Synthesis of a new monomer for sulfonated poly(arylene ether sulfones)

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4-({2,4-Bis[(4-chlorophenyl)sulfonyl]phenyl}thio)benzenesulfonic acid was synthesized based on the scheme suggested from the results of retrosynthetic analysis. This compound is a new monomer for the preparation of sulfonated poly(arylene ether sulfones) used as a solid polymer electrolyte in fuel cells. The structure of the aromatic disulfone containing a sulfo group was suggested based on the data on the influence of chemical structure of structural elements of polysulfone proton-conducting membranes on their operational characteristics.

Key words: poly(arylene ether sulfones), retrosynthetic analysis, aromatic nucleophilic substitution, sulfonation.

At the present time, fuel cells (FCs) are considered as an alternative to traditional sources of energy. Among them, great attention is attracted by FCs with solid polymer electrolyte, which is a polymeric film, proton-conducting membrane (PCM) used for the selective transport of protons from the FC working space, thus providing continuos work of the FCs.

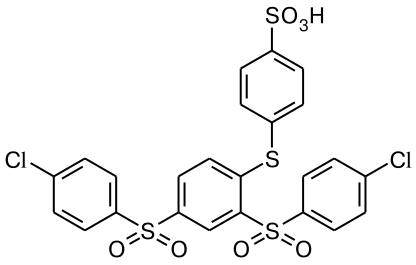
Analysis of literature data[1] showed that one of the promising classes of aromatic condensation polymers for the development of PCM are the sulfonated poly(arylene ether sulfones) (HSO_3-PAESs). Two approaches are used for their preparation: 1) the synthesis of PAESs from bis-phenols and aromatic dihalo- or dinitrosulfones by the reaction of nucleophilic polysubstitution with subsequent electrophilic introduction of a sulfo group in the polymer;[2] 2) the preparation of HSO_3-PAESs directly from monomers containing a sulfo group.[3] The second approach is more convenient for the preparation of polymers having a strictly ordered structure and a certain amount of protogenic groups.

It is known that the operational characteristics of polymers depend on chemical structure of repeating units and on their distribution pattern in the chain. The purpose of the present work is the synthesis of a new highly active in S_NAr reactions aromatic sulfone monomer containing a sulfo group and suitable for development of HSO_3-PAESs.

Results and Discussion

Based on the analysis of literature data on the structure and properties of sulfone monomers and PAESs obtained on their basis, we suggested an AA-type monomer not described in the literature. In its development, we were governed by the following ideas. First, the presence of two highly active reaction centers for the reaction of aromatic nucleophilic polysubstitution should facilitate preparation of high-molecular-weight polymers. Second, the protogenic group should be, if possible, in the side substituent, since its presence in the fragments of the main polymeric chain can impair physicomechanical properties of the obtained membranes.[4] Therefore, for the sulfo group to be introduced by the electrophilic substitution reaction the side fragment of the monomer should contain a highly active center. Third, it is desirable that the side group would have been bonded to the main chain through bridging atoms or groups, which would have decreased the rigidity of the macromolecules and improved their solubility.[5] Fourth, the presence of two sulfone groups in the elementary unit can increase the stability of the obtained polymeric material to oxidation.[6]

Bearing these reasons in mind, we suggested the structure **1** as a monomer for the development of HSO_3-PAESs.



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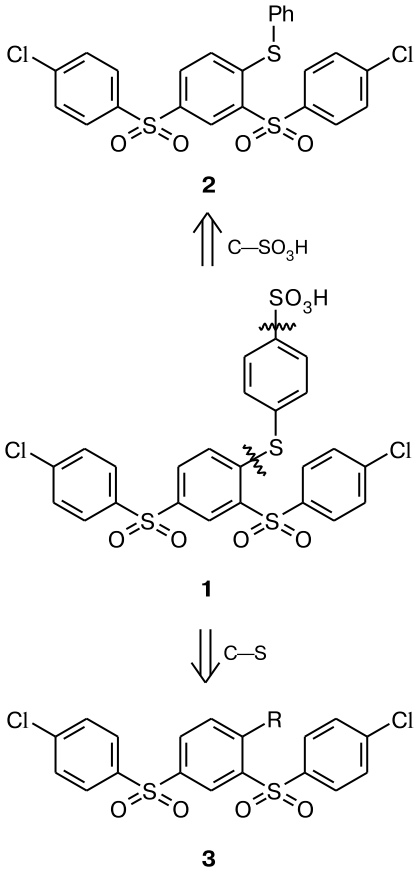
To choose the most optimal pathway for the synthesis of monomer **1**, we carried out retrosynthetic analysis,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 0545—0551, March, 2017.

which is widely used at the present time in the development of optimal strategies for the synthesis of compounds with a required structure.[7] The retrosynthetic schemes show possible reagents corresponding to the synthons obtained after the virtual cleavage of bonds or functional group interconversion (FGI).

