 H, *J* = 8.8 (H-2′, H-6′); 7.17 d, 1 H, *J*(*trans*) = 15.9 (H-a); 6.57 d, 2 H, *J* = 8.8 (H-3′, H-5′); 3.37 t, 4 H, *J* = 6.6 ($N(CH_2)_2$); 2,05 m, 4 H (2 × CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 174.05 (C-2); 158.18 (C-3a); 149.32 (C-4′); 144.25 (C-6); 141.58 (CH-b); 134.44 (C-7a); 129.78 (CH-2′, 6′); 121.96 (C-1′); 121.94 (CH-4); 121.87 (CH-5);

117.81 (CH-7); 115.32 (CH-a); 111.89 (CH-3′, 5′); 47.59 ($N(CH_2)_2$); 25.47 (2 × CH_2). UV/VIS ($CHCl_3$), λ_{max} (ε): 466 (49 400).

2-[(E)-4,6-Dinitro-2-(4-pyrrolidin-1-ylphenyl)vinyl]benzothiazole (**3r**). M.p. 217–220 °C. For $C_{19}H_{16}N_4O_4S$ (396.4) calculated: 57.57% C, 4.07% H, 14.13% N, 8.09% S; found: 57.90% C, 3.98% H, 14.14% N, 8.22% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.98 d, 1 H, *J*(5,7) = 2.1 (H-5); 8.89 d, 1 H, *J*(7,5) = 2.1 (H-7); 7.67 d, 1 H, *J*(*trans*) = 15.9 (H-b); 7.50 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.28 d, 1 H, *J*(*trans*) = 15.9 (H-a); 6.56 d, 2 H, *J* = 9.0 (H-3′, H-5′); 3.41–3.36 m, 4 H (2 × CH_2); 2.08–2.04 m, 4 H (2 × CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 178.99 (C-2); 151.73 (C-3a); 150.02 (C-4′); 145.46 (CH-b); 141.52 (C-6); 138.49 (C-7a); 138.50 (C-4); 130.80 (C-2′, C-6′); 121.06 (C-1′); 122.63 (CH-7); 118.50 (CH-5); 115.23 (CH-a); 112.13 (C-3′, C-5′); 47.85 ($N(CH_2)_2$); 25.30 (2 × CH_2). UV/VIS ($CHCl_3$), λ_{max} (ε): 268 (9 400), 330 (6 700), 534 (15 200).

2-{(E,E)-4-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}-6-nitrobenzothiazole (**3s**). M.p. 228–230 °C. For $C_{19}H_{17}N_3O_2S$ (351.4) calculated: 64.94% C, 4.88% H, 11.96% N, 9.12% S; found: 65.12% C, 4.72% H, 12.00% N, 9.01% S. ^{1}H NMR (300 MHz, $CDCl_3$): 8.74 d, 1 H, *J*(7,5) = 2.4 (H-7); 8.31 dd, 1 H, *J*(5,4) = 9.0, *J*(5,7) = 2.4 (H-5); 7.97 d, 1 H, *J*(4,5) = 9.0 (H-4); 7.46 dd, 1 H, *J*(*trans*) = 15.3, *J* = 9.9 (H-b); 7.43 d, 1 H, *J* = 12.6 (H-d); 7.41 d, 2 H, *J* = 8.7 (H-2′, H-6′); 6.84 d, 1 H, *J* = 15.3 (H-a); 6.81 dd, 1 H, *J*(*trans*) = 15.3, *J* = 9.9 (H-c); 6.69 d, 2 H, *J* = 8.7 (H-3′, H-5′); 3.03 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 172.17 (C-2); 158.07 (C-3a); 151.06 (C-4′); 144.43 (C-6); 142.19 (CH-b); 140.95 (CH-d); 134.61 (C-7a); 128.84 (2 × CH-2′, 6′); 124.12 (C-1′); 122.33, 122.27, 121.91, 121.47 (CH-4, CH-5, CH-a, CH-b); 117.86 (CH-7); 112.06 (2 × CH-3′, 5′); 40.02 ($N(CH_3)_2$). UV/VIS (methanol), λ_{max} (ε): 206 (7 000), 262 (4 400), 310 (3 700), 460 (3 700). UV/VIS ($CHCl_3$), λ_{max} (ε): 471 (59 800).

2-{(E)-2-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}-4,6-dinitrobenzothiazole (**3t**). M.p. 210–211.5 °C. For $C_{19}H_{16}N_4O_4S$ (369.4) calculated: 57.57% C, 4.07% H, 14.13% N, 8.09% S; found: 57.63% C, 4.06% H, 14.26% N, 8.19% S. ^{1}H NMR (300 MHz, $CDCl_3$): 9.00 d, 1 H, *J*(5,7) = 2.1 (H-5); 8.93 d, 1 H, *J*(7,5) = 2.1 (H-7); 7.61 dd, 1 H, *J*(*trans*) = 14.7, *J* = 11.1 (H-b); 6.95 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.02 d, 1 H, *J*(*trans*) = 15.0 (H-d); 6.95 d, 1 H, *J*(*trans*) = 15.0 (H-a); 6.84 dd, 1 H, *J*(*trans*) = 15.0, *J* = 11.1 (H-c); 6.70 d, 2 H, *J* = 9.0 (H-3′, H-5′); 3.05 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 174.51 (C-2); 157.06 (C-3a); 151.41 (C-4′); 145.28 (CH-b); 143.45 (CH-d); 142.15 (C-6); 138.71 (C-4); 130.50 (C-7a); 129.42 (C-2′, C-6′); 123.71 (C-1′); 121.96 (CH-c); 121.47 (CH-7); 118.80 (CH-5); 118.61 (C-3′, C-5′); 105.60 (CH-a); 40.17 ($N(CH_3)_2$). UV/VIS ($CHCl_3$), λ_{max} (ε): 262 (33 800), 304 (17 800), 360 (13 600), 536 (23 100).

Synthesis of Derivatives of 2,3-Dimethylbenzothiazolium Iodide **4b**–**4e**.
General Procedure

A mixture of 2-methylbenzothiazole-6-carbonitrile (**1b**; 0.87 g, 5 mmol) or a nitro derivative of 2-methylbenzothiazoles **1d**–**1f** (0.97 g, 5 mmol) and iodomethane (2.13 g, 15 mmol) in methanol (4 ml) was irradiated in microwave apparatus for 40 min. The resulting precipitate was collected and washed with cold methanol. Yields and other conditions are in Table III.

