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Methyl and Trifluoromethyl Vinyl Sulfones: Steric and Electronic Structure

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Abstract—The potential functions of internal rotation around the C_{sp^2}–S bond in the compounds $H_2C{=}CHSO_2CY_3$ (Y = H or F) were obtained; the stationary points were revealed and identified by solving vibrational problems [MP2(full)/6-31+G(d), B3PW91/6-31+G(d), B3PW91/6-311+G(3df,p)]. The energetically favorable conformations were determined, and the internal rotation barriers and geometric parameters of the molecules were estimated. The wave functions [MP2(full)/6-31+G(d)] were analyzed by the NBO method. The energies, populations, and dipole moments of natural orbitals of bonds and lone electron pairs, the main types of donor–acceptor interactions, the bond orders (Wiberg indices), and the natural charges on atoms were estimated. The steric and electronic structures of vinyl sulfoxides and sulfones are compared.

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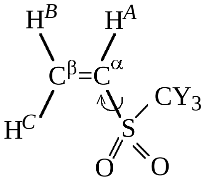
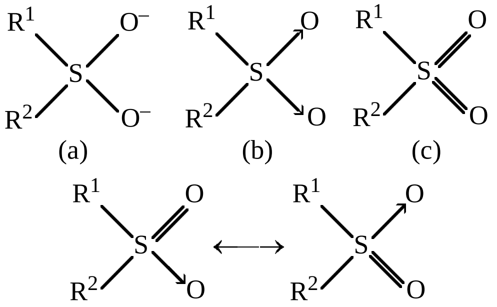
In the previous paper [1] we considered the steric and electronic structure of methyl and trifluoromethyl vinyl sulfoxides. Proceeding with these studies, we examined the corresponding vinyl sulfones. The steric isomerism of methyl and trifluoromethyl vinyl sulfones is associated with rotation of the SO_2CY_3 group (Y = H, F) around the C_{sp^2}–S bond.



The stationary points in the potential functions of internal rotation around the C_{sp^2}–S bonds can be characterized by the torsion angles between the $C^\beta{=}C^\alpha$–S and C^α–S=O planes (θ) or between the $C^\beta{=}C^\alpha$–S and C^α–S–C^Y planes (φ). According to the existing interpretation of the IR spectra, methyl vinyl sulfone in the crystal exists in the *gauche* (close to eclipsed) conformation with the *cis* arrangement of the S=O and C=C bonds, and in the liquid state this conformation exists in an equilibrium with the less stable *s-trans* conformation [2]. In the gas phase (80°C), according to electron diffraction, methyl vinyl sulfone exists in two conformations: with *s-cis* arrangement of the methyl and vinyl groups (φ 0°) and eclipsed *gauche* conformation (φ ~100°). Naumov and Kitaeva [4] believe that the eclipsed *gauche* form is more stable, and in the gas phase at 80°C the relative content of the conformer of approximate C_s symmetry may increase. According to quantum-chemical calculations [MP2/6-31G(d)], methyl vinyl sulfone exists in the eclipsed *gauche* conformation [5]. This compound was studied by molecular mechanics (MM3) calculations [6]. No conformational studies were performed with trifluoromethyl vinyl sulfone.

The electronic nature of the S=O bonds in the sulfonyl group was studied by theoretical and physicochemical methods (see, e.g., [7–18]). These bonds are considered as polar (a), semipolar (b), covalent double (c), or intermediate (d) [18].



The traditional concept (structure c) is the most common in chemistry. Reed and Schleyer [14] made a significant contribution to understanding the nature of chemical bonding in the sulfonyl group. Natural population analysis of the compounds $R^1SO^2R^2$ ($R^1 = R^2$ = Cl, CH_3; R^1 = Cl, $R^2 = CH_3$) showed that the S=O bond is partially ionic. The hyperconjugation of the oxygen lone electron pairs with the σ* orbitals of the S–R bonds by the n_π(O) → $\sigma^*_{S–R}$ mechanism make a decisive contribution, whereas the $n_{\pi}(O) \rightarrow d_{\pi}(S)$ interaction is of secondary significance. A QT-AIM calculation [19] showed that the S=O covalent bond is strongly polarized toward the O atom and the oxygen lone electron pairs provide considerable back-bonding [20–23].

The effect of the SO_2CY_3 groups (Y = H or F) on the electron density distribution is interpreted in organic chemistry in terms of the concepts of induction and resonance interactions. In the correlation analysis, the contribution of these interactions is formally estimated by the constants σ_I and σ_R [24–26]: SO_2CH_3 0.55 (σ_I), 0.16 (σ_R) and SO_2CF_3 0.73, 0.78 (σ_I), 0.31 (σ_R). The acceptor induction properties of the SO_2CY_3 groups are caused by the high electronegativity of the O and F atoms in these groups, and the acceptor resonance properties, by the interaction of the vacant *d* orbitals of the S atom with the π system of the unsaturated fragment (d,π conjugation) [27–29]. The first UV and IR studies of vinyl sulfones revealed no evidences of conjugation of the vinyl fragment with the SO_2 group [30, 31]. However, in other studies [32, 33] the optical spectra of these compounds are interpreted as confirming the occurrence of such interaction. The dipole moments of vinyl sulfones are discussed in [34]. In the NMR spectra of alkyl vinyl sulfones, changes in the shielding of the ^{13}C atoms of the double bonds are ascribed to the polarization and steric effects of the RSO_2 groups. [35]. The photoelectron spectra of alkyl vinyl sulfones are discussed in [36], and the X-ray fluorescence spectra, in [37].