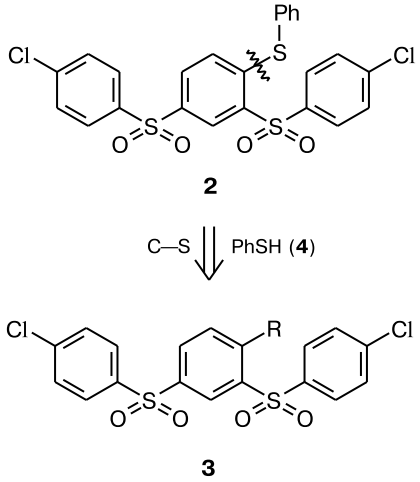
The presence of the protogenic group in the structure of a monomer can be achieved using two means (Scheme 1): the introduction of a sulfo group in the thiophenyl radical of compound **2** by the S_EAr-type reaction or as a result of the reaction of compound **3** with 4-mercaptobenzenesulfonic acid. The second method seems less convenient due to the following reasons: 4-mercaptosulfonic acid is a poorly available and expensive reagent, while thiophenols containing strong electron-withdrawing groups are weak nucleophiles, which would require drastic conditions for carrying out the S_NAr-type reactions with their involvement. At the same time, sulfonation is widely used in organic synthesis and proceeds readily for substrates with electron-donating substituents. The product is obtained through the formation of a sulfonyl chloride, which hydrolyzes upon treatment of the reaction mixture with water. Thus, the first step of the retrosynthetic scheme is the "C—SO_3H bond cleavage".

Scheme 1



Compound **2** can be easily obtained by the S_NAr reaction of thiophenol **4** with aromatic disulfone **3** containing a good nucleofuge (R), such as F and Cl atoms or a nitro group. The presence of two acceptor groups should considerably facilitate the course of the substitution reaction. Consequently, the step of the "C—S bond cleavage" can be represented by Scheme 2.

Scheme 2

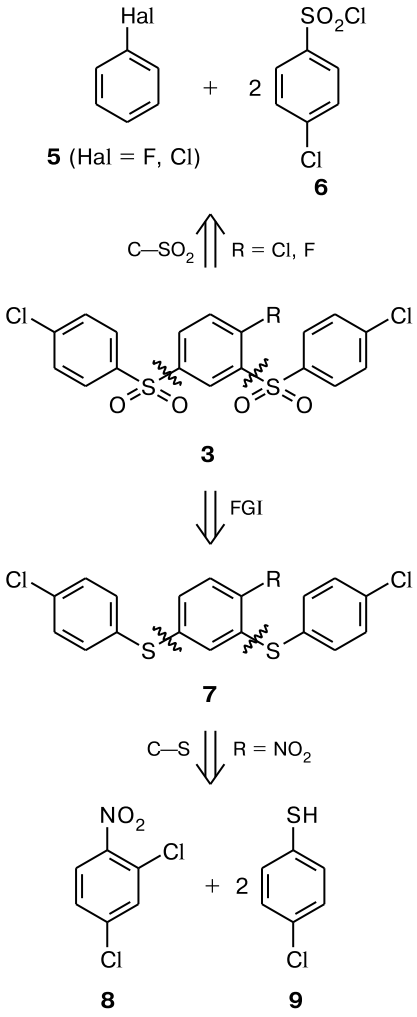


The shortest pathway for the synthesis of compound **3** is the Friedel—Crafts reaction of chloro- or fluorobenzene **5** with 4-chlorobenzenesulfonyl chloride **6** (2 equiv.) in the presence of anhydrous $AlCl_3$ (Scheme 3). A principal disadvantage of this method consists in the difficulty of the introduction of the second electrophilic species in the forming diphenyl sulfone, which does not contain electron-donating substituents. Using the IFG method, a simpler and more efficient pathway can be suggested. It is known[8] that diphenyl sulfones can be obtained easily and in high yield by oxidation of diphenyl sulfides with the mixture of H_2O_2—AcOH. After the cleavage of the C—S bond, the building blocks can be suggested, from which the polynuclear structure **7** would be assembled. These are 2,4-dichloronitrobenzene (**8**) and 4-chlorothiophenol (**9**), highly active reagents for the S_NAr reaction (see Scheme 3). The conditions for this process are described in detail in the literature for the reaction of 4-chloronitrobenzene with different nucleophiles.[9]

Thus, using retrosynthetic analysis we have designed a scheme for the preparation of a new monomer **1** for the development of PAESs containing a sulfo group (Scheme 4).