6-Cyano-2,3-dimethylbenzothiazolium iodide (**4b**). M.p. 250–251 °C. For $C_{10}H_9IN_2S$ (316.2) calculated: 37.99% C, 2.87% H, 8.86% N, 10.14% S; found: 37.69% C, 2.84% H, 8.74% N, 10.14% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.95 d, 1 H, *J*(7,5) = 1.2 (H-7); 8.50 d, 1 H, *J*(4,5) = 8.7 (H-4); 8.36 dd, 1 H, *J*(5,4) = 8.7, *J*(5,7) = 1.2 (H-5); 4.22 s, 3 H (N-CH_3); 3.21 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 181.63 (C-2); 144.02 (C-3a); 132.25 (CH-7); 129.69 (CH-5); 129.48 (C-7a); 118.15 (CH-4); 117.66 (CN); 110.37 (CH-6); 36.29 (N-CH_3); 17.75 (CH_3).

2,3-Dimethyl-5-nitrobenzothiazolium iodide (**4c**). M.p. 255–257 °C. For $C_9H_9IN_2O_2S$ (336.2) calculated: 32.16% C, 2.70% H, 8.33% N, 9.54% S; found: 32.09% C, 2.69% H, 8.34% N, 9.44% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.19 d, 1 H, J(4,6) = 2.4 (H-4); 8.70 d, 1 H, J(7,6) = 9.0 (H-7); 7.71 dd, 1 H, J(6,7) = 9.0, J(6,4) = 2.4 (H-6); 4.31 s, 3 H (N-CH_3); 3.23 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 181.90 (C-2); 147.87 (C-3a); 141.76 (C-5); 135.00 (C-7a); 126.22 (CH-7); 122.30 (CH-6); 112.86 (CH-4); 36.88 (N-CH_3); 17.79 (CH_3).

2,3-Dimethyl-6-nitrobenzothiazolium iodide (**4d**). M.p. 260–261 °C; ref.[26] gives m.p. 240 °C (nitromethane). ^{1}H NMR (300 MHz, DMSO-d_6): 9.43 d, 1 H, J(7,5) = 2.1 (H-7); 8.68 dd, 1 H, J(5,4) = 9.0, J(5,7) = 2.4 (H-5); 8.51 d, 1 H, J(4,5) = 9.0 (H-4); 4.25 s, 3 H (N-CH_3); 3.24 s, 3 H (CH_3).

2,3-Dimethyl-7-nitrobenzothiazolium iodide (**4e**). M.p. 179–180 °C. For $C_9H_9IN_2O_2S$ (336.2) calculated: 32.16% C, 2.70% H, 8.33% N, 9.54% S; found: 32.07% C, 2.71% H, 8,33% N, 9.53% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.79 dd, 1 H, J(4,5) = 8.4, J(4,6) = 0.6 (H-4); 8.68 dd, 1 H, J(6,5) = 8.4, J(6,4) = 0.6 (H-6); 8.19 t, 1 H, J = 8.4 (H-5); 4.30 s, 3 H (N-CH_3); 3.27 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 181.03 (C-2); 143.10 (C-7); 142.17 (C-3a); 130.37 (CH-4); 124.57 (CH-5); 123.97 (C-7a); 123.88 (CH-6); 37.13 (N-CH_3); 17.22 (CH_3).

Synthesis of 3-Methyl-2-((*E*)-styryl)benzothiazol-3-ium Iodide (**5a**)

2-Styrylbenzothiazole (**3a**; 1.19 g, 5 mmol) and iodomethane (2.84 g, 1.85 ml, 20 mmol) was refluxed in nitromethane for 12 h. The resulting precipitate was collected, washed with nitromethane and recrystalized from ethanol. Yield 1.35 g (75%). M.p. 230–233 °C; ref.[27] gives m.p. 223 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 8.46 d, 1 H, J(7,6) = 7.5 (H-7); 8.28 d, 1 H, J(4,5) = 7.5 (H-4); 8.24 d, 1 H, J(*trans*) = 15.0 (H-b); 8.09–8.06 m, 2 H (H-Ar); 8.07 d, 1 H, J(*trans*) = 15.0 (H-a); 7.93–7.87 m, 1 H (H-5); 7.84–7.79 m, 1 H (H-6); 7.60–7.54 m, 3 H (H-Ar); 4.38 s, 3 H (N-CH_3). ^{13}C NMR data are consistent with ref.[28].

Reaction of 2,3-Dimethylbenzothiazolium Iodide Derivatives with Aromatic Benzaldehydes. General Procedure

A mixture of 2,3-dimethylbenzothiazolium iodide (**4a**; 0.58 g 2 mmol) or 6-cyano-2-methylbenzothiazolium iodide (**4b**; 0.63 g, 2 mmol) or a nitro derivative of 2,3-dimethylbenzothiazolium iodides **4c**–**4e** (0.67 g, 2 mmol), the corresponding aldehyde (2 mmol) and basic catalyst (pyridine or piperidine 0.3 mmol) or, alternatively, without any catalyst in methanol (5 ml) was refluxed for 6–12 h. The resulting precipitate was collected, washed with cold methanol and recrystalized from methanol. The results are summarized in Table IV.

2-{(E)-2-[4-(Dimethylamino)pheny]vinyl}-3-methylbenzothiazol-3-ium iodide (**5b**). M.p. 262.5–264 °C; ref.[29] gives m.p. 249–250 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 8.29 d, 1 H, J(7,6) = 8.0 (H-7); 8.09 d, 1 H, J(4,5) = 8.4 (H-4); 8.06 d, 1 H, J(*trans*) = 15.3 (H-b); 7.90 d, 2 H, J = 8.5 (H-2′, H-6′); 7.78 t, 1 H, J = 7.9 (H-5); 7.69 t, 1 H, J = 7.9 (H-6); 7.65 d, 1 H, J(*trans*) = 15.3 (H-a); 6.83 d, 2 H, J = 8.7 (H-3′, H-6′); 4.23 s, 3 H (CH_3); 3.03 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 171.40 (C-2); 153.59 (C-4′); 150.20 (CH-b); 142.00 (C-3a); 132.90 (C-2′, C-6′); 128.98 (CH-5); 127.55 (CH-6); 126.85 (C-7a); 123.79 (CH-7); 121.50 (C-1′); 115.98 (CH-4); 112.03 (C-3′, C-5′); 106.24 (CH-a); 39.83 (N(CH_3)$_2$); 35.62 (N-CH_3). UV/VIS data are consistent with ref.[30]. UV/VIS (methanol), λ_{max} (ε): 220 (30 200), 318 (7 800), 520 (67 900).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-3-methylbenzothiazol-3-ium hydrogen sulfate (**5c**). M.p. 295–296 °C. For $C_{18}H_{20}N_2O_4S_2$ (392.2) calculated: 55.08% C, 5.14% H, 7.14% N,

