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Synthesis and Transformations of Bis(polychloroethylideneaminosulfonyl)- and Bis(polychloroethylaminosulfonyl)-Substituted Derivatives of Biphenyl, Diphenyl Oxide, and Diphenylmethane

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Abstract—Reactions of *N,N,N',N'*-tetrachlorobiphenyl-4,4'-disulfonamide, 4,4'-methylenebis(*N,N*-dichlorobenzenesulfonamide), and 4,4'-oxybis(*N,N*-dichlorobenzenesulfonamide) with 1,2-dichloroethylene and trichloroethylene open convenient synthetic approach to highly electrophilic bissulfonylimines of dichloroacetic aldehyde and chloral: *N,N'*-bis(polychloroethylidene)biphenyl-4,4'-disulfonamides, 4,4'-methylenebis[*N*-(polychloroethylidene)benzenesulfonamides] and 4,4'-oxybis[*N*-(polychloroethylidene)benzenesulfonamides]. The synthetic opportunities of the bisazomethines obtained were demonstrated by examples of their reactions with water, methanol, chloroacetamide, and toluene where products of O-, N-nucleophiles addition to the azomethine bond and products of C-amidoalkylation of aromatic compound with imines were formed.

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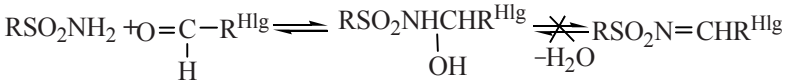
The synthetic importance of imines of polyhalogeneted aldehydes and ketones originates from the presence in their structure of an activated azomethine group. The considerable polarization of the C=N bond by strong electron-withdrawing substituents notably activates the electrophilic properties of the azomethine carbon, and this fact is successfully used to solve versatile synthetic problems. Thus N-sulfonyl-, -carbonyl-, -alkoxycarbonyl-, and -phosphonylimines of polyhalocarbonyl compounds are active in reactions with O-, N-, S-, and P-nucleophiles and polynucleophiles, these imines are reactive amidoalkylating agents, heterodienes and heterodienophiles,; therefore synthetic approaches have been developed to a wide range of polyfunctional nitrogen-containing acyclic and heterocyclic compounds, among them many of a doubtless practical interest [1].

The classic procedure of azomethines preparation, condensation of carbonyl compounds with amino group containing substances, is hardly acceptable for *N*-acyl- and *N*-sulfonylimines of polyhaloaldehydes, for the process stops at the stage of intermediate hydroxyamidals (Scheme 1) whose dehydration is either difficult or impossible because of strong electron-withdrawing substituents [1]. Therefore an urgent problem is a development of alternative preparation methods for imines containing electron-withdrawing sulfonyl and polyhalomethyl substituents at the azomethine moiety.

One of the most convenient synthetic approaches to the polychloroaldehydes sulfonylimines is based on the reaction of sulfonic acids *N,N*-dichloroamides with 1,2-polychloroethenes. The advantages of the method (simple experiment, high yields, cheap commercial reagents, unique possibility to obtain a number of azomethine derivatives of polychloroaldehydes) we demonstrated formerly by preparation of arenesulfonyl and trifluoromethylsulfonylimines of chloral and dichloroacetic aldehyde [1–5].

Scheme 1.



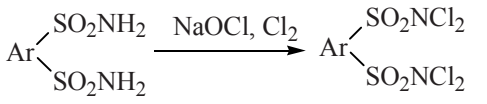
In this study we continued the systematic investigation of reactions between *N,N*-dichloroamides and polyhaloethenes, synthesized previously unknown 4,4'-bis(*N,N*-dichloroaminosulfonyl)-substituted derivatives of biphenyl (**Ia**), diphenylmethane (**Ib**), and diphenyl oxide (**Ic**), and examined their reactions with 1,2-dichloroethylene and trichloroethylene in order to find synthetic approach to new bisazomethine compounds. The interest attracted by these imines is caused by the presence in their structure of two activated azomethine groups that can be used in preparation of formerly unknown functionalized halogen-containing polyamide ensembles, in particular, of oligomer and macroheterocyclic structure.

Dichloroamides **Ia–Ic** were obtained by chlorination of the corresponding disulfonic acids bisamides.

It was established that the boiling of a mixture containing dichloroamide **Ia–Ic** and 10–20-fold excess of 1,2-polychloroethene under an argon atmosphere for 7–9 h led to the formation of *N,N'*-bis(polychloroethylidene)biphenyl-4,4'-disulfonamides **IIa** and **IIb**, 4,4'-methylenebis[*N*-(polychloroethylidene)benzenesulfonamides] **IIIa** and **IIIb**, and 4,4'-oxybis[*N*-(polychloroethylidene)benzenesulfonamides] **IVa** and **IVb** in high yields. The reaction was accompanied by chlorine liberation; the latter added to the corresponding polychloroethene (Scheme 2).

