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

^{13}C–^{13}C Spin–Spin Coupling Constants in Structural Studies: XLI. Stereochemical Study on *N*-(Polychloroethylidene)-arenesulfonamides and *N*′-Arylsulfonylformimidamides

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Abstract—The second-order polarization propagator approach (SOPPA) was used to calculate ^{13}C–^{1}H, ^{13}C–^{13}C, and ^{15}N–^{1}H coupling constants for a series of *N*-(polychloroethylidene)arenesulfonamides and *N*′-arylsulfonylformimidamides, and their configuration with respect to the C=N bond was determined by comparing the calculated data with the experimental values. All the examined compounds were found to exist in solution exclusively as the corresponding *E* isomers. The most favorable conformations and relative energies of the *E* and *Z* isomers in the gas phase were determined in terms of the second-order perturbation theory (MP2/6-311G**). *N*′-Arylsulfonylformimidamides are characterized by restricted internal rotation of the dialkylamino group about the C–N bond having an increased order.

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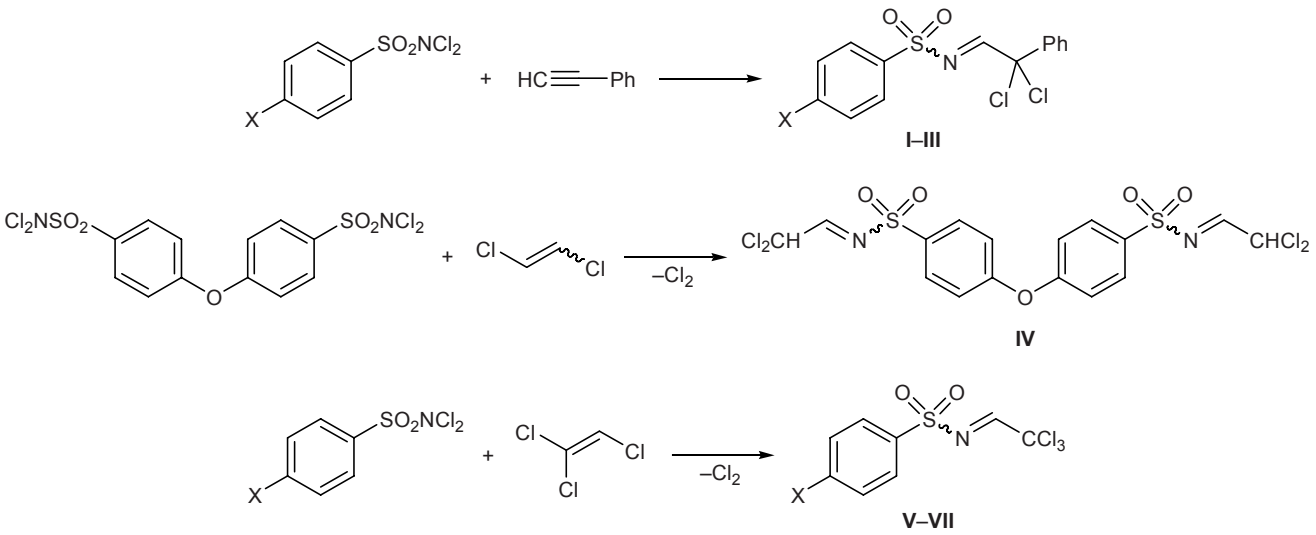
N-Substituted polyhalogenated aldehyde imines are important reagents for fine organic synthesis [1]. The presence in their molecules of an azomethine bond activated by strong electron-withdrawing substituents is responsible for their enhanced reactivity toward various nucleophiles, as well as in C-amidoalkylation of arenes and cycloaddition processes. These reactions provide synthetic routes to a large number of polyfunctional halogen-containing cyclic and acyclic sulfonamide derivatives as potential biologically active substances and precursors of α-amino aldehydes, α-amino acids, and heterocyclic systems.

First representatives of trichloroacetaldehyde imines were reported at the beginning of XXth century, and synthetic potential of activated halogen-containing Schiff bases has been explored during several decades [1]. However, physicochemical studies on Schiff bases derived from polychlorinated aldehydes were limited to identification of these compounds as reaction products. Exceptions are our previous works [2] where a number of *N*-arylsulfonyl imines were studied by ^{35}Cl NQR spectroscopy. No detailed stereochemical studies on halogen-containing Schiff bases have been performed up to now. Therefore, in the present work we synthesized a series of *N*-arylsulfonyl-substituted di- and trichloroacetaldehyde imines **I**–**VII** and a series of structurally related *N*′-arylsulfonylformimidamides **VIII**–**XVI** and examined stereochemical structure of these compounds by NMR spectroscopy and high-level quantum-chemical calculations.

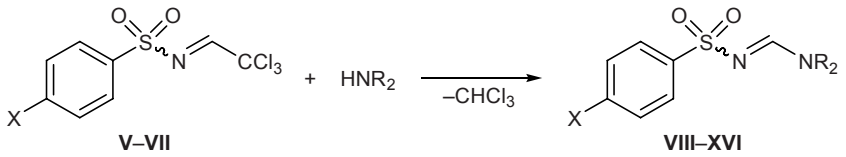
The most convenient synthetic approaches to *N*-sulfonyl polychloroaldehyde imines are based on reactions of *N*,*N*-dichloro sulfonamides with 1,2-polychloroethenes and phenylacetylene [1, 3]. These procedures are advantageous due to experimental simplicity (one-step process), high yields, and the use of low-expensive and accessible reagents, including large-scale commercial products. *N*-(Polychloroethylidene)-arenesulfonamides **I**–**VII** were prepared as shown in Scheme 1. Formimidamides **VIII**–**XVI** were synthesized by treatment of trichloroacetaldehyde imines **V**–**VII** with secondary amines (Scheme 2), which was accompanied by elimination of chloroform (like haloform reaction) [4].

