Russian Journal of General Chemistry, Vol. 73, No. 5, 2003, pp. 731–742. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 5, 2003, pp. 773–785.

Potential Functions of Internal Rotation around the C_{sp^2}–X Bonds and Intermolecular Interactions in the Compounds CH_2=CHXCH_3 (X = O, S, Se)

V. M. Bzhezovskii, E. G. Kapustin, and B. A. Trofimov

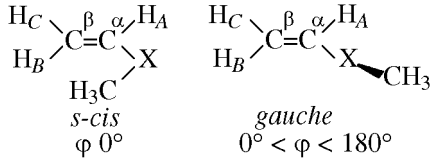
Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine
Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

Received April 28, 2001

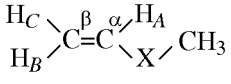
Abstract—The potential functions of internal rotation around the C_{sp^2}–X bonds in the CH_2=CHXCH_3 molecules (X = O, S, Se) were determined by MP2/6-31G* and MP2/6-31G** calculations. The stationary points were identified by solution of vibrational problems. The rotation barriers were evaluated taking into account the zero-point vibration energy. The intramolecular interactions were considered in terms of the method of natural bond orbitals. The degrees of hybridization, energies, and populations of the orbitals of the lone electron pairs of the O, S, and Se atoms, the energies of their donor–acceptor interaction with the antibonding σ* and π* orbitals of the double bond, and the natural atomic charges in various conformations were determined.

The CH_2=CHXCH_3 and CH_2=CHXH molecules (X = O, S, Se) are the simplest representatives of α,β-unsaturated compounds containing a Group VIA element at the double bond. These molecules are highly reactive; also, interaction of chalcogen atoms with unsaturated bonds is an interesting theoretical problem. These facts stimulate studies of the steric and electronic structure of these compounds. Numerous studies of vinyl chalcogenides by physicochemical methods are summarized in monographs [1, 2] and reviews [3, 4]. Therefore, below we briefly describe only the main results.

The steric structure of vinyl methyl ether, sulfide, and selenide is characterized by a more complex potential function of internal rotation around the C_{sp^2}–X bonds as compared to anisole, thioanisole, and selenoanisole [5–7]. Vinyl methyl chalcogenides can exist in two planar conformations (*s-cis* and *s-trans*) and in nonplanar *gauche* ("skewed") conformation:



s-cis φ 0° *gauche* 0° < φ < 180°



s-trans φ 180°

Here φ is the $C^{\beta}C^{\alpha}XCH_3$ torsion angle.

The Kerr constants show that the most stable conformation of the CH_2=CHOCH_3 molecule is the *s-cis* form [8, 9], with the nonplanar (approximately orthogonal) *gauche* conformer (φ 90° ± 20°) being the second most stable [9]. An electron diffraction study [10] showed that the planar *s-cis* conformer is the most favorable energetically in the gas phase. The second conformer is also approximately orthogonal (φ 80°–110°). The difference between the energies of the rotamers is estimated at 5.0 kJ mol^{-1}. In a later study [11], Samdal and Seip concluded that the electron diffraction data are also consistent with the *s-trans* structure of the second conformer. Microwave spectroscopic data show that the *s-cis* conformer is more favorable energetically, and the second conformer is believed to be nonplanar [12]. Combined analysis of the electron diffraction and microwave spectroscopic data shows that the second conformer is "skewed," with its content not exceeding 5% [13]. Examination of the IR and Raman spectra in [14–17] and of the photoelectron spectra in [18–20] led the authors to a conclusion that the less stable conformer coexisting with the major *s-cis* conformer is *s-trans*. However, the vibration spectra in [21–23] suggest that the less stable conformer is "skewed." The difference between the enthalpies of the *s-cis* and *gauche* forms is estimated at 6.02 ± 0.67 [21] and 7.11 ± 0.38 kJ mol^{-1} [22]. Durig and Compton [23] concluded that the torsion angle φ in the *gauche* conformer is 144°, and the rotation barriers are 26.48 (*cis/gauche*), 21.21

1070-3632/03/7305-0731 $25.00

(*gauche/cis*), and 3.47 kJ mol^{-1} (*gauche/gauche*). Thus, the results of all physicochemical studies agree in that the *s-cis* conformer of CH_2=$CHOCH_3$ is the most favorable energetically. At the same time, there is disagreement concerning the structure of the second conformer [nonplanar *gauche* ("skewed") or planar *s-trans*].