It was established in this study that dichloroamides **Ia–Ic** could not be involved in the chlorination of 1,2-dichloroethylene to trichloroethylene. Therefore their reactions with 1,2-dichloroethylene did not lead to the formation of side products trichloroethylidene- and trichloroethylamides in contrast to formerly investigated arenesulfonic acids *N,N*-dichloroamides [6].

Scheme 2.



Ar = 4-$C_6H_4C_6H_4$-4' (**Ia, IIa, IIb**), 4-$C_6H_4CH_2C_6H_4$-4' (**Ib, IIIa, IIIb**), 4-$C_6H_4OC_6H_4$-4' (**Ic, IVa, IVb**); X = Cl (**a**), H (**b**).

The reaction proceeds by the radical mechanism for it does not occur in the presence of the inhibitors of radical processes.

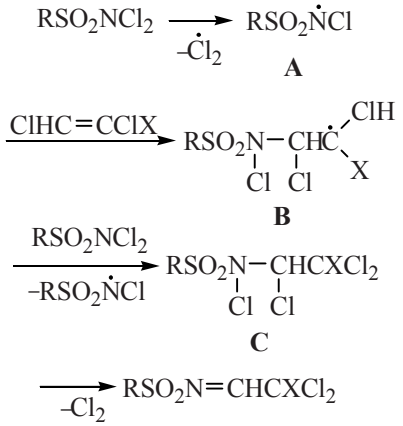
Apparently azomethines **IIa, IIb–IVa, IVb** result from a chain radical process starting with the formation of amidyl radical **A.** Radical **A** adds further to dichloroethylene or trichloroethylene giving a radical-adduct **B** carrying on the chain propagation with the formation of saturated adduct **C** unstable under the reaction conditions whose dehydrochlorination yields the final azomethine (Scheme 3). Previously this path of imines formation was proved by similar transformations of *N,N*-dichloroamides of arenesulfonic acids and trifluoromethanesulfonic acid [7].

The application to the process of *cis*- or *trans*-isomer of 1,2-dichloroethylene or the isomers mixture does not affect the course of the reaction. The tetrachloroethylene does not enter into these reactions.

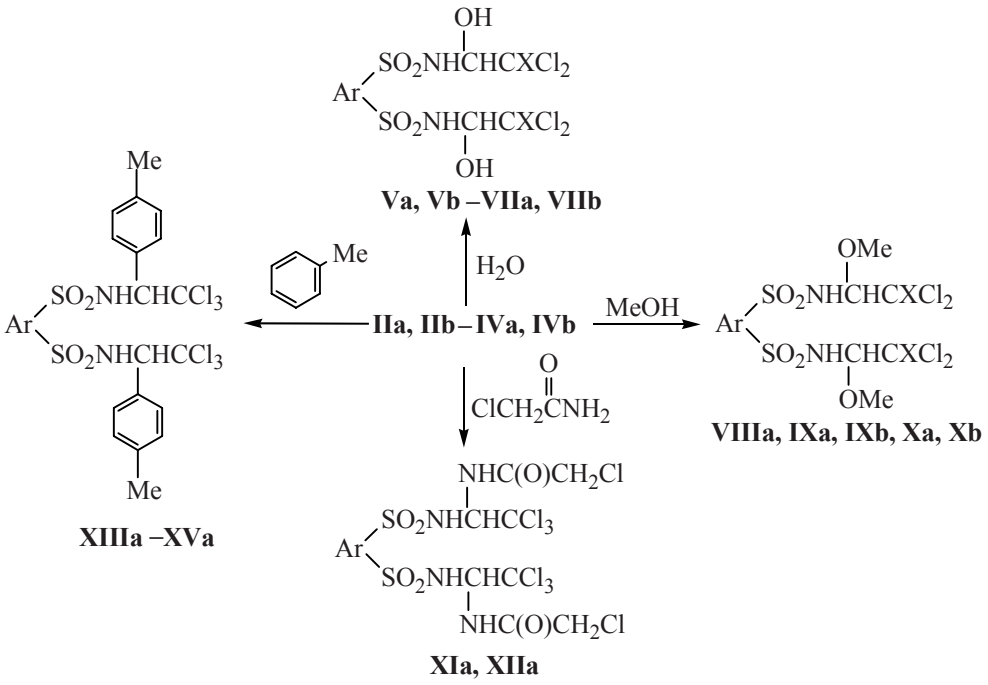
The formation of bisazomethines **IIa, IIb–IVa, IVb** was confirmed by NMR and IR spectroscopy. The comparison of the spectral characteristics of compounds obtained in this study and those of previously investigated sulfonylimines of chloral and dichloacetic aldehyde reveals their analogy [3, 5, 7] thus also supporting the structures of compounds **IIa, IIb–IVa, IVb**. The signals of the hydrogen and carbon atoms of the azomethine groups appear in the ^1H and ^{13}C NMR spectra in the region 8.3–8.5 and 164–166 ppm respectively. Beside these signals the NMR spectra of azomethine compounds **IIa, IIb–IVa, IVb** contain signals corresponding to the aromatic and polychloromethyl fragments.

