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Photochromic Properties of *ortho*-Methylnitrobenzothiazoles in Solution

M. R. Matveev, A. I. Ponyaev, and A. V. El'tsov†

St. Petersburg State Institute of Technology, St. Petersburg, Russia

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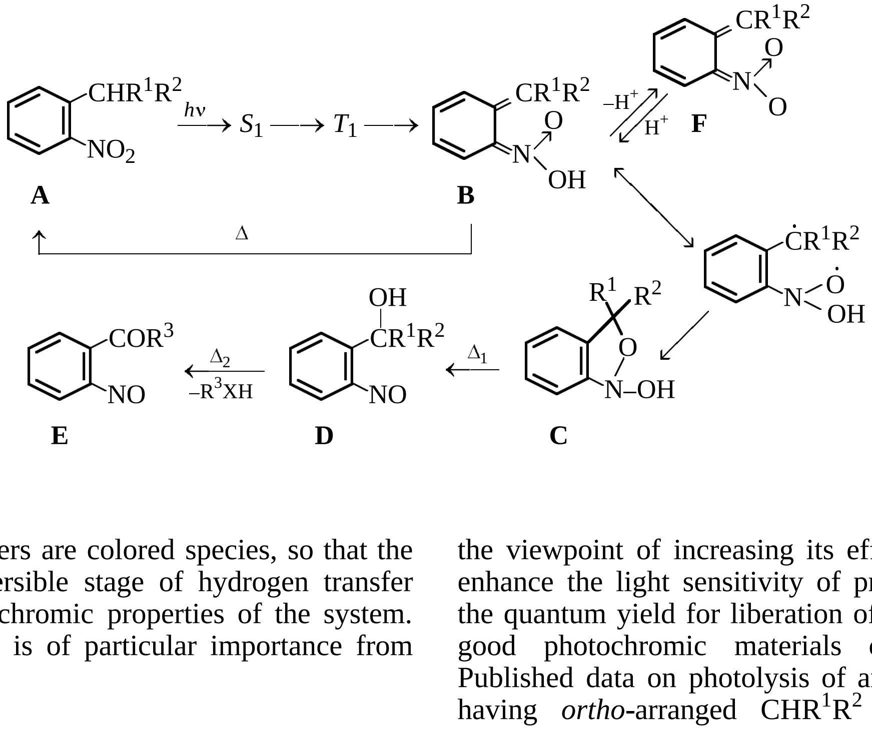
Abstract—Isomeric benzothiazoles having the nitro and methyl groups *ortho* to each other are converted into tautomeric *aci*-nitro derivatives on irradiation in heptane solution; in water, the corresponding more deeply colored anions are formed. The efficiency of photochromic transformations strongly depends on the position of the nitro and methyl groups in the benzene ring of the benzothiazole molecule.

Hydrogen transfer from the medium to the nitro group is a primary process occurring on photoexcitation of nitro compounds. When a nitroaromatic compound has a CHR^1R^2 substituent in the *ortho* position with respect to the nitro group (structure **A**), this process (as a way of dissipation of electron excitation energy) may follow intramolecular path with formation of *aci*-nitro tautomer **B** [1]. Provided that the R^1 substituent is an alkoxy, carboxy, amino, or analogous group (R^1 = XR^3, where X = O or NH), tautomer **B** can be stabilized in the form of 2,1-benzoxazole intermediate **C** which is capable of undergoing irreversible ring opening to nitroso derivative **D**. The latter readily decomposes (e.g., when R^2 = H) to give nitroso aldehyde **E** and R^3XH species. When R^3 possesses labile hydrogen atoms, the R^3XH species can be protected with the aid of an *ortho*-nitrobenzyl group which can readily be removed (as nitroso derivative **E**) by irradiation [2, 3]. Such photochemical processes are used in prodrug design [4] and fine organic synthesis [5], for generation of the active R^3XH component in photolithographic materials [6], etc.



aci-Nitro tautomers are colored species, so that the first thermally reversible stage of hydrogen transfer gives rise to photochromic properties of the system. Study of this stage is of particular importance from the viewpoint of increasing its efficiency in order to enhance the light sensitivity of protective group and the quantum yield for liberation of R^3XH; as a result, good photochromic materials could be created. Published data on photolysis of aromatic compounds having *ortho*-arranged CHR^1R^2 and NO_2 groups (**A**) deal mainly with the effect of the R^1 and R^2

