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N-(2,2-Dichloro-2-phenylethylidene)arenesulfonamides in Reactions with Secondary Amines

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Abstract—*N*-(2,2-Dichloro-2-phenylethylidene)arenesulfonamides were synthesized by a modified procedure, and their reactions with secondary amines were studied for the first time. Reactions of imines with dialkylamines proceed at room temperature to afford α,α-dichloromethylbenzene and *N,N*-dialkyl-*N'*-(arenesulfonyl)formamidines arising from the haloform cleavage of the initially formed unstable *N*-(1-dialkylamino-2,2-dichloro-2-phenylethyl)arenesulfonamides. When the reaction is carried out upon cooling to 0°C, the products of the nucleophilic addition of secondary amines to azomethines, *N*-(1-dialkylamino-2,2-dichloro-2-phenylethyl) are formed in yields of no higher than 5%. Nonempirical calculations of $^{13}C–^{1}H$ spin–spin coupling constants and their experimental measurements for the series of the synthesized *N*-arenesulfonamides were performed to show that these compounds exist in solutions exclusively as *E* isomers. Preferable conformations of the investigated compounds and the relative energies of their *E* and *Z* isomers in the gas phase were determined by quantum-chemical calculations at the MP2/6-311G** level of theory. The NMR spectral data revealed restricted rotation of the *N,N*-dialkylamino group about the partially double C–$NAlk_2$ bond in the molecules of *N*-arenesulfonylformamidines.

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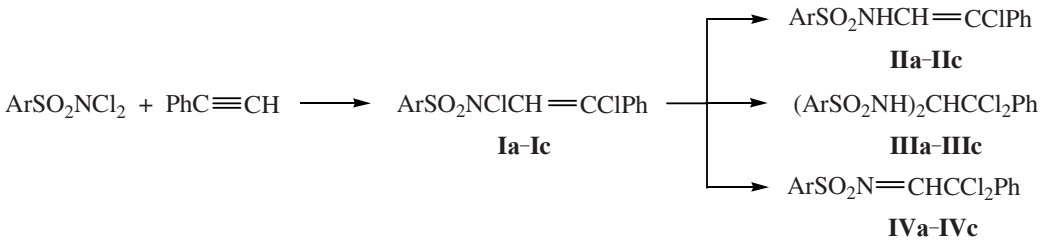
The combination of the electron-deficient azomethine group and the dichloromethylene fragment in the molecules of *N*-(2,2-dichloro-2-phenylethylidene)-arenesulfonamides allows these compounds to be considered as promising reagents for various synthetic applications, like preparation of various polyfunctional cyclic or acyclic amides containing pharmacophore fragments, which are of interest as NH acids, potential ligands, and monomers. However, unlike chloral arenesulfonylimines, arenesulfonylimines derived from α,α-dichlorophenylacetaldehyde are less studied. Many important synthetic routes using these representatives of activated azomethines as key reagents could not be realized mainly due to the absence of convenient methods of their synthesis.

In this connection, an actual problem was to improv of the protocol for preparation of *N*-sulfonylimines derived from dichlorophenyl-acetaldehyde, based on the reaction of *N,N*-dichloroarenesulfonamides with phenylacetylene, and further develop of the chemistry of these azomethines.

Earlier we showed [1–5] that the reaction of *N,N*-dichloroarenesulfonamides with phenylacetylene results in formation of mixtures of arenesulfonamide derivatives **I–IV**, of which *N*-chloro-*N*-(2-chloro-2-phenylvinyl)amides **Ia–Ic**, *N*-(2-phenyl-2-chlorovinyl)-amides **IIa–IIc**, 1,1-bis(arenesulfonylamino)-2,2-dichloro-2-phenylethanes **IIIa–IIIc**, and *N*-(arenesulfonyl)dischlorophenylacetaldimines **IVa–IVc** were isolated in 40–75% yields.

A plausible mechanism of the formation of imines **IVa–IVc** in this reaction should involve the step of addition of dichloroamides to phenylacetylene to form adducts **Ia–Ic** and their subsequent isomerization, as discussed in detail in [1–3].

No alternative synthetic approaches to imines **IVa–IVc** have so far been developed. The known schemes for synthesis of halogenated imines, based on condensation of amides, isocyanates, or sulfonyl isocyanates with aldehydes [6], are not used for



Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-MeC_6H_4 (**c**).

azomethine derivatives of α,α-dichlorophenylacetaldehyde, apparently due to a highly laborous experiment and poor availability of dichlorophenylacetaldehyde.

We could optimize conditions for the reaction of *N,N*-dichlorosulfonamides with phenylacetylene to improve the yield of imines **IVa–IVc** and to simplify the procedure.