The chemical theory of molecular structure is based on the concept of localized electron density of bonds. Since in the description of molecules in terms of the formalism of canonical molecular orbitals there is no direct correspondence with postulates of the traditional chemical theory, a problem arises: How to pass from the results of MO calculations to the concepts accepted in chemistry? The natural bond orbital (NBO) method [38–40] allows one to mathematically correctly pass from the quantum-chemical description of molecules to the concepts and terminology of the traditional chemical structural theory. Therefore, we consider it urgent to apply this method to various classes of organic compounds with the aim to generalize the views on the electronic structure and intramolecular interactions within the framework of a common quantum-chemical concept.

The goals of this study are as follows:

(1) analysis of the potential functions of internal rotation around the C_{sp^2}–S bonds in compounds $H_2C=CHSO_2CY_3$ (Y = H or F; **I** and **II**, respectively), determination and identification of stationary points, estimation of internal rotation barriers and parameters of molecular structure;

(2) NBO analysis of the wave functions; estimation of the energies, populations, and dipole moments of natural orbitals of bonds and lone electron pairs, discussion of the nature of intramolecular interactions and electron density distribution;

(3) comparison of the steric and electronic structures of vinyl sulfoxides and sulfones, based on the results obtained on the same level of quantum-chemical calculations.

Calculation procedures. Quantum-chemical calculations were performed using the GAUSSIAN-98W (Rev. A.7) [41] and GAMESS [42] program packages. The potential functions were obtained by rotation of fragments around the C_{sp^2}–S bonds in the range of torsion angles θ from 0° to 360° with a step of 15° and full optimization of the other geometric parameters. The stationary points were determined at full optimization of the geometry (including the torsion angle θ) and were identified by solving the vibration problems in the MP2(full)/6-31+G(d), B3PW91/6-31+G(d), and B3PW91/6-311+G(3df,p) approximations [43]. Standard criteria of convergence of the density matrix and energy gradient were used. In the vibration problems, all the frequencies are positive in the minima and one imaginary frequency is observed in the Hesse matrix in the saddle points (transition states). The rotation barriers were corrected for the zero-point vibration energy. The wave functions obtained in the MP2(full)/6-31+G(d) approximation were analyzed using the NBO formalism [38–40] with the NBO 5.0 program [44].

Conformation and parameters of molecular structure. The potential functions of internal rotation of fragments around the C_{sp^2}–S bonds in **I** and **II** are plotted in Figs. 1 and 2, respectively. The characteristics of the stationary points and the barriers to internal rotation of fragments around the C_{sp^2}–S bond in **I** and **II** are given in Tables 1 and 2, respectively. The potential function of **I** obtained in the MP2(full)/6-31+G(d) approximation has two degenerate minima (Min-1 and Min-2) corresponding to the same conformation. The B3PW91/6-31+G(d) and B3PW91/6-311+G(3df,p) calculations also give two degenerate minima (Min-1 and Min-2) corresponding to the same conformation, but in addition a shallow local energy minimum (Min-3) is observed at θ 114.9°–115.1°. The difference between the energies of Min-1 (or Min-2) and Min-3 is 11.09 [MP2(full)/6-31+G(d)] or 9.78 kJ mol^{-1} [B3PW91/6-31+G(d)]. The rotation barriers Min-3/TS-1 and Min-3/TS-3 are less than *kT*. The other rotation barriers appreciably exceed *kT*. The

Table 1. Characteristics of the stationary points of the potential functions of internal rotation around the C_{sp^2}–S bond in **I**: torsion angles (deg), total energies (E_{tot}, au), corrections for zero-point vibration energy (Z_0, Hartree/particle), imaginary frequencies (ν, cm^{-1}), and internal rotation barriers ($\Delta H^{\neq}$, kJ mol^{-1})

Structure	∠θ	∠φ	$-E_{tot}$	Z_0	ν	$\Delta H^{\neq}$
MP2(full)/6-31+G(d) method						
Min-1	2.6	248.7	665.170298	0.092128	–	
Min-2	225.0	111.3	665.170298	0.092128	–	
TS-1	114.7	0.0	665.165167	0.091881	–20.8	12.82$^{a, b}$
TS-2	294.0	180.0	665.163508	0.091576	–134.8	16.38$^{a, b}$
B3PW91/6-31+G(d) method						
Min-1	0.9	246.7	666.337941	0.090680		
Min-2	226.8	113.2	666.337941	0.090680		
Min-3	114.9	359.8	666.333578	0.090539		
TS-1	76.6	321.2	666.333106	0.090407	–78.7	11.99,^{a} 0.89^{c}
TS-2	294.1	180.0	666.331772	0.090115	–122.3	14.72$^{a, b}$
TS-3	152.3	38.5	666.333106	0.090407	–75.9	11.99,^{b} 0.89^{c}
B3PW91/6-311+G(3df,p) method						
Min-1	0.4	245.9	666.504218	0.090293		
Min-2	228.1	114.3	666.504218	0.090293		
Min-3	115.1	359.2	666.500311	0.090112		
TS-1	71.3	315.8	666.499386	0.089965	–95.1	11.83,^{a} 2.04^{c}
TS-2	294.4	180.1	666.498155	0.089740	–125.8	14.48^{a},^{b}
TS-3	158.1	44.1	666.499386	0.089965	–90.3	11.83,^{b} 2.04^{c}