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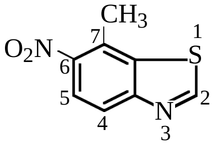
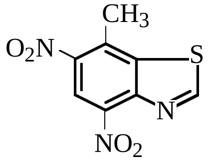
† Deceased.

groups, while the role of the structure of the parent aromatic compound remains unclear [1]. We previously found that isomeric *ortho*-methylnitrobenzimidazoles are characterized by different parameters of the overall phototautomerization process and thermal conversion into the initial molecules [7]. For example, no interaction between the methyl and nitro groups was observed for 6-methyl-5-nitroquinoxaline in aqueous alcohol at a flash duration of 5×10^{-5} s [8]. The present communication reports the results of our study of the light-induced intramolecular hydrogen transfer in the series of regioisomeric *ortho*-methylnitrobenzothiazoles (there are no equivalent positions in the benzene ring of the benzothiazole molecule).

New *ortho*-methylnitrobenzothiazoles **II**, **III**, and **V**–**VIII** were synthesized by nitration of the corresponding methylbenzothiazoles. Compound **IV** was obtained by cyclization of 2-bromo-4-methyl-5-nitroformanilide (**XII**) with Na_2S, and known product **I** was prepared by the procedure described in [9]. The structure of the newly synthesized compounds was proved by spectral data; the structure of dinitro derivatives **V** and **VIII** was additionally proved by independent synthesis from the corresponding mononitro compounds: **III**, **IV** and **VI**, **VII**. The IR spectra of all isomeric methylnitrobenzothiazoles contained absorption bands typical of nitro groups. Compounds **I**, **III**, and **VII** showed in the ^{1}H NMR spectra AB spin systems corresponding to protons located in the *ortho* position with respect to each other.



I



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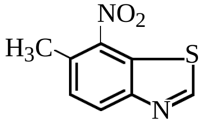

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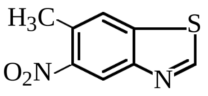
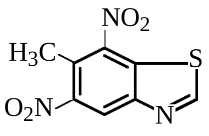
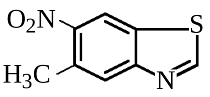


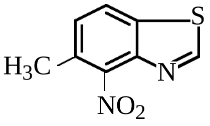
IV



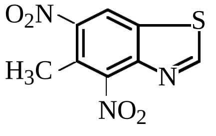
V



VI



VII



VIII

According to PM3 (RHF) quantum-chemical calculations, only in molecule **I** the nitro group lies in the benzene ring plane; in molecules of the other compounds the nitro groups are turned through an angle of 47 to 90° relative to the benzene ring plane. All methylnitrobenzothiazoles show appreciable variation of the bond lengths and bond angles, as compared to unsubstituted benzothiazole: the C^4-C^5 bond length changes from 1.380 to 1.397 Å in the series **I**, **III**, **II**, **V**, **IV**, **VI**, **VII**, **VIII**; the C^5-C^6 bond length changes from 1.406 to 1.417 Å in the series **III**, **VII**, **II**, **IV**, **VI**, **I**, **V**, **VIII**; and the C^6-C bond length changes from 1.394 to 1.404 Å in the series **VII**, **IV**, **VIII**, **VI**, **III**, **II**, **V**, **I**.

Despite the strong differences in the structure of the ground state, solutions of all compounds in heptane or aqueous phosphate buffer with pH 6.86 (containing 1% of EtOH) give rise to interaction between the *ortho*-arranged methyl and nitro groups (Table 1) under the action of light flash. Flash irradiation results in coloration of solutions. The color disappears with time; the half-conversion period ranges from 20 μs to 1–2 s, depending on the medium and isomer structure. Aqueous solutions are characterized by more intense color as compared to heptane, and dinitro derivatives give a more intense color than mononitro compounds (Fig. 1), the substrate concentrations and flash energies being equal. As shown in [10, 11], strongly acidic *aci*-nitro tautomers derived from 2,4- and 2,6-dinitrotoluenes on flash photolysis in polar acetonitrile and methanol undergo dissociation with formation of more deeply colored anions. Therefore, the stronger color of aqueous solutions of compounds **I**–**VIII** can be attributed to formation of mesomeric anions of *aci*-nitro tautomers [12] (structure **F**). No dissociation occurs in heptane, and the detectable products are the corresponding neutral *aci*-nitro forms which absorb at shorter wavelengths.

