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Nucleophilic Substitution in Nitrofluorenones

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Abstract—The reaction of 2,4,5,7-tetranitrofluorenone with amines, thiols, and phenol in a polar aprotic solvent led to the preferable substitution of the nitro group in the position *2*, and in the reaction of 2,4,7-trinitrofluorenone first the nitro group in the position *4* was replaced. The different regioselectivity is due evidently to the steric hindrances to the nucleophilic attack on the atom C^4 caused by the nitro group in the position *5* of tetranitrofluorenone.

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Polynitrofluorenones are used as efficient sensitizers for electrophotography [1]. The nucleophilic substitution of nitro groups in nitrofluorenones is a simple way to the modification of their structure. The comparison of the reactions of tetranitro- and trinitrofluorenones with O-, N-, and S-nucleophiles provides a possibility to conclude on the dependence of the substitution regioselectivity on the structure of the reagent and the substrate.

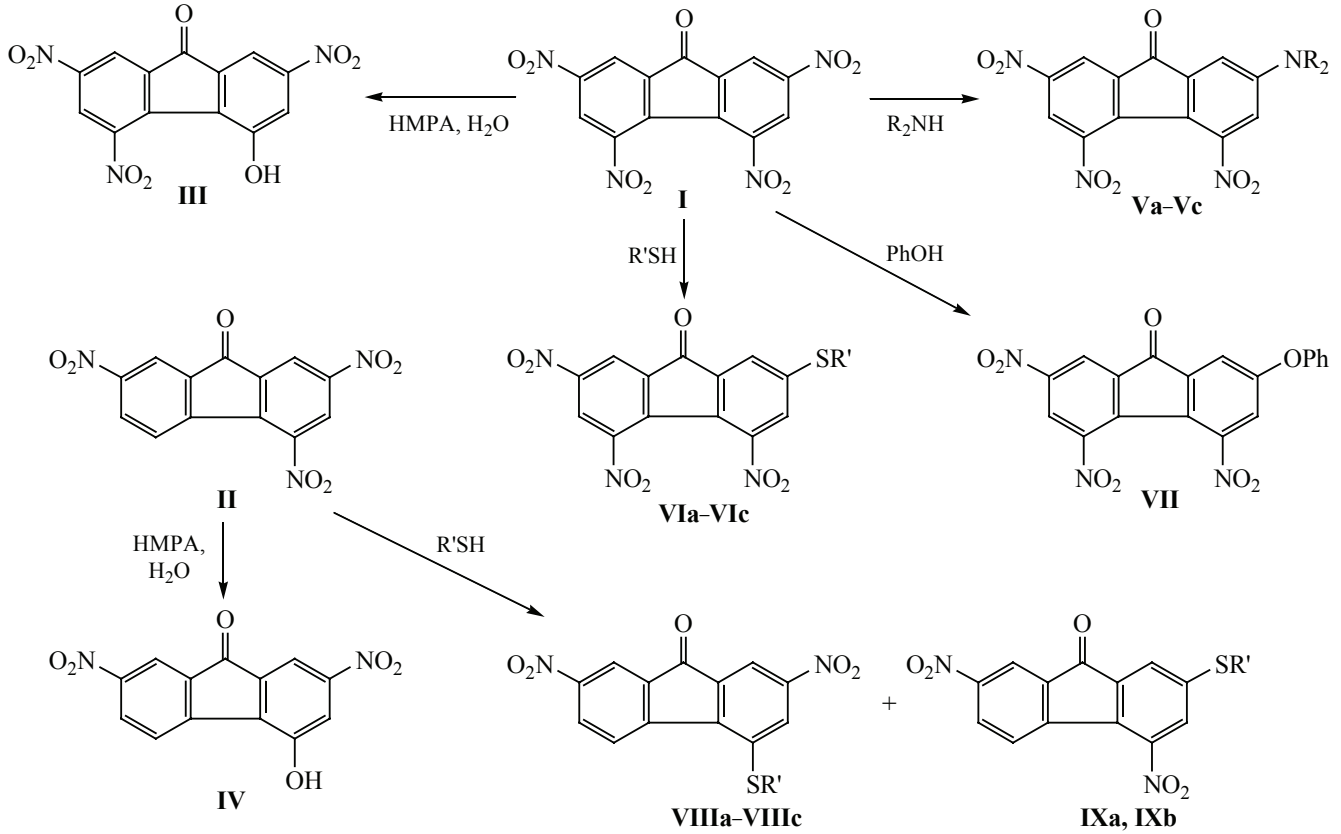
It was formerly established that in 2,4,5,7-tetranitrofluorenone (**I**), 2,4,7-trinitrofluorenone (**II**) [2], and also in the 2,4,7-trinitrofluorenone-5-carbonitrile [3] in HMPA at room temperature the nitro group in the position *4* is replaced by the hydroxy group with the formation of 4-hydroxy-2,5,7-trinitro-fluorenone (**III**), 4-hydroxy-2,7-dinitrofluorenone (**IV**), and 4-hydroxy-2,7-dinitrofluorenone-5-carbonitrile respectively. The heating of tetranitrofluorenone **I** in HMPA results in the formation alongside 4-hydroxy-substituted (**III**) of the isomeric 2-hydroxy-4,5,7-trinitrofluorenone, and the heating of the 2,4,7-trinitrofluorenone-4-carbonitrile provides only the 4-hydroxy derivative. Presumably the nucleophilic agent attacking the nitro group is water contained in HMPA. Adding water to dry HMPA accelerates the reaction.

