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Dedicated to Full Member of the Russian Academy of Sciences G.A. Tolstikov on his 75th anniversary

Reactions of *N*-(Polychloroethylidene)arene- and -trifluoromethanesulfonamides with Indoles

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Abstract—*N*-(Polychloroethylidene)arene- and -trifluoromethanesulfonamides reacted with indole and N-substituted indoles to give the corresponding *N*-[2,2-dichloro(or 2,2,2-trichloro)-1-(1*H*-indol-3-yl)ethyl]-substituted sulfonamides. Unlike *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide, less electrophilic *N*-(polychloroethylidene)arenesulfonamides failed to react with 1-(4-nitrophenyl)-1*H*-indole. Previously unknown *N*,*N*′-bis(2,2-dichloroethylidene)biphenyl-4,4′-disulfonamide reacted with 1-benzyl-1*H*-indole at both azomethine fragments. Likewise, reactions of 1,6-bis(1*H*-indol-1-yl)hexane and 1,4-bis(1*H*-indol-1-ylmethyl)benzene with *N*-sulfonyl trichloroacetaldehyde imines involved both indole rings in the former.

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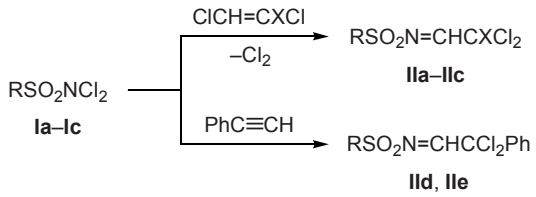
We previously showed [1] that indole and 1- and 2-methylindoles readily react with *N*-(2,2,2-trichloroethylidene)arenesulfonamides in the absence of a catalyst to give the corresponding *N*-[2,2,2-trichloro-1-(1*H*-indol-3-yl)ethyl]arenesulfonamides. These compounds attract interest due to unique combination in their molecules of an indole fragment and sulfonylamino and trichloromethyl groups which are responsible for their biological activity and ability to undergo further transformations. For example, amidotrichloroethyl-substituted indoles were used to synthesize biologically active *N*-substituted α-indolylglycines, i.e., heteroauxin derivatives modified with a sulfonylamino group [2]. Development of new procedures for the introduction of aminopolyhaloethyl substituents into indole and substituted indole molecules could provide convenient synthetic approaches to new amidoalkyl-substituted indoles as precursors of amino acids containing an indole ring, aminocarbonyl compounds, and heterocyclic systems; therefore, the importance of studies in this line is beyond doubt.

The present works continues our studies on the amidoalkylating activity of Schiff bases activated by strong electron-withdrawing substituents. We examined reactions of a series of *N*-sulfonyl polychloroacetaldehyde imines with indoles and some N-substituted indoles. Schiff bases **IIa**–**IIe** were synthesized by reactions of *N*,*N*-dichloroarene- and trifluoromethanesulfonamides **Ia**–**Ic** with trichloroethylene, 1,2-dichloroethylene, or phenylacetylene as shown in Scheme 1 [3–6]. Advantages of these procedures were demonstrated previously [7]. They include experimental simplicity, high yields of the target products, and the use of low-expensive and accessible reagents.

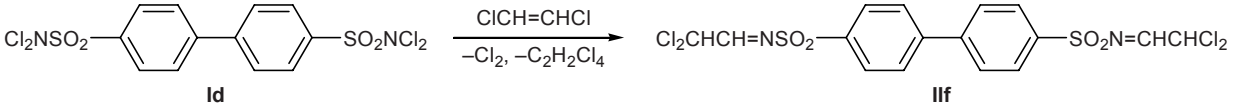
Scheme 1.



Ia, **IIa**, **IIc**, R = CF_3; **Ib**, **IIb**, **IId**, R = 4-ClC_6H_4; **Ic**, **IIe**, R = Ph; **IIa**, **IIb**, X = Cl; **IIc,** X = H.

Previously unknown *N*,*N*′-bis(2,2-dichloroethylidene)biphenyl-4,4′-disulfonamide (**IIf**) was obtained from *N*,*N*,*N*′,*N*′-tetrachlorobiphenyl-4,4′-disulfonamide (**Id**) [8] and 1,2-dichloroethylene (Scheme 2) by heating the reactants [molar ratio 1 : (20–30)] at the boiling

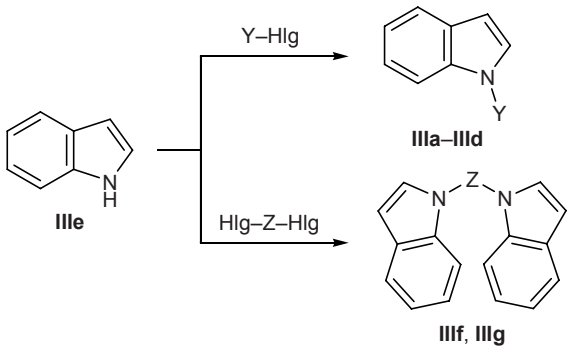
Scheme 2.



point over a period of 8 h. Unlike previously studied reactions of *N*,*N*-dichloroarenesulfonamides with 1,2-dichloroethylene, which resulted in the formation of mixtures of di- and trichloroethyl derivatives [9], the reaction of compound **Id** with 1,2-dichloroethylene selectively afforded *N*,*N*′-bis(2,2-dichloroethylidene)-substituted derivative **IIf**. A probable reason is lower reactivity of tetrachloro amide **Id** in the chlorination of 1,2-dichloroethene to trichloroethene; as a result, no sulfonamide and trichloroethylidene derivatives are formed as by-products.

Substituted indoles **IIIa**–**IIIc** were prepared according to the procedure reported in [10] for the synthesis of 1-methyl-1*H*-indole, by alkylation of indole (**IIIe**) with butyl bromide, allyl bromide, and benzyl chloride, respectively, in DMSO in the presence of alkali (Scheme 3). Considerable reduction of the amounts of solvent (by a factor of 2 to 3) and alkali (by a factor of 1.5) allowed us to increase the yield of substituted indoles **IIIa**–**IIIc** by 10–15%. 1-(4-Nitrophenyl)-1*H*-indole (**IIId**), 1,6-bis(1*H*-indol-1-yl)hexane (**IIIf**), and 1,4-bis(1*H*-indol-1-ylmethyl)benzene (**IIIg**) were synthesized in a similar way, by alkylation of unsubstituted indole (**IIIe**) with 4-fluoronitrobenzene, 1,6-dichlorohexane, and 1,4-bis(chloromethyl)benzene, respectively. The yields of **IIIa**–**IIIg** were 85–95%.

