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Note

Configurational assignment of *N*-arylsulfonylimines of α-polychloroaldehydes

Leonid B. Krivdin,* Kirill A. Chernyshev, Gulnur N. Rosentsveig, Irina V. Ushakova, Igor B. Rosentsveig and Galina G. Levkovskaya

A. E. Favorsky Institute of Chemistry, Irkutsk, Siberian Branch of the Russian Academy of Sciences, Favorsky St. 1, 664033 Irkutsk, Russia

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Configurational assignment of seven synthesized *N*-arylsulfonylimines of α-polychloroaldehydes has been carried out by means of experimental measurements and high-level *ab initio* calculations of their $^{13}C-^{13}C$, $^{13}C-^{1}H$ and $^{15}N-^{1}H$ spin–spin coupling constants. The title compounds were shown to exist in solution solely in the form of *E* isomers, in line with thermodynamic reasoning. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: NMR; spin–spin coupling constant; SOPPA; configurational assignment; *N*-arylsulfonylimines of polychloroaldehydes

INTRODUCTION

Functional derivatives of polyhaloaldimines are widely used in organic synthesis, which is mainly due to the presence of the azomethine moiety in their structure activated by strong electron-withdrawing substituents.[1] As an example, the electron-deficient character of the azomethine group of polyhalogenaldimines promotes their interaction with numerous nucleophiles, amidoalkylation of aromatic and heteroaromatic compounds as well as cycloaddition reactions which open the efficient and versatile route to the wide variety of cyclic and open-chain polyfunctional, halogen-containing, biologically active amides,[2] the precursors of α-amino aldehydes and α-amino acids.

In spite of the fact that first syntheses of chloral imines were reported as long as a century ago and synthetic potential of the halogen-containing azomethines had been heavily exploited during past several decades,[1] physicochemical investigations of the azomethine derivatives of polychloroaldehydes are currently limited to the identification of their structure with the only exception of the detailed ^{35}Cl NQR study of several chloral arylsulfonylimines.[3]

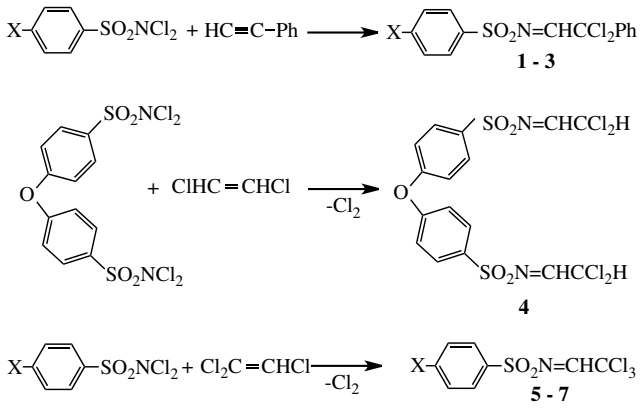
In the present paper, seven representative members of the α-polychloroaldimines series including arylsulfonylimines of phenyldichloroacetaldehyde **1**–**3**, dichloroacetaldehyde **4** and chloral **5**–**7** were synthesized for the detailed stereochemical study by means of NMR substantiated by the high-level *ab initio* calculations. The most convenient route to the sulfonylimines of α-polychloroaldehydes used in the present study is based on the one-pot interaction of *N*,*N*-dichloroamides of sulfonic acids with 1,2-polychloroethenes or phenylacetylene,[1] as shown in Scheme 1.

RESULTS AND DISCUSSION

It is noteworthy that all synthesized arylsulfonylimines of α-polychloroaldehydes **1**–**7** exist in solution in the individual imine form with no traces of the possible enamide tautomer, as follows from the analysis of their ^{13}C NMR spectra. Signal assignments of ^{13}C resonances were based on the 2D INADEQUATE tracing out of their carbon skeletons, as exemplified in Fig. 1 for *N*-(2-phenyl-2,2-dichloroethylidene)-4-methylbenzenesulfonamide (**2**). Configurational ascertainments of **1**–**7** were performed on the basis of $^{1}J(C,H)$, $^{1}J(C,C)$ and $^{2}J(N,H)$ coupling constants measured accordingly from the proton-coupled and 1D INADEQUATE ^{13}C NMR spectra and 2D HMBC $^{15}N-^{1}H$ experiments substantiated by their theoretical calculations performed at the second-order polarization propagator approach (SOPPA)[4] level taking into account all four coupling contributions, namely Fermi contact, J_{FC}, spin–dipolar, J_{SD}, diamagnetic spin–orbital, J_{DSO}, and paramagnetic spin–orbital, J_{PSO}, terms (for details, see 'Experimental').