16.34% S; found: 54.85% C, 5.05% H, 7.25% N, 16.44% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.28 d, 1 H, *J*(7,6) = 8.1 (H-7); 8.09 d, 1 H, *J*(4,5) = 8.4 (H-4); 8.03 d, 1 H, *J*(*trans*) = 15.3 (H-b); 7.89 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.77 t, 1 H, *J* = 7.2 (H-5); 7.67 t, 1 H, *J* = 7.2 (H-6); 7.60 d, 1 H, *J*(*trans*) = 15.3 (H-a); 6.80 d, 2 H, *J* = 9.0 (H-3′, H-6′); 4.22 s, 3 H (CH_3); 3.08 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 171.31 (C-2); 153.43 (C-4′); 150.08 (CH-b); 141.92 (C-3a); 132.81 (C-2′, C-6′); 128.85 (CH-5); 127.42 (CH-6); 126.80 (C-7a); 123.77 (CH-7); 121.44 (C-1′); 115.92 (CH-4); 111.91 (C-3′, C-5′); 106.24 (CH-a); 39.75 ($N(CH_3)_2$); 35.52 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 206 (38 300), 522 (71 500).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-3-methyl-5-nitrobenzothiazol-3-ium iodide (**5d**). M.p. 242–243 °C. For $C_{18}H_{18}IN_3O_2S$ (467.3) calculated: 46.26% C, 3.88% H, 8.99% N, 6.86% S; found: 46.12% C, 3.85% H, 8.79% N, 6.75% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.82 d, 1 H, *J*(4,6) = 1.9 (H-4); 8.52 d, 1 H, *J*(7,6) = 8.8 (H-7); 8.44 dd, 1 H, *J*(6,7) = 8.8, *J*(6,4) = 1.9 (H-6); 8.12 d, 1 H, *J*(*trans*) = 15.2 (H-b); 7.96 d, 2 H, *J* = 8.9 (H-2′, H-6′); 7.59 d, 1 H, *J*(*trans*) = 15.2 (H-a); 6.81 d, 2 H, *J* = 9.0 (H-3′, H-6′); 4.26 s, 3 H (CH_3); 3.12 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 173.50 (C-2); 154.10 (C-4′); 152.13 (CH-b); 147.55 (C-5); 142.44 (C-3a); 133.66 (C-2′, C-6′); 133.51 (CH-7a); 125.00 (CH-7); 121.52 (C-6); 121.40 (C-1′); 112.15 (C-3′, C-5′); 111.00 (CH-4); 105.54 (CH-a); 48.55 ($N(CH_3)_2$); 35.86 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 548 (58 800). UV/VIS ($CHCl_3$), λ_{max} (ε): 282 (6 700), 576 (42 600).

2-{(E)-2-[3-(Dimethylamino)phenyl]vinyl}-3-methyl-5-nitrobenzothiazol-3-ium iodide (**5e**). M.p. 224–225 °C. For $C_{18}H_{18}IN_3O_2S$ (467.3) calculated: 46.26% C, 3.88% H, 8.99% N, 6.86% S; found: 46.05% C, 3.81% H, 8.69% N, 6.84% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.10 d, 1 H, *J*(4,6) = 1.8 (H-4); 8.71 d, 1 H, *J*(7,6) = 8.7 (H-7); 8.61 dd, 1 H, *J*(6,7) = 8.7, *J*(6,4) = 1.8 (H-6); 8.30 d, 1 H, *J*(*trans*) = 15.9 (H-b); 8.02 d, 1 H, *J*(*trans*) = 15.9 (H-a); 7.42–7.35 m, 3 H (H-Ar); 7.00–6.96 m, 1 H (H-Ar); 4.47 s, 3 H (CH_3); 3.00 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 175.64 (C-2); 151.96 (CH-b); 150.62 (C-3′); 147.91 (C-5); 142.41 (C-3a); 134.43, 134.21 (CH-7a, C-1′); 129.79 (CH-5′); 125.84 (CH-7); 122.52 (CH-6); 118.27, 117.10 (CH-a, CH-6′); 113.55 (CH-2′); 113.42 (CH-4′); 112.62 (CH-4); 40.17 ($N(CH_3)_2$); 37.10 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 206 (30 900), 218 (32 600), 256 (22 400), 272 (21 800), 384 (20 600).

2-{(E)-2-[2-(Dimethylamino)phenyl]vinyl}-3-methyl-5-nitrobenzothiazol-3-ium iodide (**5f**). M.p. 213–214 °C. For $C_{18}H_{18}IN_3O_2S$ (467.3) calculated: 46.26% C, 3.88% H, 8.99% N, 6.86% S; found: 46.15% C, 3.79% H, 8.72% N, 6.77% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.09 d, 1 H, *J*(4,6) = 1.8 (H-4); 8.64 d, 1 H, *J*(7,6) = 9.0 (H-7); 8.59 dd, 1 H, *J*(6,7) = 9.0, *J*(6,4) = 1.8 (H-6); 8.38 d, 1 H, *J*(*trans*) = 16.1 (H-b); 8.09 dd, 1 H, *J*(6′,5′) = 7.5, *J*(6′,4′) = 1.5 (H-6′); 8.09 d, 1 H, *J*(*trans*) = 15.9 (H-a); 7.55 dt, 1 H, *J*(4′,5′,6′) = 7.8, *J*(4′,6′) = 1.5 (H-4′); 7.26–7.16 m, 2 H (H-3′, H-5′); 4.43 s, 3 H (CH_3); 2.87 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 175.94 (C-2); 155.11 (C-2′); 147.92 (CH-b); 147.45 (C-5); 142.49 (C-3a); 133.93 (C-7a); 133.83 (CH-4′); 129.84 (C-1′); 125.98, 125.66 (CH-7, CH-6′); 122.53, 122.20 (CH-6, CH-5′); 119.09 (CH-3′); 112.53, 112.51 (CH-4, CH-a); 45.27 ($N(CH_3)_2$); 36.83 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 268 (17 000), 368 (18 400), 464 (8 700).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-3-methyl-6-nitrobenzothiazol-3-ium iodide (**5g**). M.p. 255–258 °C. For $C_{18}H_{18}IN_3O_2S$ (467.3) calculated: 46.26% C, 3.88% H, 8.99% N, 6.86% S; found: 46.29% C, 3.85% H, 8.98% N, 6.52% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.28 d, 1 H, *J*(7,5) = 1.2 (H-7); 8.56 dd, 1 H, *J*(5,4) = 8.8, *J*(5,7) = 1.2 (H-5); 8.26 d, 1 H, *J*(4,5) = 9.0 (H-4); 8.22 d, 1 H, *J*(*trans*) = 15.1 (H-b); 7.99 d, 2 H, *J* = 8.5 (H-2′, H-6′); 7.62 d, 1 H, *J*(*trans*) = 15.1 (H-a); 6.89 d, 2 H, *J* = 8.5 (H-3′, H-6′); 4.23 s, 3 H (CH_3); 3.19 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 174.32 (C-2); 154.26 (C-4′); 152.57 (CH-b); 145.98 (C-3a); 145.22

(CH-6); 133.91 (C-2′, C-6′); 127.67 (C-7a); 124.01 (CH-5); 121.73 (C-1′); 120.19 (CH-7); 116.19 (CH-4); 112.26 (C-3′, C-5′); 105.68 (CH-a); 39.90 ($N(CH_3)_2$); 35.86 ($N-CH_3$). UV/VIS (methanol), λ_{max} (ε): 562 (32 700). UV/VIS ($CHCl_3$), λ_{max} (ε): 304 (2 500), 596 (18 700).