Whereas at the hydrolysis in HMPA at room temperature in 2,4,5,7-tetranitrofluornone (**I**) only the nitro group in the position *4* is exchanged for the hydroxy group, at the action of amines, thiols, phenol in the polar aprotic solvents the nitro group in the position *2* is substituted. As a result of the reaction with dimethylamine in DMF without heating within 3 days 2-dimethylamino-4,5,7-trinitrofluorenone (**Va**) was obtained with insignificant impurity of 4-dimethylamino-2,5,7-trinitrofluorenone. At the use of the appropriate secondary amines 2-diethylamino-4,5,7-trinitrofluorenone (**Vb**) and 2-dibutylamino-4,5,7-trinitrofluorenone (**Vc**) were synthesized.

The reaction of 2,4,5,7-tetranitrofluorenone (**I**) with butane-1-thiol in DMSO at heating or in HMPA at room temperature gave 2-butylsulfanyl-4,5,7-trinitrofluorenone (**VIb**) [4]. At boiling tetranitrofluorenone (**I**) in DMSO 2-methylsulfanyl-4,5,7-trinitro-fluorenone (**VIa**) formed because of the thermal decomposition of the solvent [5]. In the reaction of fluorenone **I** with thiophenol also the nitro group in the position *2* suffered the substitution to afford 2-phenylsulfanyl-4,5,7-trinitrofluorenone (**VIc**) in a 78% yield. At heating compound **I** with phenol in HMPA at 100°C 2-phenoxy-4,5,7-trinitrofluorenone (**VII**) was obtained. The reactions with thiols and phenol do not require the presence of a base usually added to increase the nucleophilicity. This fact demonstrates the high electron-deficiency of the polynitrofluorenones.

Compounds **Va, VIa** possess the properties of sensitizers for the organic electrophotographic layers [6, 7].

The boiling of 2,4,7-trinitrofluorenone (**II**) in DMSO led to the formation of a mixture of 4-methylsulfanyl-2,7-dinitrofluorenone (**VIIIa**) and 2-methylsulfanyl-4,7-dinitrofluorenone (**IXa**) in the ratio ~4:1. Treating 2,4,7-trinitrofluorenone (**II**) with excess butanethiol



V, R = Me (**a**), Et (**b**), Bu (**c**); **VI, VIII, IX**, R' = Me (**a**), Bu (**b**), Ph (**c**).

in DMSO at room temperature in the course of 2 days resulted in the formation of a mixture of 4-butylsulfanyl-2,7-dinitrofluorenone (**VIIIb**) and 2-butylsulfanyl-4,7-dinitrofluorenone *(***IXb**) in the ratio 3:1 and an overall yield 74%. In the reaction of trinitrofluorenone **II** with thiophenol exclusively the nitro group in the position *4* underwent the substitution, and the sole reaction product was 4-phenylsulfanyl-2,7-dinitrofluorenone (**VIIIc**) (yield 87–89%).