Characteristic ^{13}C chemical shifts together with the experimental $^{1}J(C,H)$, $^{1}J(C,C)$ and $^{2}J(N,H)$ coupling constants confirming the structures of **1**–**7** are compiled in Table 1, while the results of their theoretical calculations in the model *N*-(2,2-dichloroethylidene)sulfinamide (**8**) and *N*-(2,2,2-trichloroethylidene)sulfinamide (**9**) are given in Table 2. All SOPPA calculations of spin–spin coupling constants were performed using the MP2/6-311G** optimized equilibrium geometries of **8** and **9** (Fig. 2). It follows from the

*Correspondence to: Leonid B. Krivdin, Institute of Chemistry, Irkutsk, Siberian Branch of the Russian Academy of Sciences, Favorsky St. 1, 664033 Irkutsk, Russia.
E-mail: krivdin_office@irioch.irk.ru; http://krivdin.irk.ru



X = H (**1**, **5**), CH3 (**2**, **6**), Cl (**3**, **7**).

Scheme 1. Synthesis of *N*-arylsulfonylimines of α-polychloroaldehydes **1**–**7**.

analysis of data presented in Table 2 that generally a good agreement between calculated ^1J(C,H), ^1J(C,C) and ^2J(N,H) coupling constants (J_{calc}) and their experimental values (J_{exp}) is achieved. It is noteworthy that the Fermi contact contribution by far dominates the values of ^1J(C-1,H$^\alpha$) and ^1J(C-1,C-2), while in the case of ^2J(N,H$^\alpha$) it totals to only *ca* 65% leaving as much as *ca* 35% to the paramagnetic spin–orbital contribution to the total value of this spin–spin coupling, which emphasizes the importance of the noncontact contributions to be taken into account in the analysis of stereoelectronic effects.

Comparison of the experimental values of ^1J(C-1,H$^\alpha$), ^1J(C-1,C-2) and ^2J(N,H$^\alpha$) measured in **1**–**7** (Table 1) with their theoretical values calculated in **8** and **9** (Table 2) leaves no doubt that all synthesized arylsulfonylimines of α-polychloroaldehydes under study have the *E* configuration at the C=N bond, in line with thermodynamic reasoning: hypothetical diverse *Z* isomers of arylsulfonylimines of α-polychloroaldehydes are less stable by *ca* 42 kJ/mol due to the pronounced steric effects at the C=N bond, as found at the MP2/6-311G** level for **8** and **9**. Indeed, steric strain in *Z* isomers is monitored by the increased values of their bond angles ∠C(1)–C(2)–N and ∠C(2)–N–S by *ca* 12° as compared to the corresponding *E* isomers (Fig. 2).

Dramatic difference of ^1J(C-1,H$^\alpha$), ^1J(C-1,C-2) and ^2J(N,H$^\alpha$) in *E* and *Z* isomers of arylsulfonylimines of α-polychloroaldehydes, which is used here for the configurational assignment of **1**–**7**, should be ascribed to the well-known orientational nitrogen lone pair effect in azomethines (for guideline, see very recent review by Krivdin and Contreras[5] and references quoted therein). In the case of arylsulfonylimines of α-polychloroaldehydes **1**–**7**, this lone pair effect should result in larger values (in absolute magnitude) of ^1J(C-1,H$^\alpha$) and ^2J(N,H$^\alpha$) and in smaller values of ^1J(C-1,C-2) in *Z* as compared to *E* isomers.