The CH_2=$CHSCH_3$ molecule, according to microwave spectroscopic data, exists in the planar *s-cis* conformation [24]. The electron diffraction data suggest coexistence of the *s-cis* and *gauche* conformers in the 33 : 67 [25] or 38 : 62 [11] ratio. At the same time, the electron diffraction data in [26] were interpreted as suggesting 11–21% content of the *gauche* conformer. Samdal *et al*. [27] examined the results of [11, 24–26] and also the microwave and Raman spectra of vinyl methyl sulfide using static and dynamic models. The differences in the estimated conformer ratio are due to inadequacy of the static model. The photoelectron spectra measured in [28] revealed a single planar conformer. However, the photoelectron spectra taken by Muller *et al*. [29] in the temperature range from 20 to 600°C suggest a temperature-dependent equilibrium between the *s-cis* and *gauche* rotamers. Based on the IR data obtained at various temperatures and on the quantum model of rotational isomerism, Keiko *et al*. [30] determined the parameters of the potential function of internal rotation around the C_{sp^2}–S bond. The planar *s-cis* conformer is the most favorable energetically, and the less favorable *gauche* conformer is characterized by a local energy minimum at the torsion angle φ 132° ±3°. The barrier to transition between the *s-cis* and *gauche* forms is 9.8–10.6 kJ mol^{-1}, and the barrier separating the *gauche* forms is 2.5–2.9 kJ mol^{-1}; the difference between the energies of the lowest *gauche* and cis levels is ~3.8–4.2 kJ mol^{-1}. Durig *et al*. [31] evaluated the rotation barriers from the vibration spectra and obtained the following values (kJ mol^{-1}): 21.03 (*cis/gauche*), 5.93 (*gauche/gauche*), and 11.92 (*gauche/cis*). Despite appreciable disagreement between [30] and [31] in the barrier height, the common conclusion of these two studies is that the *s-cis* conformer of CH_2=$CHSCH_3$ is the most favorable energetically and that this molecule also has two quasi-degenerate *gauche* forms separated by a barrier at φ 180°.

The CH_2=$CHSeCH_3$ molecule, in contrast to its O and S analogs, is poorly studied by physicochemical methods. Surushkin *et al*. [32] assigned the bands in the IR and Raman spectra of vinyl methyl selenide on the basis of normal mode calculation. The IR spectra of the neat liquid and solutions in the range 193–353 K suggest existence of rotational isomers. The UV spectra are interpreted in [33], and the UV spectrum is analyzed in [34] taking into account photoelectron spectroscopic data.

The CH_2=$CHOCH_3$ [35–41] and CH_2=$CHSCH_3$ [41–45] molecules were subjects of numerous early quantum-chemical studies (for review, see [3, 4, 46]). Gallinella and Cadioli [47] calculated the CH_2=CHO–CH_3 molecule on ate MP2(fc)/6-31G*//HF/6-31G* and MP3(fc)/6-31G*//HF/6-31G* levels, i.e., without taking into account the correlation correction for core electrons and using the geometry optimized on the HF/6-31G* level. According to these calculations, the energies of the minima corresponding to the *s-cis* and *s-trans* forms differ by 8.3 and 9.9 kJ mol^{-1}, respectively. According to HF/6-31G* calculations of the CH_2=$CHSCH_3$ molecule, the most stable is the *s-cis* conformer (φ 0°), and the second most stable *gauche* conformer (134.4°) lies higher on the energy scale by 2.42 kJ mol^{-1} [48]. The MP2(f)/6-31G* calculations in [31] revealed potential energy minima at φ 0° and 138.7° and gave the following barriers to rotation around the C_{sp^2}–S bond (kJ mol^{-1}): 13.40 (*cis/gauche*), 3.30 (*gauche/gauche*), and 8.70 (*gauche/cis*) [31]. The two conformers differ in the energy by 4.71 kJ mol^{-1}. The CH_2=$CHSeCH_3$ molecule was studied at the STO/3G and HF/3-21G* levels [41].

Thus, although the steric structure of CH_2=CHX–CH_3 molecules was examined in numerous papers, it was not studied systematically by modern quantum-chemical methods at the same theoretical level. Our goal was to obtain the potential functions of internal rotation around the C_{sp^2}–X bonds in the CH_2=CHX–CH_3 molecules (X = O, S, Se) by *ab initio* quantum-chemical calculations taking into account the electron correlation, to find and identify the stationary points (maxima and minima), and to discuss intramolecular interactions in terms of the method of natural bond orbitals (NBO).

