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Methyl and Trifluoromethyl Vinyl Sulfoxides. Steric and Electronic Structure

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Abstract—Potential functions of internal rotation about the C_{sp^2}–S bond in $H_2C=CHSOCY_3$ (Y = H or F) were determined and stationary points were identified by vibrational analysis at the MP2(full)/6-31+G(d), B3PW91/6-31+G(d), and B3PW91/6-311+G(3df,p) levels. Energetically favorable conformations were established, and rotation barriers and molecular geometry parameters were evaluated. Wave functions [MP2(full)/6-31+G(d)] were analyzed by the NBO method. Energies and dipole moments of bond and lone-pair orbitals, principal types of donor–acceptor interactions, bond orders, and atomic charges were determined.

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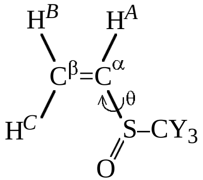
Alkyl vinyl sulfoxides are widely used in organic synthesis but fairly poorly studied by physicochemical methods. These compounds have been studied by dipole moment measurements [1], as well as ^{13}C NMR [2] and optical spectroscopy [3–6]. Prilezhaeva *et al.* [7] have discussed the basicity of vinyl sulfoxides. The steric structure of methyl vinyl sulfoxide has not been studied by direct structural methods but computed at various levels of theory [8–10]. Trifluoromethyl vinyl sulfoxides has been studied by UV spectroscopy only [11]. To compare the barriers to internal rotation, intermolecular interactions, and charge distributions in these two compounds, we have performed their computations at the same level of theory, with subsequent analysis of wave functions in terms of the natural bond orbital (NBO) method [12].

The aim of the present work was to obtain potential functions of internal rotation around the C_{sp^2}–S bond in $H_2C=CHSOCH_3$ and $H_2C=CHSOCF_3$ at the same level of quantum-chemical computations including electron correlation effects [MP2(full)/6-31+G(d), B3PW91/6-31+G(d) or B3PW91/6-311+G(3df,p)], to identify stationary points, to evaluate barriers to internal rotation and molecular geometry parameters, to analyze wave functions [MP2(full)/6-31+G(d)] in terms of the NBO formalism, as well as to study the electronic structure, intramolecular interactions, and electron density distribution in energetically favorable conformations.

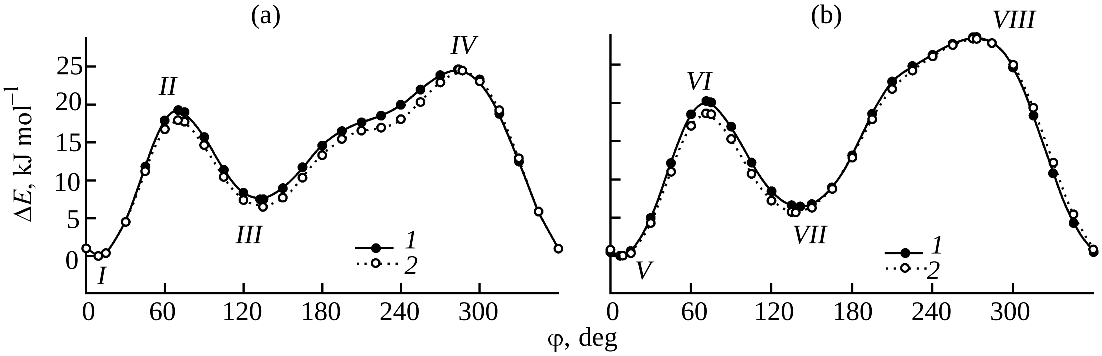
Methods. Potential functions were obtained by rotating fragments around the C_{sp^2}–S bond, with the torsion angle θ (between the $C^{\beta}=C^{\alpha}$–S and C^{α}-S=O planes) varied from 0° to 360° at 15° steps and the other geometric parameters fully optimized. Stationary points were determined with full optimization of geometric parameters (including θ) and identified by vibrational analysis at the MP2(full)/6-31+G(d), B3PW91/6-31+G(d), and B3PW91/6-311+G(3df,p) levels [13]. Standard criteria for density matrix and energy gradient convergence were applied. The barriers to internal rotation were corrected for zero-point energies (ZPE). The computations were performed using the GAMESS program package [14]. The NBO [12] analysis of wave functions [MP2(full)/6-31+G(d)] was performed using the NBO 5.0 program [15].