Scheme 1.



I, **V**, X = H; **II**, **VI**, X = Me; **III**, **VII**, X = Cl.

Scheme 2.

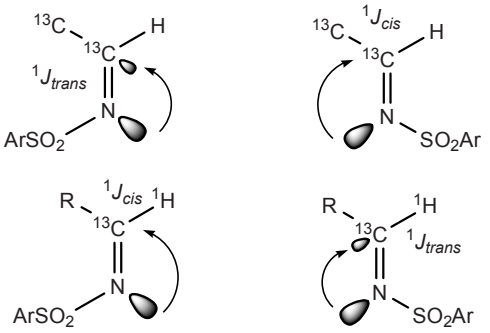


VIII, **XII**, **XIV**, R = Me; **IX**, **XIII**, **XV**, R = Et; **X**, **XVI**, R = Pr; **XI**, R = Bu; **VIII**–**XI**, X = H; **XII**, **XIII**, X = Me; **XIV**–**XVI**, X = Cl.

Despite different reactivities, *N*-(polychloroethylidene)arenesulfonamides **I**–**VII** and *N*′-arylsulfonylformimidamides **VIII**–**XVI** have a common structural fragment, Ar–SO_2–N=C, which gives rise to *E*/*Z* isomerism about the C=N bond and rotational isomerism with respect to the N–S bond; the latter aspect was of our prime interest.

According to the ^1H and ^{13}C NMR data, compounds **I**–**XVI** in solution exist as a single isomer. The structure of that isomer was determined as a rule by comparing in pairs direct ^{13}C–^{13}C coupling constants in the 1D-INADEQUATE spectrum, as shown in Fig. 1 for *N*-(2,2-dichloro-2-phenylethylidene)-4-methylbenzenesulfonamide (**II**) as an example. In addition, signals in the ^1H and ^{13}C NMR spectra were assigned using two-dimensional homo- and heteronuclear correlation techniques (2D-NOESY, HSQC, HMBC), as well as 2D-INADEQUATE experiments which revealed direct correlations between carbon nuclei, as shown in Fig. 2 for the same compound. The ^{13}C chemical shifts and direct ^{13}C–^{13}C and ^{13}C–^1H coupling constants of compounds **I**–**XVI** are given in Table 1.

The configuration of compounds **I**–**XVI** was determined by comparing the experimental and theoretical ^{13}C–^{13}C, ^{13}C–^1H, and ^{15}N–^1H coupling constants that are very sensitive to orientation of the lone electron pair (LEP) on the nitrogen atom in Schiff bases. This was demonstrated by us for the first time using oximes as examples [5]. Difference in the direct ^{13}C–^{13}C and ^{13}C–^1H coupling constants involving the C=N carbon atom results from through-space interaction between the nitrogen LEP and the neighboring C–C bond oriented *cis* with respect to the LEP. This interaction gives rise to an additional channel for transmission of spin–spin coupling, which produces a positive contribution to the total value of $^1J_{cis}$. On the other hand, electron density transfer from the nitrogen LEP to the antibonding orbital of the *trans*-oriented C–C bond (n_σ,σ* interaction) weakens that C–C bond, the corresponding coupling constant decreases, and the contribution to $^1J_{trans}$ is negative. The nature of this effect was studied in detail in a series of theoretical works [6], and it is widely used to assign configurations of various Schiff bases [7].



Analogous pattern is observed for geminal $^{15}N–^{1}H$ coupling constants. The coupling constant $^{2}J_{cis}$ for *Z* isomers in absolute value exceeds $^{2}J_{trans}$ for *E* isomers by a factor of 3 to 5 due to the same additional coupling transmission channel (involving lone electron pair on the nitrogen atom) in the former. The gyromagnetic ratio for ^{15}N is negative; correspondingly, the total $^{15}N–^{1}H$ coupling constants should be negative, and they should be compared with account taken of their sign. The results of our calculations showed that the geminal $^{15}N–^{1}H$ coupling constants $^{2}J_{cis}$ and $^{2}J_{trans}$ have opposite signs ($^{2}J_{cis}$ is negative, while $^{2}J_{trans}$ is positive) due to opposite signs of the corresponding Fermi-contact contributions (see below).

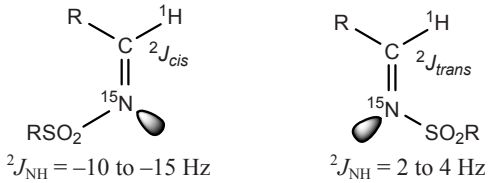


Table 2 contains the calculated and experimental $^{13}C–^{13}C$, $^{13}C–^{1}H$, and $^{15}N–^{1}H$ coupling constants for *E*