Following the Scheme 4, 2,4-dichloronitrobenzene **8** and 4-chlorothiophenol **9** were used to obtain 2,4-bis[(4-chlorophenyl)thio]-1-nitrobenzene **7** in 96% yield. To increase the conversion of the substrate and to decrease the reaction time, the substitution was carried out upon treatment with ultrasound for 1 h under conditions described by us in the work.[10]

Scheme 3



The aromatic disulfide **7** was oxidized with 33% aqueous solution of hydrogen peroxide in glacial acetic acid (see Scheme 4). The data on the influence of temperature of oxidation on the yield of product **3** are given below.

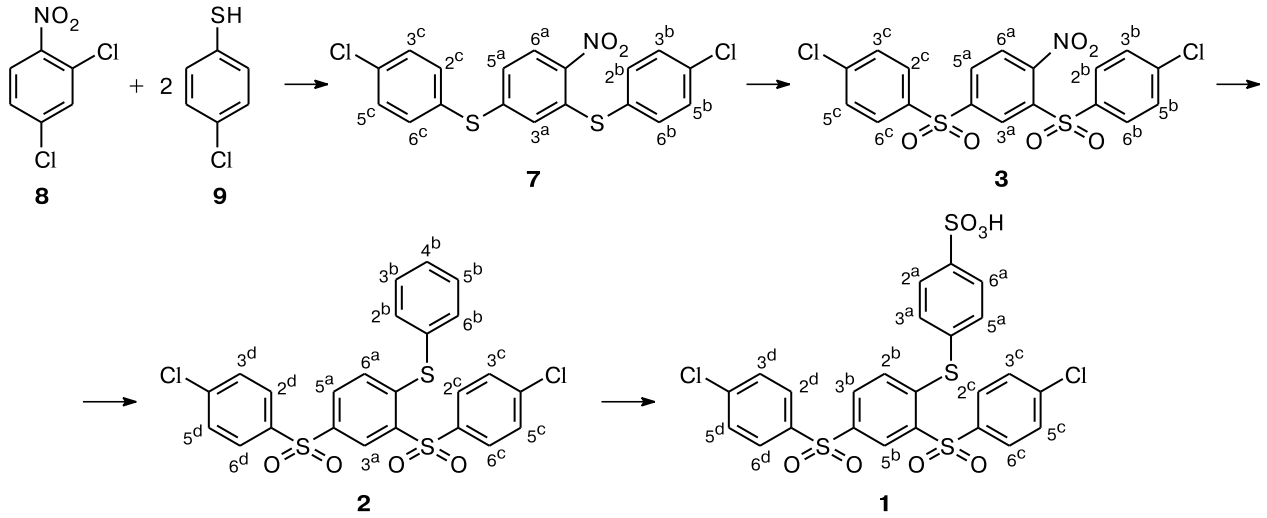
T/°C	70	75	80	85	90	95	100
Yield (%)	71	80	83	84	89	97	95

At the temperatures below 90 °C, the yield of 2,4-bis-[(4-chlorophenyl)sulfonyl]-1-nitrobenzene (**3**) did not exceed 84%. This can be explained by the poor solubility of the substrate **7** in acetic acid, as a result, the reaction proceeded under heterophase conditions. As a result, the target product **3** contained a considerable impurity of the starting compound, which cannot be completely removed by recrystallization. Pure product **3** was obtained by carrying out the reaction at 95 °C for 3 h. After cooling the reaction mixture, compound **3** crystallized as colorless crystals and did not require additional purification. The yield of aromatic disulfone **3** was 97%.