Some chemical modifications of compounds **IIa, IIb–IVa, IVb** (Scheme 4) also reliably prove their structure and provide a possibility to a certain extent to estimate

Scheme 3.



Scheme 4.



Ar = 4-$C_6H_4C_6H_4$-4' (**Va, Vb, VIIIa, XIa, XIIIa**), 4-$C_6H_4CH_2C_6H_4$-4' (**VIa, VIb, IXa, IXb, XIVa**), 4-$C_6H_4OC_6H_4$-4' (**VIIa, VIIb**, **Xa, Xb, XIIa, XVa**); X = Cl (**a**), H (**b**).

the synthetic prospects of imines containing the azomethine groups activated by electron-withdrawing substituents.

Compounds **IIa, IIb–IVa, IVb** show high activity in reactions with O-, N-nucleophiles. They quicly add the atmospheric moisture giving in a quantitative yield hemiaminals **Va, Vb–VIIa, VIIb**. The structure of hydroxyethylamides **Va, Vb–VIIa, VIIb** was proved also by an independent synthesis by reaction of the corresponding bissulfonic acids diamides with chloral.

By an example of reaction with methanol proceeding with heat evolution the activity of imines **IIa, IIb–IVa, IVb** toward alcohols was demonstrated; the reaction products were alkoxyaminals **VIIIa, IXa, IXb, Xa**, **Xb**. The short heating resulted in addition to the activated azomethine group of even weak N-nucleophiles like chloroacetamide providing polyamide systems **XIa** and **XIIa**.

Imines **IIa, IIb–IVa, IVb** proved to be relatively active C-amidoalkylating agents capable of reacting with aromatic compounds. They reacted with toluene in the presence of oleum providing in good yields, trichloroethylamides **XIIIa–XVa**. The substitution at the amidoalkylation occurred specifically into the *para*-position of the aromatic ring.

The described chemical transformations were carried out aiming at preparation of potential biologically active substances and semiproducts for further reactions. Polyfunctionsl halogen-containing ethylamides of sulfonic acids are initial compounds for preparation of amino acids [8], amidine derivatives of amino acids [9], and heterocyclic compounds [10, 11]. They are interesting as potential ligands, strong NH-acids, possible reagents for asymmetric synthesis and supramolecular chemistry.

The structure of functionalized arenesulfonamides **V–XV** was proved by IR and NMR spectroscopy and confirmed by elemental analysis.

In the IR spectra of compounds **V–XV** characteristic absorption bands are observed of NH and SO_2 groups, in the spectra of hemiaminals **Va, Vb–VIIa, VIIb**, of OH groups.

In the ^1H and ^{13}C NMR spectra of bissulfonamides derivatives **V–XV** signals are present from NHCH fragments with the coupling constant $^3J_{CH–NH}$ 10–12 Hz, and also signals of polyhalomethyl and aromatic fragments in keeping with the assumed structures.

The synthesized sulfonamides derivatives **II–XV** are colorless crystalline substances, readily soluble in highly

polar organic solvents (acetone, DMSO), sparingly soluble in aromatic solvents and halogeneted hydrocarbons, insoluble in aliphatic hydrocarbons and in water.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-400 (operating frequencies 400.13 and 100.61 MHz respectively), internal reference HMDS. IR spectra were recorded on a spectrophotometer Specord 75IR from KBr pellets.

***N,N,N',N'*-Tetrachlorobiphenyl-4,4'-disulfonamide (Ia)**. Through a solution of 4.0 g (100 mmol) of NaOH in 50 ml of water was passed chlorine till the end of heat evolution. Then to the reaction mixture 6.24 g (20 mmol) of biphenyl-4,4'-disulfonamide was added, and at continuous passing of chlorine the mixture was stirred for 3 h maintaining the temperature below 10°C. The precipitate of compound **Ia** was filtered off, washed with water till negative reaction for chloride ion, dried, and recrystallized from chloroform or dichloro-methane. Yield 7.65 g(85%), mp 125°C. IR spectrum, ν, cm^{-1}: 1160, 1360 (SO_2), 3100 (CH_{arom}). ^{1}H NMR spec-trum ($CDCl_3$), δ, ppm: 7.98, 8.22 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$). Found, %: C 31.75; H 2.02; Cl 30.76; N 5.93; S 14.11. $C_{12}H_8Cl_4N_2O_4S_2$. Calculated, %: C 32.02; H 1.79; Cl 31.50; N 6.22; S 14.24.

4,4'-Methylenebis(*N,N*-dichlorobenzenesulfonamide) (Ib) was similarly obtained from 6.52 g (20 mmol) of 4,4'-methylenedibenzenesulfonamide. Yield 8.17 g (88%), mp 113–116°C. IR spectrum, ν, cm^{-1}: 1150, 1360 (SO_2), 3100 (CH_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.28 s (2H, CH_2), 7.48, 8.06 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$). Found, %: C 33.25; H 2.22; Cl 30.76; N 5.93; S 14.11. $C_{13}H_{10}Cl_4N_2O_4S_2$. Calculated, %: C 33.64; H 2.17; Cl 30.55; N 6.04; S 13.81.