The efficiency of intramolecular hydrogen transfer in the series of compounds **I**–**VIII** was estimated by the integral optical absorption $S = \int D \partial \nu$ of the photoinduced colored form in the visible region of the spectrum, i.e., in the frequency range 25000–14200 cm^{-1} (Fig. 1). For each isomer, the value of S is proportinal to the oscillator strength, and the proportionality factor is the quantum yield of formation of the corresponding *aci*-nitro compound. Assuming that the oscillator strengths of *aci*-nitro tautomers, as well as of the corresponding anions, remain constant in the series **I**–**VIII** and that *aci*-nitro compounds in water dissociate completely, we have revealed parallelism in the variation of S and φ for *aci*-nitro compounds in heptane and for their anions in water in going from one benzothiazole derivative

Table 1. Spectral parameters of the photoinduced forms of compounds **I**–**XI**

Solvent	Parameter	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**
Water	λ_{max}, nm	420	635 (<400)	410	495	480	490	<400	500	405	514 (<400)	494
	D	0.0256	0.011 (0.021)	0.092	0.037	0.19	0.0225	0.0055	0.035	0.0411	0.0132 (>0.0164)	0.082
	S, cm^{-1}	86.7	130	231	167	1190	97	7.6	254	93.0	101	525
Heptane	λ_{max}, nm	<390	<390	<390	455	<435	453	400	420	–	–	–
	D	0.021	0.018	0.030	0.0167	0.125	0.012	0.0067	0.012	–	–	–
	S, cm^{-1}	37	58	46	63	>264	30	9.4	18	–	–	–

to another. Here, the ratio of *S* for the anions and acids changes from 2.5 to 4.5.

The integral optical absorption *S* of the *aci*-nitro compounds under study strongly depends on the arrangement of substituents in the benzene ring, while the degree of coplanarity of the nitro group in the nitro isomer is insignificant. Photoinduced coloration of compound **VII** is weak, and acidifying effect of the electron-acceptor thiazole ring in the excited state turnes out to be negligible. In the series of mononitrobenzothiazoles the ratio of *S* for the corresponding anions changes by a factor of up to 30. 5,7-Dinitro derivative **V** is characterized by the most intense color of the anion and *aci*-nitro compound, despite large deviations of the nitro group planes from the molecular plane (by 60 and 90°, respectively) in the ground state. The ratio of *S* for the anions of dinitro compounds changes by a factor of up to 9. The ratio of the *S* values for dinitro compound **V**, which is characterized by the most efficient coloration, and mononitro compounds **VII** and **III** showing, respectively, the least and most efficient coloration is 160 and 5.2. On the other hand, the oscillator strengths and hence the intensities of photoinduced coloration for anions (**X**) anion and then to 2,4,6-trinitrotoluene (**XI**) it derived from aromatic *aci*-nitro compounds differ to a much lesser extent: in going from the anion of 2-nitrotoluene (**IX**) to 2,4-dinitrotoluene the anion of increases by factors of 1.8 and 2.4, respectively [13]. This means that the thiazole ring strongly differentiates *ortho*-nitromethyl fragments in photochromic properties, depending on their position in the molecule.

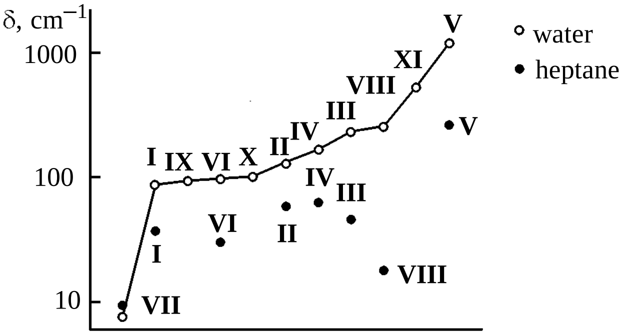


Fig. 1. Efficiency of photocoloration of *ortho*-methylnitrobenzothiazoles **I**–**VIII** and *ortho*-nitrotoluenes **IX**–**XI** in water and heptane.