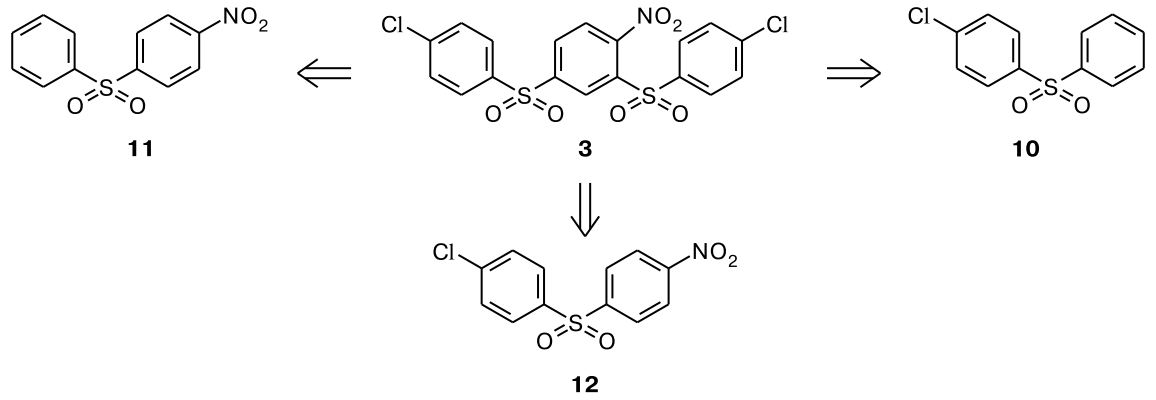
The oxidation of compound **7** resulted in the introduction of two strong electron-withdrawing groups in its structure, which promote formation of three reaction centers for the nucleophilic attack.

At first glance, only a nitro group, the nucleofugicity of which is higher than that of chlorine atoms,[11] should undergo substitution in the course of the S_NAr reaction at the stoichiometric ratios of reagents **3** : **4** = 1 : 1. In addition, the presence in compound **3** of two strong electron-withdrawing groups at *ortho*- and *para*-positions to the reaction center should also facilitate the nucleophilic attack at the C—NO_2 bond. However, when the process was carried out at 70 °C and higher (the solvent DMF, the deprotonating agent K_2CO_3, 1 h), a difficult to separate mixture of products was obtained. Carrying out the reaction at 20 °C did not give pure target product **2** either, since

Scheme 4



Scheme 5



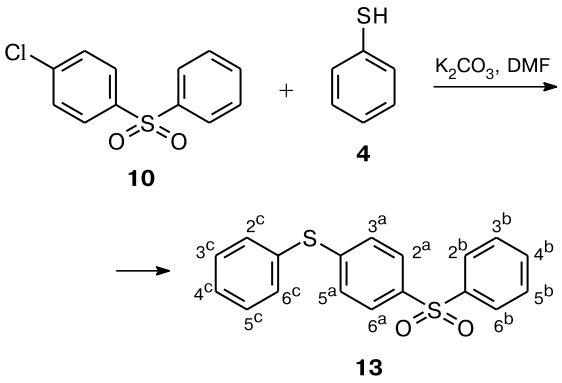
about 20—25% of the nitro compound remained unreacted. In this case, an increase in the time of the synthesis did not lead to any significant change in the conversion of nitroarene **3**.

To identify the side processes proceeding in the course of the reaction of aromatic nucleophilic substitution in nitrobenzene **3**, the complicated structure of this substrate was virtually transformed into simpler compounds **10**—**12** (Scheme 5), containing possible reaction centers for the nucleophilic attack, and the reactions of these compounds with thiophenol **4** were studied (Schemes 6—8).

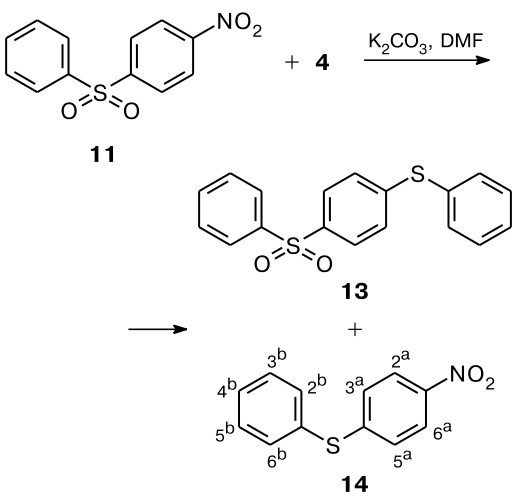
In the reaction of 1-chloro-4-(phenylsulfonyl)benzene (**10**) with nucleophile **4** (DMF, K_2CO_3) at 70 °C, the conversion of compound **10** after 1 h was only 21% (Scheme 6). An increase in the temperature to 100 °C and the S_NAr reaction time to 8 h allowed us to obtain the individual product in 91% yield. The ^{1}H NMR spectrum of compound **13** exhibited the signals for 14 aromatic protons, with the signals for the protons H(2^c) and H(6^c) being observed in the more high-field region of the spectrum (at δ 7.21) as compared to other signals. These data, as well as the *m/z* value of 327.0516 $[M + 1]^+$, correspond to 1-(phenylsulfonyl)-4-(phenylthio)benzene (**13**). The formation in this reaction of the only product **13** indicated the presence in the structure of **10** of only one reaction center.