Calculation procedure. The *ab initio* calculations taking into account the correlation energy for all the electrons were performed in the approximation of the second-order Møller–Plesset perturbation theory [49–51] in the 6-31G* basis set: MP2(f)/6-31G*. For the ether and sulfide, we also performed MP2 calculations without taking into account the correlation energy for the core electrons, in the 6-311G** basis set: MP2(fc)/6-311G**. The calculations were performed for the torsion angle φ varied from 0° to 180° at a 15° step, with optimization of the other geometric parameters. The stationary points on the potential functions of internal rotation around the C_{sp^2}–X bonds were sought for with complete optimization of the geometry, including the torsion angle φ, and identified by

Table 1. Total energy ($-E_{tot}$, au) of CH_2=CHXCH_3 molecules (X = O, S, Se) in the range of the torsion angle φ from 0° to 180°. The energies (ΔE, kJ mol^{-1}) of particular conformers relative to the global minimum of the potential function of internal rotation are given in parentheses

φ, deg	CH_2=CHOCH_3		CH_2=CHSCH_3		CH_2=CHSeCH_3, MP2(f)/6-31G*
	MP2(f)/6-31G*	MP2(fc)/6-311G**	MP2(f)/6-31G*	MP2(fc)/6-311G**	
0	192.4 930 767 (0.00)	192.6 094 929 (0.00)	515.1 109 600 (0.00)	515.2 120 702 (0.00)	2515.2 205 387 (0.00)
15	192.4 921 896 (2.33)	192.6 085 773 (2.40)	515.1 103 417 (1.62)	515.2 114 361 (1.66)	2515.2 201 130 (1.12)
30	192.4 897 873 (8.64)	192.6 060 980 (8.91)	515.1 087 087 (5.91)	515.2 097 613 (6.06)	2515.2 190 430 (3.93)
45	192.4 866 567 (16.86)	192.6 028 703 (17.39)	515.1 068 351 (10.83)	515.2 078 249 (11.15)	2515.2 179 798 (6.72)
60	192.4 841 627 (23.40)	192.6 002 290 (24.18)	515.1 058 083 (13.53)	515.2 066 997 (14.10)	2515.2 177 485 (7.33)
75	192.4 833 886 (25.44)	192.5 994 285 (26.42)	515.1 058 664 (13.37)	515.2 066 205 (14.31)	2515.2 183 646 (5.71)
90	192.4 839 581 (23.94)	192.5 999 889 (24.95)	515.1 065 857 (11.48)	515.2 072 092 (12.76)	2515.2 191 205 (3.72)
105	192.4 852 447 (20.56)	192.6 013 780 (21.31)	515.1 076 144 (8.78)	515.2 081 839 (10.20)	2515.2 196 501 (2.33)
120	192.4 866 835 (16.79)	192.6 029 925 (17.07)	515.1 085 820 (6.24)	515.2 091 886 (7.57)	2515.2 199 053 (1.66)
135	192.4 878 192 (13.80)	192.6 042 779 (13.69)	515.1 090 977 (4.89)	515.2 097 841 (6.00)	2515.2 198 712 (1.75)
150	192.4 883 927 (12.30)	192.6 049 164 (12.02)	515.1 089 443 (5.35)	515.2 096 701 (6.30)	2515.2 195 001 (2.73)
165	192.4 884 391 (12.18)	192.6 049 507 (11.93)	515.1 082 443 (7.13)	515.2 089 872 (8.09)	2515.2 189 279 (4.23)
180	192.4 883 460 (12.42)	192.6 048 277 (12.25)	515.1 078 266 (8.23)	515.2 085 372 (9.28)	2515.2 186 233 (5.03)

solving the vibrational problems. Calculations were performed with the GAUSSIAN 98W software [52]. The population analysis of the wave functions obtained in the MP2(f)/6-31G* approximation was performed by the NBO method [53–55] using the NBO Ver. 3.1 program (link 607, GAUSSIAN 98W) [56].