Note: Height of rotation barriers relative to ^{a} Min-1, ^{b} Min-2, and ^{c} Min-3.

potential function of internal rotation in **II**, obtained in the MP2(full)/6-31+G(d), B3PW91/6-31+G(d), and B3PW91/6-311+G(3df,p) approximations, has two degenerate minima (Min-1 and Min-2) corresponding to the same conformation. The rotation barrier heights exceed *kT*. Thus, compounds **I** and **II** mainly exist in the *gauche* (close to eclipsed) conformations with the *cis* arrangement of the S=O and C=C bonds.

The parameters of the molecular structures of **I** and **II** are given in Table 3. The S=O bond in **II** is shorter than in **I** by 0.008 (B3PW91) or 0.009 Å (MP2). The S–CH_3 bond is shorter than the S–CF_3 bond by 0.075 (MP2) or 0.094 Å (B3PW91). The S–C^{α} bond in **II** is shorter than in **I** by 0.007 (MP2) or 0.010 Å (B3PW91). The C=C bond lengths differ insignificantly (0.001 Å). The C^{α}–SC^{Y} bond angles in **I** are larger than in **II** by 2.8° (MP2) or 1.8° (B3PW91). The $C^{\beta}C^{\alpha}S$ bond angles in **I** are larger than in **II** by 0.7° (MP2) or 0.8° (B3PW91). The OSO bond angles in **I** are smaller than in **II** by 2.1° (MP2) or 1.9° (B3PW91). The calculated parameters of the molecular structure of **I** reasonably agree with the electron diffraction data [3].

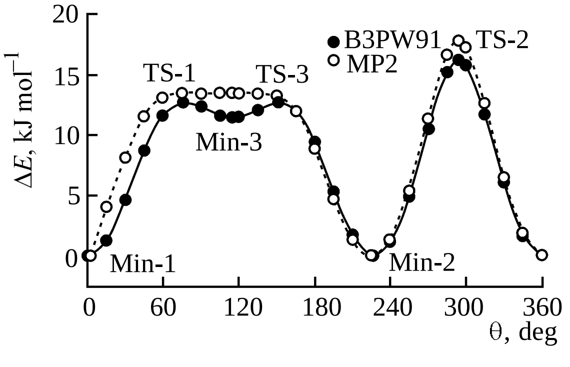


Fig. 1. Potential function of internal rotation of fragments around the C_{sp^2}–S bond in **I** (TS denotes transition state).

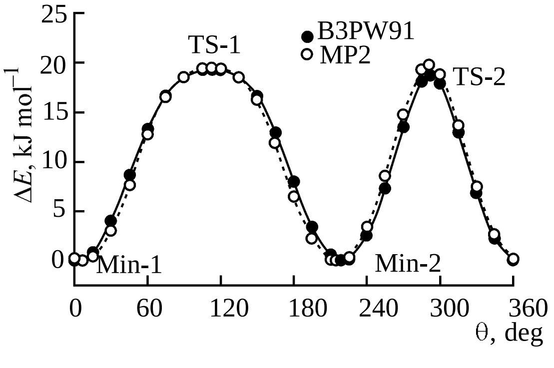


Fig. 2. Potential function of internal rotation of fragments around the C_{sp^2}–S bond in **II**.

Table 2. Characteristics of the stationary points of the potential functions of internal rotation around the C_{sp^2}–S bond in **II**: torsion angles (deg), total energies (E_{tot}, au), corrections for zero-point vibration energy (Z_0, hartree/particle), imaginary frequencies (ν, cm^{-1}), and internal rotation barriers ($\Delta H^{\neq}$, kJ mol^{-1})

Structure	∠θ	∠φ	$-E_{tot}$	Z_0	ν	$\Delta H^{\neq}$ [a]
			MP2(full)/6-31+G(d) method			
Min-1	6.4	255.6	962.264518	0.068105		
Min-2	215.3	104.4	962.264518	0.068105		
TS-1	112.3	0.0	962.257067	0.067800	–58.5	18.76
TS-2	291.2	180.0	962.256980	0.067562	–124.5	18.37
			B3PW91/6-31+G(d) method			
Min-1	3.5	251.7	963.944366	0.067188		
Min-2	219.6	108.3	963.944366	0.067188		
TS-1	113.4	0.4	963.936984	0.066843	–46.4	18.49
TS-2	291.6	179.9	963.937233	0.066703	–124.3	17.47
			B3PW91/6-311+G(3df,p) method			
Min-1	3.2	251.3	964.217892	0.067345		
Min-2	220.1	108.7	964.217892	0.067345		
TS-1	108.1	354.7	964.210934	0.066975	–25.2	17.31
TS-2	291.8	180.0	964.210823	0.066879	–123.2	17.34

[a] Height of rotation barriers relative to Min-1 and Min-2 (equal values).