As it was expected, the reactivity of 1-nitro-4-(phenylsulfonyl)benzene (**11**) in the reaction with **4** was higher (Scheme 7). At 70 °C, 36% of the substrate was consumed in the reaction already after 1 h. However, this reaction proceeded with the formation of two products. The compound **11** was completely converted when the substitution process was carried out for 5 h at 100 °C. This resulted in the formation of a mixture of products **13** and **14** in the ratio of 3 : 1, which was separated by fractional crystallization in a binary mixture of solvents Pr^{i}OH—hexane. The structures of compounds **13** and **14** were confirmed by ^{1}H NMR spectroscopy and mass spectrometry. ^{1}H NMR spectrum of 1-nitro-4-(phenylthio)benzene (**14**)

Scheme 6



Scheme 7



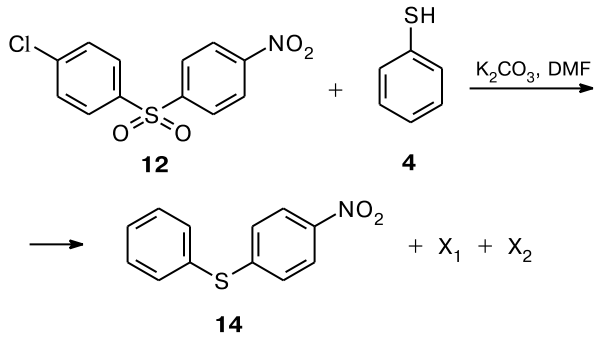
contains the signals for the nine protons of mono- and disubstituted benzene rings. A signal with the double intensity attributed to the protons C(2^b) and C(6^b) was found in the high-field region of the spectrum at δ 7.27. A signal at δ 8.11 belongs to the weakly shielded protons H(2^a) and

H(6^a) at *ortho*-positions to the nitro group. The other five protons resonate as a multiplet in the region of δ 7.48—7.58. The high resolution mass spectrum exhibits a molecular ion with m/z 232.0435 $[M + 1]^+$.

The data obtained allow us to draw a conclusion that in compound **11** both the nitro group and the phenylsulfone fragment can act as a nucleofuge.

The nucleophilic substitution reaction between 1-chloro-4-[(4-nitrophenyl)sulfonyl]benzene (**12**) and thiophenol **4** at 100 °C reached completion within 5 h (Scheme 8). This resulted in the formation of a mixture containing three products, which were not isolated in the individual state, however, diphenyl sulfide **14** was identified as one of the products by gas chromatography. The retention times of two other products (X_1 and X_2; see Scheme 8) are higher than that of the starting compound **12**. Products X_1 and X_2 are most likely formed as a result of the substitution of the nitro group and the chlorine atom in substrate **12**. This indicates a possibility for the S_NAr reaction to follow three directions.

Scheme 8



Thus, based on the results of the studies we draw a conclusion on a possibility of the nucleophilic attack on several reaction centers of 2,4-bis[(4-chlorophenyl)-sulfanyl]-1-nitrobenzene **3**: the chlorine atoms, the nitro group, and the phenylsulfone fragments can act as nucleofuges.

To increase the selectivity of the reaction of nitro compound **3** with *S*-nucleophile **4**, the temperature of the process was varied in the range 30—60 °C with a 5 °C step. The nucleophilic agent was added to the reaction mixture gradually.