2-{(E)-2-[3-(Dimethylamino)phenyl]vinyl}-3-methyl-6-nitrobenzothiazol-3-ium iodide (**5h**). M.p. 255–227 °C. For $C_{18}H_{18}IN_3O_2S$ (467.3) calculated: 46.26% C, 3.88% H, 8.99% N, 6.86% S; found: 46.01% C, 3.90% H, 8.71% N, 6.59% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.46 d, 1 H, *J*(7,5) = 2.4 (H-7); 8.67 dd, 1 H, *J*(5,4) = 9.3, *J*(5,7) = 2.4 (H-5); 8.45 d, 1 H, *J*(4,5) = 9.3 (H-4); 8.35 d, 1 H, *J*(*trans*) = 15.9 (H-b); 8.02 d, 1 H, *J*(*trans*) = 15.9 (H-a); 7.42–7.36 m, 3 H (H-Ar); 7.00–6.97 m, 1 H (H-Ar); 4.41 s, 3 H (CH_3); 3.01 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 176.76 (C-2); 152.39 (CH-b); 150.70 (C-3′); 146.16 (C-6); 145.71 (C-3a); 134.48 (C-1′); 129.77 (CH-5′); 128.74 (C-7a); 124.36 (CH-5); 120.91 (CH-7); 118.06 (CH-a); 117.83 (CH-6′); 117.06 (CH-4); 113.71 (CH-2′); 113.53 (CH-4′); 40.18 ($N(CH_3)_2$); 37.06 ($N-CH_3$). UV/VIS (methanol), λ_{max} (ε): 218 (14 600), 390 (23 700).

2-{(E)-2-[2-(Dimethylamino)phenyl]vinyl}-3-methyl-6-nitrobenzothiazol-3-ium iodide (**5i**). M.p. 208–209.8 °C. For $C_{18}H_{18}IN_3O_2S$ (467.3) calculated: 46.26% C, 3.88% H, 8.99% N, 6.86% S; found: 46.34% C, 3.85% H, 8.91% N, 6.82% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.36 d, 1 H, *J*(7.5) = 2.4 (H-7); 8.66 dd, 1 H, *J*(5,4) = 9.2, *J*(5,7) = 2.4 (H-5); 8.44 d, 1 H, *J*(4,5) = 9.3 (H-4); 8.31 d, 1 H, *J*(*trans*) = 15.9 (H-b); 8.09 dd, 1 H, *J*(6′,5′) = 5.1, *J*(6′,4′) = 1.2 (H-6′); 8.02 d, 1 H, *J*(*trans*) = 15.9 (H-a); 7.58–7.53 m, 1 H (H-4′); 7.26–7.15 m, 2 H (H-3′, H-5′); 4.48 s, 3 H (CH_3); 2.86 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 176.94 (C-2); 155.13 (CH-2′); 147.78 (C-b); 146.06 (C-6); 145.78 (C-3a); 133.86 (CH-4′); 129.94 (C-1′); 128.39 (C-7a); 125.94 (CH-6′); 124.35 (CH-5); 122.12 (CH-5′); 120.65 (CH-7); 119.03 (CH-3′); 117.73 (CH-4); 112.62 (CH-a); 45.26 ($N(CH_3)_2$); 36.88 ($N-CH_3$). UV/VIS (methanol), λ_{max} (ε): 376 (20 300), 476 (9 100).

2-{(E)-2-[4-(Dimethylamino)phenyl]vinyl}-3-methyl-7-nitrobenzothiazol-3-ium iodide (**5j**). M.p. 218.5–220 °C. For $C_{18}H_{18}IN_3O_2S$ (467.3) calculated: 46.26% C, 3.88% H, 8.99% N, 6.86% S; found: 46.03% C, 3.79% H, 8.75% N, 6.74% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.54 d, 1 H, *J*(6,5) = 8.1 (H-6); 8.47 d, 1 H, *J*(4,5) = 8.1 (H-4); 8.38 d, 1 H, *J*(*trans*) = 15.0 (H-b); 8.00 t, 1 H, *J*(5,4,6) = 8.2 (H-5); 7.96 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.61 d, 1 H, *J*(*trans*) = 15.0 (H-a); 6.85 d, 2 H, *J* = 9.0 (H-3′, H-5′); 4.24 s, 3 H (CH_3); 3.14 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 172.70 (C-2); 154.20 (C-4′); 152.57 (CH-b); 143.96 (C-7); 141.73 (C-3a); 133.83 (2 × CH-2′, 6′); 129.72 (C-7a); 123.07 (CH-4); 122.80 (CH-5); 121.95 (C-1′); 121.80 (CH-6); 112.21 (2 × CH-3′, 5′); 105.22 (CH-a); 40.06 ($N(CH_3)_2$); 35.95 ($N-CH_3$). UV/VIS (methanol), λ_{max} (ε): 556 (51 700). UV/VIS ($CHCl_3$), λ_{max} (ε): 244 (31 400), 586 (69 900).