Hydrogen transfer in *ortho*-nitrobenzyl compounds, as well as in nitrotoluenes, is believed to occur in the $^3(n\pi^*)$ state localized on the nitro group [3, 14]. The results of our PM3/UHF calculations show that the spin density in the lower triplet state of compound **V** (which is the most efficient photochrome, judging by the parameter *S*) is localized mainly on the 7-nitro group (Fig. 2a). By contrast, the spin density in compound **VII** which exhibits weak photochromic properties is localized mainly on the sulfur atom of the heteroring, while the 4-nitro group is characterized by a negligible spin density (Fig. 2b). In the other benzothiazole derivatives (compounds **I**–**IV**, **VI**, and **VIII**) the spin density is delocalized over the fused ring system with more or less contribution of the nitro groups (Fig. 2c). Therefore, the different photochromic properties of compounds **I**–**VIII** may be attributed at least to differences in the fine structure of lower triplet states whose participation in the hydrogen transfer process may be characterized by different quantum yields.

Obviously, polycyclic *ortho*-methylnitro derivatives open the way to effective control of photochromic properties and light sensitivity of *ortho*-nitrobenzyl moieties.

EXPERIMENTAL

The elemental compositions (Table 2) were determined using a Hewlett–Packard C,H,N-analyzer. The melting points were measured with the aid of a Kofler heating device coupled with a microscope; heating rate 2.5 deg/min. The ^{1}H NMR spectra of compounds **I**–**VIII** were recorded on a Bruker AM-500 spectrometer (500 MHz) (Table 3). The electronic absorption spectra were measured on a Specord M-40 spectrophotometer using 1-cm quartz cells (Table 4). Solvents were purified by standard procedures [15]. Photochromic properties of compounds **I**–**XI** ($c = 5 \times 10^{-5}$ M, 20 ± 1°C) in water (phosphate buffer, pH 6.86, 1% of EtOH) and heptane were studied by flash photolysis on a setup with a time resolution of 2 ms [16]. Solutions were irradiated with an IFP-5000 xenon lamp (full spectrum, 125 J) using quartz cells (l = 20 cm). The solutions under study were not deoxygenated. Preliminary experiments showed that deaeration affects neither the rate of decoloration nor the optical density of photoinduced forms. The optical densities were averaged from the results of several experiments (accuracy ±5%). Thin-layer chromatography was performed on Silufol UV-254 plates.

7-Methyl-6-nitrobenzothiazole (I). 6-Nitrobenzothiazole, mp 175–175.5°C [17], 1.7 g, was dissolved under argon in 40 ml of anhydrous THF, and 6.7 ml of a 2.82 M solution of CH_3MgCl in anhydrous THF was added at –10°C. The mixture was stirred for 5 min at –10°C and for 5 min at 0°C, and a solution of 1 g $KMnO_4$ in 30 ml of 50% acetone was added (dropwise) very slowly under vigorous stirring at –10 to –15°C. The mixture was kept for 0.5 h at room temperature and filtered. The precipitate of MnO_2 was extracted with hot acetone (3 × 10 ml), and the extracts were combined with the filtrate. The solvent was distilled off, and the product was extracted from the residue into chloroform (2 × 10 ml); the extract was dried over Na_2SO_4 and evaporated. The residue was subjected to vacuum sublimation followed by recrystallization from 10 ml of hexane. Yield 0.178 g (9.7%), colorless crystals with mp 126–127°C [9]. Repeated crystallization from hexane did not increase the melting point. R_f 0.66 (chloroform–ether, 4 : 1).

7-Methyl-4,6-dinitrobenzothiazole (II). 7-Methyl-6-nitrobenzothiazole, 0.038 g, was dissolved in 2 ml of 92% H_2SO_4, 0.050 g of $NaNO_3$ was added, and the mixture was kept for 2 h at 120°C. It was then poured onto ~20 g of ice while stirring. The precipitate was filtered off and washed with water until neutral washings. The yellowish crystals, 0.024 g, were purified by vacuum sublimation. Yield 0.019 g (41%), mp 134–135°C (subl.). Recrystallization from hexane did not increase the melting point. R_f 0.56 (chloroform–ether, 4 : 1).