Conformation and molecular geometry parameters. The steric isomerism in alkyl vinyl sulfoxides is associated with the possibility of rotation of the SOAlk group around the C_{sp^2}–S bond (configuration **A**).

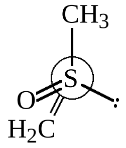


A

Energetically favorable conformations and transition states can be characterized by the magnitude of the torsion angle θ between the $C^{\beta}=C^{\alpha}$–S and C^{α}–S=O planes. The figure shows the potential functions of internal rotation of the fragments around the C_{sp^2}–S bond. Table 1 lists the characteristics of stationary points and the ZPE-corrected total energy



Potential functions of internal rotation of fragments about the C_{sp^2}–S bond in (a) $H_2C{=}CHSOCH_3$ and (b) $H_2C{=}CHSOCF_3$. (*1*) MP2(full)/6-31+G(d) and (*2*) B3PW91/6-31+G(d).



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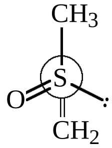

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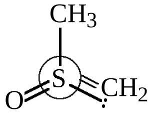

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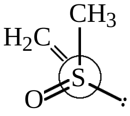

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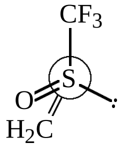

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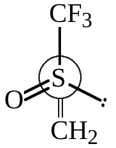

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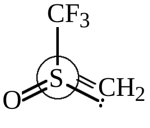

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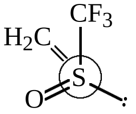


VIII

differences between the global and local minima. The profiles of the potential functions of internal rotation around the C_{sp^2}–S bond in the two compounds are fairly similar to each other: The global minimum (Min-1) is observed at θ = 9.0°–9.6° (Y = H) and θ = 7.2°–9.3° (Y = F), and the local minimum (Min-2) at θ = 132.6°–134.6° (Y = H) and θ = 137.7°–141.5° (Y = F). The transition states TS-1 are observed at θ = 69.1°–70.2° (Y = H) and θ = 70.2°–71.5° (Y = F), whereas TS-2, at θ = 283.5°–289.3° (Y = H) and θ = 272.3°–277.2° (Y = F). The minima and transition states were identified by vibrational analysis. The energy gap between the global and local minima in the compounds in hand is fairly large (from 4.87 to 7.07 kJ mol^{-1}). The Boltzmann populations of Min-1 at 25°C, as given by MP2(full)/6-31+G(d), B3PW91/6-31+G(d), and B3PW91/-6-311+G(3df,p) calculations are ~95, 92, and 91% in $H_2C{=}CHSOCH_3$ and 92, 89, and 88% in $H_2C{=}CHSOCF_3$, respectively.

Table 2 lists the barriers to internal rotation about the C_{sp^2}–S bond. The barriers are higher than *kT*. As seen, the $\Delta H^{\neq}$ values at Y = F are generally higher than those at Y = H. In our opinion, the reason lies in different steric parameters of the CY_3 groups ($CF_3 > CH_3$). Thus, in standard conditions $H_2C{=}CHSOCH_3$ and $H_2C{=}CHSOCF_3$ prefer the Min-1 conformation. This conformation can be described as close to eclipsed with S=O located *s-cis* to C=C. In what follows we will consider the electronic structure of and intramolecular interactions in this conformation only.