4,4'-Oxybis(*N,N*-dichlorobenzenesulfonamide) (Ic) was similarly obtained from 6.56 g (20 mmol) of 4,4'-oxidibenzenesulfonamide. Yield 8.11 g (87%), mp 68–70°C. IR spectrum, ν, cm^{-1}: 1160, 1360 (SO_2), 3090 (CH_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.30, 8.15 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$). Found, %: C 31.05; H 1.92; Cl 30.76; N 5.96; S 14.13. $C_{12}H_8Cl_4N_2O_5S_2$. Calculated, %: C 30.92; H 1.73; Cl 30.42; N 6.01; S 13.76.

***N,N'*-Bis(2,2,2-trichloroethylidene)biphenyl-4,4'-disulfonamide (IIa).** A mixture of 4.50 g (10 mmol) of compound **Ia** and 26 g (200 mmol) of trichloroethylene was boiled under constant argon flow till the end of chlorine evolution (7–9 h). For isolation of pure bisimine **IIa** the reaction mixture was maintained at ~ 0°C for 24 h, the formed precipitate of compound **IIa** was separated by decanting, washed with CCl_4, and dried in a vacuum desiccator over P_2O_5. In the syntheses bisimine **IIa** was used without isolation from the reaction mixture. Yield 5.60 g (98%), mp 139–141°C. IR spectrum, ν, cm^{-1}: 1160, 1345 (SO_2), 1640 (C=N), 3100 (CH_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.82, 8.11 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$), 8.52 s (2H, N=CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 92.15 (CCl_3), 128.22, 129.51, 140.10, 146.27 (4,4'-$C_6H_4C_6H_4$), 164.80 (N=CH).

Compounds **IIb, IIIa, IIIb, IVa**, and **IVb** were obtained by the same procedure.

***N,N'*-Bis(2,2-dichloroethylidene)biphenyl-4,4'-disulfonamide (IIb)** was obtained from 4.50 g (10 mmol) of compound **Ia** and 20 g (200 mmol) of dichloroethylene. Yield 4.80 g (96%), mp 157–159°C. IR spectrum, ν, cm^{-1}: 1150, 1340 (SO_2), 1640 (C=N), 3100 (CH_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.12 d (2H, $CHCl_2$, ^3J 6.8 Hz), 7.79, 8.05 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$), 8.40 d (2H, N=CH, ^3J 6.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 66.91 ($CHCl_2$), 128.49, 129.30, 139.15, 145.12 (4,4'-$C_6H_4C_6H_4$), 165.84 (N=CH).

4,4'-Methylenebis[*N*-(2,2,2-trichloroethylidene)-benzenesulfonamide] (IIIa) was obtained from 4.64 g (10 mmol) of compound **Ib** and 26 g (200 mmol) trichloroethylene. Yield 5.70 g (97%), mp 160–161°C. IR spectrum, ν, cm^{-1}: 1140, 1320 (SO_2), 1630 (C=N), 2930 (CH_{Alk}), 3150 (C–H_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.15 s (2H, CH_2), 7.36, 7.91 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$), 8.47 C (2H, N=CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 42.35 (CH_2), 93.18 (CCl_3), 129.67, 130.07, 137.24, 145.57 (4,4'-$C_6H_4CH_2C_6H_4$), 164.30 (N=CH).

4,4'-Methylenebis[N-(2,2-dichloroethylidene)-benzenesulfonamide] (IIIb) was obtained from 4.64 g (10 mmol) of compound **Ib** and 20 g (200 mmol) of dichloroethylene. Yield 5.0 g (97%), mp 154–155°C. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 1630 (C=N), 2920 (CH_{Alk}), 3150 (CH_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.14 s (2H, CH_2), 6.15 d (2H, $CHCl_2$, ^3J 6.4 Hz), 7.36, 8.35 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$), 8.35 d (2H, N=CH, ^3J 6.4 Hz).

4,4'-Oxibis[N-(2,2,2-trichloroethylidene)-benzenesulfonamide] (IVa) was obtained from 4.66 g

(10 mmol) of compound **Ic** and 26 g (200 mmol) of trichloroethylene. Yield 5.50 g (95%), mp 175°C. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 1630 (C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.22, 8.01 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$), 8.50 s (2H, N=CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 93.87 (CCl_3), 119.87, 131.46, 138.89, 161.46 (4,4'-$C_6H_4OC_6H_4$), 164.42 (N=CH).

4,4'-Oxybis[*N*-(2,2-dichloroethylidene)benzenesulfonamide] (IVb) was obtained from 4.66 g (10 mmol) of compound **Ic** and 20 g (200 mmol) of dichloroethylene. Yield 5.0 g (97%), mp 145–147°C. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 1635 (C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.12 d (2H, $CHCl_2$, ^3J 6.5 Hz), 7.94, 8.06 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$), 8.35 d (2H, N=CH, ^3J 6.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 67.80 ($CHCl_2$), 120.61, 132.12, 137.18, 161.80 (4,4'-$C_6H_4OC_6H_4$), 166.39 (N=CH).