Table 3. Bond lengths (Å) and bond angles (deg) in $H_2C{=}CHSO_2CY_3$ (Y = H or F) obtained in the approximations (a) MP2(full)/6-31+G(d) and (b) B3PW91/6-311+G(3df,p); (c) electron diffraction data [3][a]

Parameter	Method	Y = H	Y = F	Parameter	Method	Y = H	Y = F
$d(S{=}O)$	*a*	1.473.2	1.464 × 2	$d(C^{\beta}–H^{B})$	*a*	1.086	1.086
	b	1.440.2	1.432 × 2		*b*	1.085	1.085
	c	1.429(4)					
$d(S–C^{Y})$	*a*	1.783	1.858	$d(C^{\beta}–H^{C})$	*a*	1.085	1.085
	b	1.778	1.872		*b*	1.085	1.085
	c	1.776(–)					
$d(S–C^{\alpha})$	*a*	1.772	1.765	$\angle C^{\alpha}SC^{Y}$	*a*	103.6	100.8
	b	1.769	1.759		*b*	103.6	101.8
	c	1.774(8)			*c*	103.2(1.6)	
$d(C^{\alpha}{=}C^{\beta})$	*a*	1.336	1.337	$\angle C^{\beta}C^{\alpha}S$	*a*	120.2	119.5
	b	1.322	1.323		*b*	120.5	119.7
	c	1.347(16)			*c*	118.4(2.1)	
$d(C^{\alpha}–H^{A})$	*a*	1.087	1.086	∠OSO	*a*	121.3	123.4
	b	1.085	1.084		*b*	120.5	122.4
	c	120.0(1.5)					

[a] In the methyl group, *d*(C–H) 1.093, 1.091, 1.092 (a); 1.091, 1.089, 1.090 (b). In the trifluoromethyl group, *d*(C–F) 1.336, 1.343, 1.346 (a); 1.322, 1.326, 1.331 (b).

Main characteristics of natural bond orbitals. The energies ($E_{A–B}$), populations ($P_{A–B}$), natural atomic hybrid coefficients (c_A, c_B), dipole moments [$\mu_{A–B}$(NBO)], and Wiberg indices [$W_{A–B}$(NAO)] of the bonding natural bond orbitals are given in Table 4. The coefficients c_A and c_B show the contributions to the bonding natural orbital of the A–B bond made by natural atomic hybrids of each of the atoms A and B [38, 39, 44]. They reflect the electron density introduced by the atom into the bonding natural bond orbital (% of its population). Therefore, c_A and c_B can serve as a measure of the polarization of the natural bond orbital and show the direction of its dipole moment. The Wiberg index is the relative measure of the

Table 4. Main characteristics of NBO of bonds: energy ($E_{A–B}$, eV), population ($P_{A–B}$, e), natural atomic hybrid coefficients (c_A, c_B, %), dipole moments ($\mu_{A–B}$, D), and Wiberg indices ($W_{A–B}$)

A–B bond	$H_2C{=}CHSO_2CH_3$						$H_2C{=}CHSO_2CF_3$					
	$-E_{A–B}$	$P_{A–B}$	c_A	c_B	$\mu_{A–B}$	$W_{A–B}$	$-E_{A–B}$	$P_{A–B}$	c_A	c_B	$\mu_{A–B}$	$W_{A–B}$
σ(S–O)	32.9	1.954	33.9	66.1	1.50	1.16	34.3	1.953	34.2	65.8	1.46	1.19
	33.1	1.955	33.8	66.2	1.50	1.16	34.4	1.953	34.1	65.9	1.46	1.19
σ(S–C^Y)	24.0	1.944	47.3	52.7	0.55	0.81	24.6	1.920	45.0	55.0	0.63	0.66
σ(S–C^α)	24.5	1.937	46.6	53.4	0.56	0.80	25.7	1.935	47.8	52.2	0.42	0.81
σ(C^α=C^β)	28.3	1.963	51.2	48.8	0.12	1.83	28.9	1.963	51.5	48.5	0.13	1.81
π(C^α=C^β)	11.5	1.911	54.7	45.3	0.53		12.1	1.901	56.1	43.9	0.69	
σ(C^α–H^A)	20.8	1.956	63.6	36.4	1.69	0.86	21.4	1.956	64.4	35.6	1.60	0.85
σ(C^β–H^B)	20.4	1.959	61.9	38.1	1.74	0.89	21.0	1.958	62.3	37.7	1.70	0.88
σ(C^β–H^C)	20.3	1.960	62.9	37.1	1.63	0.88	21.0	1.960	63.0	37.0	1.61	0.88

bond order [45]. In what follows, the natural bond orbitals will be shortly termed bond orbitals.