2-{(E)-6-Cyano-2-[4-(dimethylamino)phenyl]vinyl}-3-methylbenzothiazol-3-ium iodide (**5k**). M.p. 246.5–249 °C. For $C_{19}H_{18}IN_3S$ (447.3) calculated: 51.01% C, 4.06% H, 9.39% N, 7.17% S; found: 50.89% C, 4.01% H, 9.14% N, 7.20% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.79 bs, 1 H (H-7); 8.21 bs, 2 H (H-5, H-4); 8.19 d, 1 H, *J*(*trans*) = 15.0 (H-b); 7.96 d, 2 H, *J* = 9.3 (H-2′, H-6′); 7.96 d, 1 H, *J*(4,5) = 9.0 (H-4); 7.61 d, 1 H, *J*(*trans*) = 15.0 (H-a); 6.88 d, 2 H, *J* = 9.0 (H-3′, H-6′); 4.19 s, 3 H (CH_3); 3.15 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 173.37 (C-2); 154.26 (C-4′); 152.28 (CH-b); 144.77 (C-3a); 133.76 (C-2′, C-6′); 132.12 (CH-5); 128.47 (CH-7); 127.47 (C-7a); 121.62 (C-1′); 117.94 (CN); 116.62 (CH-4); 112.20 (C-3′, C-5′); 109.00 (CH-6); 105.53 (CH-a); 39.89 ($N(CH_3)_2$); 35.76 ($N-CH_3$). UV/VIS (methanol), λ_{max} (ε): 554 (64 000). UV/VIS ($CHCl_3$), λ_{max} (ε): 582 (49 400).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}-3-methylbenzothiazol-3-ium iodide (**5l**). M.p. 232–234 °C. For $C_{28}H_{23}IN_2S$ (543.5) calculated: 61.54% C, 4.24% H, 5.13% N, 5.87% S; found: 61.03% C, 4.44% H, 5.14% N, 5.75% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.37 d, 1 H, *J*(7,6) =

8.1 (H-7); 8.19 d, 1 H, *J*(4,5) = 8.1 (H-4); 8.13 d, 1 H, *J*(*trans*) = 15.6 (H-b); 7.62 d, 2 H, *J* = 8.7 (H-2′, H-6′); 7.87–7.81 m, 1 H (H-5); 7.78–7.73 m, 1 H (H-6); 7.78 d, 1 H, *J*(*trans*) = 15.6 (H-a); 7.47–7.42 m, 4 H (H-Ar); 7.27–7.19 m, 6 H (H-Ar); 6.92 d, 2 H, *J* = 8.7 (H-3′, H-5′); 4.29 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 171.72 (C-2); 151.37 (C-4′); 148.60 (CH-b); 145.51 (2 × C); 142.01 (C-3a); 131.85 (2 × CH-2′, 6′); 130.05 (4 × CH); 129.19 (CH-5); 128.03 (CH-6); 127.36 (2 × C-1′, 7a); 126.19 (4 × CH); 125.50 (2 × CH); 124.06 (CH-7); 119.00 (2 × CH-3′, 5′); 116.50 (CH-4); 110.11 (CH-a); 36.05 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 356 (28 300), 508 (20 200). UV/VIS ($CHCl_3$), λ_{max} (ε): 294 (23 400), 358 (23 000), 554 (46 500).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}-3-methyl-5-nitrobenzothiazol-3-ium iodide (**5m**). M.p. 225 °C. For $C_{28}H_{23}IN_2O_2S$ (591.5) calculated: 56.86% C, 3.75% H, 7.10% N, 5.42% S; found: 56.62% C, 3.84% H, 7.03% N, 5.72% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.00 d, 1 H, *J*(4,6) = 2.1 (H-4); 8.62 d, 1 H, *J*(7,6) = 9.0 (H-7); 8.30 dd, 1 H, *J*(6,7) = 9.0, *J*(6,4) = 2.1 (H-6); 8.25 d, 1 H, *J*(*trans*) = 15.6 (H-b); 7.95 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.48–7.43 m, 4 H (H-Ar); 7.30–7.22 m, 6 H (H-Ar); 7.79 d, 1 H, *J*(*trans*) = 15.3 (H-a); 6.90 d, 2 H, *J* = 9.3 (H-3′, H-5′); 4.36 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 174.64 (C-2); 152.01 (CH-b); 147.76 (C-5); 145.23 (C-4′); 142.45 (C-3a); 133.92 (C-7a); 132.53 (2 × CH-2′, 6′); 130.10 (4 × CH); 129.52 (2 × C); 126.43 (4 × CH); 125.88 (2 × CH); 125.83 (CH-7); 125.47 (C-1′); 122.57 (CH-6); 118.53 (2 × CH-3′, 5′); 112.00 (CH-4); 109.91 (CH-a); 36.05 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 208 (51 500), 296 (22 200), 542 (30 000). UV/VIS ($CHCl_3$), λ_{max} (ε): 244 (31 100), 286 (30 400), 580 (71 400).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}-3-methyl-6-nitrobenzothiazol-3-ium iodide (**5n**). M.p. 240–240.5 °C. For $C_{28}H_{23}IN_2O_2S$ (591.5) calculated: 56.86% C, 3.75% H, 7.10% N, 5.42% S; found: 56.72% C, 3.65% H, 7.23% N, 5.55% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.36 d, 1 H, *J*(7,5) = 2.4 (H-7); 8.61 dd, 1 H, *J*(5,4) = 9.0, *J*(5,7) = 2.4 (H-5); 8.33 d, 1 H, *J*(4,5) = 9.0 (H-4); 8.26 d, 1 H, *J*(*trans*) = 15.5 (H-b); 7.96 d, 2 H, *J* = 8.8 (H-2′, H-6′); 7.76 d, 1 H, *J*(*trans*) = 15.5 (H-a); 7.47–7.43 m, 4 H (H-Ar); 7.31–7.23 m, 6 H (H-Ar); 6.90 d, 2 H, *J* = 8.7 (H-3′, H-5′); 4.27 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 175.59 (C-2); 152.04 (CH-b); 151.11 (C-4′); 145.73 (C-3a); 145.65 (C-6); 145.06 (2 × C); 132.58 (2 × CH-2′, 6′); 130.02 (4 × CH); 129.42 (C-7a); 128.16 (C-1′); 126.38 (4 × CH); 125.80 (2 × CH); 124.10 (CH-5); 120.46 (CH-7); 118.30 (2 × CH-3′, 5′); 117.02 (CH-4); 109.57 (CH-a); 36.35 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 210 (57 200), 288 (18 800), 350 (19 400), 552 (23 600). UV/VIS ($CHCl_3$), λ_{max} (ε): 244 (27 300), 284 (20 000), 364 (11 800), 602 (75 200).