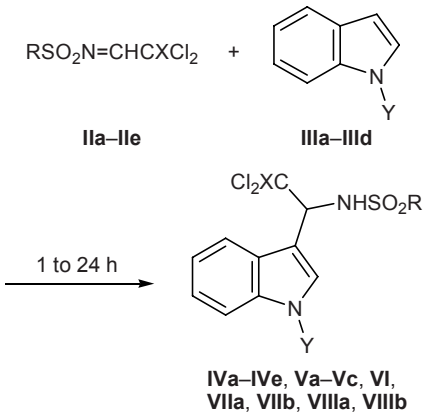
Scheme 3.



Y = Bu (**a**), CH_2=$CHCH_2$ (**b**), $PhCH_2$ (**c**), 4-$O_2NC_6H_4$ (**d**); Z = $(CH_2)_6$ (**f**), *p*-$CH_2C_6H_4CH_2$ (**g**).

Schiff bases **IIa**–**IIc** and **IIf** can be brought into reaction with indoles without isolation from the reaction mixture, which considerably simplifies the experimental procedure. The reactions of **IIa**–**IIe** with indoles **IIIa**–**IIIe** required neither catalyst nor elevated temperature and were accompanied by heat evolution. As a result, the corresponding C-amidoalkylation products, 3-substituted indoles **IV**–**VIII**, were formed in 50–97% yield (Scheme 4).

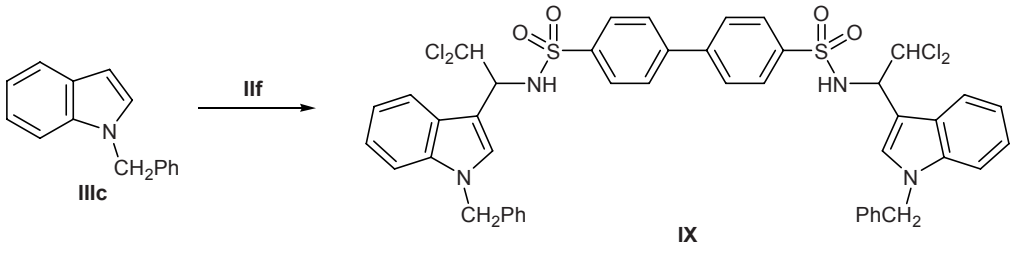
Scheme 4.



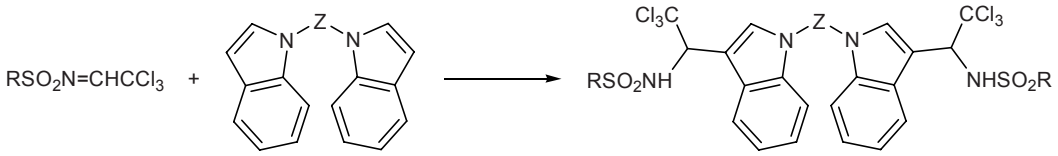
IIa, **IVa**–**IVg**, X = Cl, R = CF_3; **IIb**, **Va**–**Ve**, X = Cl, R = 4-ClC_6H_4; **IIc**, **VI**, X = H, R = CF_3; **IId**, **VIIa**, **VIIb**, X = Ph, R = 4-ClC_6H_4; **IIe**, **VIIIa**, **VIIIb**, X = R = Ph; **IIIa**, **IVa**, **Va**, Y = Bu; **IIIb**, **IVb**, **Vb**, Y = CH_2=$CHCH_2$; **IIIc**, **IVc**, **Vc**, **VI**, **VIIb**, **VIIIb**, Y = $PhCH_2$; **IIId**, **IVd**, Y = 4-$O_2NC_6H_4$; **IIIe**, **IVe**, **VIIa**, **VIIIa**, Y = H.

According to our previous data [4, 11], *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide (**IIa**) is more reactive than analogous N-substituted arenesulfonamides toward nucleophiles, as well as in C-amidoalkylation of arenes and hetarenes. Our present results also showed higher reactivity of compound **IIa** as compared to arenesulfonamides. For instance, 4-chloro-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide (**IIb**) failed to react with 1-(4-nitrophenyl)-1*H*-indole (**IIId**) even on prolonged heating in the presence of a catalyst (oleum, $BF_3 \cdot OEt_2$). Obviously, the C=N carbon atom in **IIb** is less electrophilic than that in **IIa**. The presence of a powerful electron-withdrawing trifluoromethylsulfonyl group activates Schiff base **IIa** so strongly that its reaction with unsubstituted indole (**IIIe**) is accompanied by heat evolution and tarring, which cannot be avoided even by cooling and dilution of the reaction mixture. As a result, the yield of substituted indole **IVe** considerably decreases, and its isolation from the reaction mixture is complicated. Less

Scheme 5.



Scheme 6.



R = CF_3 (**a**), 4-ClC_6H_4 (**b**); **IIIf**, **X**, Z = $(CH_2)_6$; **IIIg**, **XI**, Z = *p*-$CH_2C_6H_4CH_2$.

active *N*-(2,2,2-trichloroethylidene)arenesulfonamides reacted with unsubstituted indole to give about 40% of the corresponding C-amidoalkylation products, in keeping with our previous data [1]. Further decrease in electrophilicity of the azomethine fragment is observed in going to *N*-(2,2-dichloro-2-phenylethylidene)arenesulfonamides **IId** and **IIe**. No appreciable heat evolution was observed in the reactions of **IId** and **IIe** with indole (**IIIe**), the process was not accompanied by tarring, and the yields of **VIIa** and **VIIIa** attained 95%.

Thus the yields of amidoalkylated indole derivatives decrease as the electrophilicity of the CH=N carbon atom in Schiff bases **II** increases, presumably as a result of strong tarring. On the other hand, introduction of a substituent into position *1* of the indole ring ensures selective C-amidoalkylation with Schiff bases possessing different electrophilicities and good yields of the target products. *N*,*N*′-Bis(2,2-dichloroethylidene)biphenyl-4,4′-disulfonamide (**IIf**) reacted with 1-benzyl-1*H*-indole (**IIIc**) at a molar ratio of 1 : 2.2, both CH=N groups in the former being involved (Scheme 5). In this case, reduced electrophilicity of the $CHCl_2CH$=N fragment as compared to CCl_3CH=N does not hamper alkylation of *N*-benzylindole.