It was found that the yields of target imines **IVa–IVc** reach a maximum, when the reaction of *N,N*-dichloroarenesulfonamides with acetylene is performed under argon in CCl_4. Therewith, reagent addition order is of principal importance. When *N,N*-dichloroamide is added to a solution of phenylacetylene, the yields of imines **IVa–IVc** are substantially higher than when the reagents are mixed in the reverse order (90–95 vs. 40–64%). The reaction has an inductive period after which it proceeds with a notable self-heating (up to 50°C). It is important that the reaction mixture is heated for 3 h at 50–60°C after the exothermic process has been complete.

It can be suggested that the found conditions unfavor side reactions, such as chlorination and oligomerization of phenylacetylene and addition of excess dichloroamide to initially formed *N*-chloroenamides **Ia–Ic**, while heating at the final reaction stage favors 1,3-chlorotropic rearrangement, thus increasing the yields of target azomethines **IVa–IVc**.

Imines **IVa–IVc** precipitate upon cooling of the reaction mixture and can be readily separated and used for further synthetic transformations without additional crystallization. When the reaction mixture is kept cool for a long time after imines **IVa–IVc** have been separated, by-product diaminoethanes **IIIa–IIIc** precipitate. It is noteworthy that no *N*-chloro-*N*-(2-chloro-2-phenylvinyl)amides **Ia–Ic** and *N*-(2-phenyl-2-chlorovinyl)amides **IIa–IIc** are present in the reaction mixture.

Therefore, conditions were found that allowed us to substantially improve the yields of target azomethines **IVa–IVc** and exclude fomation of hardly separable by-products.

The formation of diamides **IIIa–IIIc** and imines **IVa–IVc** is proved by spectral data. Physicochemical characteristics of these are consistent with published data [4, 5] (Tables 1 and 2).

Reported reactions of dichlorophenylacetaldimines with N-nucleophiles were limited to reactions with carboxamides and arenesulfonamides [4, 5], acrylamide [7], thioacetamide, and thiourea [8]. The amides

Table 1. Yields, melting points, and elemental analyses of 1,1-bis(arenesulfonylamino)-2,2-dichloro-2-phenylethanes **IIIa–IIIc** and *N*-(2,2-dichloro-2-phenylethylidene)arenesulfonamides **IVa–IVc**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	Cl	N	S		C	Cl	N	S
IIIa	6	210–213	50.02	14.15	6.02	13.92	$C_{20}H_{18}Cl_2N_2O_4S_2$	49.49	14.61	5.77	13.21
IIIb	3	217–219	43.09	25.22	5.53	12.02	$C_{20}H_{16}Cl_4N_2O_4S_2$	43.34	25.58	5.05	11.57
IIIc	7	200–202	50.98	13.42	5.89	12.98	$C_{22}H_{22}Cl_2N_2O_4S_2$	51.46	13.81	5.46	12.49
IVa	90	101–102	50.90	21.43	4.61	9.45	$C_{14}H_{11}Cl_2NO_2S$	51.23	21.60	4.27	9.77
IVb	95	104–105	46.04	29.24	4.03	8.29	$C_{14}H_{10}Cl_3NO_2S$	46.37	29.33	3.86	8.84
IVc	91	105–106	52.37	20.29	4.37	9.04	$C_{15}H_{13}Cl_2NO_2S$	52.64	20.72	4.09	9.37

Table 2. IR and ^{1}H NMR spectra of 1,1-bis(arenesulfonylamino)-2,2-dichloro-2-phenylethanes **IIIa–IIIc** and *N*-(2,2-dichloro-2-phenylethylidene)arenesulfonamides **IVa–IVc**

Comp. no.	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum (DMSO-d_6), δ, ppm			$^3J_{NH-CH}$, Hz
	NH	SO_2	другие	CH	NH	Ar	
IIIa	3220	1160, 1340	3040 (=C–H_{arom})	5.90 t	8.86 d	7.40–7.52 m	11
IIIb	3220	1160, 1320	3040 (=C–H_{arom})	5.79 t	9.02 d	7.27–7.98 m	11.5
IIIc	3220	1165 1340	3045 (=C–H_{arom})	5.38 t	8.28 d	7.29–7.67 m	9.3
IVa	–	1160, 1310	1620 (C=N)	8.51 s	–	7.33–7.83 m	–
IVb	–	1170, 1310	1630 (C=N)	8.58 s	–	7.35–7.90 m	–
IVc	–	1650, 1310	1630 (C=N)	8.55 s	–	7.30–7.82 m	–

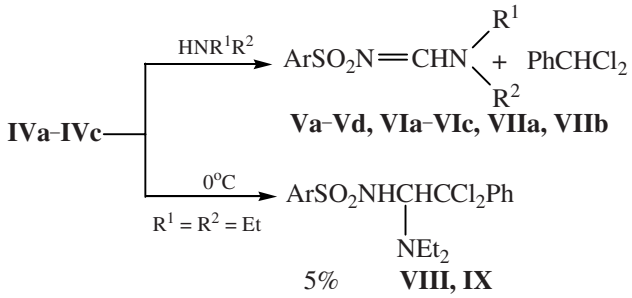
were shown to add to the imino group to afford the corresponding diamides.