6-Methyl-7-nitrobenzothiazole (III). 6-Methylbenzothiazole, mp 15–16°C [18], 0.9 g, was dissolved in 5 ml H_2SO_4 (92.2%, chemically pure grade) while stirring with no external cooling, and 3.5 ml of 93% HNO_3 was added dropwise over a period of 5 min

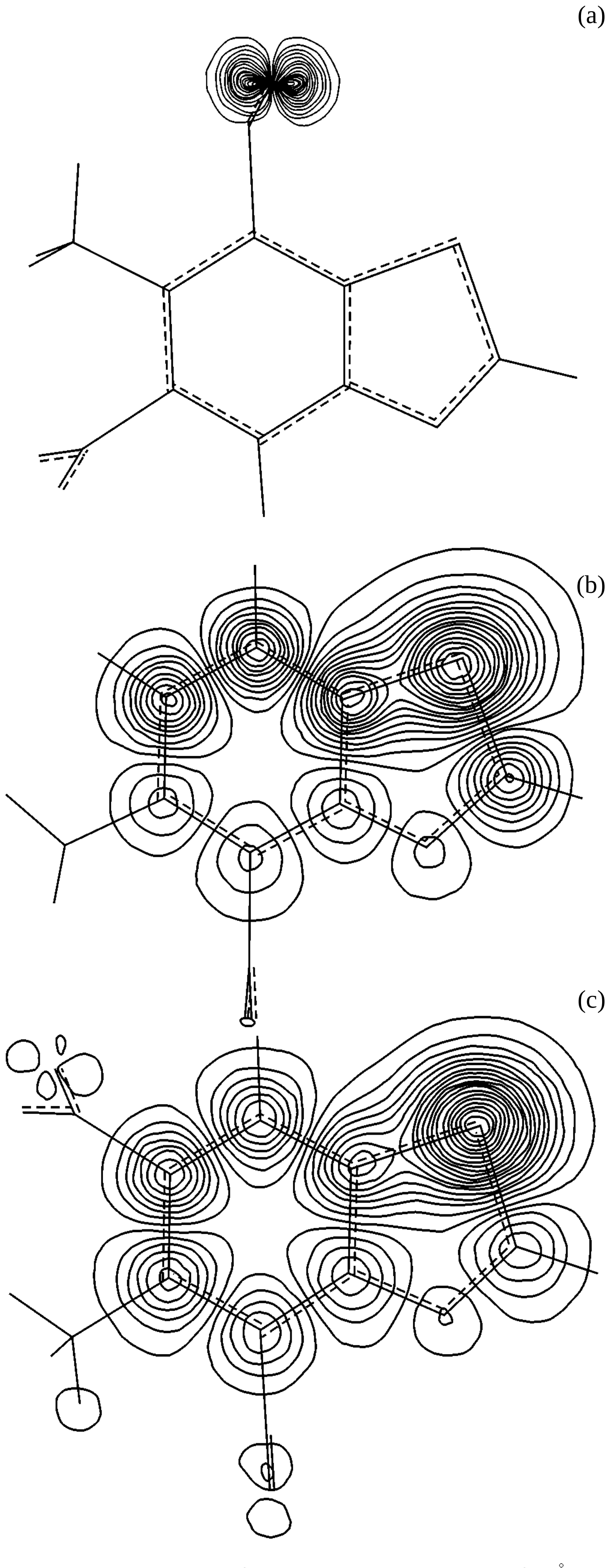


Fig. 2. Distribution of spin density at a distance of 1 Å from the molecular plane of compounds (a) **V**, (b) **VII**, and (c) **VIII** in the lower triplet state.

