

Long-Range ^{19}F – ^1H Spin–Spin Coupling as an Indication of Conformational Equilibrium of Fluoro-Substituted Aryl Vinyl Sulfides

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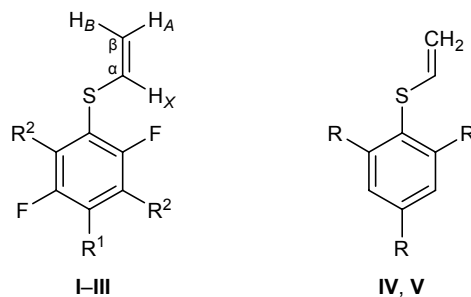
Abstract—Long-range ^{19}F – ^1H spin–spin coupling with participation of vinyl group protons, observed in the ^1H NMR spectra of fluoro-substituted aryl vinyl sulfides, indicates that these compounds exist as equilibrium mixtures of *s-cis* and *s-trans* rotational isomers.

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Steric structure of vinyl sulfides having various substituents was studied by several physicochemical methods [1, 2]. It was found that alkyl vinyl sulfides give rise to rotational isomerism related to internal rotation about the S–C $_{\alpha}$ bond. According to the results of nonempirical quantum-chemical calculations with account taken of electron correlation in terms of the second-order perturbation theory using Pople's triple-split basis set, the molecule of methyl vinyl sulfide adopts preferentially planar *s-cis* conformation [3]. The second, less energetically favorable conformer is represented by two quasi-degenerate nonplanar *gauche* structures separated by a low rotational barrier corresponding to the planar *trans* conformer [3]. Therefore, it can be regarded as quasi-*s-trans* conformer in which molecular fragments move with a large amplitude. Alkyl vinyl sulfides with branched alkyl groups are characterized by predominant *s-trans* (*gauche*) conformation [1, 2]. On the other hand, there are no published data on rotational isomerism in the series of aryl vinyl sulfides, though electronic structure of these compounds was examined on the basis of their ^{13}C NMR spectra [4]. Furthermore, ^1H and ^{13}C NMR studies on hetaryl vinyl sulfides revealed some conformation-related parameters which can be used to identify predominant spatial configuration [5, 6].

We previously synthesized several fluoro-substituted aryl vinyl sulfides [7, 8] which were used as initial compounds in the synthesis of a large number of more complex derivatives possessing an analogous

fragment [9–13]. These compounds clearly displayed in the ^1H NMR spectra long-range spin–spin couplings between ^{19}F nuclei and proton in the α -position of the vinyl group, and the observed couplings were used to identify regioisomers [10, 11]. However, long-range ^{19}F – ^1H coupling with other protons in the vinyl group was not observed previously, and stereochemical conditions ensuring observation of such coupling were not discussed in studies on the synthesis of fluoro-substituted aryl vinyl sulfides. The present communication reports on the use of long-range ^{19}F – ^1H spin–spin couplings involving α - and β -protons in the vinyl group, as well as of other conformation-dependent ^1H and ^{13}C NMR parameters, in experimental study on rotational isomerism of fluorine-containing aryl vinyl sulfides **I–III**. The populations of different rotamers of **I–III** and unsubstituted phenyl vinyl sulfide **IV** were compared on the basis of other conformation-related parameters of their ^1H and ^{13}C NMR spectra.



I, R¹ = CH₂=CHS, R² = F; **II**, R¹ = Cl, R² = F; **III**, R¹ = R² = CH₂=CHS; **IV**, R = H; **V**, R = Me.

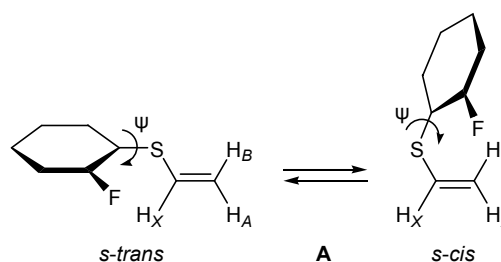
^1H and ^{13}C NMR spectra of aryl vinyl sulfides I–V

Compound no.	Chemical shifts δ , δ_{C} , ppm						Coupling constants, Hz			
	H_A	H_B	H_X	$\Delta\delta$	C^α	C^β	$^3J(\text{H}_A, \text{H}_X)$	$^3J(\text{H}_B, \text{H}_X)$	$^6J(\text{F}, \text{H}_B)$	$^5J(\text{F}, \text{H}_X)$
I	5.41	5.32	6.39	-0.09	128.39	116.81	9.4	16.4	0.55	0.35
II	5.40	5.29	6.35	-0.11	128.56	116.61	9.4	16.5	0.95	0.55
III	5.32	5.19	6.40	-0.13	129.88	114.98	9.5	16.5	0.95	0.30
IV	5.33	5.31	6.52	-0.02	131.92	115.33	9.4	16.7	–	–
V	4.98	4.50	6.23	-0.48			9.5	16.7		

The ^1H and ^{13}C NMR parameters of aryl vinyl sulfides I–IV are given in table. The ^{13}C NMR spectra of sulfides I–IV show excess shielding of the β -carbon atom in the vinyl group as compared to ethylene (δ_{C} 115–117 and 123 ppm, respectively), which indicates essential p - π interaction in the vinylsulfanyl group [1, 2]. Therefore, conformational equilibrium of aryl vinyl sulfides I–IV may be considered assuming the presence of *s-cis* and *s-trans* conformers in which high-amplitude vibrations of molecular fragments and considerable deviations from their coplanar arrangement are possible; the corresponding *gauche* conformer lacks p - π interaction in the vinylsulfanyl group [1, 2].