We have continued our systematic reactivity research and studied reactions of arenesulfonylimines **IVa–IVc** with secondary amines.

It was found that compounds **IVa–IVc** react with excess dialkylamines in carbon tetrachloride without heating by way of haloform cleavage to form *N*-(dialkylaminomethylidene)arenesulfonamides **V–VII** in good yields.

The formation of α,α-dichloromethylbenzene was proved by NMR spectroscopy. Thus, the ^{1}H NMR spectra of the reaction mixtures contained a signal at 6.6 ppm, which is consistent with the spectrum of an authentic sample.

Furthermore, the reactions of imines **IVa** and **IVb** with diethylamine under cooling involve addition of the secondary amine to the imino group to form compounds **VIII** and **IX**. We failed to isolate pure adducts **VIII** and **IX** because of their low stability. The yields of these products were no higher 5% as judged from the NMR spectra.



Ar = Ph (**Va–Vd, VIII**), 4-ClC_6H_4 (**VIa–VIc, IX**), 4-MeC_6H_4 (**VIIa, VIIb**), $R^1 = R^2$ = Et (**Va, VIa, VIIa**), Pr (**Vb, VIb**), Bu (**Vc**), R^1 = Me, R^2 = Pr (**Vd, VIc, VIIb**).

The presence of compounds **VIII** and **IX** in the reaction mixtures was proved by physicochemical methods (see Experimental). The ^{1}H NMR spectra contain signals of the NH–CH fragment and signals of the aromatic rings and dialkylamino groups with expected integral intensities.

The formation of amidines **V–VII** is confirmed by spectral methods. Compounds **Va–Vc**, **VIa, VIb**, and **VIIa** were described earlier [9, 19], and their physicochemical characteristics are consistent with published data (Tables 3 and 4). Amidines **Vd, VIc**, and **VIIb** were synthesized for the first time.

As follows from the ^{1}H and ^{13}C NMR spectra, formamidines **Va–Vd, VIa–Vc, VIIa**, and **VIIb** exist in solutions as individual isomers, and it was one of the aims of the present work to assign their configuration. The structure of these compounds was established by means of two-dimensional homo- and heteronuclear correlation techniques 2D-NOESY, HSQC, and HMBC. The measured ^{1}H and ^{13}C NMR chemicals shifts and ^{13}C–^{1}H coupling constants, that confirm the structure of all the studied compounds, are listed in Tables 4 and 5.

To establish the configuration of the obtained formamidines, we made use of a method based on experimental measurement and theoretical calculation of ^{13}C–^{1}H coupling constants which are quite sensitive to the orientation of the lone electron pair (LEP) on the nitrogen atom in azomethines, as was first shown with oximes [10]. The drastic difference of the direct ^{13}C–^{1}H coupling constants with the imine carbon atom is, first, due to through-space interaction of the nitrogen LEP with an adjacent bond *cis* to the LEP. This opens an additional channel for transmission of spin–spin coupling interaction, leading to a positive contribution into the total $^1J_{cis}$ constant. Second, the electron density

Table 3. Yields, melting points, and elemental analyses of *N,N*-dialkyl-*N'*-(arenesulfonyl)formamidines **Va–Vd, VIa–VIc, VIIa**, and **VIIb**

Comp. no.	Yield, %	mp, °C (mp [9])	Found, %				Formula	Calculated, %			
			C	H	N	S		C	H	N	S
Va	83	72–73 (73–75)	55.41	6.68	11.82	13.83	$C_{11}H_{16}N_2O_2S$	54.98	6.71	11.66	13.34
Vb	75	63–66 (60–65)	58.15	7.43	10.62	11.14	$C_{13}H_{20}N_2O_2S$	58.18	7.51	10.44	11.95
Vc	77	43–47 (36–45)	60.38	8.07	9.73	11.01	$C_{15}H_{24}N_2O_2S$	60.78	8.16	9.45	10.82
Vd[a]	62	–	54.75	6.31	11.16	12.99	$C_{11}H_{16}N_2O_2S$	54.98	6.71	11.66	13.34
VIa	89	78–81 (75–80)	48.23	5.38	10.52	11.85	$C_{11}H_{15}ClN_2O_2S$	48.09	5.50	10.20	11.67
VIb	81	82–85 (80–83)	51.75	6.23	9.51	10.74	$C_{13}H_{19}ClN_2O_2S$	51.56	6.32	9.25	10.59
VIc	67	79–80	47.63	5.13	10.53	11.32	$C_{11}H_{15}ClN_2O_2S$	48.09	5.50	10.20	11.67
VIIa	73	57–61 (55–60)	56.53	7.06	11.47	12.82	$C_{12}H_{18}N_2O_2S$	56.67	7.13	11.01	12.60
VIIb[a]	59	–	56.38	7.08	11.38	12.95	$C_{12}H_{18}N_2O_2S$	56.67	7.13	11.01	12.60

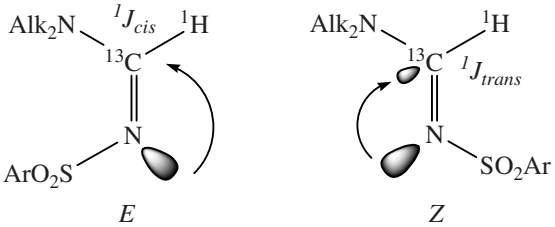
[a] Tarry compounds.