***N,N'*-Bis(2,2,2-trichloro-1-hydroxyethyl)biphenyl-4,4'-disulfonamide (Va).** *a*. In an open air was kept for 5 h 2.86 g (5 mmol) of bisimine **IIa**, and therewith disulfonamide **Va** formed in a quantitative yield 3.03 g.

b. A mixture of 3.12 g (10 mmol) of 1,1'-biphenyl-4,4'-disulfonamide, 4.41 g (30 mmol) of chloral, 50 ml of CCl_4, and 0.1–0.2 ml of concn. H_2SO_4 was stirred for 3 h at 60°C. The precipitate formed in the reaction was filtered off, washed with water till neutral washings, and dried in a vacuum desiccator over P_2O_5. Yield 5.46 g (90%), mp 172єC. IR spectrum, ν, cm^{-1}: 1140, 1330 (SO_2), 3250 (NH), 3450 (OH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.24 d (2H, NCH, $^3J_{CH–NH}$ 9.2 Hz), 7.96, 8.02 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$), 9.02 d (2H, NH, $^3J_{CH–NH}$ 9.2 Hz). Found, %: C 31.55; H 2.29; Cl 35.56; N 4.43; S 10.71. $C_{16}H_{14}Cl_6N_2O_6S_2$. Calculated, %: C 31.65; H 2.32; Cl 35.04; N 4.61; S 10.56.

***N,N'*-Bis(2,2-dichloro-1-hydroxyethyl)biphenyl-4,4'-disulfonamide (Vb)** was synthesized by procedure *a* from 2.50 g (5 mmol) of bisimine **IIb**. Yield 2.65 g (98%), mp 151–153єC. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 3230 (NH), 3450 (OH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.06 d.d (2H, NCH, $^3J_{CH–CH}$ 4.0, $^3J_{CH–NH}$ 8.9 Hz), 6.02 d (2H, $CHCl_2$, $^3J_{CH–CH}$ 4.0 Hz), 7.94, 7.98 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$), 8.72 d (2H, NH, $^3J_{CH–NH}$ 8.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 74.90 ($CHCl_2$), 80.73 (NCH), 127.45, 127.55, 141.89, 142.22 (4,4'-$C_6H_4C_6H_4$). Found, %: C 35.56; H 2.91; Cl 26.77; N 5.03; S 12.26. $C_{16}H_{16}Cl_4N_2O_6S_2$. Calculated, %: C 35.70; H 3.00; Cl 26.35; N 5.20; S 11.91.

4,4'-Methylenebis[*N*-(2,2,2-trichloro-1-hydroxyethyl)benzenesulfonamide] (VIa) was synthesized by procedure *a* from 2.93 g (5 mmol) of bisimine **IIIa** in the yield 3.00 g (97%) and by method *b* from 3.26 g (10 mmol) of 4,4'-methylenedibenzenesulfonamide in the yield 5.40 g (87%), mp 163–165°C. IR spectrum, ν, cm^{-1}: 1140, 1330 (SO_2), 3250 (NH), 3400 (OH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.12 s (2H, CH_2), 5.20 d (2H, CH, $^3J_{CH–NH}$ 9.3 Hz) 7.48, 7.84 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$), 8.85 d (2H, NH, $^3J_{CH–NH}$ 9.3 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 41.18 (CH_2), 85.70 (NCH), 102.34 (CCl_3), 127.11, 129.27, 139.91, 145.26 (4,4'-$C_6H_4CH_2C_6H_4$). Found, %: C 32.60; H 2.67; Cl 34.60; N 5.01; S 10.41. $C_{17}H_{16}Cl_6N_2O_6S_2$. Calculated, %: C 32.87; H 2.60; Cl 34.25; N 4.51; S 10.32.

4,4'-Methylenebis[*N*-(2,2-dichloro-1-hydroxyethyl)benzenesulfonamide] (VIb) was synthesized by procedure *a* from 2.58 g (5 mmol) of bisimine **IIIb**. Yield 2.62 g (95%), mp 133–135°C. IR spectrum, ν, cm^{-1}: 1150, 1320 (SO_2), 3250 (NH), 3400 (OH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.11 s (2H, CH_2), 5.00 d.d (2H, NCH, $^3J_{CH–CH}$ 4.0, $^3J_{CH–NH}$ 8.3 Hz), 5.97 d (2H, $CHCl_2$, $^3J_{CH–CH}$ 4.0 Hz), 7.44, 7.79 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$), 8.55 d (2H, NH, $^3J_{CH–NH}$ 8.3 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 41.05 (CH_2), 75.51 ($CHCl_2$), 81.34 (NCH), 126.68, 129.78, 140.88, 145.17 (4,4'-$C_6H_4CH_2C_6H_4$). Found, %: C 36.80; H 3.21; Cl 25.62; N 5.03; S 11.73. $C_{17}H_{18}Cl_4N_2O_6S_2$. Calculated, %: C 36.97; H 3.29; Cl 25.68; N 5.07; S 11.61.