While developing procedures for the synthesis of polyfunctional derivatives of hitherto unknown linearly bridged bis-indoles, we examined reactions of bis-indoles **IIIf** and **IIIg** with *N*-(2,2,2-trichloroethylidene)sulfonamides **IIa** and **IIb**. These reactions were complete in 2–4 h at room temperature and were accompanied by slight heat evolution, and the products were compounds **Xa**, **Xb**, **XIa**, and **XIb** resulting from C-amidoalkylation at both indole rings.

The structure of compounds **IV**–**XI** was proved by spectral data and elemental analyses (see Experimental). The ^{1}H NMR spectra of indole derivatives **IV**–**XI** lacked signal from proton in the 3-position (δ 6.7 ppm in the spectra of initial indoles **IIIa**–**IIIe**). The $NHCHCCl_2X$ fragment in trichloroethyl derivatives **IVa**–**IVe**, **Va**–**Vc**, **Xa**, **Xb**, and **XIb** and dichloro(phenyl)ethyl derivatives **VII** and **VIII** gives rise to two doublets with a coupling constant $^3J_{HH}$ of 9.5–10.3 Hz; *N*-(2,2-dichloroethyl) amides **VI**–**IX** displayed two doublets from the NH and CCl_2H protons and a doublet of doublets from the NCH proton, in keeping with published data for structurally related *N*-polychloroethyl sulfonamides [3–6]. Protons in the NH groups are exchangeable with deuterium on prolonged storage of solutions in deuterated solvents. Aromatic protons resonate as a multiplet in the region δ 6.9–7.8 ppm, and the signal intensity ratio is consistent with the assumed structures.

In the ^{1}H NMR spectra of *N*-benzylindole derivatives **IVc**, **Vc**, **VI**, **VIIb**, and **VIIIb** and bis-indoles **XIa** and **XIb**, signals from diastereotopic protons in the benzylic CH_2 group appear as an *AB* spin system. Magnetic nonequivalence of these protons originates from the absence of a mirror symmetry plane and the presence of asymmetric centers in the side chain [12]. Figure 1 shows some fragments of the ^{1}H NMR spectra of *N*-benzylindole derivatives. It should be noted that the distances between the signals from diastereo-

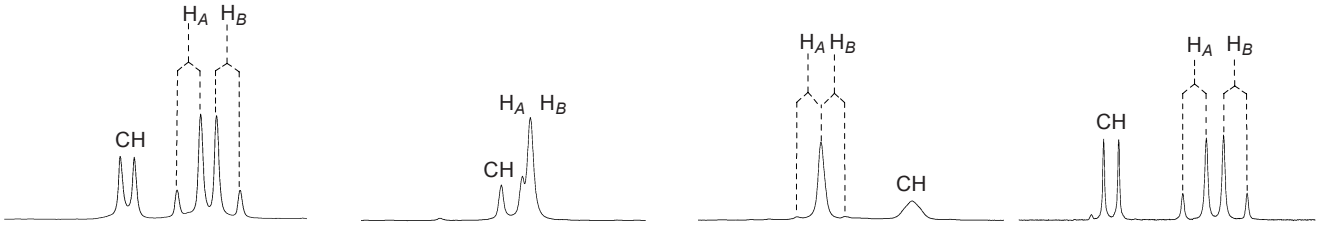


Fig. 1. Fragments of the ^{1}H NMR spectra of substituted *N*-benzylindoles **IVc**, **Vc**, **VI**, and **VIIb** in DMSO-d_6 in the resonance regions corresponding to the NCH_2 and NHC**H** protons.

topic CH_2 protons (Δδ) in compounds **IVc**, **Vc**, **VI**, and **VIIb** differ considerably due to different steric structures of substituents responsible for the formation of diastereoisomer pairs.

Even more interesting pattern was observed in the ^{1}H NMR spectrum of bis-indole **XIa** (Fig. 2). Two benzylic CH_2 groups in the chemically equivalent fragments of molecule **XIa** are characterized by different ^{1}H chemical shifts. Moreover, the difference in the resonance frequencies of the methylene protons depends on the solvent. In $CDCl_3$ two symmetric NHCH fragments give rise to two doublets from the CH protons and two doublets from the NH protons, while in DMSO-d_6 the same protons resonate as singlets as a result of exchange processes. We believe that the observed nonequivalence of protons in the two methylene groups of bis-indole **XIa** in DMSO-d_6 and $CDCl_3$ (Fig. 2) originates from formation of intra- or intermolecular hydrogen bonds. It should be noted that the appearance of the methylene proton signals in the ^{1}H NMR spectra of compound **VIIb** does not depend on the solvent nature to an appreciable extent; the difference in the chemical shifts of the CH_2 protons is 0.056 ppm in DMSO-d_6 and 0.052 ppm in $CDCl_3$ (cf. Δδ = 0.2 ppm for bis-indole **XIa**; Fig. 2).

Temperature effects in the ^{1}H NMR spectrum of bis-indole **XIa** in DMSO-d_6 are also interesting. Raising the temperature to 100°C leads to coalescence of the methylene proton signals to give a singlet typical of an A_2 spin system. In contrast, the difference in the chemical shifts of the methylene protons in the ^{1}H NMR spectrum of **VIIb** increases from 0.056 ppm at 25°C to 0.065 ppm at 100°C. The ^{1}H NMR spectra of *N*-alkyl (**IVa**, **Va**) and *N*-allyl derivatives (**IVb**, **Vb**) in the NCH_2 resonance region conform to ABX_2 and *ABX* spin systems, respectively.

To conclude, we have studied how the structure of *N*-(polychloroethyl) sulfonamides affects their C-amidoalkylating activity toward indole and its N-substituted derivatives. We have developed convenient preparative procedures for the synthesis of 3-(2-polychloro-1-sulfonylaminoethyl)-substituted indoles and bridged 1,6-bis(1*H*-indol-1-yl)hexane and 1,4-bis(1*H*-indol-1-ylmethyl)benzene, as well as of the C-amidoalkylation product of 1-benzyl-1*H*-indole with newly synthesized bis-imine, *N*,*N*′-bis(2,2-dichloroethylidene)biphenyl-4,4′-bis(sulfonamide). The compounds obtained in the present work attract interest as potential biologically active substances and substrates for further transformations.