Table 2. Elemental analyses of compounds **I–XIII**

Comp. no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
I	49.51	3.2	14.39	$C_8H_6N_2O_2S$	49.48	3.09	14.43
II	40.22	2.10	17.51	$C_8H_5N_3O_4S$	40.17	2.09	17.57
III	49.77	3.08	14.18	$C_8H_6N_2O_2S$	49.48	3.09	14.43
IV	49.54	3.30	14.61	$C_8H_6N_2O_2S$	49.48	3.09	14.43
V	40.31	2.07	17.50	$C_8H_5N_3O_4S$	40.17	2.09	17.57
VI	49.43	3.11	14.41	$C_8H_6N_2O_2S$	49.48	3.09	14.43
VII	49.56	3.19	14.39	$C_8H_6N_2O_2S$	49.48	3.09	14.43
VIII	40.12	2.05	17.62	$C_8H_5N_3O_4S$	40.17	2.09	17.57
XII	37.15	2.81	10.90	$C_8H_7BrN_2O_3$	37.07	2.70	10.81
XIII	49.08	3.31	14.58	$C_8H_6N_2O_2S$	49.48	3.09	14.43

Table 3. ^1H NMR spectral parameters of compounds **I–VIII** in acetone-d_6

Comp. no.	Chemical shifts δ, ppm				
	H^2	H^4	H^5	H^7	CH_3^1
I[a]	9.599	8.215	8.159	–	2.862
II	9.857	–	8.909	–	3.058
III[a]	9.431	8.359	7.746	–	2.901
IV	9.475	8.693	–	8.288	2.735
V	9.669	8.935	–	–	2.879
VI	9.575	8.193	–	8.905	2.755
VII[a]	9.445	–	7.61[b]	8.32	2.547
VIII	9.754	–	–	9.175	2.652

[a] The spin–spin coupling constants for the *ortho*-arranged protons in the aromatic ring of compounds **I**, **III**, and **VII** are as follows: $J_{4,5}$ = 8.65, $J_{4,5}$ = 8.60, and $J_{6,7}$ = 8.35 Hz, respectively. [b] δ(H^6).

under vigorous stirring at 20°C. The mixture was heated for 5 min at 45°C (water bath) and was poured (under vigorous stirring) onto 60 g of ice. The colorless precipitate was filtered off, washed with a 5% solution of NaOH and then with 50 ml water to pH 6, and dried at 50°C. Yield of the crude product 0.902 g, mp 129–130°C. It was recrystallized from 12 ml of hot ethanol. Yield 0.749 g (64.2%), mp 131.5°C (subl.). Recrystallization from hexane did not increase the melting point. R_f 0.72 (toluene–acetone, 1:1), 0.74 (ethyl acetate), 0.56 (chloroform–ether, 4:1).

2-Bromo-4-methyl-5-nitroformanilide (XII). A solution of 3 g of 2-bromo-4-methyl-5-nitroaniline, mp 121°C [19, 20], in 36 ml of 85% HCOOH was refluxed for 3 h, ~25 ml of HCOOH was distilled off, and the mixture was left overnight. The large cream-colored needles were filtered off. Yield 3.02 g (90%), mp 172.5–173.5°C. Recrystallization from 85% HCOOH did not increase the melting point. R_f 0.77 (2-propanol), 0.26 (ether–heptane, 2:1), 0.1 (ether–heptane, 1:1).

6-Methyl-5-nitrobenzothiazole (IV). 2-Bromo-4-methyl-5-nitroformanilide, 1 g, was dissolved in 33 ml of boiling ethanol, and 0.933 g of $Na_2S \cdot 9H_2O$ was added. The mixture was refluxed for 1 h and poured into 200 ml of water, and the yellow precipitate of 2-bromo-4-methyl-5-nitroaniline, 0.391 g (44.3%), was filtered off; it can be used for repeated synthesis of 2-bromo-4-methyl-5-nitroformanilide without additional purification. The red filtrate was acidified with 0.1 N H_2SO_4 to pH 4–5, and the yellow precipitate of crude 6-methyl-5-nitrobenzothiazole, 0.319 g (43%), was filtered off. The crude product was dissolved in 65 ml of boiling heptane, and the hot solution was filtered from red–brown impurity and cooled. After cooling, the precipitate was filtered off. Yield 0.155 g (20%), mp 149–151.5°C (subl.). Recrystallization from hexane did not increase the melting point. R_f 0.27 (hexane–ether, 1:1), 0.64 (chloroform–ether, 4:1).