Table 4. IR and ^{1}H NMR spectra of *N,N*-dialkyl-*N'*-(arenesulfonyl)formamidines **Va–Vd, VIa–VIc, VIIa**, and **VIIb**

Comp. no.	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum ($CDCl_3$), δ, ppm			
	C=N	SO_2	CH_{alkyl}	HC=N	*s-cis*-Alk[a]	*s-trans*-Alk[b]	Ar
Va	1620	1160, 1290	2950–2980	8.16	3.48 q; 1.14 t	3.38 q; 1.26 t	7.47–7.89
Vb	1610	1160, 1290	2960–2985	8.08	3.26 t; 1.47 m; 0.74 t	3.18 t; 1.52 m; 0.78 t	7.37–7.77
Vc	1610	1140, 1290	2945–2970	8.15	3.41 t; 1.52 m; 1.27 m; 0.87 t	3.30 t; 1.59 m; 1.30 m; 0.95 t	7.44–7.88
Vd (*s-cis*)	1620	1150, 1290	2950–2980	8.13	3.38 t; 1.56 m; 0.84 t	3.08 c	7.42–7.93
Vd (*s-trans*)	1620	1150, 1290	2950–2980	8.16	2.97 s	3.29 t; 1.62 m; 0.88 t	7.42–7.93
VIa	1620	1160, 1310	2950–2980	8.14	3.48 q; 1.15 t	3.39 q; 1.27 t	7.43–7.82
VIb	1620	1150, 1310	2940–2970	8.14	3.37 t; 1.58 m; 0.87 t	3.28 t; 1.65 m; 0.92 t	7.43–7.81
VIc (*s-cis*)	1620	1160, 1290	2945–2980	8.13	3.40 t; 1.59 m; 0.87 t	3.11 s	7.43–7.82
VIc (*s-trans*)	1620	1160, 1290	2945–2980	8.16	2.99 s	3.31 t; 1.65 m; 0.91 t	7.43–7.82
VIIa	1620	1140, 1330	2940–2990	8.01	3.34 q; 1.01 t	3.27 q; 1.13 t	7.13–7.61
VIIb (*s-cis*)	1620	1160, 1310	2950–2990	8.14	3.40 t; 1.61 m; 0.87 t	3.09 s	7.26–7.76
VIIb (*s-trans*)	1620	1160, 1310	2950–2990	8.17	2.98 s	3.29 t; 1.65 m; 0.91 t	7.26–7.76

[a] N–Alk group is *s-cis* to the C=N bond. [b] N–Alk group is *s-trans* to the C=N bond.

is transferred from the nitrogen LEP orbital to the antibonding orbital of a bond *trans* to the LEP (n_σ–σ* interaction). As a result, the latter bond is elongated, the spin-spin coupling gets weaker, and the coupling constant decreases. All this leads to a negative contribution into the total $^1J_{trans}$ constant. The nature of this effect is well studied in a series of theoretical works [11] and widely used for configurational assessment of azomethines of various structures [12].



The coupling constants were calculated using by the use of a well-established nonempirical *Second Order Polarization Propagator Approach* (SOPPA) [13], including all the four spin–spin coupling contributions at the nonrelativistic level: Fermi contact (J_{FC}), spin–dipole (J_{SD}), diamagnetic spin–orbital (J_{DSO}), and paramagnetic spin–orbital (J_{PSO}), using

Table 5. ^{13}C NMR chemical shifts and $^{13}C–^{1}H$ coupling constants of *N,N*-dialkyl-*N'*-(arenesulfonyl)formamidines **Va–Vd, VIa–VIc, VIIa**, and **VIIb**