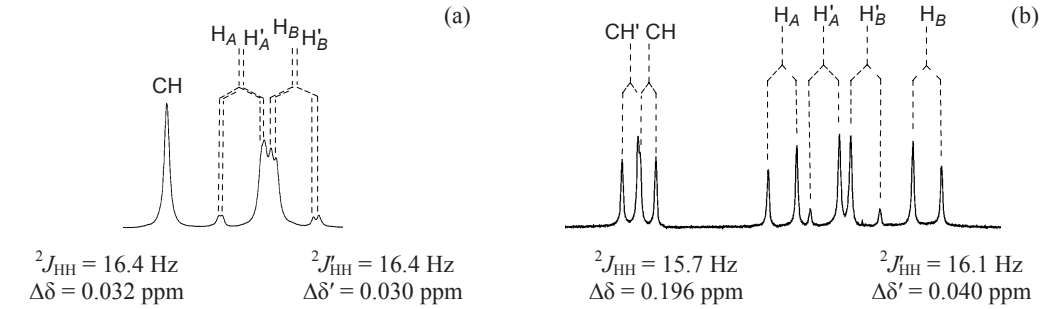


Fig. 2. Fragments of the ^{1}H NMR spectra of 1,6-bis[3-(2,2,2-trichloro-1-trifluoromethylsulfonylaminoethyl)-1*H*-indol-1-yl]hexane (**Xa**) in the resonance regions corresponding to the NCH_2 and NHC**H** protons, recorded in (a) DMSO-d_6 and (b) $CDCl_3$.

EXPERIMENTAL

The IR spectrum was recorded in KBr on a Specord 75IR spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 spectrometer at 400.13 and 101.61 MHz, respectively, from solutions in chloroform-*d* or DMSO-d_6. The chemical shifts were measured relative to tetramethylsilane with an accuracy of 0.01 ppm, and the coupling constants (J_{HH} and J_{CF}) were determined with an accuracy of 0.1 Hz.

Initial Schiff bases **IIa** [4], **IIb** [3], **IIc** [5], **IId**, and **IIe** [6] were synthesized by known methods.

***N*,*N*′-Bis(2,2-dichloroethylidene)biphenyl-4,4′-bis(sulfonamide) (IIf).** A solution of 4.5 g (0.01 mol) of tetrachloroamide **Id** in 20 ml of 1,2-dichloroethylene was heated under reflux in a continuous stream of argon until chlorine no longer evolved (7–9 h). The mixture was kept for 24 h at 0°C, and the precipitate was separated by decanting, washed with carbon tetrachloride, and dried over P_2O_5 under reduced pressure. Yield 4.81 g (96%), mp 157–159°C. IR spectrum, ν, cm^{-1}: 1150, 1340 (SO_2); 3100 (C–H_{arom}); 1640 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.12 d (2H, $CHCl_2$, $^3J_{HH}$ = 6.8 Hz), 7.79 d and 8.05 d (8H, H_{arom}, *AA′BB′* system), 8.40 d (2H, N=CH, $^3J_{HH}$ = 6.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 66.91 ($CHCl_2$); 128.49, 129.30, 139.15, 145.12 (C_{arom}); 165.84 (N=CH). Found, %: C 38.59; H 2.36; Cl 27.65; N 5.42; S 12.43. $C_{16}H_{12}Cl_4N_2O_4S_2$. Calculated, %: C 38.17; H 2.41; Cl 28.24; N 5.58; S 12.77.

General procedure for the synthesis of 1-substituted indoles. Indole (**IIIe**), 11.71 g (0.1 mol), was added to a solution of 12 g (0.3 mol) of sodium hydroxide in 50 ml of DMSO, the mixture was stirred for 15–20 min and cooled to 10–15°C, and the corresponding alkylating agent [0.05 mol of 1,6-dichlorohexane, 0.05 mol of 1,4-bis(chloromethyl)benzene, or 0.1 mol of 4-fluoronitrobenzene], was slowly added dropwise (in portions). The mixture was stirred for 3 h at room temperature and poured into 200 ml of ice-cold water, and the precipitate was filtered off, washed with water, dried, washed with diethyl ether, and dried again.

1-(4-Nitrophenyl)-1*H*-indole (IIId). Yield 22.3 g (93%), mp 127–129°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.78 s (1H, 3-H), 7.18 t (1H, 5-H), 7.26 t (1H, 6-H), 7.66–7.75 m (3H, 3-H, 4-H, 7-H), 7.85 d and 8.39 d (4H, C_6H_4, *AA′BB′* system). ^{13}C NMR spectrum, δ_C, ppm: 106.35, 111.22, 121.89, 121.94, 123.71, 123.96, 125.92, 128.29, 130.87, 135.70, 145.49, 145.57. Found, %: C 70.27; H 4.20; N 11.81. $C_{14}H_{10}N_2O_2$. Calculated, %: C 70.58; H 4.23; N 11.76.

1,6-Bis(1*H*-indol-1-yl)hexane (IIIf). Yield 14.5 g (92%), mp 82–85°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 br.s (4H, CH_2), 1.76 m (4H, CH_2), 4.12 t (4H, NCH_2), 6.42 s (2H, 3-H), 7.01 t (2H, 5-H), 7.12 t (2H, 6-H), 7.19 s (2H, 2-H), 7.37 d (2H, 4-H), 7.55 d (2H, 7-H). ^{13}C NMR spectrum, δ_C, ppm: 26.69, 30.45, 46.16, 101.06, 109.97, 119.37, 121.08, 121.51, 128.51, 129.30, 136.63. Found, %: C 83.22; H 7.68; N 8.72. $C_{22}H_{24}N_2$. Calculated, %: C 83.50; H 7.64; N 8.85.

1,4-Bis(1*H*-indol-1-ylmethyl)benzene (IIIg). Yield 15.2 g (90%), mp 140–143°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.17 s (4H, CH_2), 6.48 d (2H, 3-H), 6.93 s (4H, C_6H_4), 7.00–7.18 m (8H, 2-H, 4-H, 5-H, 6-H), 7.58 d (2H, 7-H). ^{13}C NMR spectrum, δ_C, ppm: 48.83 (CH_2), 101.05, 110.13, 119.14, 120.52, 121.22, 127.22, 128.36, 129.07, 135.77, 137.44. Found, %: C 85.75; H 5.92; N 8.26. $C_{24}H_{20}N_2$. Calculated, %: C 85.68; H 5.99; N 8.33.

General procedure for the C-amidoalkylation of indoles. A solution of 0.01 mol of indole **IIIa–IIId** or 0.005 mol of bis-indole **IIIf** or **IIIg** in 3–4 ml of anhydrous carbon tetrachloride was added in portions (insoluble indoles were added in portions as solids) to a reaction mixture containing 0.01 mol of Schiff base **IIa**, **IIb**, or **IIc**. After 6 h, the precipitate was filtered off, washed on a filter with cold hexane, and dried under reduced pressure.