The position of the substituent arising at the replacement of the nitro group by the nucleophile was established from the ^{1}H NMR spectra. At the exchange in the position *2* for an electron-donor group the doublet signals of the protons located in the position *1* appear in essentially stronger field than the signals of the same protons at the substitution in the position *4* when in the *ortho*-position to them remains the electron-acceptor nitro group. The corresponding chemical shifts in 2-dimethylamino-substituted **Va** and its 4-dimethylamino-substituted isomer are observed at 7.38 and 7.55 ppm, in 2-methylsulfanyl-substituted **IXa** and its isomer **VIIIa**, at 7.98 and 8.32 ppm, in 2-butyl-substituted **IXb** and its isomer **VIIIb**, at 7.99 and 8.35 ppm. The doublet signals from the protons in the position *3* for these isomeric pairs are observed at 7.67 and 7.79, 8.30 and 8.42, 8.31 and 8.51 ppm respectively. In the combination with the interpretation of the other signals in the ^{1}H NMR spectra (see Experimental) it is possible to distinguish between the substitution in the position *2* or *4*. The structure of 4-phenylsulfanyl-substituted compound **VIIIc** was established by X-ray analysis [8].

Therefore in 2,4,5,7-tetranitrofluorenone (**I**) the hydroxy group substituted predominantly the nitro group in the position *4*, and dialkylamino-, alkylsulfanyl-, phenylsulfanyl-, and phenoxy groups replace the nitro group in the position *2*. In 2,4,7-trinitrofluorenone (**II**) prevailingly the nitro group in the position *4* is substituted. The regioselectivity of the nucleophilic substitution in the polynitrofluorenones depends on the relative reactivity of the certain position occupied by the nitro group, and on its spatial accessibility which in its turn is governed by the extent of shielding of the site of the attack and by the volume of the attacking species. In the absence of steric hindrances the position *4* is obviously more active, and the substitution with water occurs just in this place

since water does not find any hindrances due to its small molecule. The X-ray analysis data for 2,4,5,7-tetranitrofluorenone [9] and 2,4,5-trinitrofluorenone [10] confirm the existence of the steric hindrances because of the nitro groups in the positions *4* and *5* of the fluorenone. At the attack of a bulky species of dialkylamine or thiophenol in 2,4,5,7-tetranitrofluorenone (**I**) the less hindered nitro group in the position *2* undergoes the exchange. At the lack of a nitro group in the position *5* the hindrance to the attack decreases, therefore in 2,4,7-trinitrofluorenone (**II**) the substitution in the position *4* becomes possible.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Jeol ECX-400 (operating frequency 400.13 MHz) in DMSO-d_6, chemical sifts are reported with respect to TMS. IR spectra were recorded on a spectrophotometer Perkin Elmer-598 from pellets with KBr. The reaction progress was monitored and the homogeneity of compounds obtained was checked by TLC on aluminum plates with a fixed layer of silica gel (Silufol UV-254), development with a mixture of solutions of $SnCl_2$ and 4-dimethylaminobenzaldehyde in aqueous ethanol containing HCl. The preparative column chromatography was performed using Silicagel L40/100μ and L 100/160μ (Chemapol, Czechia). Melting points were measured on a Boëtius heating block.

2-Dimethylamino-4,5,7-trinitro-9*H*-fluoren-9-one (Va) and **4-dimethylamino-4,5,7-trinitro-9*H*-fluoren-9-one.** To a solution of 36.0 g (100 mmol) of compound **I** in 75 ml of DMF was added at 20–25°C and while stirring 40 ml of 20% water solution of dimethylamine. After 3 days the solution was poured into 300 ml of 5% hydrochloric acid, the separated dark brown precipitate was filtered off, washed with water, and dried. We obtained 23.85 g of compound **Va**. Additional 0.71 g of this compound was isolated by evaporation of the filtrate to dryness, dissolution of the residue in benzene and chromatographing this solution (eluent benzene). Overall yield 24.56 g (69%). Violet crystals, R_f 0.25 (benzene), mp 272–272.5°C (acetonitrile). IR spectrum, ν, cm^{-1}: 1735 (C=O), 1540, 1530, 1340 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.81 s (6H, CH_3), 7.38 d (1H, H*1*, ^4J 2.1 Hz), 7.67 d (1H, H*3*, ^4J 2.1 Hz), 8.53 d (1H, H*8*, ^4J 1.8 Hz), 8.82 d (1H, H*6*, ^4J 1.8 Hz). UV spectrum (benzene), λ_{max}, nm (log ε): 485 (4.09). Found, %: C50.02; H 2.90; N 15.47. $C_{15}H_{10}N_4O_7$. Calculated, %: C 50.29; H 2.81; N 15.64.