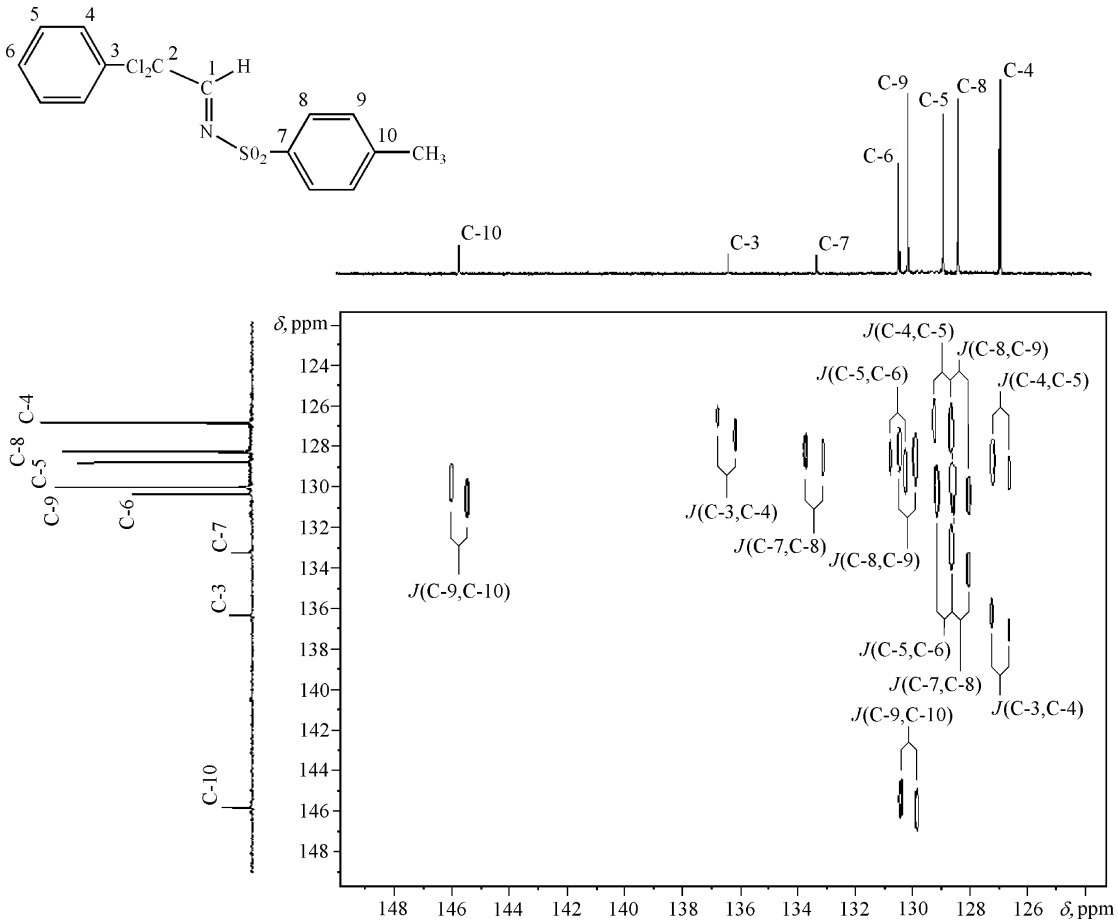


Figure 1. The 2D INADEQUATE spectrum of (*E*)-*N*-(2-phenyl-2,2-dichloroethylidene)-4-methylbenzenesulfonamide (**2**) in $CDCl_3$ (100.61 MHz).