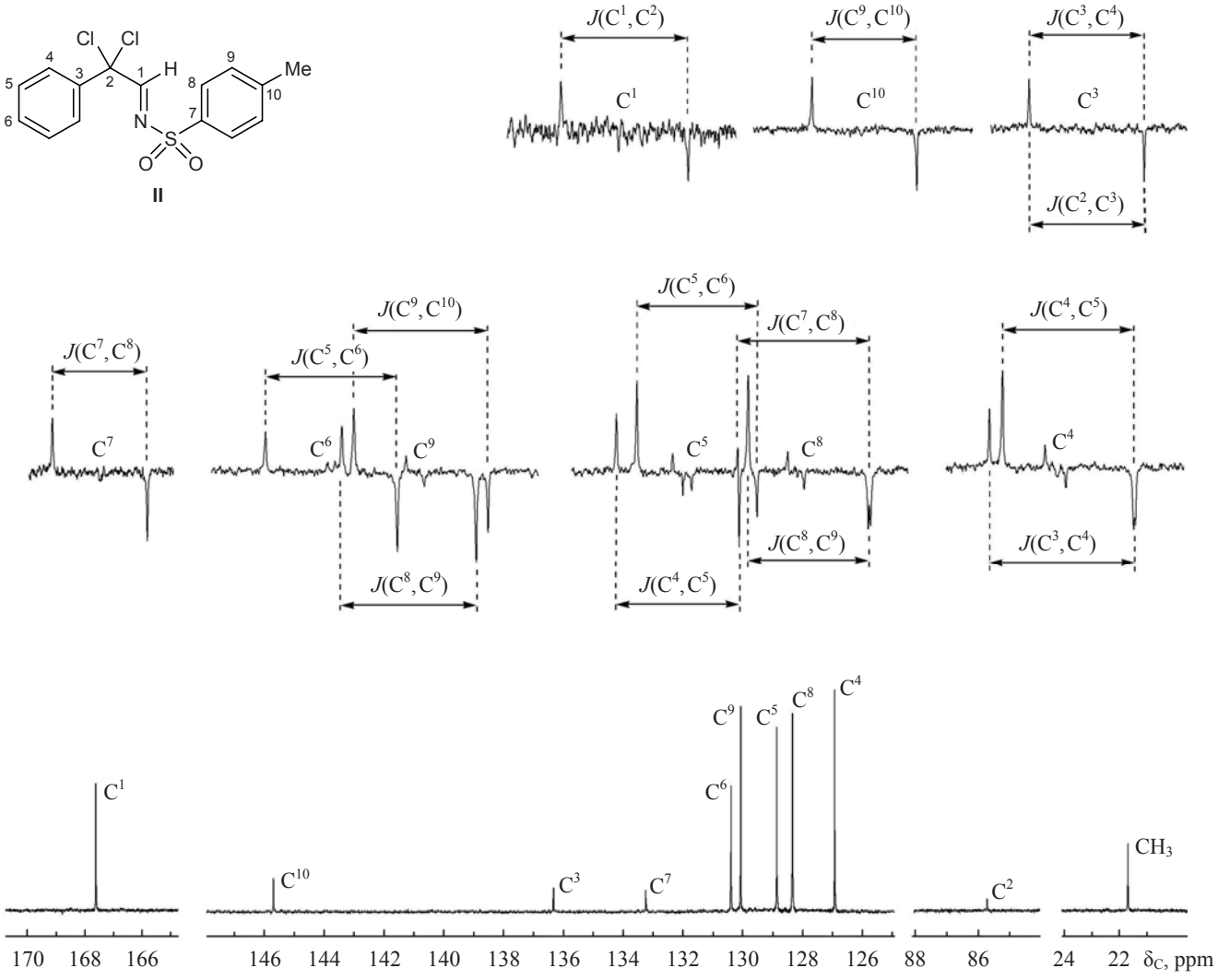


Fig. 1. Direct $^{13}C–^{13}C$ coupling constants in the 1D-INADEQUATE spectrum of *N*-(2,2-dichloro-2-phenylethylidene)-4-methylbenzenesulfonamide (**II**) ($CDCl_3$, 100.61 MHz).