Comp. no.	^{13}C NMR chemicals shifts ($CDCl_3$), δ, ppm							*J*, Hz
	C=N	C^i	C^o	C^m	C^p	*s-cis*-Alk[a]	*s-trans*-Alk[b]	$^{1}J(C^{\alpha},H^{\alpha})$
Va	157.95	142.40	128.37	125.84	131.39	46.80; 11.71	40.62; 14.12	180.3
Vb	158.92	142.64	128.40	125.97	131.39	54.02; 19.62; 10.51	47.67; 21.56; 10.87	180.3
Vc	158.78	142.58	128.47	126.05	131.50	52.16; 28.48; 19.40; 13.40	45.80; 30.44; 19.71; 13.48	180.9
Vd (*s-cis*)	159.28	142.54	128.63	126.23	131.70	49.68; 19.28; 10.96	39.51	180.5
Vd (*s-trans*)	159.02	142.43	128.68	126.32	131.78	33.48	56.32; 21.14; 10.61	180.9
VIa	158.08	141.17	128.74	127.67	137.72	47.05; 11.88	40.87; 14.28	180.3
VIb	158.99	141.26	128.87	127.77	137.89	54.30; 19.90; 10.77	47.88; 21.78; 11.14	180.9
VIc (*s-cis*)	159.25	142.34	128.98	127.96	138.11	49.90; 19.34; 11.11	39.68	180.5
VIc (*s-trans*)	158.99	141.14	129.68	126.32	138.78	33.65	56.53; 21.31; 10.75	181.4
VIIa	157.88	139.57	126.01	129.07	142.08	46.86; 11.82	40.76; 14.25	180.9
VIIb (*s-cis*)	159.18	140.08	126.46	129.33	142.34	49.79; 19.44; 11.12	39.56	180.3
VIIb (*s-trans*)	158.92	139.71	126.56	129.38	142.46	33.57	56.42; 21.55; 10.77	180.3

[a] N–Alk group is *s-cis* to the C=N bond. [b] N–Alk group is *s-trans* to the C=N bond.

special Dunning's correlation-consistent basis sets [14] augmented with functions icluding intrinsic correlation effects [15] and the Sauer's basis set [16], as described in [17].

Comparison of the experimental $^{13}C–^{1}H$ coupling constants with the calculated values (Tables 5 and 6) shows that N-arenesulfonylformamidines all exist in solution as individual *E* isomers. Indeed, the experimental $^{13}C–^{1}H$ coupling constants of the studied formamidines are nicely reproduced by those calculated for the *E* isomer of the corresponding model amidine **X** and substantially differ from the calculated spin–spin coupling constants for a hypothetical *Z* isomer, that allows unambiguous assessment of *E* configuration to formamidines **V–VII**.

Spin–spin coupling constants were calculated for preferable rotamers of the *E* and *Z* isomers optimized at the MP2/6-311G** level. The geometries and relative energies are shown in Fig 1. It should be noted that for the *E* isomer of model compound **X** is 7.8 kcal mol^{-1} more stable than the corresponding *Z* isomer in their preferable conforma-tions. This is in line with the above-discussed results based on the experimental measurement and theoretical calculation of $^{13}C–^{1}H$ coupling constants, which provide unambiguos evidence in favor of the *E* configuration of all the studied amidines.

Internal rotation about the C–$NAlk_2$ bond in formamidines **V–VII** is restricted due to its partially double character caused by conjugation of the dialkylamino nitrogen LEP with the azomethine π system. This is also proved by the calculated barriers to internal rotation and the dynamic temperature effects observed in the NMR spectra. The nitrogen LEP in both the *E* and the *Z* isomers of model formamidine **X** in the optimized preferable conformations is orthogonal to the plane of the azomethine fragment. In the gas phase, according to the MP2/6-311G** results for compound **X**, the activation barrier of free rotation is 23 kcal mol^{-1}. Actually, the alkyl substituents in the *N,N*-dialkylamino groups in all the studied *N*-arenesulfonylformamidines are structurally nonequivalent and give two sets of signals in the ^{1}H and ^{13}C NMR spectra, which is caused by the partially double character of the C–$NAlk_2$ bond and,

Table 6. Calculated (SOPPA) and experimental $^{1}J(C^{I},H)$ coupling constants (Hz) for model formamidine **X**

Isomer	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	*J*	Experiment
E	1.3	–0.6	0.7	177.1	178.5	180.3[a]
Z	1.2	–0.4	0.5	187.3	188.6	

[a] For compound **Va**.

consequently, a high barrier to restricted internal rotation in these compounds. Analogous effects were observed earlier in similar sulfonylformamidines $H_3SO_2N{=}CHNR_2$ (R = Me, Et) [18] and *N,N*-dimethyl derivatives of arenesulfonylformamidines [9].

Assignment of alkyl group signals to different rotamers in the ^{1}H NMR spectra of compounds **Va–Vd, VIa–Vc, VIIa**, and **VIIb** was made by the use of the 2D-NOESY method which allows one to observe a characteristic cross-peak of the N–CH_2 protons of the *s-cis* alkyl group and the azomethine proton. As an illustration, we present in Fig. 2 the 2D-NOESY spectrum of *N'*-(benzenesulfonyl)-*N,N*-dibutylformamidine (**Vc**).