According to the NBO model, the S atom in the sulfonyl group is bonded with each of the O atoms by a covalent σ bond. The energy levels of the orbitals of the S–O σ bonds in **II** lie lower by 1.3 and 1.4 eV compared to **I**. The populations of the orbitals of the S–O σ bonds differ insignificantly (by ≤0.002 e). The electron density of the orbitals of the $S^{\delta+}$–$O^{\delta-}$ σ bonds is polarized toward the O atom by 16.1 or 16.2% (Y = H) and by 15.8 or 16.2% (Y = F) relative to the symmetrical distribution. The $\mu_{S–O}$ value in **I** exceeds that in **II** by 0.04 D. The $W_{S–O}$(NAO) indices are intermediate between those corresponding to single and double bonds, which is indicative of the increased multiplicity of the S–O bond. The $W_{S–O}$(NAO) values in **II** are larger than those in **I** by 0.03.

The energy level of the S–CF_3 bond orbital lies lower than that of the S–CH_3 orbital by 0.6 eV. The population of the S–CH_3 bond orbital is higher than that of the S–CF_3 orbital by 0.024 e. The electron density of the S–C^Y bond orbitals is polarized toward the C atom by 2.7 (S–CH_3) and 5.0% (S–CF_3) relative to the symmetrical distribution. The $\mu_{S–C}$ value for the S–CF_3 bond orbital is 0.08 D higher compared to the S–CH_3 bond. The $W_{S–C}$(NAO) index for the S–CH_3 bond is close to that characteristic of single bonds, whereas that for the S–CF_3 bond is appreciably lower, indicating that this bond is electron-deficient.

The energy level of the S–C^α bond orbital in **II** lies lower than that in **I** by 1.2 eV. The population of the S–C^α bond orbital in **I** is higher than that in **II** by 0.002 e. The electron density of the S–C^α bond orbital is polarized toward the C atom by 3.4 (Y = H) and 2.2% (Y = F) relative to the symmterical distribution. The $\mu_{S–C}$ value for the S–C^α orbital in **I** is 0.14 D larger compared to **II**. The $W_{S–C}$(NAO) indices are close to those characteristic of single bonds.

The energy levels of the orbitals of the σ and π bonds in the vinyl fragment of **II** lie 0.6 eV lower than in that of **I**. The population of the σ orbital of the double bond is insensitive to Y (H or F) on the chosen level of accuracy. The population of the π orbital in **I** is 0.010 e higher than in **II**. The electron densities of the σ and π orbitals of the double bond are polarized toward the α-C atom by 1.2 (σ, Y = H), 1.5 (σ, Y = F), 4.7 (π, Y = H), and 6.1% (π, Y = F) relative to the symmetrical distribution. The dipole moments of the σ and π orbitals of the double bond in II are 0.01 (σ) and 0.16 D (π) larger than those in **I**. The $W_{C=C}$(NAO) indices of the double bond in the vinyl fragment of **I** and **II** are similar.

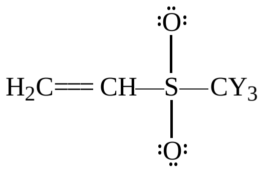
The energy of the C^α–H^A, C^β–H^B, and C^β–H^C σ bond orbitals varies from –20.3 to –20.8 eV in **I** and from –21.0 to –21.4 eV in **II**. The population of these orbitals varies from 1.956 to 1.960 e. The dipole moments of the orbitals of these bonds are directed toward the carbon atom ($C^{\delta-}$–$H^{\delta+}$) and vary from 1.60 to 1.74 D.

Main characteristics of the natural orbitals of the oxygen lone electron pairs and donor–acceptor interactions. The energies (E_n), populations (P_n), and dipole moments [μ_n(NBO)] of the natural orbitals of the lone pairs (hereinafter, lone-pair orbitals) of the O and S atoms and the fractions of the *s* constituent (*s*) in the corresponding hybrids are given in Table 5.

In the sulfonyl group, the electron density of the π bond is mainly localized on the O atom, which, in terms of the NBO model, formally corresponds to the presence of three lone pair orbitals on this atom.

Table 5. Main characteristics of NBO of lone electron pairs (LEP) of O and S atoms: energy (E_n, eV), population (P_n, e), dipole moments (μ_n, D), and fraction of *s* constituent (*s*, %)

LEP	$H_2C{=}CHSO_2CH_3$				$H_2C{=}CHSO_2CF_3$			
	$-E_n$	P_n	μ_n	*s*	$-E_n$	P_n	μ_n	*s*
n_σ(O)	28.8	1.960	2.46	76	29.7	1.960	2.45	76
	28.9	1.960	2.44	76	29.8	1.961	2.44	76
n_π^1(O)	12.2	1.799	0.12	<1	13.0	1.780	0.13	<1
	12.3	1.800	0.10	<1	13.1	1.775	0.18	<1
n_π^2(O)	12.0	1.760	0.28	<1	12.8	1.738	0.30	<1
	12.2	1.764	0.32	<1	12.9	1.748	0.29	<1



$$H_2C{=}CH{-}\overset{\ddot{O}:}{\underset{:\ddot{O}:}{S}}{-}CY_3$$

The hybrid orbital of one of the oxygen lone electron pairs has ~76% *s* character (n_σ), and the other two lone pairs are virtually “pure” *p* orbitals with less than 1% contribution of the *s* constituent (n_π). The energy levels of the n_σ orbitals are lower than those of the n_π orbitals, and the population of the n_σ orbitals is higher than that of the n_π orbitals. The μ_n values for the n_σ orbitals considerably exceed those for the n_π orbitals.