Steric structure. The total energies (E_{tot}, au) of rotamers of CH_2=CHXCH_3 molecules with the torsion angle φ varied from 0° to 180° at a 15° step are listed in Table 1. The energies (ΔE_{tot}, kJ mol^{-1}) of particular rotamers relative to the global minimum of the potential function of internal rotation are given in parentheses. The potential functions of internal rotation around the C_{sp^2}–X bonds, obtained by MP2(f)/6-31G* calculations, are plotted in Fig. 1. To refine the positions of stationary points and identify them, we fully optimized their geometry (including φ) and solved the vibrational problems.

CH_2=CHOCH_3. According to the MP2(fc)/6-311G** calculations, to the global minimum corresponds the planar *s-cis* form with φ 0.000° (E_{tot} –192.6094929 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 247.06 cm^{-1}). The correction for the zero-point vibration energy (ZPVE) is 0.081825 hartree per particle (here and hereinafter, the scaling factor in this approximation is 0.9496 [57]). The transition state is revealed at φ 75.157° (E_{tot} –192.5994428 au). In this point, the Hesse matrix has one negative eigenvalue (–162.35 cm^{-1}). The ZPVE correction is 0.080605 hartree per particle. The minimum corresponding to the second conformer is observed at φ 158.000° (E_{tot} –192.6049900 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 80.73 cm^{-1}). The ZPVE correction is 0.080932 hartree per particle. The point at φ 180.000° (E_{tot} –192.6048277 au) is also identified as transition state.

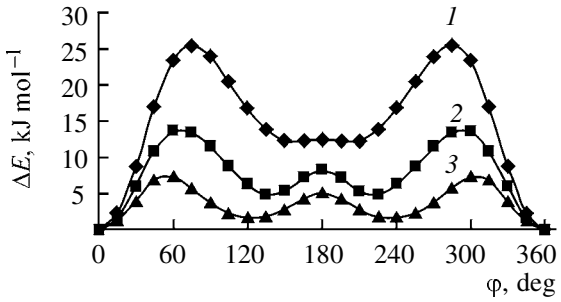


Fig. 1. Potential functions of internal rotation around the C_{sp^2}–X bond, obtained in the MP2/6-31G* approximation for (*1*) CH_2=$CHOC_3$, (*2*) CH_2=$CHSCH_3$, and (*3*) CH_2=$CHSeCH_3$.

In this point, the Hesse matrix has one negative eigenvalue (–61.31 cm^{-1}). The rotation barriers corrected for ZPVE, according to MP2(fc)/6-311G** calculations, are 23.18 (*cis/gauche*) and 13.71 kJ mol^{-1} (*gauche/cis*). The barrier separating two nonplanar *gauche* forms at refined energies of the maximum and minimum is as low as 0.43 kJ mol^{-1}. The difference between the energies of the minima corresponding to the *cis* and *gauche* forms is 11.82 kJ mol^{-1}.

According to the MP2(f)/6-31G* calculations, to the global minimum also corresponds the planar *s-cis* form (φ 0.002°, E_{tot} –192.4930767 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 239.24 cm^{-1}). The ZPVE correction (here and hereinafter, the scaling factor in this approximation is 0.9661 [57]) is 0.084355 hartree per particle. The transition state is revealed at φ 74.743° (E_{tot} –192.4833885 au). In this point, the Hesse matrix has one negative eigenvalue (–159.53 cm^{-1}). The ZPVE correction is 0.0831001 hartree per particle. The minimum corresponding to the second conformer is observed at φ 158.149° (E_{tot} –192.4884654 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 76.24 cm^{-1}). The ZPVE correction is 0.0833522 hartree per particle. The point at φ 180.000° (E_{tot} –192.4883459 au) is also identified as transition state. In this point, the Hesse matrix has one negative eigenvalue (–52.05 cm^{-1}). The rotation barriers corrected for the zero-point vibration energy, according to the MP2(f)/6-31G* calculations, are 22.14 (*cis/gauche*) and 12.67 kJ mol^{-1} (*gauche/cis*). The barrier separating two nonplanar *gauche* forms at refined energies of the maximum and minimum is as low as 0.31 kJ mol^{-1}. The difference between the energies of the minima corresponding to the *cis* and *gauche* forms is 12.11 kJ mol^{-1}.

Thus, the potential function of internal rotation around the C_{sp^2}–O bond exhibits a pronounced "sharp" energy minimum in the vicinity of the energetically favorable planar *s-cis* conformation. The less favorable *gauche* form is characterized by two quasi-degenerate minima at φ 158° and 202°, separated by a very low (<0.5 kJ mol^{-1}) barrier. Therefore, the *gauche* conformer can actually be considered as a nonrigid conformer with a large amplitude of the mutual motion of the fragments about the center at φ 180°.