5,7-Dinitro-6-methylbenzothiazole (V). *a.* To 2.6 g of 6-methylbenzothiazole we added while stirring 11.1 ml of 92% H_2SO_4 without external cooling. A colorless 6-methylbenzothiazolium sulfate dropped, and dissolved on heating to 40°C. A 8-ml portion of 97% HNO_3 was added dropwise with stirring at 20°C, and the mixture was kept for 3 h at 120°C, cooled to 15°C, and poured onto 100 g of ice under vigorous stirring. The bright yellow precipitate was filtered off and washed with water (3 × 7 ml), 4 ml of

Table 4. UV and IR spectra of compounds **I–VIII**

Comp. no.	λ_{max}, nm ($\log \varepsilon$)	Solvent	IR spectrum (KBr), ν, cm^{-1}
I	215 (4.40), 286 (3.98)	Water	1510 s, 1350 s (NO_2), 3100 m (C^2H), 1600 m ($C^2{=}N$)
	217 (4.38), 275 (4.00), 319 sh (3.64)	Heptane	
II	207 (4.06), 276 (3.89), 318 sh (3.69)	Water	1530 s, 1330 s (NO_2), 1530 s, 1360 s (NO_2), 3080 m (C^2H), 1610 m ($C^2{=}N$)
	216 (4.30), 255 (4.20), 282 sh (4.01), 317 sh (3.66)	Heptane	
III	208 (4.35), 241 (3.93), 323 (3.80)	Water	1520 s, 1320 s (NO_2), 3135 w (C^2H), 1615 m ($C^2{=}N$)
	209 (4.36), 245 (4.08), 305 (3.77)	Heptane	
IV	208 (4.34), 248 (4.33), 298 (3.68)	Water	1520 s, 1350 s (NO_2), 3100 m (C^2H), 1610 m ($C^2{=}N$)
	200 (4.38), 244 (4.42), 280 sh (3.73)	Heptane	
V	208 (4.28), 232 (4.19), 311 sh (3.74)	Water	1530 s, 1330 s (NO_2), 1560 s, 1360 s (NO_2), 3090 m (C^2H), 1610 m ($C^2{=}N$)
	231 (4.31), 296 sh (3.74)	Heptane	
VI	217 (4.28), 287 (3.83)	Water	1510 s, 1320 s (NO_2), 3120 m (C^2H), 1620 m ($C^2{=}N$)
	222 (4.25), 278 (3.81), 320 sh (3.41)	Heptane	
VII	212 (4.48), 254 (3.67), 294 (3.37)	Water	1530 s, 1370 s (NO_2), 3100 m (C^2H), 1610 m ($C^2{=}N$)
	213 (4.47), 252 (3.94), 295 (3.42)	Heptane	
VIII	214 (4.44), 273 (3.91)	Water	1540 s, 1360 s (NO_2), 1560 s, 1370 s (NO_2), 3110 m (C^2H), 1620 m ($C^2{=}N$)
	215 (4.53), 270 sh (4.07)	Heptane	

a 30% solution of Na_2CO_3 to pH 8, and water again (2×10 ml) to pH 6–7. The precipitate turned beige. Yield of the crude product 1.61 g. It was recrystallized thrice from 95% ethanol (plates) and once from 80% ethanol (needles). Yield 0.64 g (15.3%), mp 127.5°C (subl.). R_f 0.53 (heptane–ether, 1:1), 0.71 (chloroform–ether, 4:1).

b. A 0.0125-g portion of 6-methyl-5-nitrobenzothiazole was dissolved in 1 ml 92% H_2SO_4, 0.050 g of $NaNO_3$ was added, and the mixture was kept for 2.5 h at 120°C. The mixture was then transferred on cooling into 4 ml of ice water, neutralized with aqueous ammonia, and extracted with ether (3×2 ml). The extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from a small amount of 50% EtOH. Yield of **V** 0.005 g (32%). No depression of the melting point was observed on mixing samples obtained as described in *a* and *b*. Their TLC and spectral parameters were also identical.