Table 3 lists the geometric parameters of the Min-1 conformers of $H_2C{=}CHSOCH_3$ and $H_2C{=}CHSOCF_3$. When comparing parameters obtained by the same method, we can see that the S=O bond in $H_2C{=}CHSOCF_3$ is shorter than in $H_2C{=}CHSOCH_3$ by 0.013 (*a*), 0.012 (*b*), or 0.010 Å (*c*). The S–CH_3 bond is shorter by 0.058 (*a*), 0.069 (*b*), or 0.077 Å (*c*) that S–CF_3. The S–C^{α} bond lengths are almost the same. The C=C bond lengths, too, are quite close to each other (within 0.001 Å) and smaller that the C=C bond lengths in ethylene, calculated by the respective methods [1.339 (*a*), 1.333 (*b*), or 1.324 Å (*c*)]. The $C^{\alpha}SC^{Y}$ at Y = H is larger than at Y = F by 2.5° (*a*), 1.7° (*b*), or 2.0° (*c*). The $C^{\beta}C^{\alpha}S$ bond angle at Y = H is larger than at Y = F by 0.9° (*a*), 1.0° (*b*), or 1.1° (*c*). The $C^{\alpha}SO$ angle at Y = H is smaller than at Y = F by 0.9° (*a*), 0.5° (*b*), or 0.6° (*c*).

Principal characteristics of natural bond orbitals. Table 4 lists the populations ($P_{A\text{–}B}$), coefficients of natural atomic hybrides (c_A and c_B), NBO dipole moments ($\mu_{A\text{–}B}$), and Wiberg indices

Table 1. Torsion angles (θ), total energies (E_{tot}), zero-point corrections (Z_0), imaginary frequencies (ν), and differences in the energies of the global and local minima (ΔE_{min})[a]

Parameter	Method	$H_2C{=}CHS(O)CH_3$		$H_2C{=}XHS(O)CF_3$	
		Min-1	Min-2	Min-1	Min-2
θ, deg	*a*	9.6	132.6	7.2	141.5
	b	9.2	134.6	9.3	138.1
	c	9.0	132.6	9.3	137.7
$-E_{tot}$, au	*a*	590.125272	590.122436	887.227550	887.225108
	b	591.152633	591.150172	888.766163	888.764006
	c	591.268981	591.266539	888.989464	888.987451
Z_0, Hartree/particle	*a*	0.086450	0.086299	0.062661	0.062538
	b	0.085057	0.084912	0.061860	0.061692
	c	0.084389	0.084137	0.061736	0.061578
ΔE_{min}, kJ mol^{-1}	*a*	7.05	6.09		
	b	6.08	5.22		
	c	5.80	4.87		
		TS-1	TS-2	TS-1	TS-2
θ, deg	*a*	70.2	283.5	71.5	272.3
	b	70.1	286.9	71.3	272.9
	c	69.1	289.3	70.2	277.2
$-E_{tot}$, au	*a*	590.117946	590.115912	887.219862	887.216686
	b	591.145816	591.143333	888.759083	888.755357
	c	591.261927	591.259390	888.982269	888.978515
Z_0, Hartree/particle	*a*	0.085992	0.086427	0.062234	0.062558
	b	0.084545	0.084843	0.061399	0.061639
	c	0.084082	0.084247	0.061317	0.061520
ν, cm^{-1}	*a*	–137.20	–99.70	–123.92	–84.56
	b	–134.86	–117.77	–127.78	–93.62
	c	–141.24	–126.54	–130.30	–94.45

Notes: Here and in the other tables: [a] MP2(full)/6-31+G(d), [b] B3PW91/6-31+G(d), and [c] B3PW91/6-311+G(3df,p).

($W_{A–B}$) of bonding NBOs. The coefficients c_A and c_B show the contribution into the bonding natural orbital of the A–B bond of the natural atomic hybrids of the A and B atoms [12, 16]. These coefficients relate to the quantity of the electron density of the bond (in percent of its population), contributed by each atom into the bonding NBO. Therefore, they can serve as a measure of polarization of the electron density of the NBO and indicate direction of the dipole moment of the bond. The Wiberg indices $W_{A–B}$(NAO) are a relative measure of bonding NBO orders. In what follows we call NBOs and natural orbitals of lone electron pairs “bond orbitals” and “lone-pair orbitals.”