4,4'-Oxybis[*N*-(2,2,2-trichloro-1-hydroxyethyl)-benzenesulfonamide] (VIIa) was synthesized by procedure *a* from 2.94 g (5 mmol) of bisimine **IVa** in the yield 3.10 g (98%) and by procedure *b* from 3.28 g (10 mmol) of 4,4'-oxydibenzenesulfonamide in the yield 5.73 g (92%), mp 183єC. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 3220 (NH), 3470 (OH). ^1H NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 5.46 d (2H, NCH, $^3J_{CH–NH}$ 9.6 Hz), 7.23, 8.02 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$), 7.77 d (2H, NH, $^3J_{CH–NH}$ 9.6 Hz). ^{13}C NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 86.83 (NCH), 102.55 (CCl_3), 119.98, 130.63, 138.42, 160.43 (4,4'-$C_6H_4OC_6H_4$). Found, %: C 30.75; H 2.18; Cl 34.48; N 4.64; S 10.52. $C_{16}H_{14}Cl_6N_2O_7S_2$. Calculated, %: C 30.84; H 2.26; Cl 34.14; N 4.50; S 10.29.

4,4'-Oxybis[*N*-(2,2-dichloro-1-hydroxyethyl)-benzenesulfonamide] (VIIb) was synthesized by procedure *a* from 2.60 g (5 mmol) of bisimine **IVb**. Yield 2.65 g (96%), mp 110–113°C. IR spectrum, ν, cm^{-1}: 1150, 1340 (SO_2), 3250 (NH), 3450 (OH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.01 d.d (2H, CH–N, $^3J_{CH–CH}$ 4.2,

$^3J_{CH–NH}$ 8.8 Hz), 6.00 d (2H, $CHCl_2$, $^3J_{CH–CH}$ 4.2 Hz), 7.22, 7.91 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$), 8.62 d (2H, NH, $^3J_{CH–NH}$ 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 75.31 ($CHCl_2$), 81.11 (CHN), 119.40, 129.79, 138.08, 159.13 ($C_6H_4OC_6H_4$). Found, %: C 34.65; H 2.88; Cl 25.52; N 4.98; S 11.48. $C_{16}H_{16}Cl_4N_2O_7S_2$. Calculated, %: C 34.67; H 2.91; Cl 25.59; N 5.05; S 11.57.

***N,N'*-Bis(2,2,2-trichloro-1-methoxyethyl)biphenyl-4,4'-disulfonamide (VIIIa).** To a solution of bisimine **IIa** in trichloroethylene obtained as described above was poured 4 ml (100 mmol) of anhydrous methanol. The reaction mixture was left standing for 24 h, evaporated in a vacuum, and the residue was recrystallized from a mixture acetone–chloroform, 1:1, and dried in a vacuum desiccator over P_2O_5. Yield 4.70 g (74%), mp 93–95°C. IR spectrum, ν, cm^{-1}: 1160, 1330 (SO_2), 3280 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.30 s (6H, OCH_3), 5.10 d (2H, NCH, $^3J_{CH–NH}$ 9.0 Hz), 7.94, 8.05 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$), 8.78 d (2H, NH, $^3J_{CH–NH}$ 9.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 58.36 (OCH_3), 93.11 (CH), 100.41 (CCl_3), 127.04, 128.87, 141.75, 145.83 (4,4'-$C_6H_4C_6H_4$). Found, %: C 34.25; H 3.02; Cl 33.20; N 4.37; S 10.18. $C_{18}H_{18}Cl_6N_2O_6S_2$. Calculated, %: C 34.04; H 2.86; Cl 33.49; N 4.41; S 10.09.

Compounds **IXa, IXb, Xa**, and **Xb** were similarly obtained.

4,4'-Methylenebis[*N*-(2,2,2-trichloro-1-methoxyethyl)benzenesulfonamide] (IXa) was obtained from bisimine **IIIa**. Yield 4.54 g (70%), mp 84–86°C. IR spectrum, ν, cm^{-1}: 1140, 1340 (SO_2), 3250 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.23 s (6H, OCH_3), 4.14 s (2H, CH_2), 4.95 d (2H, NCH, $^3J_{CH–NH}$ 9.0 Hz), 7.40, 7.86 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$), 8.78 d (2H, NH, $^3J_{CH–NH}$ 9.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 40.90 (CH_2), 57.71 (OCH_3), 93.12 (NCH), 100.06 (CCl_3), 127.52, 129.61, 140.35, 145.91 (4,4'-$C_6H_4CH_2C_6H_4$). Found, %: C 30.75; H 3.15; Cl 32.48; N 4.44; S 10.21. $C_{19}H_{20}Cl_6N_2O_6S_2$. Calculated, %: C 35.15; H 3.11; Cl 32.77; N 4.31; S 9.88.