***N*-[1-(1-Butyl-1*H*-indol-3-yl)-2,2,2-trichloroethyl]trifluoromethanesulfonamide (IVa)** was obtained from compound **IIa** and 1.73 g of *N*-butylindole. Yield 3.84 g (85%), mp 144–146°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.28 m (2H, CH_2), 1.81 m (2H, CH_2), 4.13 d.t (2H, CH_2, $^3J_{HH}$ = 7.0, $^2J_{HH}$ = 2.9 Hz), 5.57 d (1H, CH, $^3J_{HH}$ = 10.1 Hz), 6.17 d (1H, NH, $^3J_{HH}$ = 10.1 Hz), 7.15 t (1H, 5-H), 7.22 t (1H, 6-H), 7.28 s (1H, 2-H), 7.31 d (1H, 7-H), 7.66 d (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 13.62 (CH_3), 19.93 (CH_2), 32.02 (CH_2), 46.49 (CH_2), 66.66 (CH), 101.53 (CCl_3), 107.96 (C^3), 109.99 (C^7), 119.03 (C^4), 120.58 (C^5), 122.50 (C^6), 127.15 (C^{3a}), 127.43 (C^2), 135.48 (C^{7a}), 114.41, 117.60, 120.79, 123.98 q (CF_3, $^1J_{CF}$ = 320.8 Hz). Found, %: C 39.59; H 3.54; Cl 23.48; N 6.24; S 7.15. $C_{15}H_{16}Cl_3F_3N_2O_2S$. Calculated, %: C 39.88; H 3.57; Cl 23.55; N 6.20; S 7.10.

***N*-[1-(1-Allyl-1*H*-indol-3-yl)-2,2,2-trichloroethyl]-trifluoromethanesulfonamide (IVb)** was obtained from Schiff base **IIa** and 1.57 g of *N*-allylindole. Yield 4.01 g (92%), mp 145°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.82 d (1H, CH_2, $^3J_{HH}$ = 17.1 Hz), 4.88 d (1H, NCH_2, $^3J_{HH}$ = 4.4 Hz), 5.14 d (1H, CH=, $^3J_{HH}$ = 10.2 Hz), 5.57 s (1H, $CHCCl_3$), 6.03 m (1H, CH_2=), 7.12 t (1H, 5-H), 7.18 t (1H, 5-H), 7.46 d (1H, 7-H), 7.75 m (2H, 2-H, 4-H), 11.03 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 48.15 (NCH_2), 65.97 (CHNH), 102.23 (CCl_3), 107.80 (C^3), 110.47 (C^7), 116.35 (=CH_2), 118.70 (C^4), 120.15 (C^5), 121.82 (C^6), 127.16 (C^{3a}), 129.46 (C^2), 134.10 (CH=), 135.10 (C^{7a}), 114.35, 117.55, 120.76, 123.96 q (CF_3, $^1J_{CF}$ = 322.5 Hz). Found, %: C 38.46; H 2.75; Cl 24.32; N 6.45; S 7.39. $C_{14}H_{12}Cl_3F_3N_2O_2S$. Calculated, %: C 38.60; H 2.78; Cl 24.41; N 6.43; S 7.36.

***N*-[1-(1-Benzyl-1*H*-indol-3-yl)-2,2,2-trichloroethyl]trifluoromethanesulfonamide (IVc)** was obtained from Schiff base **IIa** and 2.07 g of *N*-benzylindole. Yield 4.71 g (97%), mp 178–180°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.34 and 5.39 (1H each, CH_2, *AB* system, $^2J_{HH}$ = 16.1 Hz), 5.50 d (1H, CH, $^3J_{HH}$ = 9.5 Hz), 7.00–7.28 m (8H, C_6H_5, 7-H, 5-H, 6-H), 7.67 m (1H, 4-H), 7.77 s (1H, 2-H), 10.42 d (1H, NH, $^3J_{HH}$ = 9.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 49.92 (CH_2), 66.00 (CHNH), 102.24 (CCl_3), 108.64 (C^3), 109.95 (C^7), 118.63 (C^4), 120.15 (C^5), 121.96 (C^6), 126.33, 127.42, 127.62 (C^{3a}), 128.50, 129.56 (C^2), 135.17 (C^{7a}), 137.04, 114.41, 117.62, 120.82, 123.02 q (CF_3, $^1J_{CF}$ = 322.2 Hz). Found, %: C 44.39; H 2.90; Cl 22.03; N 5.70; S 6.67. $C_{18}H_{14}Cl_3F_3N_2O_2S$. Calculated, %: C 44.51; H 2.91; Cl 21.90; N 5.77; S 6.60.

***N*-{2,2,2-Trichloro-1-[1-(4-nitrophenyl)-1*H*-indol-3-yl]ethyl}trifluoromethanesulfonamide (IVd)** was obtained from Schiff base **IIa** and 2.38 g of *N*-(4-nitrophenyl)indole. Yield 4.91 g (95%), mp 155–157°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.70 s (1H, $CHCCl_3$), 7.27–7.35 m (2H, 5-H, 6-H), 7.75 d (1H, 7-H), 7.98 d (1H, 4-H), 8.24 s (1H, 2-H), 7.88 and 8.47 (4H, C_6H_4, *AA′BB′* system), 11.12 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 65.44 (CH), 101.53 (CCl_3), 110.98 (C^3), 112.67 (C^7), 118.32 (C^4), 119.74 (C^5), 122.08 (C^6), 123.73, 125.73, 128.41 (C^{3a}), 128.80 (C^2), 133.99 (C^{7a}), 143.76, 145.16, 114.30, 117.50, 120.70, 123.78 q (CF_3, $^1J_{CF}$ = 322.2 Hz). Found, %: C 39.37; H 2.15; Cl 20.45; N 8.15; S 6.18. $C_{17}H_{11}Cl_3F_3N_3O_4S$. Calculated, %: C 39.52; H 2.15; Cl 20.58; N 8.13; S 6.20.