The most interesting in the ^1H NMR spectra of compounds I–III is long-range coupling between the H_B and H_X protons in the vinyl group, on the one hand, and ^{19}F nuclei, on the other [$^6J(\text{F}, \text{H}_B)$ and $^5J(\text{F}, \text{H}_X)$; see table]. In keeping with the experimental data and theoretical calculations, such interaction could be effectively transmitted through a system of bonds if the molecular fragment separating the interacting nuclei is planar and all bonds therein are *trans*-configured [14, 15]. In our case, no such fragment exist, so that the observed long-range ^{19}F - ^1H spin-spin coupling in sulfides I–III should be regarded as through-space interaction which requires that the distance between the interacting hydrogen and fluorine atoms be about the sum of their van der Waals radii (2.5–3.0 Å) [14–17]. This conclusion is consistent with the fact that the remote H_A proton in the vinyl group displays no coupling with ^{19}F . Through-space ^{19}F - $^1\text{H}_X$ interaction is feasible in the *s-trans* conformers of aryl vinyl sulfides I–III, whereas analogous ^{19}F - $^1\text{H}_B$ interaction requires an appreciable population of the *s-cis* conformer (structure A). Thus, the ^{19}F - ^1H couplings observed experimentally in the ^1H NMR spectra of fluorinated aryl vinyl sulfides I–III indicate the existence of conformational equilibrium involving *s-cis* and *s-trans* conformers. However, quantitative estimation

of the populations of *s-cis* and *s-trans* conformers on the basis of the experimental coupling constants $^6J(\text{F}, \text{H}_B)$ and $^5J(\text{F}, \text{H}_X)$ in compounds I–III is difficult because of high sensitivity of these coupling constants to the interatomic distance $^{19}\text{F}\cdots^1\text{H}$ [14–17].



Nonempirical quantum-chemical calculations showed that restricted rotation about the $\text{C}_{\text{Ph}}\text{-S}$ bond in aromatic sulfides is characterized by a low barrier; as a result, weight-average torsion angles between the benzene ring and C-S-C planes are fairly large, which corresponds to intermediate state between the planar and orthogonal conformations [18, 19]. Analogous pattern might be expected for fluoroaryl vinyl sulfides I–III, and the torsion angle Ψ between the planes of the benzene ring and vinylsulfanyl group in sterically strained *s-cis* conformer should be especially large. This is consistent with more upfield position of the H_B signal (the H_B proton is oriented *cis* with respect to the sulfur atom) relative to the signal of H_A which is oriented *trans* with respect to the sulfur atom (the value $\Delta\delta = \delta\text{H}_B - \delta\text{H}_A$ is negative; see table). When the aromatic fragment is strongly tilted relative to the vinylsulfanyl group plane, the H_B proton appears below the benzene ring plane (see structure A) and is shielded by the ring current [20, 21]. Hetaryl vinyl sulfides exist preferentially as *s-trans* conformers due to specific intramolecular interactions, and the H_B proton therein resonates in a weaker field as compared to H_A (the value $\Delta\delta = \delta\text{H}_B - \delta\text{H}_A$ is positive) [5, 6]. Increase in the population of the *s-cis* conformer of vinyl sulfides having an aromatic ring on the sulfur

atom may be judged by decrease of the parameter $\Delta\delta$, which is positive when *s-trans* conformer prevails and negative when conformational equilibrium includes an appreciable fraction of *s-cis* conformer [5, 6].

Taking the above stated into account, conformational behavior of fluoro-substituted aryl vinyl sulfides **I–III** can be compared with that of phenyl vinyl sulfide (**IV**). The parameter $\Delta\delta$ for phenyl vinyl sulfide (**IV**) is somewhat greater than those found for aryl vinyl sulfides **I–III** ($\Delta\delta = -0.02$ and -0.09 to -0.13 ppm, respectively; see table). Presumably, the main reason is not reduced population of the *s-cis* conformer but smaller torsion angle Ψ about the $\text{C}_{\text{Ph}}\text{--S}$ bond (due to smaller van der Waals radius of hydrogen compared to fluorine), for the H_X proton in the vinyl group of **IV** also resonates in a stronger field (by 0.12–0.17 ppm; see table). Analogous pattern is seen more clearly in the spectrum of 2,4,6-trimethylphenyl vinyl sulfide (**V**). Steric effect of two methyl groups in the *ortho* positions of the benzene ring in molecule **V** should lead to considerable increase of the weight-average torsion angle Ψ . As might be expected, the value of $\Delta\delta$ for sulfide **V** is considerably lower (-0.48 ppm), and the H_X signal is displaced upfield by 0.12–0.29 ppm relative to the corresponding signal of sterically unhindered sulfides **I–IV**. Taking into account variable effect of magnetically anisotropic aromatic fragment on the chemical shifts of H_B and H_X in the vinyl group of compounds **I–V**, it may be concluded that rotational *s-cis*–*s-trans* isomerism is intrinsic to all aryl vinyl sulfides to greater or lesser extent.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 instrument at 250.1 and 62.9 MHz, respectively, using CDCl_3 as solvent and HMDS as internal reference; sample concentration 5–10 wt % for ^{13}C NMR spectra and 0.1 wt % for ^1H NMR spectra.

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