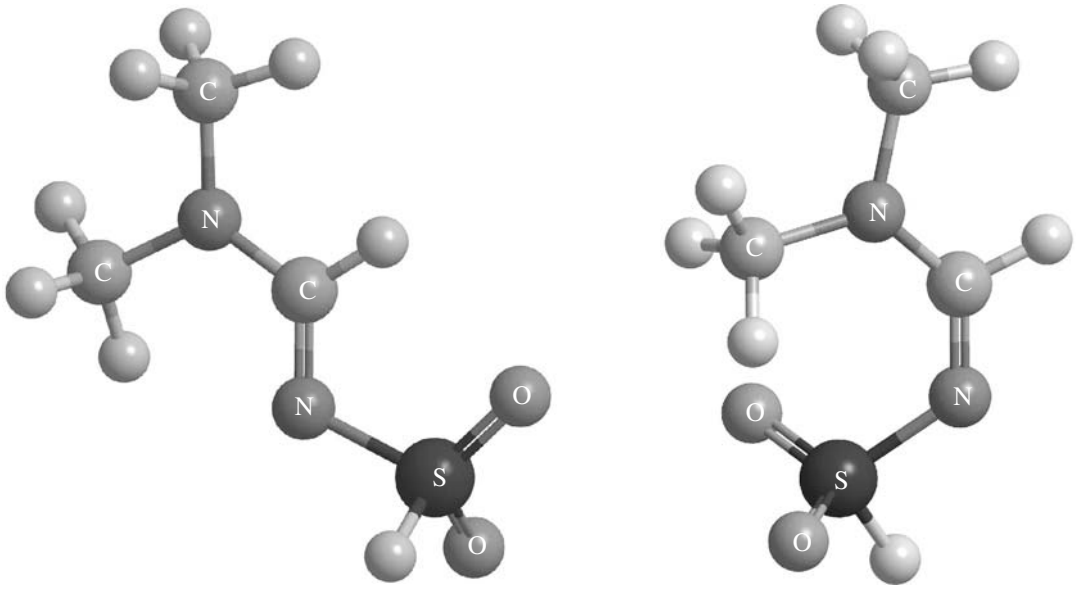
It is interesting to mention that in the case of *N*-methyl-*N*-propylformamidines **Vd, VIc**, and **VIIb** we can observe restricted rotation on an NMR time scale: The equilibrium *s-trans*:*s-cis* ratio of 70:30 is reached within 2–3 h (Fig. 3).

Therefore, in the present work the method of preparation of arenesulfonylimines derived from dichlorophenylacetaldehyde, based on the reaction of *N,N*-dichloroarenesulfonamides with phenylacetylene, was substantially optimized. The ability of *N*-(2,2-chloro-2-phenylethylidene)arenesulfonamides to suffer haloform cleavage under the action of secondary amines was demonstrated for the first time, and a convenient synthesis of *N*-arenesulfonyl-*N'*,*N'*-dialkylformamidines, alternative to that patented earlier [19], was developed. The structure of the synthesized compounds was studied by physicochemical methods.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were registered on a Bruker DPX-400 spectrometer at 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C for 5–10% solutions in $CDCl_3$ and DMSO-d_6, internal reference HMDS. The ^{13}C–^{1}H coupling constants were measured using 2D HSQC and HMBC pulse sequences with the following parameters: spectrum width 800 Hz (^{1}H) and 5 kHz (^{13}C), pulse length 6 μs (^{1}H) and 14 μs (^{13}C), relaxation delay 2.5 s, acquisition time 2 s, digital resolution 0.1 Hz/point (^{1}H) and 0.5 Hz/point (^{13}C).

***N*-(2,2-Dichloro-2-phenylethylidene)benzenesulfonamide (IVa) and 1,1-bis(benzenesulfonylamino)-2,2-dichloro-2-phenylethane (IIIa).** To a solution of 4 ml of phenylacetylene in 20 ml of carbon tetrachloride, 6.78 g of *N,N*-dichlorobenzenesulfonamide was added in portions (0.4–0.5 g) with stirring and argon bubbling. Each further portion of the



X(*E*), 0.0 kcal mol^{-1} **X**(Z), 7.8 kcal mol^{-1}

Fig. 1. Predominant conformations and relative energies of the *E* and *Z* isomers of model formamidine **X**, calculated by the MP2/6-311G** method.