4,4'-Methylenebis[*N*-(2,2-dichloro-1-methoxyethyl)benzenesulfonamide] (IXb) was obtained from bisimine **IIIb**. Yield 4.17 g (72%), mp 65–67°C. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 3250 (NH). ^{1}H NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 3.71 s (6H, OCH_3), 4.64 s (2H, CH_2), 5.34 d (2H, NCH, $^3J_{CH–CH}$ 3.6 Hz), 6.43 d (2H, $CHCl_2$, $^3J_{CH–CH}$ 3.6 Hz), 7.90, 8.33 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$). ^{13}C NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 40.89 (CH_2), 56.18 (OCH_3), 72.54 ($CHCl_2$), 88.35 (NCH), 127.52, 129.61, 140.35, 145.91 (4,4'-$C_6H_4CH_2C_6H_4$). Found, %: C 39.08; H 3.58; Cl 24.15; N 4.64; S 11.12. $C_{19}H_{22}Cl_4N_2O_6S_2$. Calculated, %: C 39.32; H 3.82; Cl 24.44; N 4.83; S 11.05.

4,4'-Oxybis[*N*-(2,2,2-trichloro-1-methoxyethyl)benzenesulfonamide] (Xa) was obtained from bisimine **IVa**. Yield 5.20 g (80%), mp 80–82°C. IR spectrum, ν, cm^{-1}: 1140, 1320 (SO_2), 3280 (NH). ^{1}H NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 3.59 s (6H, OCH_3), 4.97 d (2H, NCH, $^3J_{CH–NH}$ 9.7 Hz), 5.70 d (2H, NH, $^3J_{CH–NH}$ 9.7 Hz), 7.10, 7.94 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$). ^{13}C NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 58.49 (OCH_3), 92.69 (NCH), 99.03 (CCl_3), 119.60, 129.23, 136.26, 159.78 (4,4'-$C_6H_4OC_6H_4$). Found, %: C 33.12; H 2.71; Cl 32.88; N 4.07; S 9.35. $C_{18}H_{18}Cl_6N_2O_7S_2$. Calculated, %: C 33.20; H 2.79; Cl 32.67; N 4.30; S 9.85.

4,4'-Oxybis[*N*-(2,2-dichloro-1-methoxyethyl)benzenesulfonamide] (Xb) was obtained from bisimine **IVb**. Yield 4.36 g (75%), mp 75–77°C. IR spectrum, ν, cm^{-1}: 1140, 1320 (SO_2), 3250 (NH). ^{1}H NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 3.41 s (6H, OCH_3), 5.01 d (2H, NCH, $^3J_{CH–NH}$ 3.6 Hz), 6.12 d (2H, $CHCl_2$, $^3J_{CH–CH}$ 3.6 Hz), 7.35, 8.10 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$). ^{13}C NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 56.96 (OCH_3), 73.29 ($CHCl_2$), 89.17 (NCH), 119.85, 128.72, 130.43, 158.67 (4,4'-$C_6H_4OC_6H_4$). Found, %: C 36.85; H 3.28; Cl 24.15; N 4.67; S 10.58. $C_{18}H_{20}Cl_4N_2O_7S_2$. Calculated, %: C 37.13; H 3.46; Cl 24.35; N 4.81; S 11.01.

***N,N'*-{Biphenyl-4,4'-diylbis[sulfonylimino-(2,2,2-trichloroethane-1,1-diyl)]}bis(2-chloroacetamide) (XIa).** To a solution of imine **IIa** in trichloroethylene was added 3.76 g (40 mmol) of chloroacetamide preliminary dried for 5 h in a vacuum over P_2O_5 at 90–100°C. The reaction mixture was stirred for 8 h at 70–80°C. The precipitate was filtered off, washed with 20 ml of chloroform, and dried. Yield 4.77 g (65%), mp 168–170°C. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 1670 (C=O), 3230 br.s (NH), 3330 br.s (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.93 *AB* (4H, CH_2Cl), 5.91 d.d (2H, NCH, $^3J_{CH–NHC(O)}$ 9.0, $^3J_{CH–NHSO_2}$ 9.5 Hz), 8.95 d (2H, $NHSO_2$, $^3J_{CH–NHSO_2}$ 9.5 Hz), 9.19 d [2H, NHC(O), $^3J_{CH–NHC(O)}$ 9.0 Hz], 7.87, 7.95 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 42.21 (CH_2Cl), 85.73 (CHN), 102.15 (CCl_3), 128.33, 129.53, 142.25, 146.31 ($C_6H_4C_6H_4$), 165.22 (C=O). Found, %: C 31.71; H 2.42; Cl 37.15; N 7.34; S 8.48. $C_{20}H_{18}Cl_8N_4O_6S_2$. Calculated, %: C 31.69; H 2.39; Cl 37.41; N 7.39; S 8.46.