By chromatography also 0.63 g (2%) of 4-dimethylamino derivative was isolated. Violet crystals, R_f 0.36 (benzene), mp 192–194°C (acetonitrile). IR spectrum, ν, cm^{-1}: 1720 (C=O), 1535, 1520, 1335 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.83 s (6H, CH_3), 7.55 d (1H, H*1*, ^4J 2.1 Hz), 7.79 d (1H, H*3*, ^4J 2.1 Hz), 8.55 d (1H, H*8*, ^4J 1.8 Hz), 8.85 d (1H, H*6*, ^4J 1.8 Hz). Found, %: C 50.18; H 2.76; N 15.59. $C_{15}H_{10}N_4O_7$. Calculated, %: C 50.29; H 2.81; N 15.64.

2-Diethylamino-4,5,7-trinitro-9*H*-fluoren-9-one (Vb). To a solution of 3 mmol of compound **I** in 10 ml of DMF was added dropwise at 20–25°C while stirring 2 ml of diethylamine. The mixture was stirred for 20 min and poured into 50 ml of 5% hydrochloric acid. The separated dark brown precipitate was filtered off, washed with water, dried, and recrystallized from acetonitrile. Yield 0.79 g (73%). Violet crystals, R_f 0.25 (benzene), mp 261–263°C (acetonitrile). IR spectrum, ν, cm^{-1}: 1730 (C=O), 1535, 1335 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.15 t (6H, CH_3, ^3J 7.2 Hz), 3.36 q (4H, CH_2, ^3J 7.2 Hz), 7.40 d (1H, H*1*, ^4J 2.1 Hz), 7.69 d (1H, H*3*, ^4J 2.1 Hz), 8.58 d (1H, H*8*, ^4J 1.8 Hz), 8.85 d (1H, H*6*, ^4J 1.8 Hz). Found, %: C 52.78; H 3.57; N 14.56. $C_{17}H_{14}N_4O_7$. Calculated, %: C52.85; H 3.63; N 14.51.

2-Dibutylamino-4,5,7-trinitro-9*H*-fluoren-9-one (Vc) was obtained similarly by the reaction with dibutylamine. Yield 0.92 g (69%). Violet crystals, R_f 0.47 (benzene), mp 168–169°C (acetonitrile). IR spectrum, ν, cm^{-1}: 1730 (C=O), 1530, 1330 (NO_2). ^{1}H NMR spectrum, δ, ppm: 0.97 t (6H, CH_3, ^3J 7.2 Hz), 1.36 m (4H, CH_2CH_3), 1.57 m (4H, $CH_2CH_2CH_3$), 3.40 q (4H, NCH_2, ^3J 7.8 Hz), 7.38 d (1H, H*1*, ^4J 2.2 Hz), 7.67 d (1H, H*3*, ^4J 2.2 Hz), 8.56 d (1H, H*8*, ^4J 1.8 Hz), 8.83 d (1H, H*6*, ^4J 1.8 Hz). Found, %: C 56.92; H 5.02; N 12.64. $C_{21}H_{22}N_4O_7$. Calculated, %: C 57.01; H 4.98; N 12.67.

2-Methylsulfanyl-4,5,7-trinitro-9*H*-fluoren-9-one (VIa). A solution of 3.6 g (10 mmol) of compound **I** in 30 ml of DMSO was boiled for 9 h, cooled to room temperature, and poured into 200 ml of 3% hydrochloric acid. The separated dark brown precipitate was filtered off, treated with a mixture of 50 ml of acetone and 150 ml of benzene, the obtained solution was chromatographed on a column packed with silica gel (eluent acetone–benzene, 1 : 3). Yield 1.86 g (52%), bright yellow crystals. R_f 0.7 (benzene), mp 214–215°C (acetic acid). IR spectrum, ν, cm^{-1}: 1730 (C=O), 1560, 1540, 1340 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.81 s (3H, CH_3), 8.07 d (1H, H*1*,

^4J 1.8 Hz), 8.30 d (1H, H^3, ^4J 1.8 Hz), 8.70 d (1H, H^8, ^4J 2.3 Hz), 8.94 d (1H, H^6, ^4J 2.3 Hz). Found, %: C 46.78; H 2.05; N 11.49; S 8.83. $C_{14}H_7N_3O_7S$. Calculated, %: C 46.54; H 1.91; N 11.63; S 8.86.