Table 2. Barriers to internal rotation about the C_{sp^2}–S bond with zero-point corrections ($\Delta H^{\neq}$, kJ mol^{-1}) in $H_2C{=}CHSOCY_3$ (Y = H or F)

Parameter	Method	Y = H	Y = F
Min-1/TS-1	*a*	18.03	19.06
	b	16.55	17.38
	c	17.73	17.79
Min-1/TS-2	*a*	24.51	28.25
	b	23.86	27.79
	c	24.83	28.18
Min-2/TS-1	*a*	10.98	12.98
	b	10.47	12.16
	c	11.93	12.92
Min-2/TS-2	*a*	17.46	22.16
	b	17.78	22.57
	c	19.03	23.31

S–O. According to the NBO model, the sulfur and oxygen atoms in the sulfinyl group of $H_2C{=}CHSO \cdot CY_3$ (Y = H or F) are linked by a covalent σ bond. The population of S–O σ bond orbitals in these compounds scarcely depends on the electronic nature of the CY3 group (differences within 0.001 e). The

Table 3. Bond lengths (Å) and bond angles (deg) in the energetically preferred conformation (Min-1) in $H_2C{=}CHSOCY_3$ (Y = H or F)[a]

Parameter	Method	Y = H	Y = F	Parameter	Method	Y = H	Y = F
$d(S{=}O)$	*a*	1.519	1.506	$d(C^{\beta}–H^{B})$	*a*	1.087	1.087
	b	1.511	1.499		*b*	1.087	1.087
	c	1.483	1.473		*c*	1.084	1.084
$d(C^{\alpha}{=}C^{\beta})$	*a*	1.336	1.335	$d(C^{\beta}–H^{C})$	*a*	1.085	1.085
	b	1.330	1.330		*b*	1.089	1.088
	c	1.323	1.322		*c*	1.086	1.086
$d(S–C^{\alpha})$	*a*	1.788	1.791	$\angle C^{\alpha}SC^{Y}$	*a*	95.7	93.2
	b	1.800	1.800		*b*	96.2	94.5
	c	1.782	1.782		*c*	96.4	94.4
$d(S–C^{Y})$	*a*	1.809	1.867	$\angle C^{\beta}C^{\alpha}S$	*a*	119.5	118.6
	b	1.828	1.897		*b*	119.8	118.8
	c	1.811	1.888		*c*	119.9	118.8
$d(C^{\alpha}–H^{A})$	*a*	1.089	1.087	$\angle C^{\alpha}SO$	*a*	107.3	108.2
	b	1.089	1.088		*b*	107.5	108.0
	c	1.087	1.085		*c*	107.8	108.4

[a] CH_3, d(C–H), Å: (*a*) 1.092, 1.094, 1.093; (*b*) 1.093 × 2, 1.095; and (*c*) 1.091 × 2, 1.092. CF_3, d(C–F), Å: (*a*) 1.353, 1.343, 1.338; (*b*) 1.335, 1.345, 1.331; and (*c*) 1.327, 1.336, 1.322.

Table 4. Principal characteristics of bonding NBOs [populations ($P_{A–B}$, e), coefficients of atomic hybrids (c_A and c_B, %), NBO dipole moments ($\mu_{A–B}$, D), and NAO Wiberg indices ($W_{A–B}$)], and O and S lone-pair orbitals [*s* contributions (*s*, %), populations (P_n, e), and dipole moments (μ_n, D)]

A–B bond	Natural bond orbitals									
	$H_2C^{\beta}{=}C^{\alpha}HSOCH_3$ (Min-1)					$H_2C^{\beta}{=}C^{\alpha}HSOCF_3$ (Min-1)				
	$P_{A–B}$	c_A	c_B	$\mu_{A–B}$	$W_{A–B}$	$P_{A–B}$	c_A	c_B	$\mu_{A–B}$	$W_{A–B}$
$\sigma(S–O)$	1.952	35.8	64.2	1.38	1.14	1.951	35.6	64.4	1.35	1.18
$\sigma(S–C^{Y})$	1.943	46.6	53.4	0.39	0.86	1.921	43.6	56.4	0.44	0.74
$\sigma(S–C^{\alpha})$	1.940	46.1	53.9	0.40	0.86	1.935	47.0	53.0	0.26	0.86
$\alpha(C^{\alpha}{=}C^{\beta})$	1.965	51.3	48.7	0.21	1.83	1.965	51.4	48.6	0.30	1.82
$\pi(C^{\alpha}{=}C^{\beta})$	1.923	53.5	46.5	0.37	–	1.916	54.6	45.4	0.57	–
$\alpha(C^{\alpha}–H^{A})$	1.957	62.9	37.1	1.76	0.87	1.956	63.7	36.3	1.68	0.86
$\sigma(C^{\beta}–H^{B})$	1.958	61.7	38.3	1.78	0.87	1.957	62.1	37.9	1.74	0.87
$\sigma(C^{\beta}–H^{C})$	1.959	63.1	36.9	1.62	0.89	1.959	63.1	36.9	1.62	0.88