***N*-[2,2,2-Trichloro-1-(1*H*-indol-3-yl)ethyl]trifluoromethanesulfonamide (IVe).** A solution of 1.17 g of indole (**IIIe**) in 5 ml of carbon tetrachloride was added dropwise under stirring to a reaction mixture containing Schiff base **IIa**, cooled to –5°C. The mixture was allowed to warm up to room temperature, and the solvent was evaporated under reduced pressure. According to the NMR data, the residue, 4.00 g, was a tarry mixture of products. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.58 d (1H, CH, $^3J_{HH}$ = 9.5 Hz), 6.69 d (1H, NH, $^3J_{HH}$ = 9.5 Hz), 7.10–7.45 m (4H, 2-H, 5-H, 6-H, 7-H), 7.65 d (1H, 4-H), 8.38 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 66.48 (CH), 101.27 (CCl_3), 109.63 (C^3), 111.61 (C^7), 118.70 (C^4), 120.86 (C^5), 122.96 (C^6), 124.26 (C^2), 126.34 (C^{3a}), 135.14 (C^{7a}), 114.30, 117.49, 120.68, 123.89 q (CF_3, $^1J_{CF}$ = 321.4 Hz).

***N*-[1-(1-Butyl-1*H*-indol-3-yl)-2,2,2-trichloroethyl]-4-chlorobenzenesulfonamide (Va)** was synthesized from Schiff base **IIb** and 1.73 g of *N*-butylindole. Yield 4.24 g (86%), mp 186–188°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.87 t (3H, CH_3, $^3J_{HH}$ = 7.3 Hz), 1.13 m (CH_2), 1.56 m (CH_2), 3.97 m (2H, CH_2), 5.33 s (1H, CH), 7.01 t (1H, 5-H), 7.09 t (1H, 6-H), 7.29 d (1H, 7-H), 7.41 s (1H, 2-H), 7.51 d (4-H), 6.97, 7.41 (4H, C_6H_4, *AA′BB′* system), 8.90 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.02 (CH_3), 19.80 (CH_2), 32.09 (CH_2), 45.73 (CH_2), 65.91 (CH), 103.26 (CCl_3), 108.03 (C^3), 110.11 (C^7), 118.85 (C^4), 120.02 (C^5), 121.81 (C^6), 127.92 (C^{3a}), 129.22 (C^2), 135.08 (C^{7a}), 128.55, 137.28, 139.41 (C_6H_4). Found, %: C 48.52; H 4.02; Cl 28.47; N 5.69; S 6.44. $C_{20}H_{20}Cl_4N_2O_2S$. Calculated, %: C 48.60; H 4.08; Cl 28.69; N 5.67; S 6.49.

***N*-[1-(1-Allyl-1*H*-indol-3-yl)-2,2,2-trichloroethyl]-4-chlorobenzenesulfonamide (Vb)** was obtained from Schiff base **IIb** and 1.57 g of *N*-allylindole. Yield 3.91 g (82%), mp 187–190°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.64 d (2H, NCH_2, $^3J_{HH}$ = 4.0 Hz), 4.79 d (1H, CH_2, $^3J_{HH}$ = 17.1 Hz), 5.11 d (1H, CH=, $^3J_{HH}$ = 10.3 Hz), 5.34 s (1H, $CHCCl_3$), 5.84 m (1H, CH_2=), 7.02 t (1H, 5-H), 7.09 t (1H, 6-H), 7.25 d (1H, 7-H), 7.43 s (1H, 2-H), 7.52 d (1H, 4-H), 7.02 and 7.41 (4H, C_6H_4, *AA′BB′*), 8.99 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 48.55 (NCH_2), 65.87 (CHNH), 103.15 (CCl_3), 108.53 (C^3), 110.37 (C^7), 117.33 (=CH_2), 118.91 (C^4), 120.21 (C^5), 121.97 (C^6), 127.95 (C^{3a}), 128.55, 128.66, 129.32 (C^2), 134.14 (CH=), 135.15 (C^{7a}), 137.36, 139.42. Found, %: C 47.61; H 3.35; Cl 29.48; N 5.88; S 6.62.

$C_{19}H_{16}Cl_4N_2O_2S$. Calculated, %: C 47.72; H 3.37; Cl 29.65; N 5.86; S 6.70.

***N*-[1-(1-Benzyl-1*H*-indol-3-yl)-2,2,2-trichloroethyl]-4-chlorobenzenesulfonamide (Vc)** was obtained from Schiff base **IIb** and 2.07 g of *N*-benzylindole. Yield 4.64 g (88%), mp 205–207°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.31 s (2H, CH_2), 5.33 d (1H, CH, $^3J_{HH}$ = 10.1 Hz), 6.80–7.44 m (12H, C_6H_5, C_6H_4, 7-H, 5-H, 6-H), 7.49 d (1H, 4-H), 7.69 s (1H, 2-H), 9.09 d (1H, NH, $^3J_{HH}$ = 10.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 49.94 (CH_2), 65.83 (CH), 103.36 (CCl_3), 108.93 (C^3), 110.55 (C^7), 119.00 (C^4), 120.30 (C^5), 122.17 (C^6), 127.77, 128.10 (C^{3a}), 128.15, 128.68, 128.72, 129.17, 129.76 (C^2), 135.12 (C^{7a}), 137.43, 138.16, 139.42. Found, %: C 52.37; H 3.45; Cl 26.70; N 5.24; S 6.95. $C_{23}H_{18}Cl_4N_2O_2S$. Calculated, %: C 52.29; H 3.43; Cl 26.84; N 5.30; S 6.07.

***N*-[1-(1-Benzyl-1*H*-indol-3-yl)-2,2-dichloroethyl]-trifluoromethanesulfonamide (VI)** was obtained from Schiff base **IIc** and 2.07 g of *N*-benzylindole. Yield 3.52 g (78%), mp 124°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.29 br.s (1H, CH), 5.45 s (2H, CH_2), 6.54 d (1H, $CHCl_2$, $^3J_{HH}$ = 4.9 Hz), 7.03–7.34 m (7H, C_6H_5, 5-H, 6-H), 7.44 d (1H, 7-H), 7.72 m (2H, 2-H, 4-H), 10.62 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 49.30 (CH_2), 59.18 (CH), 74.96 ($CHCl_2$), 109.5 (C^3), 110.54 (C^7), 118.75 (C^4), 119.79 (C^5), 121.92 (C^6), 126.03 (C^{3a}), 126.79, 127.46 (C^2), 128.55, 128.85, 135.67, 137.82, 114.49, 117.69, 120.89, 124.10 q (CF_3, $^1J_{CF}$ = 322.2 Hz). Found, %: C 47.64; H 3.30; Cl 15.58; N 6.18; S 7.71. $C_{18}H_{15}Cl_2F_3N_2O_2S$. Calculated, %: C 47.91; H 3.35; Cl 15.71; N 6.21; S 7.10.