2-{(E)-2-[4-(Diphenylamino)phenyl]vinyl}-3-methyl-7-nitrobenzothiazol-3-ium iodide (**5o**). M.p. 223–224 °C. For $C_{28}H_{23}IN_2O_2S$ (591.5) calculated: 56.86% C, 3.75% H, 7.10% N, 5.42% S; found: 56.89% C, 3.62% H, 7.15% N, 5.48% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.64 d, 1 H, *J*(6,5) = 8.4 (H-6); 8.61 d, 1 H, *J*(4,5) = 8.4 (H-4); 8.50 d, 1 H, *J*(*trans*) = 15.5 (H-b); 8.08 t, 1 H, *J* = 8.4 (H-5); 7.96 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.80 d, 1 H, *J*(*trans*) = 15.6 (H-a); 7.49–7.44 m, 4 H (H-Ar); 7.31–7.23 m, 6 H (H-Ar); 6.90 d, 2 H, *J* = 9.0 (H-3′, H-5′); 4.33 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 173.94 (C-2); 152.13 (C-4′); 151.33 (CH-b); 145.72 (2 × C); 143.87 (C-7); 141.89 (C-3a); 132.64 (2 × CH-2′, 6′); 130.11 (4 × CH), 126.48 (4 × CH); 126.00 (C-7a); 125.88 (2 × CH); 125.57 (CH-4); 123.69 (CH-5); 123.31 (C-1′); 122.89 (CH-6); 118.46 (2 × CH-3′, 5′); 109.23 (CH-a); 37.19 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 244 (25 900), 288 (25 600), 548 (39 800). UV/VIS ($CHCl_3$), λ_{max} (ε): 594 (73 000).

2-{(E)-6-Cyano-2-[4-(diphenylamino)pheny]vinyl}-3-methylbenzothiazol-3-ium iodide (**5p**). M.p. 242–243 °C. For $C_{29}H_{22}IN_3S$ (571.5) calculated: 60.95% C, 3.88% H, 7.35% N, 5.61% S; found: 60.90% C, 3.78% H, 7.27% N, 5.46% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.89 d, 1 H, *J*(7,5) = 1.2 (H-7); 8.34 d, 1 H, *J*(4,5) = 8.7 (H-4); 8.28 dd, 1 H, *J*(5,4) = 8.7, *J*(5,7) = 1.2 (H-5);

8.27 d, 1 H, *J*(*trans*) = 15.3 (H-b); 7.95 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.76 d, 1 H, *J*(*trans*) = 15.3 (H-a); 7.48–7.43 m, 4 H (H-Ar); 7.30–7.22 m, 6 H (H-Ar); 6.90 d, 2 H, *J* = 9.0 (H-3′, H-5′); 4.27 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 174.58 (C-2); 152.04 (C-4′); 150.94 (CH-b); 145.23 (2 × C); 144.72 (C-3a); 132.56 (2 × CH-2′, 6′); 132.29 (CH-5); 130.11 (4 × CH); 128.76 (CH-7); 128.03 (C-7a); 126.44 (4 × CH); 125.91 (C-1′); 125.85 (2 × CH); 118.52 (2 × CH-3′, 5′); 117.79 (CN); 117.42 (CH-4); 109.80 (CH-a); 109.54 (C-6); 36.25 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 304 (13 400), 542 (39 000). UV/VIS ($CHCl_3$), λ_{max} (ε): 286 (15 100), 350 (8 500), 592 (78 700).

3-Methyl-2-[(E)-2-(4-pyrrolidin-1-ylphenyl)vinyl]benzothiazol-3-ium iodide (**5q**). M.p. 255–256 °C. For $C_{20}H_{21}IN_2S$ (448.4) calculated: 53.58% C, 4.72% H, 6.25% N, 7.15% S; found: 53.45% C, 4.62% H, 6.33% N, 7.14% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.28 d, 1 H, *J*(7,6) = 8.1 (H-7); 8.07 d, 1 H, *J*(4,5) = 8.1 (H-4); 8.04 d, 1 H, *J*(*trans*) = 15.0 (H-b); 7.91 d, 2 H, *J* = 8.7 (H-2′, H-6′); 7.77 t, 1 H, *J* = 8.1 (H-5); 7.67 t, 1 H, *J* = 8.1 (H-6); 7.58 d, 1 H, *J*(*trans*) = 15.0 (H-a); 6.69 d, 2 H, *J* = 8.7 (H-3′, H-6′); 4.21 s, 3 H (CH_3); 3.41 t, *J* = 6.3 (2 × CH_2); 2.00 t, *J* = 6.3 (2 × CH_2). ^{13}C NMR (75 MHz, DMSO-d_6): 171.00 (C-2); 150.88 (C-4′); 150.17 (CH-b); 141.80 (C-3a); 132.94 (C-2′, C-6′); 128.66 (CH-5); 127.17 (CH-6); 126.57 (C-7a); 123.62 (CH-7); 121.13 (C-1′); 115.68 (CH-4); 112.24 (C-3′, C-5′); 105.47 (CH-a); 47.51 (N(CH_2)$_2$); 35.33 (N-CH_3); 24.77 (2 × CH_2). UV/VIS (methanol), λ_{max} (ε): 206 (35 700), 220 (26 000), 286 (6 400), 318 (4 700), 534 (72 100).

3-Methyl-6-nitro-2-[(E)-2-(4-pyrrolidin-1-ylphenyl)vinyl]benzothiazol-3-ium iodide (**5r**). M.p. 213–214 °C. For $C_{20}H_{20}IN_3O_2S$ (493.4) calculated: 48.69% C, 4.09% H, 8.52% N, 6.50% S; found: 48.50% C, 4.06% H, 8.52% N, 6.52% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.26 d, 1 H, *J*(7,5) = 2.4 (H-7); 8.55 dd, 1 H, *J*(5,4) = 9.0, *J*(5,7) = 2.4 (H-5); 8.19 d, 1 H, *J*(*trans*) = 15.0 (H-b); 8.18 d, 1 H, *J*(4,5) = 9.0 (H-4); 7.98 d, 2 H, *J* = 8.7 (H-2′, H-6′); 7.58 d, 1 H, *J*(*trans*) = 15.0 (H-a); 6.75 d, 2 H, *J* = 8.7 (H-3′, H-6′); 4.20 s, 3 H (CH_3); 3.44–3.47 m, 4 H (2 × CH_2); 2.03–1.99 m, 4 H (2 × CH_2). ^{13}C NMR (75 MHz, DMSO-d_6): 173.96 (C-2); 152.73 (C-4′); 151.87 (CH-b); 146.04 (C-3a); 145.14 (CH-6); 134.22 (C-2′, C-6′); 127.59 (C-7a); 124.00 (CH-5); 121.70 (C-1′); 120.13 (CH-7); 116.01 (CH-4); 112.88 (C-3′, C-5′); 105.06 (CH-a); 47.91 (2 × CH_2); 35.72 (N-CH_3); 24.83 (2 × CH_2). UV/VIS (methanol), λ_{max} (ε): 572 (27 300).