The energies of the donor–acceptor interaction (E_R) of the lone electron pairs of the oxygen atoms with the surrounding fragments are given in Table 6. The hybrid orbital n_σ(O) is only weakly involved in donor–acceptor interactions. The lone pairs n_π^1(O) and n_π^2(O) interact with the antibonding π* orbitals of the S–C^α and S–C^Y bonds by the hyperconjugation mechanism: $n_\pi(O) \rightarrow \sigma^*(S{-}C^\alpha)$ and $n_\pi(O) \rightarrow \sigma^*(S{-}C^Y)$. According to the E_R values, these interactions are more efficient in the compounds with Y = F owing to a more pronounced acceptor (electron-deficient) character of the S–CF_3 bonds. Also, n_π^2(O) of each O atom interacts with antibonding σ* orbital of the adjacent S–O bond by the mechanism $n_\pi^2(O^1) \rightarrow \sigma^*(S{-}O^2)$ and $n_\pi^2(O^2) \rightarrow \sigma^*(S{-}O^1)$. The mechanism of bonding of *n*(O) with the *d* orbitals of the S atom involves interactions with the Rydberg (*RY**) *d*-type orbitals: $n_\pi(O) \rightarrow > RY^*(S)$. The energy of such interactions is, on the whole, lower than the energy of the hyperconjugation bonding of n_π(O) with the σ* orbitals of the S–C bonds. The fluorine lone electron pairs interact with the σ* orbitals of the S–C^F bond by the $n(F) \rightarrow \sigma^*(S{-}C^F)$ mechanism (E_R up to 44 kJ mol^{-1}) and with those of the adjacent C–F bonds by the $n(F) \rightarrow \sigma^*(C{-}F)$ mechanism (E_R up to 66 kJ mol^{-1}).

Table 6. Energy of the main donor–acceptor interactions (E_R, kJ mol^{-1})

Donor	Acceptor	$H_2C{=}CHSO_2CY_3$	
		Y = H	Y = F
n_π^1(O)	$\sigma^*(S{-}C^\alpha)$	76.1, 61.5	103.1, 101.1
n_π^2(O)	$\sigma^*(S{-}C^\alpha)$	32.0, 53.6	11.1, 2.9
n_π^1(O)	$\sigma^*(S{-}C^Y)$	82.3, 94.8	50.5, 72.0
n_π^2(O)	$\sigma^*(S{-}C^Y)$	24.8, 10.3	101.6, 74.9
$n_\pi^2(O^{1,2})$	$\sigma^*(S{-}O^{2,1})$	138.1, 128.4	113.1, 123.8
n_π^1(O)	*RY**1(S)	50.2, 44.2	50.0, 46.5
n_π^1(O)	*RY**2(S)	31.3, 26.5	32.8, 29.5
n_π^2(O)	*RY**2(S)	43.6, 44.0	42.9, 49.0
π(C=C)	$\sigma^*(S{-}C^Y)$	15.0	24.2
π(C=C)	σ*(S–O)	14.2	11.7
π(C=C)	*RY**3(S)	5.6	9.5

The energy of the donor–acceptor interactions of the σ and π orbitals of the double bond with the surrounding fragments is relatively low. The π orbitals of the double bond interact with the antibonding σ* orbitals of the S–C^Y bonds by the $\pi(C{=}C) \rightarrow \sigma^*(S{-}C^Y)$ mechanism and with those of the S–O bond by the $\pi(C{=}C) \rightarrow \sigma^*(S{-}O)$ mechanism. The energy of the interaction by the $\pi(C{=}C) \rightarrow RY^*(S)$ mechanism is relatively low.

Electron density distribution. The natural charges (hereinafter, charges) on atoms are given in Table 7. The electron density on the functional groups SO_2CY_3 can, on the whole, be characterized by the sum of atomic charges: 0.138 (SO_2CH_3) and 0.097 e (SO_2CF_3). On replacement of H by F, the electron density on Y increases by 1.866 e and that on C^Y

Table 7. Natural charges (q, e) on atoms in the compounds $H_2C{=}CHSO_2CY_3$ (Y = H or F)[a]

Charge	SO_2CH_3	SO_2CF_3
q(X)	2.142	2.080
q(O)	–0.942, –0.948	–0.894, –0.901
$q(C^Y)$	–0.940	0.853
q(Y)	0.284, 0.270, 0.272	–0.339, –0.353, –0.349
$q(C^\alpha)$	–0.528 (–0.092)	–0.542 (–0.106)
$q(C^\beta)$	–0.367 (0.069)	–0.338 (0.098)
$q(H^A)$	0.265 (0.047)	0.281(0.063)
$q(H^B)$	0.237 (0.019)	0.245 (0.027)
$q(H^C)$	0.255 (0.037)	0.257 (0.039)
Σq_{Vin}	–0.138 (0.081)	–0.097 (0.121)
$\Delta q(C^\alpha{=}C^\beta)$	0.161	0.204

[a] In parentheses are the differences between the charges on each atom of the vinyl fragment in $H_2C{=}CHSO_2CY_3$ and ethylene [q(C) –0.436; q(H) 0.218 e] and between the sums of charges of the $CH_2{=}CH$ fragment in $H_2C{=}CHSO_2CY_3$ and ethylene.

decreases by 1.793 e, due to different electronegativities of H and F. With increasing distance from C^Y, the electronic effects rapidly weaken. The electron density on the S atom increases by 0.062 e, and that on the O atoms decreases by 0.048 and 0.047 e (by 0.095 e in total). This may be caused by increased multiplicity of the S=O bonds and hyperconjugation interactions of oxygen lone electron pairs. Thus, the major factor responsible for changes in the atomic charges in the functional groups SO_2CY_3 is the difference in the electronegativity of Y (H < F).