4-Chloro-*N*-[2,2-dichloro-1-(1*H*-indol-3-yl)-2-phenylethyl]benzenesulfonamide (VIIa). A solution of 3.62 g (0.01 mol) of Schiff base **IId** and 1.17 g (0.01 mol) of indole (**IIIe**) in 50 ml of anhydrous carbon tetrachloride was stirred for 2 h. The precipitate was filtered off and purified by reprecipitation from aqueous ammonia. Yield 4.56 g (95%), mp 128–130°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.39 d (1H, CH, $^3J_{HH}$ = 10.3 Hz), 6.80 t (1H, 5-H), 6.93–7.66 m (13H, C_6H_4, C_6H_5, 2-H, 4-H, 6-H, 7-H), 8.58 d (1H, NH, $^3J_{HH}$ = 10.3 Hz), 10.89 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 63.63 (CH), 96.97 (CCl_2), 110.10 (C^3), 111.45 (C^7), 118.34 (C^4), 119.22 (C^5), 121.27 (C^6), 126.06–140.49 (C_{arom}), 127.29 (C^{3a}), 129.58 (C^2), 135.06 (C^{7a}). Found, %: C 54.89; H 3.52; Cl 21.92; N 5.76; S 6.59. $C_{22}H_{17}Cl_3N_2O_2S$. Calculated, %: C 55.07; H 3.57; Cl 22.07; N 5.84; S 6.68.

***N*-[1-(1-Benzyl-1*H*-indol-3-yl)-2,2-dichloro-2-phenylethyl]-4-chlorobenzenesulfonamide (VIIb).** A mixture of 3.62 g (0.001 mol) of Schiff base **IId** and 2.07 g (0.001 mol) of *N*-benzylindole in 40 ml of anhydrous carbon tetrachloride was stirred for 2 h. The precipitate was filtered off and recrystallized from benzene. Yield 5.00 g (88%), mp 139–141°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.20 (2H, CH_2, *AB* system), 5.38 d (1H, CH, $^3J_{HH}$ = 10.1 Hz), 6.79 t (1H, 5-H), 6.93 t (1H, 6-H), 7.06–7.65 m (14H, C_6H_5, C_6H_4), 7.18 d (1H, 7-H), 7.21 d (1H, 4-H), 7.34 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 49.00 (CH_2), 62.98 (CH), 96.24 (CCl_2), 109.27 (C^3), 109.53 (C^7), 118.28 (C^4), 118.95 (C^5), 121.01 (C^6), 127.00–139.75 (C_{arom}), 127.08 (C^{3a}), 129.03 (C^2), 134.28 (C^{7a}). Found, %: C 60.96; H 4.15; Cl 18.35; N 4.73; S 5.52. $C_{29}H_{23}Cl_3N_2O_2S$. Calculated, %: C 61.12; H 4.07; Cl 18.66; N 4.92; S 5.63.

***N*-[2,2-Dichloro-1-(1*H*-indol-3-yl)-2-phenylethyl]-benzenesulfonamide (VIIIa).** A solution of 3.28 g (0.01 mol) of Schiff base **IIe** and 1.17 g (0.01 mol) of indole (**IIIe**) in 40 ml of anhydrous carbon tetrachloride was stirred for 2 h. The precipitate was filtered off and purified by reprecipitation from aqueous ammonia. Yield 4.09 g (92%), mp 117–119°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.42 d (1H, CH, $^3J_{HH}$ = 10.3 Hz), 6.72 t (1H, 5-H), 7.01–7.79 m (14H, C_6H_5, 2-H, 4-H, 6-H, 7-H), 7.65 d (1H, NH, $^3J_{HH}$ = 10.1 Hz), 10.01 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 65.05 (CH), 95.48 (CCl_2), 112.48 (C^3), 113.85 (C^7), 121.39 (C^4), 121.98 (C^5), 123.45 (C^6), 126.31–145.89 (C_{arom}), 126.99 (C^{3a}), 130.01 (C^2), 134.87 (C^{7a}). Found, %: C 59.75; H 4.18; Cl 15.37; N 6.55; S 7.06. $C_{22}H_{18}Cl_2N_2O_2S$. Calculated, %: C 59.33; H 4.07; Cl 15.92; N 6.29; S 7.20.

***N*-[1-(1-Benzyl-1*H*-indol-3-yl)-2,2-dichloro-2-phenylethyl]benzenesulfonamide (VIIIb).** A mixture of 3.28 g (0.01 mol) of Schiff base **IIe** and 2.07 g (0.01 mol) of *N*-benzylindole in 50 ml of anhydrous carbon tetrachloride was stirred for 2 h. The precipitate was filtered off and recrystallized from benzene. Yield 4.55 g (85%), mp 130–132°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.18 (2H, CH_2, *AB* system), 5.42 d (1H, CH, $^3J_{HH}$ = 10.0 Hz), 6.91 t (1H, 5-H), 6.99 t (1H, 6-H), 7.08–7.71 m (15H, C_6H_5), 7.21 d (1H, 7-H), 7.23 d (1H, 4-H), 7.37 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 51.98 (CH_2), 63.13 (CH), 95.15 (CCl_2), 108.67 (C^3), 110.18 (C^7), 119.95 (C^4), 120.02 (C^5), 122.31 (C^6), 126.18–144.12 (C_{arom}), 127.55 (C^{3a}), 128.62 (C^2), 135.48 (C^{7a}). Found,

%: C 65.88; H 4.58; Cl 13.63; N 5.36; S 5.52. $C_{29}H_{24}Cl_2N_2O_2S$. Calculated, %: C 65.05; H 4.52; Cl 13.24; N 5.23; S 5.99.