***N,N'*-{Oxybis[4,1-phenylenesulfonylimino-(2,2,2-trichloroethane-1,1-diyl)]}bis(2-chloroacetamide) (XIIa)** was prepared similarly from bisimine **IVa**. Yield 4.64 g (60%), mp 142–144°C. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 3230 (NH), 3350 (NH), 1660 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.99 *AB* (4H, CH_2Cl), 5.88 d.d (2H, NCH, $^3J_{CH–NHC(O)}$ 9.3, $^3J_{CH–NHSO_2}$ 9.5 Hz), 7.31, 7.84 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$), 8.89 d (2H, $NHSO_2$, $^3J_{CH–NH}$ 9.5 Hz), 9.13 d [2H, NHC(O), $^3J_{CH–NH}$ 9.3 Hz]. ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 41.70 (CH_2Cl), 85.66 (CHNH), 100.16 (CCl_3), 128.26, 129.38, 139.71, 158.31 (4,4'-$C_6H_4OC_6H_4$), 166.02 (C=O). Found, %: C 31.08; H 2.39; Cl 36.59; N 7.27; S 8.32. $C_{20}H_{18}Cl_8N_4O_7S_2$. Calculated, %: C 31.03; H 2.34; Cl 36.64; N 7.24; S 8.28.

***N,N'*-Bis[2,2,2-trichloro-1-(4-methylphenyl)ethyl]-biphenyl-4,4'-disulfonamide (XIIIa).** To a solution of bisimine **IIa** in trichloroethylene was poured 0.5 ml of oleum (5–15% SO_3) and 15–20 ml of anhydrous toluene. The reaction mixture was stirred for 5 h, diluted with 50 ml of water, the precipitate was filtered off, washed with 50 ml of 25% aqueous ammonia, dried, and additionally recrystallized from acetone. Yield 5.66 g (75%), mp 130–132°C. IR spectrum, ν, cm^{-1}: 1150, 1330 (SO_2), 3250 (NH). ^1H NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 2.16 s (6H, $C_6H_4CH_3$), 5.22 s (2H, NCH), 6.96, 7.38 *AA'BB'* (8H, $C_6H_4CH_3$), 7.43, 7.67 *AA'BB'* (8H, 4,4'-$C_6H_4C_6H_4$). ^{13}C NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 20.23 ($C_6H_4CH_3$), 72.19 (NCH), 101.44 (CCl_3), 127.31, 127.50, 127.57, 128.27, 129.74, 138.54, 140.39, 143.07 (Ar). Found, %: C 47.75; H 3.51; Cl 27.98; N 3.68; S 8.65. $C_{30}H_{26}Cl_6N_2O_4S_2$. Calculated, %: C 47.70; H 3.47; Cl 28.16; N 3.71; S 8.49.

4,4'-Methylenebis{*N*-[2,2,2-trichloro-1-(4-methylphenyl)ethyl]benzenesulfonamide} (XIVa) was prepared similarly from bisimine **IIIa**. Yield 5.77 g (75%), mp 108–110°C. IR spectrum, ν, cm^{-1}: 1150, 1340 (SO_2), 3250 (NH). ^1H NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 2.23 s (6H, $C_6H_4CH_3$), 3.91 s (2H, CH_2), 5.18 s (2H, NCH), 6.97, 7.34 *AA'BB'* (8H, $C_6H_4CH_3$), 7.02, 7.53 *AA'BB'* (8H, 4,4'-$C_6H_4CH_2C_6H_4$). ^{13}C NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 21.22 (CH_3), 41.35 (CH_2), 72.94 (NCH), 102.50 (CCl_3), 128.00, 129.14, 129.83, 130.52, 132.12, 139.47, 139.95, 145.84 (Ar). Found, %: C 47.95; H 3.65; Cl 27.68; N 3.59; S 8.55. $C_{30}H_{26}Cl_6N_2O_4S_2$. Calculated, %: C 48.39; H 3.67; Cl 27.65; N 3.64; S 8.33.

4,4'-Oxybis{*N*-[2,2,2-trichloro-1-(4-methylphenyl)ethyl]benzenesulfonamide} (XVa) was prepared similarly from bisimine **IVa**. Yield 5.40 g (70%), mp 184–186°C. IR spectrum, ν, cm^{-1}: 1145, 1330 (SO_2), 3230 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.18 s (6H, CH_3), 5.13 s (2H, NCH), 6.93, 7.32 *AA'BB'* (8H, $C_6H_4CH_3$), 6.64, 7.56 *AA'BB'* (8H, 4,4'-$C_6H_4OC_6H_4$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 20.72 (CH_3), 71.32 (NCH), 101.70 (CCl_3), 118.23, 127.91, 129.03, 129.75, 130.72, 135.81, 137.93, 158.19 (Ar). Found, %: C 46.15; H 3.22; Cl 27.35; N 4.07; S 8.03. $C_{30}H_{26}Cl_6N_2O_5S_2$. Calculated, %: C 46.71; H 3.40; Cl 27.58; N 3.63; S 8.31.

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