Lone electron pair	Natural orbitals of lone electron pairs					
	$H_2C^{\beta}{=}C^{\alpha}HSOCH_3$ (Min-1)			$H_2C^{\beta}{=}C^{\alpha}HSOCF_3$ (Min-1)		
	s	P_n	μ_n	*s*	P_n	μ_n
$n(S)$	50	1.929	5.44	55	1.929	5.32
$n_{\sigma}(O)$	80	1.970	2.33	79	1.970	2.33
$n_{\pi}^{1}(O)$	<1	1.864	0.48	<1	1.851	0.53
$n_{\pi}^{2}(O)$	<1	1.789	0.10	<1	1.754	0.12

magnitudes of the c_A and c_B coefficients show that the electron density of the S–O σ bond orbital is strongly shifted to oxygen (by 14.2% at Y = H and 14.4% at Y = F from symmetric distribution). In methyl vinyl sulfoxide, μ(S–O) is as little as 0.03 D higher than that in trifluoromethyl vinyl sulfoxide. The W_{S-O}(NAO) value in the sulfinyl group is higher than for the single bond but lower than for the double bond.

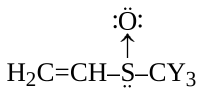
S–C^Y. The population of S–CH_3 σ bond orbitals is 0.022 e higher than that of S–CF_3 σ bond orbitals. The electron density of the S–CY bond orbital is polarized to C^Y (by 3.4% at Y = H and 6.4% at Y = F from symmetric distribution). The μ(S–C^Y) value at Y = H is 0.05 D lower than at Y = F. The W_{S-C}(NAO) value for the S–CH_3 bond is 0.12 higher than for S–CF_3, as a result of the stronger electron deficiency of the latter bond.

S–C$^\alpha$. The population of the S–C σ bond orbital at Y = H is 0.005 e higher than at Y = F. The electron density of the S–C^α bond orbital is polarized to C^α (by 3.9% at Y = H and 3.0% at Y = F from symmetric distribution). The μ(S–C^α) value at Y = H is 0.15 D higher than at Y = F. The W_{S-C}(NAO) value for the S–C^α bond in the two compounds is almost the same (within 0.01).

C$^\alpha$=C$^\beta$. The energies the σ orbitals of the double bonds vary from –21.7 (Y = H) to –22.1 eV (Y = F). At the same computational procedure, the respective value for ethylene is –26.7 eV. The populations of the σ orbitals of the double bond in the vinyl sulfoxides in study are equal to each other and 0.004 e lower than in ethylene (1.969 e). The electron density of the vinyl σ bonds are polarized to C^α by 1.3% at Y = H and 1.4% at Y = F from symmetric distribution. The μ(C^α–C^β) value for the σ bond orbital at Y = F is slightly higher (by 0.09 D) than at Y = H. The energies of π bond orbitals vary from –8.7 (Y = H) to –9.1 eV (Y = F). The respective value for ethylene is –10.2 eV. The population of the π bond orbital at Y = H is 0.007 e higher than at Y = F. At the same computational procedure, the population of the π bond orbital in ethylene (1.940 e) is higher by 0.017 e than in $H_2C{=}CHSOCH_3$ and by 0.024 e than in $H_2C{=}CHSOCF_3$. The electron density of the π bond orbital in the vinyl fragments is polarized to C^α by 3.5% at Y = H and 4.6% at Y = F from symmetric distribution. The dipole moment of the π orbital is 0.16 (Y = H) or 0.27 D (Y = F) higher than that of the σ orbital. The μ(C^α-C^β) value for the π bond orbital at Y = F is 0.20 D higher than at Y = H. The $W_{C=C}$(NAO) values for the two vinyl sulfoxides are almost equal to each other (within 0.01) and slightly lower than for ethylene (1.89).