2,4-Bis[(4-chlorophenyl)sulfonyl]-1-(phenylthio)-benzene (**2**), the product of the substitution of the nitro group containing no impurities, was obtained in 92% yield by a dropwise addition of a solution of thiophenol **4** in DMF to the reaction mixture over 30 min at 35 °C. The structure of compound **2** was confirmed using ^{1}H NMR spectroscopy. The splitting patterns of the signals confirm the structure of the fragments composing this compound, namely, the *para*-substituted, monosubstituted, and trisubstituted benzene rings. The mutual arrangement of the rings was determined using the nuclear Overhauser effect (NOE): the through-space interaction was found for the proton H(3^a) (a doublet at δ 8.66) with the protons of the *para*-substituted benzene rings H(2^c), H(6^c) and H(2^d), H(6^d) (Fig. 1). Such interaction confirms the presence of the 4-chlorophenylsulfonyl fragments at positions 2 and 4 of the central ring of the molecule. Apart from that, the experiment showed that the proton H(6^a) (a doublet at δ 7.01) is close in space with the *ortho*-protons H(2^b) and H(6^b) of the thiophenyl substituent.

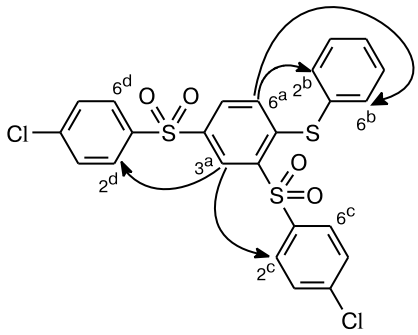


Fig. 1. The Overhauser effects in compound **2** confirming its structure.

The introduction of the sulfoxy group in compound **2** was carried out using chlorosulfonic acid, which is widely used as a sulfonating agent in organic synthesis.[12] The S_EAr reaction was carried out for 2 h at 40 °C with a two-fold excess of the electrophilic agent. Chloroform was used as the solvent. A highly pure sulfonated product **1** was obtained in 86% yield (see Scheme 4).

In conclusion, a successful synthesis of earlier unknown monomer **1** confirmed the rightful choice of the set of well studied types of reactions and available reagents suggested in the course of retrosynthetic analysis. The selection of conditions and the studies of regioselectivity of several steps of the process allowed us to obtain 4-({2,4-bis[(4-chlorophenyl)sulfonyl]phenyl}thio)benzenesulfonic acid (**1**) with high degree of purity, that is a necessary condition for the synthesis of high-molecular-weight polymers possessing required physicochemical characteristics.

Experimental

Product **7** was synthesized using an S 10 H Elmasonic ultrasonic bath (37 kHz, temperature range 30—80 °C, Elma Schmidbauer GmbH production, Germany). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer in DMSO-d_6 at 24—27 °C (500.13 and 125.76 MHz, respectively). Chemical shifts are given relative to the signal of residual protons (δ 2.5) and the signal of ^{13}C atoms of the solvent. The signals in the ^{1}H and ^{13}C NMR spectra were assigned based on the 2D ^{1}H—^{13}C HMBC spectroscopy data. The concentration of the samples for recording the NMR spectra was within the recommended

range.[13] Electrospray ionization (ESI) high resolution mass spectra were recorded on a Bruker micrOTOF II instrument. Elemental composition was determined on a Carlo Erba 1106 elemental analyzer (Italy). The course of the S_NAr reactions involving compounds **10**—**12** was monitored by gas chromatography on a Krystallyuks-4000 M chromatograph (Meta-Khrom, Russian Federation).

The following reactants purchased from Acros Organics and Sigma—Aldrich were used in the work: thiophenol (99%), 2,4-dichloronitrobenzene (97%), 1-chloro-4-(phenylsulfonyl)benzene (≥97%), 1-nitro-4-(phenylsulfonyl)benzene (99%). Solvents of the reagent grade were used without additional purification.

2,4-Bis[(4-chlorophenyl)thio]-1-nitrobenzene (7). Potassium carbonate (10.76 g, 0.078 mol) and 2,4-dichloronitrobenzene (**8**) (5.0 g, 0.026 mol) were added to a solution of 4-chlorothiophenol (**9**) (7.51 g, 0.052 mol) in DMSO (50 mL). The reaction mixture was sonicated for 1 h at 80 °C, cooled, and poured into water. A yellow precipitate formed was collected by filtration and recrystallized from DMF. The yield was 10.18 g (96%), m.p. 139—141 °C. Found: *m/z* 407.9685 $[M + H]^+$. $C_{18}H_{12}Cl_2NO_2S_2$. Calculated: M = 407.9687. ^{1}H NMR (DMSO-d_6), δ: 6.17 (d, 1 H, H(3^a), J = 2.0 Hz); 7.26 (dd, 1 H, H(5^a), J = 8.7 Hz, J = 2.0 Hz); 7.36 (d, 2 H, H(2^c), H(6^c), J = 8.5 Hz); 7.42 (d, 2 H, H(3^c), H(5^c), J = 8.5 Hz); 7.44 (s, 4 H, H(2^b), H(3^b), H(5^b), H(6^b)); 8.20 (d, 1 H, H(6^a), J = 8.7 Hz). ^{13}C NMR (DMSO-d_6), δ: 146.9 (C(4^a)), 141.5 (C(1^a)), 139.2 (C(2^a)), 137.0 (C(2^b)), 136.2 (C(2^c)), 135.6 (C(4^b)), 135.2 (C(4^c)), 130.1 (C(3^a), 130.0 (C(3^c)), 128.0 (C(1^a)), 127.2 (C(1^c)), 126.4 (C(6^a)), 123.1 (C(3^a)), 123.1 (C(5^a)). Found (%): C, 52.89; H, 2.63; N, 3.45; S, 15.71; Cl, 17.36. $C_{18}H_{11}Cl_2NO_2S_2$. Calculated (%): C, 52.95; H, 2.72; N, 3.43; S, 15.71; Cl, 17.37.