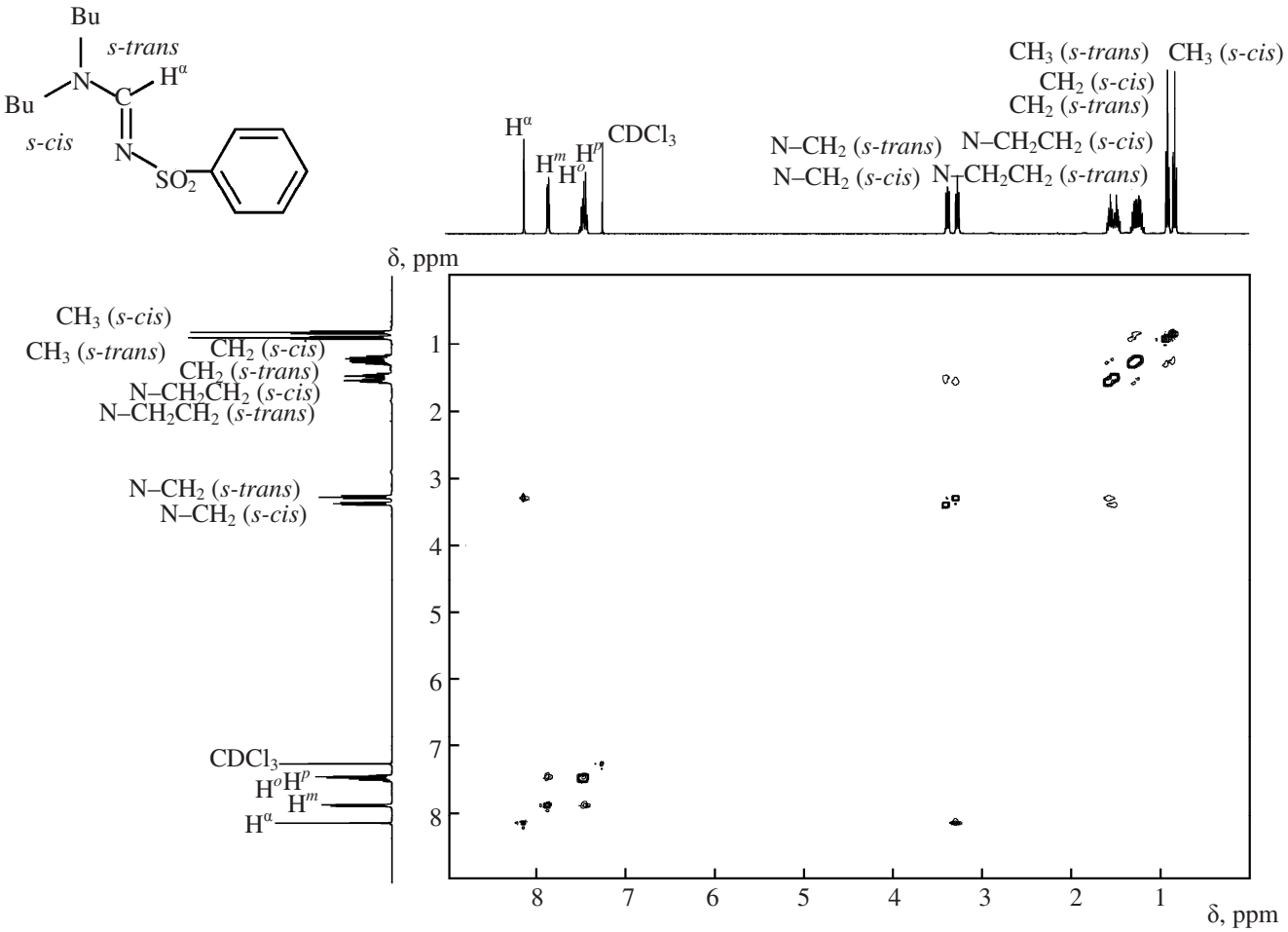


Fig. 2. 2D-NOESY spectrum of *N*'-(benzenesulfonyl)-*N,N*-dibutylformamidine (**XVI**) in $CDCl_3$ (400.13 MHz).