C$^\alpha$–H^A, *C$^\beta$–H^B*, and *C$^\beta$–H^C*. The orbital populations of respective C^α–H^A (from 1.956 to 1.959 e), C^β–H^B (from 1.957 to 1.959 e), and C^β–H^C (from 1.959 to 1.961 e) in the compounds in hand are fairly close to each other and lower than the populations of C–H bond orbitals in ethylene (1.963 e). The electron density of vinyl C–H bond orbitals is strongly polarized to carbon (from 11.7 to 13.7% from symmetric distribution). The dipole moments of these bond orbitals vary from 1.62 to 1.78 D. The W_{C-H}(NAO) values for the two sulfoxides are close to each other to W_{C-H}(NAO) for ethylene (0.90).

Principal characteristics of natural orbitals of lone electron pairs. Table 4 lists the populations (P_n) and dipole moments (μ_n) of O and S lone-pair orbitals, as well as the *s* contributions (*s*) in the corresponding hybrids. The electron density of the π bond between sulfur and oxygen in the sulfinyl group is mostly concentrated on oxygen. In terms of the NBO model, this implies the presence of three lone-pair orbitals on this atom (structure **B**).



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

B

The hybrid orbitals of one oxygen lone electron pair [n_σ(O)] are *s* orbitals by ~80%, and their energy levels are from –22.3 to –23.0 eV. The other two lone pairs [n_π^1(O) and n_π^2(O)] are almost pure *p* orbitals with the *s* contribution of no more than 1%, and their energy levels are between –8.7 to –9.9 eV. In the compound with Y = F, the oxygen lone-pair orbitals are lower in energy than the respective orbitals in the compound with Y = H. The populations of the n_σ(O) orbitals are equal to each other and higher than the populations of the n_π^1(O) and n_π^2(O) orbitals, whreseas the populations of the n_π^1(O) orbitals are higher than those of n_π^2(O). In the compound with Y = H, the populations of the n_π^1(O) and n_π^2(O) orbitals are higher than in the compound with Y = F. The dipole moments of oxygen lone-pair orbitals decrease in the series $\mu_n(n_\sigma) \rightarrow \mu_n(n_\pi^1) \rightarrow \mu_n(n_\pi^2)$. The $\mu_n(n_\sigma)$ values in the two molecules are equal to each other, and the $\mu_n(n_\pi^1)$ and $\mu_n(n_\pi^2)$ values at Y = H are lower than the respective values at Y = F.

The *s* contribution in the sulfur hybrid lone-pair orbital is about 50–55%, and the energy of this orbital span the range from –14.9 to –16.3 eV. This orbital energy at Y = H is 1.4 eV more negative than at Y = F. The populations of the *n*(S) orbitals in the two compounds are equal to each other. The dipole moment of the *n*(S) orbital is much higher than that

Table 5. Energies of principal donor–acceptor interactions (E_R, kJ mol^{-1}) in $H_2C{=}CHSOCY_3$, Y = H or F (Min-1)

Donor	Acceptor	Y = H	Y = F
n_π^1(O)	σ*(S–C$^\alpha$)	28.9	58.8
n_π^2(O)	σ*(S–C$^\alpha$)	80.8	52.8
n_π^1(O)	σ*(S–C^Y)	44.5	31.0
n_π^2(O)	σ*(S–C^Y)	59.3	127.4
n_π^1(O)	*RY**1(S)	59.5	32.8
n_π^2(O)	*RY**1(S)	7.2	28.1
n_π^1(O)	*RY**2(S)	7.0	32.6
n_π^2(O)	*RY**2(S)	43.5	28.9
n(S)	σ*(C=C)	11.7	13.0
n(S)	σ*(C=C)	18.1	11.8
n(S)	σ*(C–Y)	14.6	22.2
π(C=C)	σ*(S–CY)	11.7	19.0
π(C=C)	*RY**3(S)	7.5	7.7