In an isolated molecule, the sum of atomic charges is zero by definition. Therefore, the sum of charges on atoms of the vinyl fragment, on the whole, "compensates" the sum of charges on atoms of the corresponding functional groups with the opposite sign (Table 7, Σd_{Vin}). These electron densities are redistributed over atoms of the vinyl fragmnent in molecules with the corresponding groups SO_2CY_3. Replacement of H by F in the SO_2CY_3 group decreases the electron density on atoms of the vinyl fragment by 0.041 e. In ethylene, the sum of charges on atoms of the $CH{=}CH_2$ group is –0.218 e. Therefore, replacement of one H atom in ethylene by SO_2CY_3 groups decreases the electron density on the vinyl fragment (Table 7, Σq_{Vin} in parentheses). These values are actually the quantitative characteristic of the electron-withdrawing effect of the SO_2CY_3 groups on the vinyl fragment as a whole, relative to the effect exerted by the H atom as substituent.

The charges on the C^α and C^β atoms show that the C=C bond is polarized toward the C^α atom. On replacement of H by F, the electron density on the C^α atoms increases by 0.014 e and that on the C^β atoms decreases by 0.029 e. The stronger changes in the charge on C^β, compared to C^α, are due to specific features of multiple bonds. The charge on each atom of the vinyl fragment relative to the charge on the corresponding atom in ethylene is given in Table 7 in parentheses. These values quantitatively characterize an increase in the electron density on the C^α atoms and a decrease in the electron density on the C^β, H^A, H^B, and H^C atoms of the vinyl fragment on replacement of a hydrogen atom in ethylene by the SO_2CH_3 or SO_2CF_3 group.

The bond polarity can be characterized by the difference between the atomic charges. The differences between the charges on C^α and C^β in **I** and **II** are given in Table 7 [$\Delta q(C^\alpha{=}C^\beta)$]. The thus estimated polarity of the double bond is qualitatively similar to the dipole moments of localized molecular orbitals of bonds but reflects not only the asymmetry of the electron distribution in orbitals of the bond between these atoms but also the asymmetry of the electron distribution in the nearest surrounding. The thus estimated polarity of the double bond in **II** is considerably larger than in **I**.

Comparison of the steric and electronic structures of $H_2C{=}CHXCY_3$ (X = SO or SO_2; Y = H or F). Comparison of the results we obtained for $CH_2{=}CHSOCY_3$ in [1] and for $CH_2{=}CHSO_2CY_3$ in this study allows the following conclusions.

(1) The compounds $CH_2{=}CHSOCY_3$ and $CH_2{=}CHSO_2CY_3$ (Y = H or F) exist in the gas phase mainly in the *gauche* (close to eclpised) conformations with the *cis* arrangement of the S=O and C=C bods (the torsion angle θ varies from 2.6° to 9.6°). In these conformations, in compounds with the same Y, the S=O, $S{-}CH_3$, $S{-}CF_3$, and $S{-}C^\alpha$ bonds in vinyl sulfones are shorter than in vinyl sulfoxides. The C=C bond lengths in these compounds differ insignificantly. The $C^\alpha SC^Y$ bond angles in vinyl sulfones are larger than in vinyl sulfoxides by 7.2°–7.9°; the other bond angles differ by no more than 1°.

(2) The energy levels of the orbitals of bonds in vinyl sulfones lie lower than those of the corresponding bonds in vinyl sulfoxides, and those in the derivatives with Y = F lie lower than those in the corresponding derivatives with Y = H. The energy levels of the σ and π orbitals of the double bond in vinyl sulfones lie lower than those of the corresponding orbitals in vinyl sulfoxides by 6.6 (σ) and 2.8 eV (π) in the compounds with Y = H and by 6.8 (σ) and 3.0 eV (π) in the compounds with Y = F. The energy levels of the σ and π orbitals of the double bond in

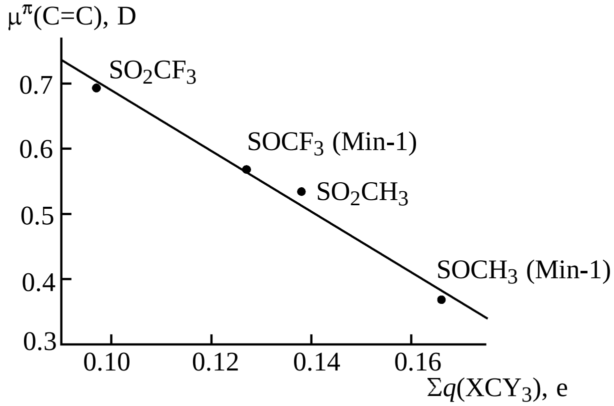


Fig. 3. Linear correlation of the dipole moment of NBO of the C=C π orbital in $H_2C=CHXCY_3$ (X = SO or SO_2, Y = H or F) with the sum of charges on atoms in the XCY_3 group: $\mu^{\pi}(C=C) = -1.16(\pm0.05) - 4.66(\pm0.40)\cdot \Sigma q(XCY_3)$, *r* 0.993, *n* 4.