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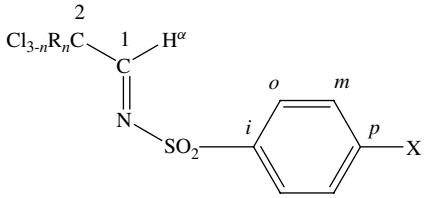
Table 1. ^{13}C Chemical shifts, $^{13}C-^{13}C$, $^{13}C-^{1}H$ and $^{15}N-^{1}H$ spin–spin coupling constants of *N*-arylsulfonylimines of α-polychloroaldehydes **1**–**7** (10% solutions in $CDCl_3$)



Compound	Chemical shifts, δ, ppm						Spin–spin coupling constants, *J*, Hz		
	C-1	C-2	C^i	C^o	C^m	C^p	^1J (C-1,C-2)	^1J(C-1,H^α)	^2J(N,H^α)
1	168.22	85.73	136.39	128.36	129.47	134.45	53.9	183.0	(+)2.8
2	167.61	85.71	133.24	128.34	130.07	145.67	53.8	182.7	(+)2.7
3	168.59	85.70	135.16	129.01	129.87	141.33	53.7	182.6	(+)2.8
4	165.72	67.07	132.14	131.35	119.84	160.72	55.1	182.4	(+)2.9
5	164.26	92.15	137.27	128.87	129.57	134.51	60.3	187.4	(+)2.9
6	163.78	91.75	133.11	128.66	130.15	146.05	59.7	188.0	(+)3.1
7	164.56	91.82	135.20	130.19	130.01	141.79	59.9	188.0	(+)3.0

CONCLUSIONS

Arylsulfonylimines of α-polychloroaldehydes **1**–**7** synthesized by the one-pot interaction of *N,N*-dichloroamides of sulfonic acids with 1,2-polychloroethanes or phenylacetylene were shown to exist in solution in the individual imine form with *E* configuration at the C═N bond with no traces of the possible enamide tautomer, as follows from the experimental measurements and SOPPA calculations of their $^{13}C-^{13}C$, $^{13}C-^{1}H$ and $^{15}N-^{1}H$ spin–spin coupling constants and in line with thermodynamic reasoning.

EXPERIMENTAL

NMR measurements

^{1}H,^{13}C, and ^{15}N NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer (^{1}H, 400.16 MHz;^{13}C, 100.61 MHz; ^{15}N, 40.55 MHz) in a 5-mm broadband probe at 25 °C in $CDCl_3$ with HMDS (or TMS) as an internal standard. Carbon–carbon coupling constants were measured from the ^{13}C satellites in the proton-decoupled ^{13}C NMR spectra and also using the 1D and 2D INADEQUATE pulse sequence adjusted for $J = 55$ Hz. Settings for the INADEQUATE experiments were as follows: 90° pulse length, 12–14 μs; spectral width, 10–15 kHz; acquisition time, 4 s; relaxation delay, 6 s; characteristic delay $\tau = 1/4J$, 2.8 ms; digital resolution 0.05–0.1 Hz/pt; accumulation time, 12 h. Carbon–hydrogen coupling constants were measured from the proton-coupled ^{13}C NMR spectra using the same spectral widths, acquisition times, relaxation delays and digital resolutions as in the INADEQUATE experiments. Nitrogen–hydrogen coupling constant were measured using the HMBC standard pulse sequence adjusted for $J = 3$ Hz. Settings for the HMBC experiments were as follows: pulse length, 6 μs (^{1}H), 27.1 μs (^{15}N); spectral width, 400 Hz (^{1}H), 20 kHz (^{15}N); acquisition time, 0.16 s; relaxation delay, 2.5 s; digital resolution 0.1 Hz; accumulation time, 4 h.

Table 2. Spin–spin coupling constants $^{13}C-^{13}C$, $^{13}C-^{1}H$ and $^{15}N-^{1}H$ of the model *N*-(2,2-dichloroethylidene)sulfinamide (**8**) and *N*–(2,2,2-trichloroethylidene)sulfinamide (**9**) calculated at the SOPPA level[a]

Compound	Isomer	Coupling constant	J_{calc}[b]	J_{exp}
8	*E*	^1J(C-1,C-2)	52.7	53.9[c]
		^1J(C-1,H^α)	179.5	183.0[c]
		^2J(N,H^α)	3.2	2.8[c]
	Z	^1J(C-1,C-2)	41.9	
		^1J(C-1,H^α)	187.4	
		^2J(N,H^α)	– 18.6	
9	*E*	^1J(C-1,C-2)	59.0	60.3[d]
		^1J(C-1,H^α)	189.2	187.4[d]
		^2J(N,H^α)	3.3	2.9[d]
	Z	^1J(C-1,C-2)	43.9	
		^1J(C-1,H^α)	200.6	
		^2J(N,H^α)	– 13.0	

[a] All couplings in Hz.