2,4-Bis[(4-chlorophenyl)sulfonyl]-1-nitrobenzene (3). A 33% aqueous solution of H_2O_2 (12 mL) was added dropwise to a solution of compound **7** (8.16 g, 0.02 mol) in glacial acetic acid (100 mL) at 95 °C over 4 h. The reaction mixture was poured into a beaker and allowed to stand for 16 h. A white precipitate formed was collected by filtration. The yield was 9.16 g (97%), m.p. 177—179 °C. Found: *m/z* 471.9487 $[M + H]^+$. $C_{18}H_{12}Cl_2NO_6S_2$. Calculated: M = 471.9484. ^{1}H NMR (DMSO-d_6), δ: 7.71 (d, 2 H, H(3^c), H(5^c), J = 8.7 Hz); 7.74 (d, 2 H, H(3^b), H(5^b), J = 8.7); 8.05 (d, 2 H, H(2^b), H(6^b), J = 8.7); 8.14 (d, 2 H, H(2^c), H(6^c), J = 8.7 Hz); 8.30 (d, 1 H, H(6^a), J = 8.4 Hz); 8.58 (dd, 1 H, H(5^a), J = 8.4 Hz, J = 2.0 Hz); 8.82 (d, 1 H, H(3^a), J = 2.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 149.9 (C(1^a)), 144.6 (C(4^a)), 140.01 (C(4^b)), 139.97 (C(4^c)), 137.72 (C(1^c)), 137.66 (C(1^b)), 135.6 (C(5^a)), 133.8 (C(2^a)), 130.10, 130.06, 130.02, 129.79 (C(2^b), C(3^b), C(5^b), C(6^b), C(2^c), C(3^c), C(5^c), C(6^c)), 129.80 (C(3^a)), 127.28 (C(6^a)). Found (%): C, 45.69; H, 2.31; N, 2.88; S, 13.58; Cl, 15.09. $C_{18}H_{11}Cl_2NO_6S_2$. Calculated (%): C, 45.77; H, 2.35; N, 2.97; S, 13.58; Cl, 15.01.

2,4-Bis[(4-chlorophenyl)sulfonyl]-1-(phenylthio)benzene (2). Potassium carbonate (3.1 g, 0.0225 mol) was added to a solution of compound **3** (7.08 g, 0.015 mol) in DMF (35 mL), followed by dropwise addition of a solution of thiophenol **4** (1.54 mL, 0.015 mol) in DMF (10 mL) over 30 min at 35 °C. Then, the reaction mixture was stirred for 30 min at 35 °C and poured into water. A white precipitate formed was collected by filtration and recrystallized from a mixture of isopropyl alcohol—DMF. The yield was 7.38 g (92%), m.p. 242—243 °C. Found: *m/z* 534.9664 $[M + H]^+$. $C_{24}H_{17}Cl_2O_4S_3$. Calculated: M = 534.9667. ^{1}H NMR (DMSO-d_6), δ: 7.01 (d, 1 H, H(5^a), J = 8.5 Hz); 7.30 (d, 2 H, H(2^b), H(6^b), J = 7.4 Hz); 7.44 (t, 2 H, H(3^b), H(5^b), J = 7.4 Hz); 7.49 (t, 1 H, H(4^b), J = 7.4 Hz); 7.68 (d, 2 H, H(3^d), H(5^d), J = 8.6 Hz); 7.71 (d, 2 H, H(3^c), H(5^c), J = 8.6 Hz); 8.02 (d, 2 H, H(2^d), H(6^d), J = 8.6 Hz); 8.04 (dd, 1 H, H(5^a), J = 8.5 Hz, J = 1.8 Hz); 8.10 (d, 2 H, H(2^c), H(6^c), J = 8.6 Hz); 8.66 (d, 1 H, H(3^a), J = 1.8 Hz). ^{13}C NMR (DMSO-d_6), δ: 146.8 (C(1^a)); 139.5 (C(4^c)); 139.3 (C(4^d)); 138.8 (C(1^d)); 138.0 (C(2^a)); 137.3 (C(1^c)); 136.6 (C(4^a)); 134.8 (C(2^b); C(6^b)); 132.7 (C(5^a)); 130.4 (C(3^b), C(4^b), C(5^b), C(6^a)); 130.2 (C(2^c), C(6^c)); 130.0 (C(3^d), C(5^d)); 129.53, 129.50 (C(3^c), C(5^c), C(2^d), C(6^d)); 128.7 (C(1^b)); 128.4 (C(3^a)). Found (%): C, 53.11; H, 2.86; S, 17.99; Cl, 13.32. $C_{24}H_{16}Cl_2O_4S_3$. Calculated (%): C, 53.83; H, 3.01; S, 17.96; Cl, 13.24.