2-Phenylsulfanyl-4,5,7-trinitro-9*H*-fluoren-9-one (VIc). To a solution of 3.6 g (10 mmol) of compound **I** in 25 ml of DMSO was added dropwise at 20–25°C 2.2 g (20 mmol) of thiophenol, and the mixture was stirred for 8 h till disappearance of initial compound **I** from the reaction mixture (TLC monitoring, benzene). The separated precipitate was filtered off, washed with water, dried in air, and crystallized from acetic acid. Yield 3.30 g (78%), orange crystals. R_f 0.53 (benzene), mp 190–191°C (acetic acid). IR spectrum, ν, cm^{-1}: 1730 (C=O), 1535, 1340 (NO_2). ^{1}H NMR spectrum, δ, ppm: 7.25 d.d (1H, H^n, ^3J 8.5, ^4J 2.0 Hz), 7.43 d.d (2H, H^O, ^3J 8.5, ^4J2.0 Hz), 7.47 d.d (2H, H^m, ^3J 8.5, ^4J 2.0 Hz), 7.70 d (1H, H^1, ^4J 2.2 Hz), 7.92 d (1H, H^3, ^4J 2.2 Hz), 8.58 d (1H, H^8, ^4J 1.8 Hz), 8.85 d (1H, H^6, ^4J 1.8 Hz). Found, %: C 53.82; H 2.09; N 9.91; S 7.92. $C_{19}H_9N_3O_7S$. Calculated, %: C 53.90; H 2.13; N 9.93; S 7.56

2-Phenoxy-4,5,7-trinitro-9*H*-fluoren-9-one (VII). To a solution of 2.0 g (5.5 mmol) of compound **I** in 20 ml of HMPA was added 1.5 g (15.9 mmol) of phenol, the mixture was heated to 100°C and stirred at this temperature for 4 h. The solution was cooled and poured on a mixture of 50 g of ice and 100 ml of 5% hydrochloric acid. The separated precipitate was filtered off, washed with water, dried, treated with benzene, the obtained solution was chromatographed on a column packed with silica gel (eluent benzene). Yield 1.04 g (46%), yellow crystals. R_f 0.56 (benzene), mp 180–181°C (acetic acid). IR spectrum, ν, cm^{-1}: 1735 (C=O), 1530, 1365, 1355 (NO_2). ^{1}H NMR spectrum, δ, ppm: 7.13 d.d (2H, H^O, ^3J 8.3, ^4J 2.2 Hz), 7.18 d.d (1H, H^n, ^3J 8.3, ^4J 2.2 Hz), 7.45 d.d (2H, H^m, ^3J 8.3, ^4J 2.2 Hz), 7.72 d (1H, H^1, ^4J 2.2 Hz), 7.92 d (1H, H^3, ^4J 2.2 Hz), 8.57 d (1H, H^8, ^4J 1.8 Hz), 8.85 d (1H, H^6, ^4J 1.8 Hz). Found, %: C 55.92; H 2.52; N 9.93. $C_{19}H_9N_3O_8$. Calculated, %: C 56.02; H 2.21; N 10.32.

4-Methylsulfanyl-2,7-dinitro-9*H*-fluoren-9-one (VIIIa) and 2-methylsulfanyl-4,7-dinitro-9*H*-fluoren-9-one (IXa). A solution of 1.0 g (3.17 mmol) of trinitrofluorenone **II** in 10 ml of DMSO was heated for 8 h at 185–190°C, cooled to room temperature, and poured into 200 ml of 3% hydrochloric acid. The separated dark brown precipitate was filtered off, washed with water, dried, dissolved in 150 ml of benzene, and chromatographed on a column packed with silica gel (eluent benzene).

Compound **VIIIa**. Yield 0.51 g (51%). Light yellow crystals. R_f 0.25 (benzene), mp 245–246°C (acetic acid). IR spectrum, ν, cm^{-1}: 1728 (C=O), 1520, 1345 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.47 s (3H, CH), 8.13 d (1H, H^5, ^3J 8.7 Hz), 8.32 d (1H, H^1, ^4J 1.8 Hz), 8.37 d (1H, H^8, ^4J 2.3 Hz), 8.42 d (1H, H^3, ^4J 1.8 Hz), 8.63 d.d (1H, H^6, ^3J 8.7, ^4J 2.3 Hz). Found, %: C 53.58; H 2.94; N 8.23; S 9.68. $C_{14}H_8N_2O_5S$. Calculated, %: C 53.16; H 2.53; N 8.86; S 10.13.