[b] All four coupling contributions, namely Fermi contact, J_{FC}, spin–dipolar, J_{SD}, diamagnetic spin–orbital, J_{DSO}, and paramagnetic spin–orbital, J_{PSO}, terms are taken into account.

[c] Measured in cmpound **1**.

[d] Measured in cmpound **5**.

Computational details

Geometric optimizations were performed with the GAMESS code[6] at the MP2 perturbation level[7] using the 6-311G** basis set of Pople and coworkers[8] without symmetry constraints, i.e. assuming the C_1 symmetry point group. Calculations of spin–spin coupling constants were carried out by taking into account all four nonrelativistic coupling contributions with the DALTON package[9] at the SOPPA level[4] using the stationary equilibrium geometries located at the MP2/6-311G** level. Correlation-consistent basis set cc-pVDZ[10] augmented with two core *s*-functions of Woon and Dunning[11] on coupled carbons, cc-pVDZ-Cs, was

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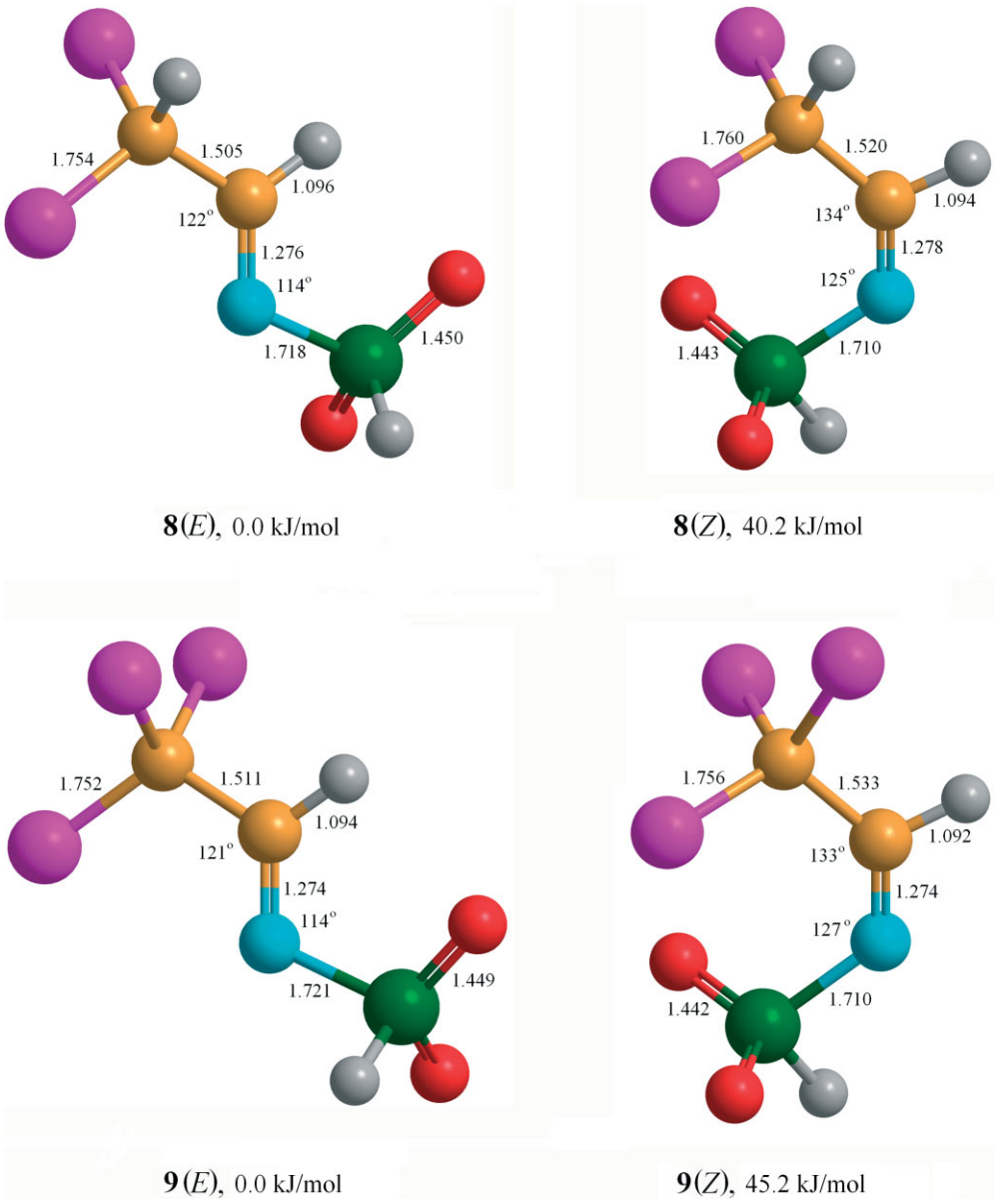