3-Nitro-4-thiocyanatotoluene (XIII). To a suspension of 18 g of 4-methyl-2-nitroaniline, mp 117°C [21], in 60 ml of water we added with stirring 33 ml 92% H_2SO_4. The mixture strongly warmed up, and a dark red solution was formed. It was cooled under stirring to 10°C, a solution of 11.4 g $NaNO_2$ in 21 ml of water was added over a period of 20 min at such a rate that the temperature did not exceed 15°C, and the mixture was stirred for 30 min at 12°C. The mixture was filtered, and the filtrate was added with stirring at the same temperature to a solution of 10.8 g of NaSCN, 1.16 g of $Fe_2(SO_4)_3 \cdot 9H_2O$, and 0.273 g of $(NH_4)_2SO_4$ in 120 ml of water. After 14 h, the precipitate was filtered off, washed with 350 ml of water, a solution of 4.13 g of Na_2CO_3 in 40 ml of water, and water again to pH 7, and dried at 50°C. Yield of 3-nitro-4-thiocyanatotoluene 20 g (87%); beige powder, mp 124.5–125°C (subl.) [22]. R_f 0.71 (2-propanol).

5-Methyl-4-nitrobenzothiazole (VII) and 5-methyl-6-nitrobenzothiazole (VI). A 1.18-g portion of 5-methylbenzothiazole, mp 79°C [23], was dissolved in 8 ml of 92% H_2SO_4 without external cooling. A mixture of 1 ml of 95% HNO_3 and 1 ml of 92% H_2SO_4 was added at 20–25°C, and the resulting mixture was kept for 15 min and slowly poured onto 50 g of ice under vigorous stirring. The crude product separated as a light brown tarry material. The mixture was neutralized with Na_2CO_3 until the tarry material and yellow precipitate no longer separated. The brown precipitate was filtered off, dried, and sublimed under reduced pressure to obtain 0.738 g (48%) of light yellow crystals. The product was recrystallized first from 16 ml of 50% 2-propanol (yield 0.63 g) and then from a mixture of 20 ml of hexane and 3 ml of chloroform. Yield of compound **VII** 0.42 g (27%); colorless prisms, mp 110–111°C (subl.). Repeated crystallization from hexane did not increase the melting point. R_f 0.73 (chloroform–ether, 4 : 1).

The mother liquor obtained after crystallization from 50% 2-propanol was evaporated under reduced pressure to obtain 0.1 g of a mixture of nitration products. It was dissolved in 1 ml of chloroform and subjected to thin-layer chromatography on Silufol UV-254 plates using chloroform–ether (4 : 1) as eluent. The upper zone, R_f 0.73, corresponded to isomer **VII**, and the lower zone, R_f 0.65, was extracted with hot chloroform (3 × 15 ml). Removal of the solvent gave 0.03 g (30%) of yellowish crystals of compound **VI**, mp 163–165°C (subl.). Recrystallization from hexane did not increase the melting point. R_f 0.65 (chloroform–ether, 4 : 1).

5-Methyl-4,6-dinitrobenzothiazole (VIII). *a.* A 0.15-g portion of 5-methyl-4-nitrobenzothiazole was dissolved in 5 ml of 92% H_2SO_4, 0.2 g of $NaNO_3$ was added, and the mixture was kept for 2 h at 120°C. It was then cooled and poured onto ~30 g of ice while stirring. The precipitate was filtered off, washed with water until neutral washings, sublimed under reduced pressure, and recrystallized from 2-propanol. Yield of **VIII** 0.117 g (41%); colorless product, mp 147–148.5°C (subl.). Repeated crystallization from hexane did not increase the melting point. R_f 0.71 (chloroform–ether, 4 : 1).

b. A 0.01-g portion of 5-methyl-6-nitrobenzothiazole (**VI**) was dissolved in 0.7 ml of 92% H_2SO_4, 0.03 g of $NaNO_3$ was added, and the mixture was kept for 2.5 h at 120°C. It was then transferred into 4 ml of ice water (on cooling), neutralized with aqueous ammonia, and extracted with ether (3 × 2 ml). The extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from a small amount of hexane. Yield 0.006 g (48.7%). No depression of the melting point was observed on mixing samples obtained as described in *a* and *b*. Their TLC and spectral parameters were also identical.

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