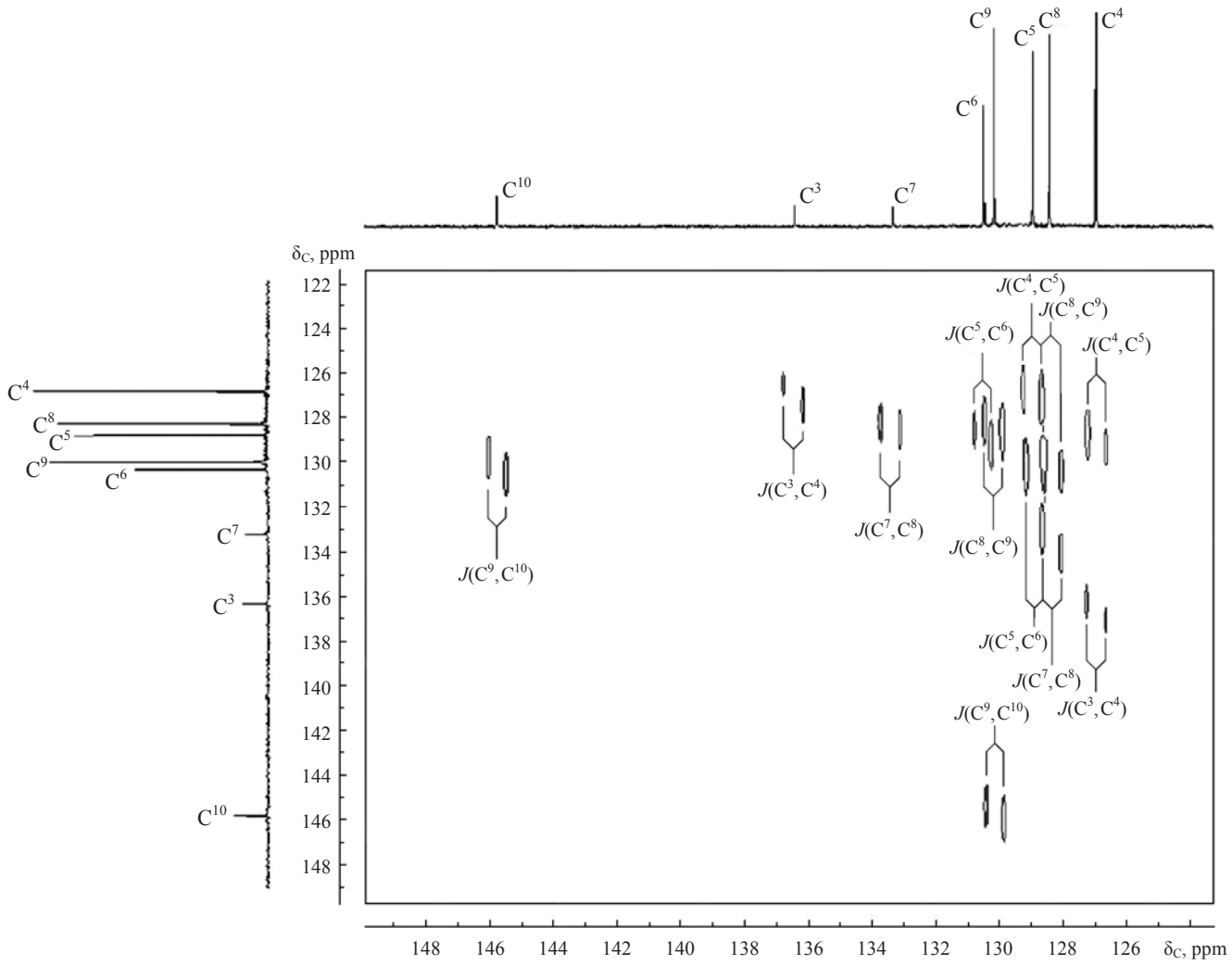


Fig. 2. Direct ^{13}C–^{13}C coupling constants in the 2D-INADEQUATE spectrum of *N*-(2,2-dichloro-2-phenylethylidene)-4-methylbenzenesulfonamide (**II**) ($CDCl_3$, 100.61 MHz).

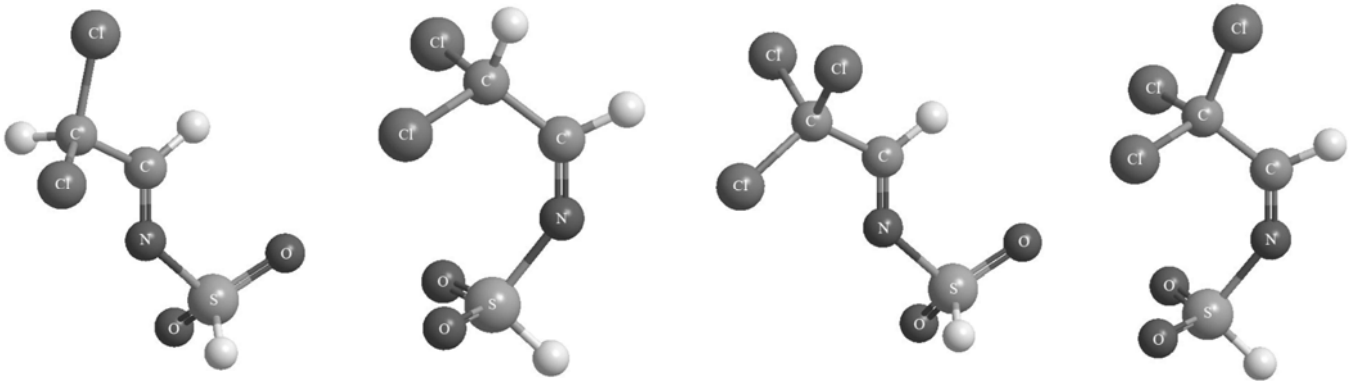
and *Z* isomers of three model compounds **XVII**–**XIX** that simulate three series of the compounds under study, *N*-(2,2-dichloroethylidene)arenesulfonamides **I**–**IV**, *N*-(2,2,2-trichloroethylidene)arenesulfonamides **V**–**VII**, and *N*′-(arylsulfonyl)formimidamides **VIII**–**XVI**, respectively. The coupling constants were calculated in terms of the second-order polarization propagator approach (SOPPA) [8] with account taken of four contributions at the nonrelativistic level: Fermi-contact (J_{FC}), spin–dipole (J_{SD}), diamagnetic spin–orbital (J_{DSO}), and paramagnetic spin–orbital (J_{PSO}); special correlation-consistent Dunning basis sets [9] supplemented by internal correlation functions [10] and Sauer basis set [11] were used as described in [12].

Comparison of the data in Tables 1 and 2 shows that all compounds **I**–**XVI** in solution exist as single *E* isomers. The experimental ^{13}C–^{13}C, ^{13}C–^{1}H, and ^{15}N–^{1}H coupling constants of **I**–**VII** and ^{13}C–^{1}H and ^{15}N–^{1}H coupling constants of **VIII**–**XVI** are well reproduced (within ~1–2 Hz) by the calculated values for the *E* isomers of the corresponding model structures **XVII**–**XIX**, and they differ considerably from those calculated for their *Z* isomers. The differences in coupling constants between the *E* and *Z* isomers of **I**–**XVI** are 10–15 Hz for ^{13}C–^{13}C, 8–10 Hz for ^{13}C–^{1}H, and 10–15 Hz (in absolute value) for ^{15}N–^{1}H; this indicates that the selected calculation method provides reliable assignment of configuration of the examined compounds.