Figure 2. The MP2/6-311G** optimized equilibrium geometries and relative energies of *E* and *Z* isomers of the model *N*-(2,2-dichloroethylidene)sulfinamide (**8**) and *N*-(2,2,2-trichloroethylidene)sulfinamide (**9**). Element colors: hydrogen – gray, carbon – yellow, nitrogen – blue, oxygen – red, sulfur – green, chlorine – violet. Bond lengths are given in Å and bond angles in degrees.

applied, as specified elsewhere.[12] Accordingly, coupled hydrogens were assigned with the basis set aug-cc-pVTZ-J of Sauer *et al.*[13] including four tight *s*-functions. Coupled nitrogens were specified with Dunning's cc-pCVDZ,[11] while the rest of atoms (uncoupled) were specified with cc-pVDZ.[10]

Synthesis

General experimental procedure for the synthesis of N-(2-phenyl-2,2-dichloroethylidene)arylsulfonamides ***1–3***

N,N-Dichloroamide of arylsulfonic acid (30 mmol) was added portionwise to the solution of phenyl acetylene (40 mmol) in CCl_4 (20 ml) under argon with stirring to avoid overheating to more than 40 °C. Once the self-heating interaction had been stopped, the reaction mixture was stirred for 3 h at 60 °C, and then allowed to stand at −5 °C till a precipitate of the imines **1–3** was formed. The precipitate was separated, washed with cold CCl_4 (3 × 1 ml) and dried in vacuum with P_2O_5.

N-(2-Phenyl-2,2-dichloroethylidene) benzenesulfonamide (***1***). Yield: 91%; mp 101–102 °C; IR (KBr, ν, cm^{-1}): 1160, 1310 (SO_2); 1620 (C=N); ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 7.33–7.93 (m, 10H, 2Ph), 8.51 (s, 1H, N=CH); ^{13}C chemical shifts, $CDCl_3$, (δ, ppm): 85.73 (CCl_2), 127.03 ($C^{o'}$), 128.36 (C^o), 128.95 ($C^{m'}$), 129.47 (C^m), 130.48 ($C^{p'}$), 134.45 (C^p), 136.39 (C^i), 136.57 ($C^{i'}$), 168.22 (N=CH).

N-(2-Phenyl-2,2-dichloroethylidene)-4-methyl benzenesulfonamide (***2***). Yield: 90%; mp 105–106 °C; IR (KBr, ν, cm^{-1}): 1150, 1310 (SO_2); 1630 (C=N); ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 2.43 (s, 3H, Me); 7.30–7.82 (m, 9H,

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Ph + C_6H_4), 8.56 (s, 1H, N=CH); ^{13}C chemical shifts, $CDCl_3$, (δ, ppm): 21.69 (CH_3), 85.71 (CCl_2), 126.92 ($C^{o\prime}$), 128.34 (C^o), 128.86 ($C^{m\prime}$), 130.07 (C^m), 130.39 ($C^{p\prime}$), 133.24 (C^i), 136.32 ($C^{i\prime}$), 145.67 (C^p), 167.61 (N=CH).