Table 6. Natural atomic charges (*q*, e) in $H_2C{=}CHSOCY_3$, Y = H or F (Min-1)[a]

Charge	Y = H	Y = F
q(S)	1.259	1.247
q(O)	–0.977	–0.928
q(C^Y)	–0.901	0.869
q(Y)	0.268, 0.252, 0.265	–0.350, –0.363, –0.348
q(C$^\alpha$)	–0.493 (–0.057)	–0.504 (–0.068)
q(C$^\beta$)	–0.412 (0.024)	–0.388 (0.048)
q(H^A)	0.249 (0.031)	0.267 (0.049)
q(H^B)	0.234 (0.016)	0.242 (0.024)
q(H^C)	0.256 (0.038)	0.256 (0.038)

[a] Parenthesized are differences of the atomic charges in the compounds studied and ethylene: *q*(C) –0.436 and *q*(H) 0.218 e.

of *n*(O). The μ_n value for the *n*(S) orbital at Y = H is higher by 0.12 D than at Y = F.

In general, the bond and lone-pair orbitals in the compound with Y = F lie deeper than the respective orbitals in the compound with Y = H. This is explained by different electronegativities of the CY_3 groups ($CF_3 > CH_3$). The different orbital populations, too, result from different electronegativities of the CY_3 groups, as well as by different donor–acceptor interactions. The higher population of the lone-pair orbital points to a higher localization of its electron density on the heteratom.

Donor–acceptor interactions. The estimated energies of donor–acceptor interactions (E_R) in $H_2C{=}CHSOCY_3$ are listed in Table 5. The n_σ(O) lone pair weakly interacts with neighboring fragments, while n_π^1(O) and n_π^2(O) effectively interact with the antibonding σ* orbitals of neighboring S–C$^\alpha$ and S–C^Y bonds by the hyperconjugation mechanism: n_σ(O) → σ*(S–C$^\alpha$) and n_σ(O) → σ*(S–C^Y). The highest E_R value is characteristic of the n_π^2(O) → σ*(S–C^F) interaction, since this bond orbital is stronger electron deficient. The mechanism of *n*(O) bonding with sulfur *d* orbitals is represented by *n*(O) interactions with sulfur *d*-type Rhydberg orbitals (*RY**) by the n_σ(O) → *RY**(S) mechanism. The energy of these interactions is lower than the energy of hyperconjugation interactions of n_σ(O) with the σ* orbitals of the S–C$^\alpha$ and S–C^Y bonds.

The lone electron pair of the sulfur atom *n*(S) fairly weakly interacts with the antibonding σ* and π* orbitals of the vinyl fragment by the *n*(S) → σ*(C=C) and *n*(S) → π*(C=C) mechanisms. The sulfur lone electron pair is in *n*(S) → σ*(C–Y) hyperconjugation with the antibonding σ* orbitals of the C–Y bonds; therewith, the interaction with the antibonding orbital of the C–H bond is less effective compared to C–F.

The vinyl π orbitals relatively weakly interact with the S–C^Y σ* orbitals by the π(C=C) → σ*(S–C^Y) mechanism, the interaction of the more electron-deficient σ* orbital of the S–C^F bond being more effective. There are also weak π(C=C) → *RY**3(S) interactions. The fluorine lone-pair orbitals interact with the σ* orbitals of the C=C bond by the *n*(F) → σ*(S–C^F) bond and with the σ* orbitals of neighboring C–F bonds by the *n*(F) → σ*(C–F) mechanism (E_R –23–67 kJ mol^{-1}).