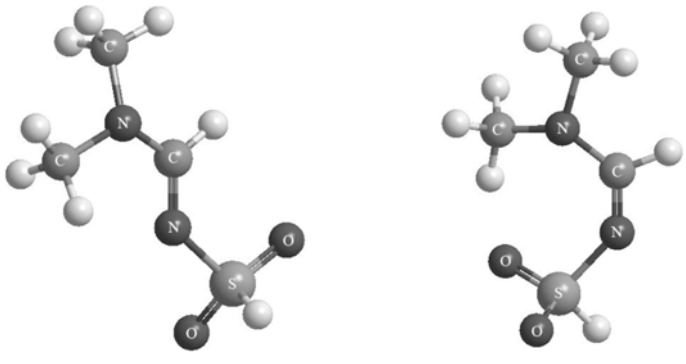
The coupling constants for model structures **XVII**–**XIX** were calculated for the most favorable rotational conformers whose geometric parameters were optimized by the MP2/6-311G** method (Fig. 3). The *E* isomers of **XVII**–**XIX** have lower energies (by 8–

Table 1. Chemical shifts and direct $^{13}C–^{13}C$ and $^{13}C–^{1}H$ coupling constants in the ^{13}C NMR spectra of compounds **I–XVI**

Compound no.	Chemical shift δ_C, ppm						Coupling constant ^1J, Hz	
	C^1	C^2	C^i	C^o	C^m	C^p	$C^1–C^2$	$C^1–H_\alpha$
I	168.22	85.73	136.39	128.36	129.47	134.45	53.9	183.0
II	167.61	85.71	133.24	128.34	130.07	145.69	53.8	182.7
III	168.59	85.70	135.16	129.01	129.87	141.33	53.7	182.6
IV	165.72	67.07	132.14	131.35	119.84	160.72	55.1	182.4
V	164.26	92.15	137.27	128.87	129.57	134.51	60.3	187.4
VI	163.78	91.75	133.11	128.66	130.15	146.05	59.7	188.0
VII	164.56	91.82	135.20	130.19	130.01	141.79	59.9	188.0
VIII	159.27	–	142.50	128.70	126.42	131.81	–	180.9
IX	157.95	–	142.40	128.37	125.84	131.39	–	180.3
X	158.92	–	142.64	128.40	125.97	131.39	–	180.3
XI	158.78	–	142.58	128.47	126.05	131.50	–	180.9
XII	159.15	–	139.62	126.56	129.38	142.52	–	180.9
XIII	157.88	–	139.57	126.01	129.07	142.08	–	180.3
XIV	159.25	–	141.16	128.81	127.86	137.90	–	181.5
XV	158.08	–	141.17	128.74	127.67	137.72	–	180.3
XVI	158.99	–	141.26	128.87	127.77	137.89	–	180.9



E-**XVII**, 0.0 kcal/mol *Z*-**XVII**, 9.6 kcal/mol *E*-**XVIII**, 0.0 kcal/mol *Z*-**XVIII**, 10.8 kcal/mol



E-**XIX**, 0.0 kcal/mol *Z*-**XIX**, 7.8 kcal/mol

Fig. 3. Most favorable conformations and relative total energies of the *E* and *Z* isomers of model compounds **XVII–XIX** according to the MP2/6-311G** calculations.

Table 2. Calculated (SOPPA) ^{13}C–^{13}C, ^{13}C–^{1}H, and ^{15}N–^{1}H spin–spin coupling constants and contributions thereto (J, Hz) for the *E* and *Z* isomers of model compounds **XVII**–**XIX** and experimental values for compounds **I**, **V**, and **VIII**

Compound no.	Isomer	Coupling	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experiment
XVII	*E*	C^1–C^2	0.4	–1.2	0.8	52.7	52.7	53.9[a]
		C^1–H	1.3	–0.8	0.7	178.3	179.5	183.0[a]
		N–H	0.1	1.1	–0.1	2.1	3.2	2.8[a]
	Z	C^1–C^2	0.4	–0.7	0.9	41.3	41.9	
		C^1–H	1.1	–0.6	0.5	186.4	187.4	
		N–H	–0.1	0.4	0.0	–18.9	–18.6	
XVIII	*E*	C^1–C^2	0.4	–1.1	0.9	58.8	59.0	60.3[b]
		C^1–H	1.4	–0.9	0.7	188.0	189.2	187.4[b]
		N–H	0.1	1.1	–0.1	2.2	3.3	2.9[b]
	Z	C^1–C^2	0.4	–0.8	1.0	43.3	43.9	
		C^1–H	1.2	–0.7	0.6	199.5	200.6	
		N–H	0.0	1.0	–0.2	–13.8	–13.0	
XIX	*E*	C^1–H	1.3	–0.6	0.7	177.1	178.5	180.9[c]
		N–H	0.1	0.7	0	1.5	2.3	1.2[c]
	Z	C^1–H	1.2	–0.4	0.5	187.3	188.6	
		N–H	0.0	0.5	–0.1	–15.6	–15.2	

[a] Compound **I**.
[b] Compound **V**.
[c] Compound **VIII**.

11 kcal/mol) than the corresponding *Z* isomers in the most favorable conformations. These data are consistent with the above results obtained by analysis of the experimental and calculated ^{13}C–^{13}C, ^{13}C–^{1}H, and ^{15}N–^{1}H coupling constants for compounds **I**–**XVI**.