*N-(2-Phenyl-2,2-dichloroethylidene)-4-chlorobenzene sulfonamide (**3**).* Yield: 95%; mp 104–105 °C; IR (KBr, ν, cm^{-1}): 1170, 1310 (SO_2); 1630 (C=N); ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 7.35–7.90 (m, 9H, Ph + C_6H_4), 8.60 (s, 1H, N=CH); ^{13}C chemical shifts, $CDCl_3$, (δ, ppm): 85.70 (CCl_2), 127.08 ($C^{o\prime}$), 129.01 (C^o), 129.84 ($C^{m\prime}$), 129.87 (C^m), 130.57 ($C^{p\prime}$), 135.16 (C^i), 136.26 ($C^{i\prime}$), 141.33 (C^p), 168.59 (N=CH).

*General experimental procedure for the synthesis of N-(2,2-dichloroethylidene)arylsulfonamide (**4**) and N-(2,2,2-trichloroethylidene)arylsulfonamides (**5–7**)*

A mixture of dichloroamide (10 mmol) and 1,2-dichloro ethylene (for the compound **4**) or trichloroethylene (for **5–7**) (200 mmol) was boiled under continuous flow of argon until chlorine evolution stopped (8 h). To obtain pure imines **4–7**, the reaction mixture was allowed to stand at ~0 °C for 24 h. The residue formed was decanted, washed with CCl_4 and dried in vacuum over P_2O_5.

*N-[2,2-Dichloroethylidene]-4-[4-([-2,2-dichloroethylidene] aminosulfonyl)phenoxy]-benzenesulfonamide (**4**).* Yield: 85%; mp 145–147 °C; IR (KBr, ν, cm^{-1}): 1145, 1330 (SO_2); 1635 (C=N); ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 6.17 (d, ^3J = 6.5 Hz, 2H, $CHCl_2$), 7.21, 7.95 (AA′BB′, 8H, 4,4′-$C_6H_4OC_6H_4$), 8.38 (d, ^3J = 6.5 Hz, 2H, N=CH); ^{13}C chemical shifts, $CDCl_3$, (δ, ppm): 67.07 ($CHCl_2$); 119.84 (C^m), 131.35 (C^o), 132.14 (C^i), 160.72 (C^p), 165.72 (N=CH).

*N-(2,2,2-Trichloroethylidene)benzenesulfonamide (**5**).* Yield: 90%; mp 89–91 °C; IR (KBr, ν, cm^{-1}): 1140, 1320 (SO_2); 1620 (C=N); ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 7.61, 8.01 (m, 5H, Ph), 8.48(s, 1H, N=CH); ^{13}C chemical shifts, $CDCl_3$, (δ, ppm): 92.15 (CCl_3); 128.87 (C^o), 129.57 (C^m), 134.51 (C^p), 137.27 (C^i), 164.26 (N=CH).

*N-(2,2,2-Trichloroethylidene)-4-methylbenzene sulfonamide (**6**).* Yield: 88%; mp 94–96 °C; IR (KBr, ν, cm^{-1}): 1135, 1330 (SO_2); 1630 (C=N); ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 2.46 (s, 3H, Me), 7.38, 7.87 (AA′BB′, 4H, C_6H_4), 8.45 (s, 1H, N=CH); ^{13}C chemical shifts, $CDCl_3$, (δ, ppm): 21.69 (Me); 91.75 (CCl_3), 128.66 (C^o), 130.15 (C^m), 133.11 (C^i), 146.05 (C^p), 163.76 (N=CH).

*N-(2,2,2-Trichloroethylidene)-4-chlorobenzene sulfonamide (**7**).* Yield: 92%; mp 111–113 °C; IR (KBr, ν, cm^{-1}): 1140, 1330 (SO_2); 1620 (C=N); ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 7.59, 7.95 (AA′BB′, 4H, C_6H_4), 8.49 (s, 1H, N=CH); ^{13}C chemical shifts, $CDCl_3$, (δ, ppm): 91.82 (CCl_3), 130.19 (C^o), 130.01 (C^m), 135.20 (C^i), 141.79 (C^p), 164.56 (N=CH).

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