2-{(E,E)-4-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}-3-methylbenzothiazol-3-ium iodide (**5s**). M.p. and ^{1}H NMR data are consistent with ref.[15]. ^{13}C NMR (75 MHz, DMSO-d_6): 171.24 (C-2); 152.86 (CH-b); 151.83 (C-4′); 148.83 (CH-d); 142.56 (C-3a); 131.18 (2 × CH-2′, 6′); 129.72 (CH-5); 128.34 (CH-6); 127.82 (C-7a); 124.61 (CH-7); 123.54 (C-1′); 122.80 (CH-c); 116.80 (CH-4); 112.82 (2 × CH-3′, 5′); 112.76 (CH-a); 40.38 (N(CH_3)$_2$); 35.88 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 206 (33 300), 220 (33 500), 338 (10 000), 580 (54 300). UV/VIS ($CHCl_3$), λ_{max} (ε): 248 (13 500), 300 (3 700), 344 (3 800), 612 (73 100).

2-{(E,E)-4-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}-3-methyl-5-nitrobenzothiazol-3-ium iodide (**5t**). M.p. 253 °C. For $C_{20}H_{20}IN_3O_2S$ (493.4) calculated: 48.69% C, 4.09% H, 8.52% N, 6.50% S; found: 48.55% C, 4.01% H, 8.33% N, 6.41% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.92 d, 1 H, *J*(4,6) = 1.8 (H-4); 8.55 d, 1 H, *J*(7,6) = 9.0 (H-7); 8.48 dd, 1 H, *J*(6,7) = 9.0, *J*(6,4) = 1.8 (H-6); 8.11 dd, 1 H, *J*(*trans*) = 14.4, *J* = 11.1 (H-b); 7.58 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.57 d, 1 H, *J* = 14.4 (H-d); 7.31 d, 1 H, *J* = 14.4 (H-a); 7.24 dd, 1 H, *J*(*trans*) = 14.4, *J* = 11.1 (H-c); 6.81 d, 2 H, *J* = 9.0 (H-3′, H-5′); 4.20 s, 3 H (CH_3); 3.07 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 172.73 (C-2); 153.36 (C-4′); 152.44 (CH-b); 150.32 (CH-d); 147.50 (C-5); 142.23 (C-3a); 133.67 (C-7a); 131.04 (2 × CH-2′, 6′); 125.09 (CH-7); 122.58, 122.12 (CH-6, CH-c); 121.51 (C-1′); 112.06 (2 × CH-3′, 5′); 111.25, 111.13 (CH-4, CH-a);

39.56 ($N(CH_3)_2$); 35.68 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 610 (68 100). UV/VIS ($CHCl_3$), λ_{max} (ε): 300 (11 300), 374 (11 300), 652 (53 700).

2-{(E,E)-4-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}-3-methyl-6-nitrobenzothiazol-3-ium iodide (**5u**). M.p. 201–203 °C. For $C_{20}H_{20}IN_3O_2S$ (493.4) calculated: 48.69% C, 4.09% H, 8.52% N, 6.50% S; found: 48.72% C, 4.12% H, 8.40% N, 6.38% S. ^{1}H NMR (300 MHz, DMSO-d_6): 9.28 d, 1 H, *J*(7,5) = 2.1 (H-7); 8.56 dd, 1 H, *J*(5,4) = 9.0, *J*(5,7) = 2.1 (H-5); 8.25 d, 1 H, *J*(4,5) = 9.0 (H-4); 8.14 dd, 1 H, *J*(*trans*) = 14.4, *J* = 11.1 (H-b); 7.58 d, 2 H, *J* = 9.0 (H-2′, H-6′); 7.57 d, 1 H, *J* = 14.4 (H-d); 7.28 d, 1 H, *J* = 14.4 (H-a); 7.24 dd, 1 H, *J*(*trans*) = 14.4, *J* = 11.1 (H-c); 6.81 d, 2 H, *J* = 9.0 (H-3′, H-5′); 4.13 s, 3 H (CH_3); 3.07 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 174.01 (C-2); 153.96 (CH-b); 152.79 (C-4′); 151.03 (CH-d); 145.84 (C-6); 145.35 (C-3a); 131.40 (2 × CH-2′, 6′); 127.94 (C-7a); 124.10 (CH-5); 122.81 (C-1′); 122.35 (CH-c); 120.30 (CH-7); 116.41 (CH-4); 112.29 (2 × CH-3′, 5′); 111.38 (CH-a); 39.67 ($N(CH_3)_2$); 35.72 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 628 (15 700). UV/VIS ($CHCl_3$), λ_{max} (ε): 384 (10 700), 676 (26 000).

2-{(E,E)-4-[4-(Dimethylamino)phenyl]buta-1,3-dien-1-yl}-3-methyl-7-nitrobenzothiazol-3-ium iodide (**5v**). M.p. 201–203 °C. For $C_{20}H_{20}IN_3O_2S$ (493.4) calculated: 48.69% C, 4.09% H, 8.52% N, 6.50% S; found: 48.55% C, 4.09% H, 8.55% N, 6.39% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.57 d, 1 H, *J*(6,5) = 8.4 (H-6); 8.53 d, 1 H, *J*(4,5) = 8.4 (H-4); 8.34 dd, 1 H, *J*(*trans*) = 15.0, *J* = 11.1 (H-b); 8.03 t, 1 H, *J* = 8.4 (H-6); 7.58 d, 2 H, *J* = 9.3 (H-2′, H-6′); 7.57 d, 1 H, *J* = 15.0 (H-d); 7.24 d, 1 H, *J* = 14.4 (H-a); 7.24 dd, 1 H, *J*(*trans*) = 14.4, *J* = 11.1 (H-c); 6.82 d, 2 H, *J* = 9.3 (H-3′, H-5′); 4.20 s, 3 H (CH_3); 3.07 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 172.08 (C-2); 154.08 (CH-b); 152.73 (C-4′); 150.95 (CH-d); 143.86 (C-7); 141.80 (C-3a); 131.38 (2 × CH-2′, 6′); 130.64 (CH-4); 123.21 (C-7a); 122.76 (C-1′); 122.43 (CH-5); 122.23 (CH-6); 112.27 (2 × CH-3′, 5′); 112.66 (CH-c); 110.92 (CH-a); 39.79 ($N(CH_3)_2$); 35.90 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 206 (32 300), 218 (31 200), 290 (9 700), 374 (8 600), 622 (60 000). UV/VIS ($CHCl_3$), λ_{max} (ε): 292 (12 800), 380 (10 700), 662 (46 800).