Apart from configuration at the double C=N bond, we were also interested in rotational isomerism arising from rotation about the N–S bond in all compounds **I**–**XVI**, C^1–C^2 bond in Schiff bases **I**–**VII**, and C–$NAlk_2$ bond in formimidamides **VIII**–**XVI**. As follows from the results of MP2/6-311G** calculations for isolated molecules, internal rotation about the N–S bond in the *E* isomers of **XVII**–**XIX** gives rise to two stable rotamers (their nature was established by harmonic analysis of vibrational spectrum containing no imaginary frequencies) in which the dihedral angle CNSH is equal to 0 and 125–128°, respectively; the relative total energy of the first of these is on the average 3 kcal/mol. Presumably, the second rotamer is stabilized via intramolecular attractive interactions between the N=CH proton and sulfonyl oxygen atom. In the most favorable conformations of the *Z* isomers of model compounds the dihedral angle CNSH is 158–161°. In this case, spatial interaction between the SO_2 group and bulky substituent on the azomethine carbon atom induces deviation of the CNSH angle from an apparently more favorable value of 180°.

The most stable rotamers formed by rotation about the C^1–C^2 bond in *N*-sulfonyl dichloroacetaldehyde imines **I**–**IV** are characterized by dihedral angles NCCH of 125.4° for the *E* isomers and 159.5° for the *Z* isomers. Energy minima for rotamers of trichloroacetaldehyde derivatives **V**–**VII** with respect to the C^1–C^2 bond correspond to NCCCl angles of 0° for the *E* isomers and 36.1° for the *Z* isomers (all dihedral angles were calculated for the model structures).

Internal rotation about the C–$NAlk_2$ bond in formimidamides **VIII**–**XVI** is restricted due to partially double character of that bond as a result of conjugation between LEP on the amino nitrogen atom and π-C=N bond; this is confirmed by the calculated barriers to internal rotation and dynamic temperature effects in the NMR spectra (see below). In the optimized conformations of both *E* and *Z* isomers of model formimidamide **XIX**, the LEP on the amino nitrogen atom is oriented orthogonally to the plane of the C=N bond. In fact, the *N*-alkyl groups in all compounds **VIII**–**XVI** are magnetically nonequivalent: two sets of signals are observed in the ^{1}H and ^{13}C NMR spectra. Analogous pattern was observed previously for structurally related