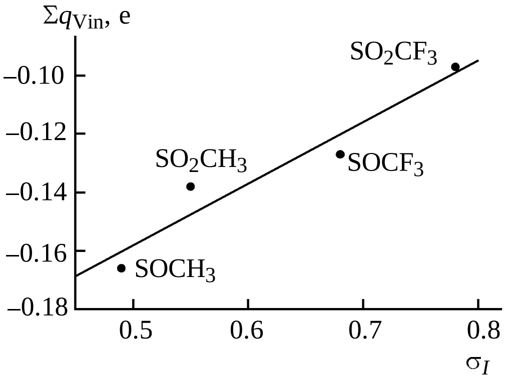


Fig. 4. Linear correlation of the sum of charges on atoms of the vinyl fragment (Σq_{Vin}) and induction constants σ_I of XCY_3 groups: $\Sigma q_{Vin} = -0.26(\pm0.02) + 0.21(\pm0.04)\sigma_I$, *r* 0.964, *n* 4.

vinyl sulfoxides lie higher, and in vinyl sulfones, lower than the energy levels of the corresponding orbitals in ethylene.

(3) The populations of the orbitals of bonds in vinyl sulfones are lower than those of the corresponding orbitals in vinyl sulfoxides (except for the S–O bonds). The population of the σ orbital of the double bond in vinyl sulfoxides and vinyl sulfones is lower by 0.004 and 0.006 e, respectively, than in ethylene (1.969 e), and the population of the π orbital is lower compared to ethylene (1.940 e) by 0.017 ($SOCH_3$), 0.024 ($SOCF_3$), 0.029 (SO_2CH_3), and 0.039 e ($SO_2\cdot CF_3$). This is due to the electron-withdrawing effect of the XCY_3 groups on the vinyl fragment compared to the effect exerted by H as substituent.

(4) The orbitals of the $S^{\delta+}–O^{\delta-}$, $C^{\delta-}–H^{\delta+}$, and $C^{\delta+}–H^{\delta-}$ bonds are strongly polarized; their dipole moments vary from 1.35 to 1.50 D (S–O), from 1.60 to 1.78 D (S–N), and from 1.84 to 1.94 D (S–F). The orbials of the $S^{\delta+}–C^{Y(\delta-)}$, $S^{\delta+}–C^{a(\delta-)}$, and $C^{\alpha(\delta-)}–C^{\beta(\delta+)}$ are polarized to a lesser extent; their dipole moments vary from 0.39 to 0.63 D (S–C^Y), from 0.26 to 0.56 D (S–C^{α}), from 0.12 to 0.30 D (σ, C=C), and from 0.37 to 0.69 D (π, C=C). In vinyl sulfoxides and vinyl sulfones, the dipole moments of the σ and π orbitals of the double bond are directed toward the C^{α} atom. The μ(C=C) values for the π orbitals of the double bond linearly correlate with the sum of charges on atoms of the functional groups XCY_3 (Fig. 3).

(5) The electronic structure of the sulfinyl and sulfonyl groups is stabilized by hyperconjugation interactions between the lone electron pairs of the O atoms and antibonding σ* orbitals of the adjacent bonds, and in the sulfonyl group, also by interaction between $n_{\pi}(O)$ and the σ* orbital of the adjacent S–O bond. The interaction with the vacant *d* orbitals of the S atom is less efficient. The strength, length, and multiplicity of the S–O bonds in the sulfinyl and sulfonyl groups are largely determined by these interactions.

(6) The electron density on the vinyl fragment decreases with an increase in the charge of the XCY_3 groups ("compensation effect"). The quantities Σq_{Vin} linearly correlate with the inductive constants σ_I (Fig. 4). The XCY_3 groups affect the electron density redistribution between the C^{α} and C^{β} atoms of the C=C bond mainly by the mechanisms of inductive and π-inductive interactions. The electron density of the vinyl fragment is polarized toward the C^{α} atom. Therefore, as compared to ethylene, in vinyl sulfoxides and vinyl sulfones the C^{α} atom of the C=C bond is electron-excessive and the terminal C^{β} atom is electron-deficient.

(7) The quantitative characteristics of the effect of the SCY_3 groups on the electron density on the vinyl fragment as a whole and on the terminal C^{β} atom in particular can be of practical significance for predicting the efficiency of nucleophilic addition to a double bond.

(8) The conformation, electronic structure, intermolecular interactions, and charge distribution in the compounds $CH_2=CHXCY_3$ are largely similar to those in the previously studied compounds $C_6H_5XCY_3$ (X = SO or SO_2; Y = H or F) [46].

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