6-Cyano-2-{(E,E)-4-[4-(dimethylamino)phenyl]buta-1,3dien-1-yl}-3-methylbenzothiazol-3-ium iodide (**5w**). M.p. 243 °C. For $C_{21}H_{20}IN_3S$ (473.4) calculated: 53.28% C, 4.26% H, 8.88% N, 6.77% S; found: 53.00% C, 4.25% H, 8.56% N, 56.52% S. ^{1}H NMR (300 MHz, DMSO-d_6): 8.79 bs, 1 H (H-7); 8.25 d, 1 H, *J*(5,4) = 9.0 (H-5); 8.23 d, 1 H, *J*(4,5) = 9.0 (H-4); 8.00 dd, 1 H, *J*(*trans*) = 14.4, *J* = 11.1 (H-b); 7.54 d, 1 H, *J* = 14.1 (H-d); 7.55 d, 2 H, *J* = 8.7 (H-2′, H-6′); 7.28 d, 1 H, *J* = 14.1 (H-a); 7.22 dd, 1 H, *J*(*trans*) = 14.1, *J* = 11.1 (H-c); 6.78 d, 2 H, *J* = 8.7 (H-3′, H-5′); 4.12 s, 3 H (CH_3); 3.06 s, 6 H (2 × CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 172.67 (C-2); 153.61 (CH-b); 152.65 (C-4′); 150.56 (CH-d); 144.66 (C-3a); 132.22 (CH-5); 131.26 (2 × CH-2′, 6′); 128.43 (CH-7); 127.77 (C-1′); 122.79 (C-7a); 122.36 (CH-c); 117.90 (CN); 116.84 (CH-4); 112.25 (2 × CH-3′, 5′); 111.30 (CH-a); 109.21 (C-6); 39.74 ($N(CH_3)_2$); 35.63 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 616 (55 300).

2-{(E,E,E)-6-[4-(Dimethylamino)phenyl]hexa-1,3,5-trien-1-yl}-3-methylbenzothiazol-3-ium iodide (**5x**). M.p. and ^{1}H NMR data are consistent with ref.[15]. ^{13}C NMR (75 MHz, DMSO-d_6): 170.50 (C-2); 151.18 (C-4′); 150.08 (CH-b); 149.10 (CH-d); 142.77 (C-3a); 141.90 (CH-f); 129.49 (2 × CH-2′, 6′); 129.12 (C-1′); 128 30 (CH-5); 127.79 (C-7a); 127.35 (CH-6); 123.96, 123.73, 123.54 (CH-7, CH-e, CH-c); 116.25 (CH-4); 113.37 (CH-a); 111.96 (2 × CH-3′, 5′); 39.74 ($N(CH_3)_2$); 35.70 (N-CH_3). UV/VIS (methanol), λ_{max} (ε): 206 (30 500), 220 (29 600), 290 (12 100), 350 (10 500), 580 (46 300). UV/VIS ($CHCl_3$), λ_{max} (ε): 636 (32 300).

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REFERENCES

1. Nalwa H. S., Miyata S. (Eds): *Nonlinear Optics of Organic Molecules and Polymers*. CRC Press, New York 1997.
2. Dalton L. R.: *Pure Appl. Chem.* **2004**, *76*, 1421.
3. Marder S. R., Gorman S. B., Tiemann B. G., Cheng. L. T.: *J. Am. Chem. Soc.* **1993**, *115*, 3006.
4. Abotto A., Bradamante S., Facchetti A., Pagani G. A.: *J. Org. Chem.* **1997**, *62*, 5755.
5. Dirk C. W., Katz H. E., Schilling M. L., King L. A.: *Chem. Mater.* **1990**, *2*, 700.
6. Hrobárik P., Zahradnik P., Fabian W. M. F.: *Phys. Chem. Chem. Phys.* **2004**, *6*, 495.
7. Moylan C. R., Twieg R. J., Lee V. Y., Swanson S. A., Betterton K. M., Miller R. D.: *J. Am. Chem. Soc.* **1993**, *115*, 12599.
8. Ćaleta I., Grdiša M., Mrvoš-Sermek D, Cetina M., Tralić-Kulenović V., Pavelić K., Karminski-Zamola G.: *Farmaco* **2004**, *59*, 297.
9. Sych E. D., Tolmachev A.: *Ukr. Khim. Zh.* **1961**, *24*, 80.
10. Veltman R. P.: *Zh. Obshch. Khim.* **1956**, *26*, 3388.
11. Mizuno Y., Adachi K.: *J. Pharm. Soc. Jpn.* **1952**, *72*, 745; *Chem. Abstr.* **1954**, *48*, 2689.
12. Mizuno Y., Adachi K.: *J. Pharm. Soc. Jpn.* **1952**, *72*, 1271; *Chem. Abstr.* **1953**, *47*, 12357.
13. Kauffman J. M., Moyna G.: *J. Org. Chem.* **2003**, *68*, 839.
14. Magdolen P., Mečiarová M., Toma Š.: *Tetrahedron* **2001**, *57*, 4781.
15. Buffa R., Zahradník P., Foltínová P.: *Heterocycl. Commun.* **2001**, *7*, 331.
16. Kanazawa R., Tokoroyama T.: *Synthesis* **1976**, 526.
17. Rodríguez J. G., Lafuente A., Martin-Vilamil R., Martínez-Alcazar M. P.: *J. Phys. Org. Chem.* **2001**, *14*, 859.
18. Dryanska V., Ivanov Ch.: *Synthesis* **1976**, 37.
19. Vompe A. F., Meshki L. M.: *Zh. Org. Khim.* **1981**, *17*, 1735.
20. Coe B. J., Harris J. A., Hall J. J., Brunschwig B. S., Hung S. T., Libaers W., Clays K., Coles S. J., Horton P. N., Light M. E., Hursthouse M. B., Garin J., Orduna J.: *Chem. Mater.* **2006**, *18*, 5907.
21. *AMPAC 5.0*. Semichem, 7128 Summit, Shawnee 1994.
22. Cuadro A., Perez-Butragueno J., Pastor-Maeso M., Alvarez-Builla J., Martinez-Grueiro M. M., Martinez-Fernandez A. R.: *Farmaco* **1992**, *47*, 477.
23. Eastman Kodak Co.: U.S. 2345094, 1941; *Chem. Abstr.* **1944**, *38*, 3558.
24. Hrobárik P., Sigmundová I., Zahradnik P.: *Synthesis* **2005**, 600.
25. Miller R. D., Lee V. Y., Moylan Ch. R.: *Chem. Mater.* **1994**, *6*, 1023.
26. Garmaise D. L., Chambers C. H., Komlossy J., McCare R. C.: *J. Med. Chem.* **1967**, *10*, 897.
27. Kiprianov A. I., Ilchenko Ya.: *Zh. Obshch. Khim.* **1965** *35*, 498.
28. Solčániová E., Čulák I.: *Magn. Reson. Chem.* **1989**, *27*, 663.
29. Zenno H.: *J. Pharm. Soc. Jpn.* **1954**, *74*, 1236; *Chem. Abstr.* **1955**, *49*, 14736.
30. Zeena S., Thomas K. G.: *J. Am. Chem. Soc.* **2001**, *123*, 7859.