***N*,*N*′-Bis[1-(1-benzyl-1*H*-indol-3-yl)-2,2-dichloroethyl]biphenyl-4,4′-bis(sulfonamide) (IX).** *N*-Benzylindole, 4.56 g (0.022 mol), was added in portions under continuous stirring to the reaction mixture obtained as described above from 4.50 g of tetrachloro amide **Id** and 20 ml of 1,2-dichloroethylene (it contained 0.01 mol of Schiff base **IIf**). The mixture was stirred for 5 h, and the precipitate was filtered off, washed with diethyl ether, and dried. Yield 6.42 g (70%), mp 122–124°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.10 d.d (2H, CH, $^3J_{HH}$ = 4.4, 8.8 Hz), 5.22 s (4H, NCH_2), 6.43 d (2H, $CHCl_2$, $^3J_{HH}$ = 4.4 Hz), 6.84–7.25 m (22H, C_6H_4, C_6H_5, 5-H, 6-H), 7.40 d (2H, 7-H), 7.54 s (2H, 2-H), 7.58 d (2H, 4-H), 8.74 d (2H, NH, J_{HH} = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 49.50 (NCH_2), 57.30 (CHNH), 74.93 ($CHCl_2$), 108.74 (C^3), 109.19 (C^4), 118.02 (C^7), 119.05 (C^5), 121.28 (C^6), 126.05, 126.40, 126.52, 126.58, 127.09, 128.08, 128.13, 134.79 (C^{7a}), 136.63, 139.89, 141.88. Found, %: C 60.32; H 4.11; Cl 15.48; N 6.03; S 7.11. $C_{46}H_{38}Cl_4N_4O_4S_2$. Calculated, %: C 60.27; H 4.18; Cl 15.47; N 6.11; S 6.99.

1,6-Bis[3-(2,2,2-trichloro-1-trifluoromethylsulfonylaminoethyl)-1*H*-indol-1-yl]hexane (Xa) was obtained from Schiff base **IIa** and 1.58 g of bis-indole **IIIf**. Yield 3.66 g (84%), mp 186–189°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.13 br.s (4H, CH_2), 1.66 br.s (4H, CH_2), 4.16 m (4H, CH_2), 5.51 s (2H, $CHCCl_3$), 7.09 t (2H, 5-H), 7.15 t (2H, 6-H), 7.44 d (2H, 7-H), 7.72 m (4H, 2-H, 4-H), 10.95 br.s (2H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.46 (CH_2), 29.22 (CH_2), 45.64 (CH_2), 65.98 (CH), 102.25 (CCl_3), 107.17 (C^3), 110.12 (C^7), 118.64 (C^4), 119.89 (C^5), 121.55 (C^6), 127.07 (C^{3a}), 129.31 (C^2), 134.83 (C^{7a}), 114.23, 117.44, 120.64, 123.85 q (CF_3, $^1J_{CF}$ = 322.5 Hz). Found, %: C 38.48; H 3.02; Cl 24.18; N 6.39; S 7.33. $C_{28}H_{26}Cl_6F_6N_4O_4S_2$. Calculated, %: C 38.51; H 3.00; Cl 24.36; N 6.42; S 7.34.

1,6-Bis{3-[2,2,2-trichloro-1-(4-chlorophenylsulfonylamino)ethyl]-1*H*-indol-1-yl}hexane (Xb) was obtained from Schiff base **IIb** and 1.58 g of bis-indole **IIIf**. Yield 4.12 g (86%), mp 182–185°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.20 s (4H, CH_2), 1.56 s (4H, CH_2), 3.96 s (4H, NCH_2), 5.31 d (2H, $CHCCl_3$), 7.00 t (2H, 5-H), 7.07 t (2H, 6-H), 7.26 d (2H, 7-H), 7.41 s (2H, 2-H), 7.50 d (2H, 4-H), 6.95 and 7.39 (8H, C_6H_4, *AA′BB′* system), 8.97 s (2H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.26 (CH_2), 30.04 (CH_2), 46.08 (CH_2), 66.07 (CH), 103.34 (CCl_3), 108.24 (C^3), 110.18 (C^7), 119.03 (C^4), 120.17 (C^5), 121.96 (C^6), 128.02 (C^{3a}), 128.63, 128.69, 129.36 (C^2), 135.17 (C^{7a}), 137.41, 139.47. Found, %: C 47.60; H 3.55; Cl 29.45; N 5.78; S 6.64. $C_{38}H_{34}Cl_8N_4O_4S_2$. Calculated, %: C 47.62; H 3.58; Cl 29.59; N 5.85; S 6.69.

1,4-Bis[3-(2,2,2-trichloro-1-trifluoromethylsulfonylaminoethyl)-1*H*-indol-1-ylmethyl]benzene (XIa) was obtained from Schiff base **IIa** and 1.68 g of bis-indole **IIIg**. Yield 3.97 g (89%), mp 131–133°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.30 t (4H, CH_2), 5.55 s (2H, $CHCCl_3$), 6.97 s (4H, C_6H_4), 7.10 m (4H, 5-H, 6-H), 7.38 m (2H, 7-H), 7.75 d (2H, 4-H), 7.87 s (2H, 2-H), 11.00 br.s (2H, NH). ^{13}C NMR spectrum, δ_C, ppm: 48.87 (CH_2), 65.80 ($CHCCl_3$), 102.08 (CCl_3), 107.84 (C^3), 110.47 (C^7), 118.66 (C^4), 120.13 (C^5), 121.80 (C^6), 126.50, 127.21 (C^{3a}), 129.94 (C^2), 134.89 (C^{7a}), 136.98, 114.19, 117.40, 120.60, 123.80 q (CF_3, $^1J_{CF}$ = 322.7 Hz). Found, %: C 40.26; H 2.44; Cl 23.85; N 6.19; S 7.15. $C_{30}H_{22}Cl_6F_6N_4O_4S_2$. Calculated, %: C 40.33; H 2.48; Cl 23.81; N 6.27; S 7.18.

1,4-Bis{3-[2,2,2-trichloro-1-(4-chlorophenylsulfonylamino)ethyl]-1*H*-indol-1-ylmethyl}benzene (XIb) was obtained from Schiff base **IIb** and 1.68 g of bis-indole **IIIg**. Yield 4.20 g (86%), mp 123°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.23 s (4H, CH_2), 5.27 d (2H, $CHCCl_3$, $^3J_{HH}$ = 10.2 Hz), 6.84–7.50 m (20H, C_6H_4, 2-H, 7-H, 5-H, 6-H), 7.64 d (2H, 4-H), 9.05 d (2H, NH, $^3J_{HH}$ = 10.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 49.45 (CH_2), 65.79 (CH), 103.32 (CCl_3), 108.93 (C^3), 110.48 (C^7), 119.06 (C^4), 120.18 (C^5), 122.03 (C^6), 127.77, 127.95 (C^{3a}), 128.60, 128.66, 129.81 (C^2), 135.10 (C^{7a}), 137.30, 137.50, 139.44. Found, %: C 49.15; H 3.12; Cl 28.76; N 5.71; S 6.49. $C_{40}H_{30}Cl_8N_4O_4S_2$. Calculated, %: C 49.10; H 3.09; Cl 28.99; N 5.73; S 6.55.

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