Electron density distribution. Table 6 lists the natural atomic charges (hereinafter "charges") in $H_2C{=}CHSOCY_3$. On replacement in the CY_3 group (Y = H or F) of hydrogens atoms by the more electronegative fluorines increases the electron density on Y by 1.848 e. Therewith, the electron density on C^Y decreases by 1.770 e. This formally implies a ~4% attenuation of the effect through one bond. Through two bonds, the charge varies much less sharply and in the opposite direction. The electron density on the sulfur atom increases by 0.012 e. This suggests that the range of charge variation decreases by ~99%, and these changes are unexplainable in terms of traditional concepts of through bond σ-inductive interactions. When H in the CY_3 group is replaced by F, the electron density through three bonds varies in different directions: It decreases on O (by 0.049 e) and increases on C$^\alpha$ (by 0.011 e). Through 4 bonds, the electron density on C$^\beta$ decreases (by 0.024 e). Therefore, it is only the transmission of the effect though one bond that can be assigned to the σ-inductive effect as such. Changes in the electron density on O, C^{α}, and C^{β} are associated with increased multiplicity of the S–O and C^{α}=C^{β} bonds. The decreased electron density on O can be explained by the more effective hyperconjugation of the lone electron pairs of this atom with C–F compared with C–H σ* orbitals (see above), and the changes of the electron density of the C^{α} and C^{β} atoms, with the fact that the vinyl π system gets stronger polarized to C^{α} on replacement of $SOCH_3$ by $SOCF_3$. The total electron density of the $SOCH_3$ and $SOCF_3$ functional groups can be characterized by the sum of atomic charges, equaling 0.166 ($SOCH_3$) and 0.127 e ($SOCF_3$). Consequently, replacement of H by F in the CY_3 group increases the total electron density on the $SOCY_3$ groups by 0.039 e.

By definition, the sum of atomic charges in an isolated molecule is equal to zero. Therefore, the sum of atomic charges of the vinyl fragment (Σq_{Vin}) "compensates" for the sum of atomic charges on the corresponding functional groups $SOCY_3$ with the opposite charge: –0.166 ($SOCH_3$) > –0.127 e ($SOCF_3$). It is these electron densities that redistribute over the vinyl fragment in each molecule. The sum of atomic charges in the H_2C=CH fragment of ethylene is –0.218 e. Thus, replacement of one hydrogen atom in ethylene by the $SOCY_3$ group decreases Σq_{Vin} by 0.051 ($SOCH_3$) or 0.092 e ($SOCF_3$). These values quantitatively measure the acceptor effect of the $SOCH_3$ and $SOCF_3$ groups on the vinyl fragment as a whole, with respect to the hydrogen atom as a substituent. As seen from the charges on the C^{α} and C^{β} atoms, the double bond in H_2C^{β}=$C^{\alpha}HSOCY_3$ is polarized to C^{α}. The charges on each vinyl carbon atom, related to the charges of the respective atoms in ethylene are given in Table 6 in parentheses. These values provide a quantitative measure of increase of the electron density on C^{α} and decrease of the electron density on the C^{β}, H^{A}, H^{B}, and H^{C} atoms of the vinyl fragment on replacement of one hydrogen atom in ethylene by the $SOCY_3$ group.

In principle, the polarity of a bond can be characterized by the difference of its atomic charges. The difference of the C^{α} and C^{β} charges increases in the series 0.072 ($SOCH_3$) < 0.116 e ($SOCF_3$). This estimate for the polarity of the double bond is qualitatively close to the above-considered dipole moments of the localized molecular orbitals of the double bond. However, the atomic charges not only reflect the asymmetry of electron distribution in σ and π bond orbitals between the C^{α} and C^{β} atoms, but also depend on the symmetry of electron distribution in the nearest environment.

Thus, the energetically preferred conformation of the H_2C=$CHSOCY_3$ compounds (Y = H or F) is a conformation close to eclipsed with the S=O bond arranged *s-cis* to C=C. The electronic structure of the sulfinyl group is stabilized primarily by hyperconjugation interactions of the lone electron pairs of the oxygen atom with the σ* orbitals of neighboring bonds. The electron density of the vinyl fragment is polarized to C^{α}. The electronic structure of and intermolecular interactions in H_2C=$CHSOCY_3$ have much in common with our previously studied compounds $C_6H_5SOCY_3$ [16].

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