4-({2,4-Bis[(4-chlorophenyl)sulfonyl]phenyl}thio)benzenesulfonic acid (1). Compound **2** (5.4 g, 0.01 mol) was dissolved in chloroform (70 mL) with stirring at 30 °C. Then, chlorosulfonic acid (1.32 mL, 0.02 mol) in chloroform (10 mL) was added dropwise to the homogeneous solution with vigorous stirring. The resulting reaction mixture was stirred for 2 h at 40 °C and concentrated to 10 mL. The residue after cooling was poured onto ice. A precipitate formed was collected by filtration and allowed to stand in 10% aqueous solution of KOH (50 mL), then treated with 9% aqueous HCl in ice to pH 5—6 and filtered. The yield was 5.3 g (86%), m.p. >290 °C. Found: *m/z* 614.9239 $[M + H]^+$. $C_{24}H_{17}Cl_2O_7S_4$. Calculated: M = 614.9235. ^{1}H NMR (DMSO-d_6), δ: 7.01 (d, 1 H, H(2^b), J = 8.6 Hz); 7.29 (d, 2 H, H(3^a), H(5^a), J = 8.1 Hz); 7.68 (d, 2 H, H(2^a), H(6^a), J = 8.2 Hz); 7.70 (d, 2 H, H(3^d), H(5^d), J = 8.6 Hz); 7.74 (d, 2 H, H(3^c), H(5^c), J = 8.6 Hz); 8.02 (d, 2 H, H(2^d), H(6^d), J = 8.6 Hz); 8.08 (dd, 1 H, H(3^b), J = 8.6 Hz, J = 1.8 Hz); 8.11 (d, 2 H, H(2^c), H(6^c), J = 8.6 Hz); 8.63 (d, 1 H, H(5^b), J = 1.7 Hz). ^{13}C NMR (DMSO-d_6), δ: 150.1 (C(1^a); 146.8 (C(1^b)); 139.6 (C(4^c)); 139.4 (C(4^d)); 138.9 (C(1^d)); 138.0 (C(6^b)); 137.3 (C(1^c)); 136.6 (C(4^b)); 134.5 (C(3^a), C(5^a)); 133.0 (C(3^b)); 130.5 (C(2^b)); 130.3 (C(2^c), C(6^c)); 130.1 (C(3^d), C(5^d)); 129.7 (C(3^c), C(5^c)); 129.6 (C(2^d), C(6^d)); 128.8 (C(4^a)); 128.5 (C(5^b)); 127.7 (C(2^a), C(6^a)). Found (%): C, 46.78; H, 2.58; Cl, 11.49; O, 18.22; S, 20.85. $C_{24}H_{16}Cl_2O_7S_4$. Calculated, %: C, 46.83; H, 2.62; S, 20.84; Cl, 11.52.

The authors of the work are grateful to the specialists of the Division of Structural Studies of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences (Moscow) for supplying with analytical data.

This work was financially supported by the President of the Russian Federation Council for Grants (Program for State Support of Young Russian Scientists-Candidates of Science (Grant MK-3839.2015.3).

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Received July 4, 2016;
in revised form October 5, 2016