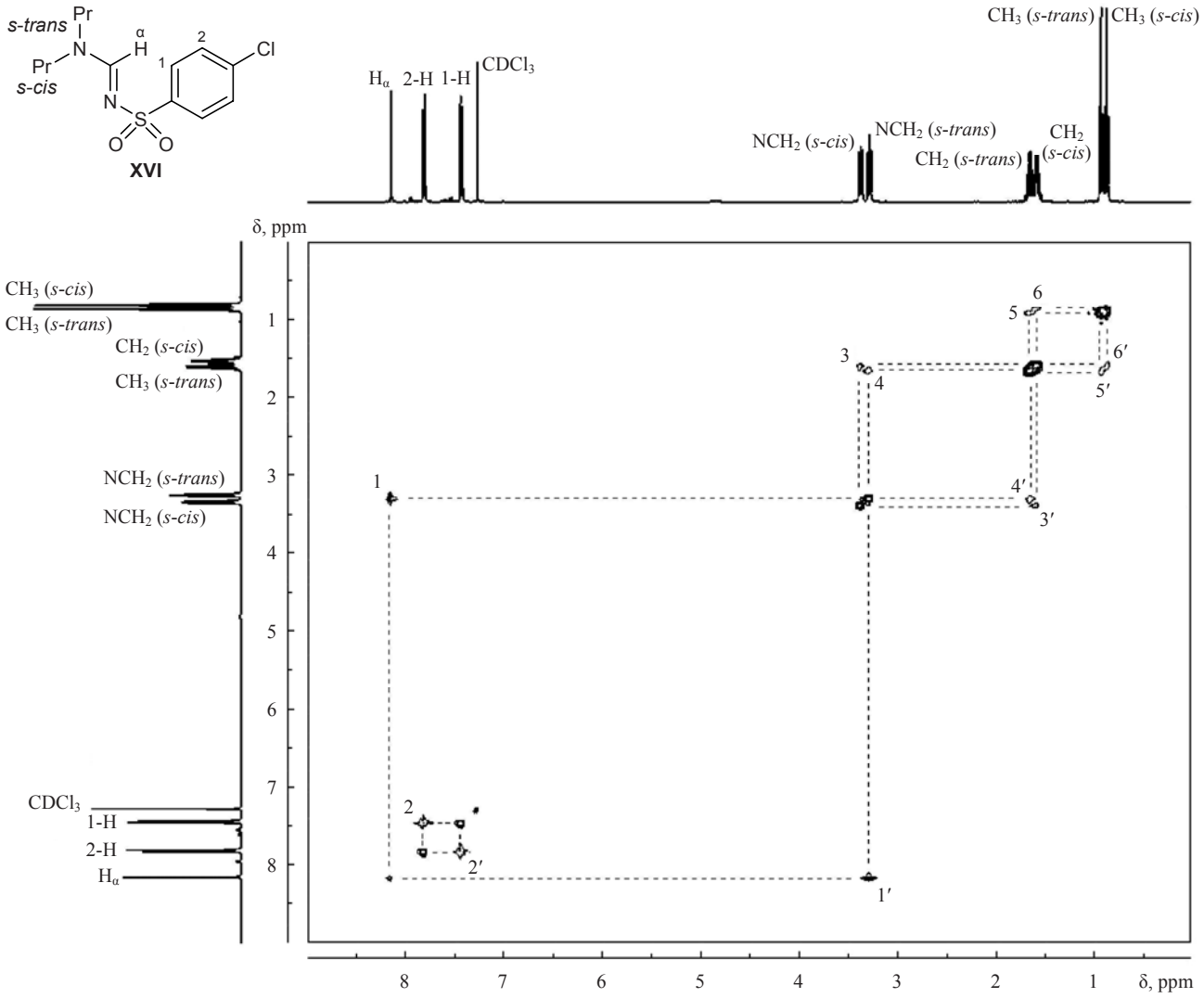


Fig. 4. 2D-NOESY spectrum of *N*′-(4-chlorophenylsulfonyl)-*N*,*N*-dipropylformimidamide (**XVI**) ($CDCl_3$, 400.13 MHz). Cross peak denotations: 1 (1′): $H_α$, CH_2N (*s-trans*); 2 (2′): 1-H, 2-H; 3 (3′): CH_2N (*s-cis*), CH_2 (*s-cis*); 4 (4′): CH_2N (*s-trans*), CH_2 (*s-trans*); 5 (5′): CH_2 (*s-trans*), CH_3 (*s-trans*); 6 (6′): CH_2 (*s-cis*), CH_3 (*s-cis*).

N,*N*-dialkyl-*N*′-methylsulfonylformimidamides $MeSO_2N{=}CHNR_2$ (R = Me, Et) [13] and *N*,*N*-dimethyl-*N*′-arylsulfonylformimidamides [4].

Signals from the *N*-alkyl groups in the ^1H NMR spectra of **VIII**–**XVI** were assigned to particular rotamers using two-dimensional NOESY technique. The NOESY spectra contained a cross peak from NCH_2 (NCH_3) protons of one alkyl group and N=CH proton. As an example, Fig. 4 shows the 2D-NOESY spectrum of *N*′-(4-chlorophenylsulfonyl)-*N*,*N*-dipropylformimidamide (**XVI**). In the ^1H and ^{13}C NMR spectra of *N*,*N*-diethyl, *N*,*N*-dipropyl, and *N*,*N*-dibutyl derivatives, downfield NCH_2 signals belong to the alkyl group in the *s-cis* position, while downfield NCH_3 signals of *N*,*N*-dimethyl derivatives and CH_3 and other CH_2 signals of *N*,*N*-dialkyl derivatives belong to the *s-trans*-oriented alkyl group, as unambiguously follows from the 2D-NOESY spectra.

The activation barrier to internal rotation in *N*′-arylsulfonylformimidamides was estimated for *N*′-(4-chlorophenylsulfonyl)-*N*,*N*-dimethylformimidamide (**XIV**) in DMSO-d_6 from the temperature dependence of the shape of methyl proton signals (Fig. 5). The coalescence temperature was determined by extrapolation of the temperature dependence of the distance between the *N*-methyl proton signals: it was ~250°C. The rate of exchange process at the coalescence temperature was estimated using the approximate formula $k_{coal} = \pi\delta\nu/\sqrt{2}$ [14]. Correspondingly, the Gibbs energy of activation calculated by the Eyring equation was