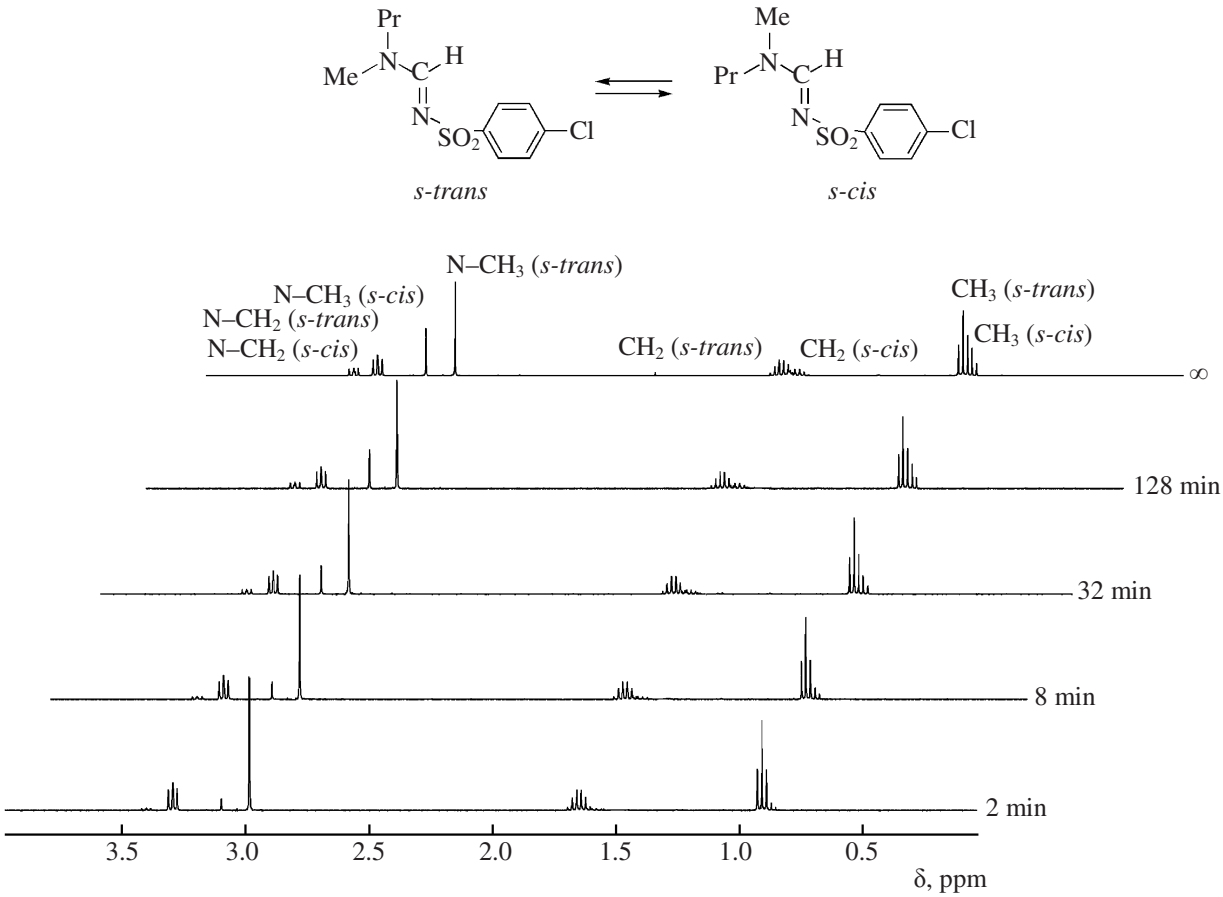
dichloroamide was added after the heat release produced by the previously added portion had been complete. The mixture was not allowed to overheat above 40°C. After all dichloroamide has been added, the reaction mixture was stirred for 2–3 h at 55–60°C, kept at –5°C until imine **IVa** precipitated. The precipitate was separated by filtration, washed on the filter with CCl_4, and dried under a vacuum over P_2O_5. When the filtrate was stored in the cold 3 days, diamide **IIIa** precipitated. The yields of compounds **IVa** and **IIIa** were 8.86 g (90%) and 0.50 g (3%), respectively.

Compounds **IIIb, IIIc** and **IVb, IVc** were obtained similarly. The yields, melting points, and spectral characteristics are given in Tables 1 and 2.

***N*'-(Benzenesulfonyl)-*N,N*-diethylformamidine (Va).** Imine **IVa**, 2.3 g, and 2.0 ml of diethylamine were stirred for 3 h in 20 ml of carbon tetrachloride, then the solvent was removed in acvacuum. The residue was washed with water, dried, and crystallized from CCl_4 or hexane. Yield 1.40 g (83%).

Formamidines **Vb–Vd, VIa–VIc, VIIa**, and **VIIb** were synthesized similarly by the reactions of azomethines **IVa–IVc** with diethylamine, dipropylamine, dibutylamine, and methylpropylamine. The yields, melting points, and spectral characteristics of compounds **Va–Vc, VIa, Vb**, and **VII** are given in Tables 3, 4, and 5.

***N*-(2,2-Dichloro-1-diethylamino-2-phenylethyl)-benzenesulfonamide (VIII)** was detected by ^{1}H NMR in the reaction mixture of imine **IVa** and diethylamine. From the ^{1}H NMR data, the yield of compound **VIII** was 5%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 t, 3.20 q [10H, $N(C_2H_5)_2$], 5.05 s (1H, CH), 6.67 s (1H, NH), 7.10–7.73 m (10H, Ar).



***N*-(2,2-Dichloro-1-diethylamino-2-phenylethyl)-4-chlorobenzenesulfonamide (IX)** was detected by ^{1}H NMR in the reaction mixture of imine **IVb** and diethylamine. From the ^{1}H NMR data, the yield of compound **IX** was 7%. ^{1}H NMR ($CDCl_3$), δ, ppm: 1.05 t, 3.12 q [10H, $N(C_2H_5)_2$], 4.98 s (1H, CH), 6.73 s (1H, NH), 7.35–7.87 m (9H, Ar).

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