Compound **IXa**. Yield 0.14 g (14%). Yellow crystals. R_f 0.42 (benzene), mp 192–193°C (acetic acid). IR spectrum, ν, cm^{-1}: 1725 (C=O), 1530, 1340 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.49 s (3H, CH), 7.88 d (1H, H^5, ^3J 8.7 Hz), 7.98 d (1H, H^1, ^4J 1.8 Hz), 8.03 d (1H, H^8, ^4J 2.3 Hz), 8.30 d (1H, H^3, ^4J 1.8 Hz), 8.52 d.d (1H, H^6, ^3J8.7, ^4J 2.3 Hz). Found, %: C 53.18; H 2.61; N 8.82; S 9.97. $C_{14}H_8N_2O_5S$. Calculated, %: C 53.16; H 2.53; N 8.86; S 10.13.

4-Butylsulfanyl-2,7-dinitro-9*H*-fluoren-9-one (VIIIb) and 2-butylsulfanyl-4,7-dinitro-9*H*-fluoren-9-one (IXb). To a solution of 1.0 g (3.17 mmol) of compound **II** in 10 ml of DMSO was added 1.0 ml of butane-1-thiol at room temperature. After 2 days the mixture was poured into 50 ml of 5% hydrochloric acid. The separated precipitate was filtered off, washed with water, dried, dissolved in benzene, and chromatographed on a column packed with silica gel (eluent benzene).

Compound **VIIIb**. Yield 0.63 g (55%). Yellow crystals. R_f 0.64 (benzene), mp 151–152°C (acetic acid). IR spectrum, ν, cm^{-1}: 1725 (C=O), 1520, 1345 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.03 t (3H, CH_3, ^3J 7.2 Hz), 1.35 m (2H, $C\underline{H}_2CH_3$), 1.61 m (2H, $C\underline{H}_2CH_2CH_3$), 2.78 q (2H, SCH_2, ^3J 7.8 Hz), 8.13 d (1H, H^5, ^3J 8.7 Hz), 8.35 d (1H, H^1, ^4J 1.8 Hz), 8.38 d (1H, H^8, ^4J 2.3 Hz), 8.51 d (1H, H^3, ^4J 1.8 Hz), 8.62 d.d (1H, H^6, ^3J 8.7, ^4J 2.3 Hz). Found, %: C 56.80; H 3.74; N 7.58; S 8.89. $C_{17}H_{14}N_2O_5S$. Calculated, %: C 56.98; H 3.91; N 7.82; S 8.94.

Compound **IXb**. Yield 0.21 g (18%). Orange crystals. R_f 0.73 (benzene), mp 146–147°C (acetic acid). IR spectrum, ν, cm^{-1}: 1730 (C=O), 1525, 1340 (NO_2). ^{1}H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, ^3J 7.2 Hz), 1.35 m (2H, $C\underline{H}_2CH_3$), 1.60 m (2H, $C\underline{H}_2CH_2CH_3$), 2.79 q (2H, SCH_2, ^3J 7.8 Hz), 7.90 d (1H, H^5, ^3J 8.7 Hz), 7.99 d (1H, H^1, ^4J 1.9 Hz), 8.06 d (1H, H^8, ^4J 2.3 Hz), 8.31 d (1H, H^3, ^4J 1.9 Hz), 8.52 d.d (1H, H^6, ^3J 8.7, ^4J 2.3 Hz). Found, %: C 56.78; H 3.80; N 7.81; S 9.06. $C_{17}H_{14}N_2O_5S$. Cal-

culated, %: C 56.98; H 3.91; N 7.82; S 8.94.

4-Phenylsulfanyl-2,7-dinitro-9*H*-fluoren-9-one (VIIIc). To a solution of 2 g (3.65 mmol) of trinitrofluorenone **III** in 20 ml of DMSO was slowly added within 20 min 1.1 g (10 mmol) of thiophenol, and the mixture was stirred at room temperature for 1 h. The separated precipitate was filtered off, washed with water, dried, and crystallized from acetic acid. Yield 2.09 g (87%), mp 218.5–219.5°C. R_f 0.58 (benzene). IR spectrum, ν, cm^{-1}: 3440, 3080, 1725 (C=O), 1520, 1340 (NO_2). Found, %: C 60.61; H 2.67; N 7.32; S 8.36. $C_{19}H_{10}N_2O_5S$. Calculated, %: C 60.32; H 2.65; N 7.41; S 8.47. The structure of compound **VIIIc** was established by X-ray analysis [8].

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