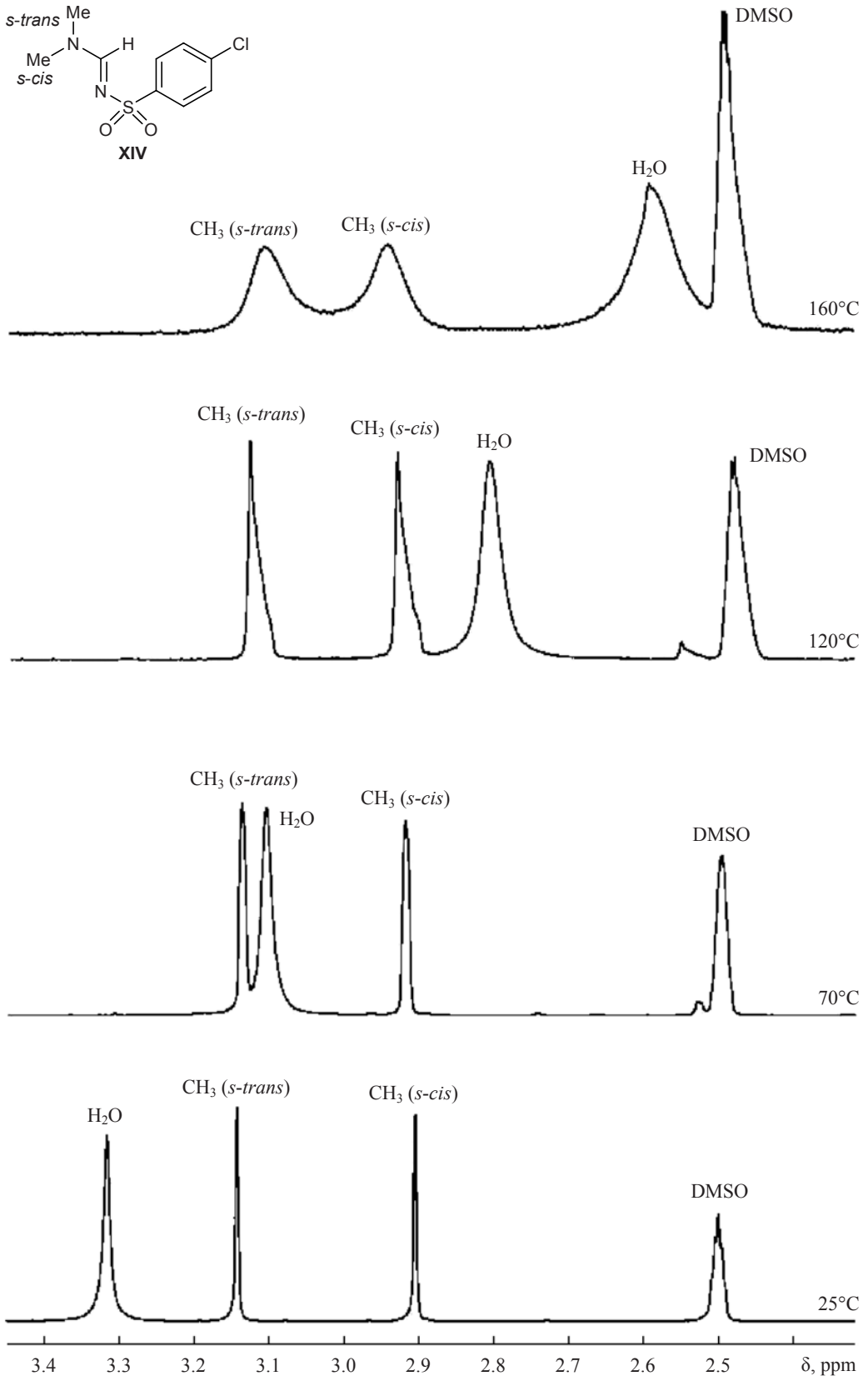


Fig. 5. Temperature dependence of the ^1H NMR spectrum (methyl proton resonance region) of *N*′-(4-chlorophenylsulfonyl)-*N*,*N*-dimethylformimidamide (**XIV**) in DMSO-d_6 (400.13 MHz).

~20 kcal/mol. According to the MP2/6-311G** calculations, the activation barrier to internal rotation in model amidine **XIX** in the gas phase is 23 kcal/mol.

Thus, the following conclusions may be drawn from the results of the present study. All *N*-(polychloroethylidene)arenesulfonamides **I–VII** and *N*′-arylsulfonylformimidamides **VIII–XVI** in solution exist as single *E* isomers. The $^{13}C–^{13}C$, $^{13}C–^{1}H$, and $^{15}N–^{1}H$ coupling constants calculated for the *E* isomers of these compounds in terms of the second-order polarization propagator approach reproduce well the experimental values, and the latter differ considerably from the calculated values for the *Z* isomers. Internal rotation about the C–$NAlk_2$ bond in *N*′-arylsulfonylformimidamides is characterized by a high activation barrier, and it gives rise to magnetic nonequivalence of the *N*-alkyl groups oriented *s-cis* and *s-trans* with respect to the lone electron pair on the nitrogen atom. Our results supplement and support our previous ^{35}Cl NQR data for crystalline *N*-arylsulfonyl aldehyde imines [2], according to which these compounds were presumed to exist in crystal as more energetically favorable *E* isomers.

EXPERIMENTAL

N-(2,2-Dichloro-2-phenylethylidene)arenesulfonamides **I–III** were synthesized by reaction of the corresponding *N*,*N*-dichloroarenesulfonamides with phenylacetylene according to the procedure reported in [15]. *N*,*N*′-Bis(2,2-dichloroethylidene)-4,4′-oxybis(benzenesulfonamide) (**IV**) was obtained by reaction of *N*,*N*,*N*′,*N*′-tetrachloro-4,4′-oxybis(benzenesulfonamide) with 1,2-dichloroethene as described in [16]. *N*-(2,2,2-Trichloroethylidene)arenesulfonamides **V–VII** [17] and *N*′-(arylsulfonyl)formimidamides **VIII–XVI** [4] were prepared by known methods. The properties of compounds **I–XVI** were consistent with published data.

The ^{1}H, ^{13}C, and ^{15}N NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13, 100.61, and 40.55 MHz, respectively, using 5-mm ampules; $CDCl_3$ or DMSO-d_6 was used as solvent (sample concentration 5–10%), and HMDS, as internal reference (^{1}H and ^{13}C). The $^{15}N–^{1}H$ coupling constants were determined using two-dimensional HMBC pulse sequence with the following parameters: band width 400 Hz (^{1}H) and 20 kHz (^{15}N), pulse duration 6 μs (^{1}H) and 27.1 μs (^{15}N), pulse delay 2.5 s, FID acquisition time 0.16 s, digital resolution 0.1 Hz per point. The $^{13}C–^{13}C$ coupling constants were measured with the following parameters of 1D-INADEQUATE sequence: band width 6 kHz, pulse duration 13.0–13.5 μs, pulse delay 4 s, FID acquisition time 4 s, digital resolution 0.1 Hz per point. The two-dimensional 2D-INADEQUATE spectrum was recorded using standard INADQFSY pulse sequence [18] with the following parameters: band width 6 and 12 kHz, pulse duration 13.0–13.5 μs, pulse delay 4 s, FID acquisition time 4 s, digital resolution 0.1 Hz per point.

Quantum-chemical calculations were performed using GAMESS [19] and DALTON programs [20] for SuSE Linux 9.0 (PC Pentium 4, CPU 3400 MHz, RAM 2 Gb, HDD 250 Gb). Geometric parameters were optimized, and total energies were calculated, at the MP2/6-311G** level (second-order Moeller–Plesset perturbation theory). The $^{13}C–^{13}C$, $^{13}C–^{1}H$, and $^{15}N–^{1}H$ coupling constants were calculated in terms of the second-order polarization propagator approach (SOPPA) using standard or modified basis sets cc-pVDZ-Cs, cc-pCVDZ, cc-pVDZ, cc-VDZ, and aug-cc-pVTZ-J (for detailed description, see [12]).

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