CH_2=$CHSCH_3$. According to the MP2(fc)/6-311G** calculations, to the global minimum corresponds the planar *s-cis* form with φ 0.000° (E_{tot} –515.2120702 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 152.77 cm^{-1}). The ZPVE correction is 0.077794 hartree per particle. The transition state is revealed at φ 68.613° (E_{tot} –515.2065536 au). In this point, the Hesse matrix has one negative eigenvalue (–109.54 cm^{-1}). The ZPVE correction is 0.077320 hartree per particle. The minimum corresponding to the second conformer is observed at φ 135.000° (E_{tot} –515.2097841 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 97.58 cm^{-1}). The ZPVE correction is 0.077520 hartree per particle. The point at φ 180.000° (E_{tot} –515.2085372 au) is also identified as transition state. In this point, the Hesse matrix has one negative eigenvalue (–105.95 cm^{-1}). The rotation barriers corrected for ZPVE, according to the MP2(fc)/6-311G** calculations, are 13.23 (*cis/gauche*), 7.96 (*gauche/cis*), and 2.19 kJ mol^{-1} (*gauche/gauche*). The difference between the energies of the minima corresponding to the *cis* and *gauche* forms is 6.00 kJ mol^{-1}.

According to the MP2(f)/6-31G* calculations, to the global minimum corresponds the planar *s-cis* form (φ 0.000°, E_{tot} –515.1109600 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 147.70 cm^{-1}). The ZPVE correction is 0.0806152 hartree per particle. The transition state is revealed at φ 66.166° (E_{tot} –515.1057251 au). In this point, the Hesse matrix has one negative eigenvalue (–115.11 cm^{-1}). The ZPVE correction is 0.0800027 hartree per particle. The energy minimum corresponding to the second conformer is observed at φ 138.746° (E_{tot} –515.1091209 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 99.69 cm^{-1}). The ZPVE correction is 0.0802462 hartree per particle. The point at φ 180.000° (E_{tot} –515.1078266 au) is also identified as transition state. In this point, the Hesse matrix has one negative eigenvalue (–101.33 cm^{-1}). The rotation barriers corrected for ZPVE, according to the MP2(f)/6-31G* calculations, are 12.14 (*cis/gauche*), 8.28 (*gauche/cis*), and 2.44 kJ mol^{-1} (*gauche/gauche*). The

difference between the energies of the minima corresponding to the *cis* and *gauche* forms is 4.83 kJ mol^{-1}.

Thus, according to the quantum-chemical calculations of the potential function of internal rotation around the C_{sp^2}–S bond, the most energetically favorable form of the CH_2=CHSCH$_3$ molecule is the planar *s-cis* form characterized by a steep potential well; also, there are two quasi-degenerate nonplanar *gauche* forms separated by a low (of the order of *kT*) but well-defined barrier. Actually, we can speak of a nonrigid state with a large amplitude of the mutual motion of fragments about the center at φ 180°. The profile and energy characterisitcs of the potential function of internal rotation reasonably agree with the temperature dependence of the IR spectra, studied in [30].

CH_2=CHSeCH$_3$. This molecule was examined only at the MP2(f)/6-31G* level. To the first minimum corresponds the planar *s-cis* form (φ 0.000°, E_{tot} –2515.2205387 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 116.90 cm^{-1}). The ZPVE correction is 0.0791893 hartree per particle. The transition state is revealed at φ 55.372° (E_{tot} –2515.2177051 au). In this point, the Hesse matrix has one negative eigenvalue (–117.69 cm^{-1}). The ZPVE correction is 0.0786241 hartree per particle. The minimum corresponding to the second conformer is observed at φ 125.753° (E_{tot} –2515.2199303 au). In this point, the Hesse matrix has only positive eigenvalues (first harmonic frequency 71.08 cm^{-1}). The ZPVE correction is 0.0789748 hartree per particle. The point at φ 180.000° (E_{tot} –2515.2186233 au) is also identified as transition state. In this point, the Hesse matrix has one negative eigenvalue (–84.08 cm^{-1}). The barriers to rotation around the C_{sp^2}–Se bond corrected for ZPVE, according to the MP2(f)/6-31G* calculations, are 5.96 (*cis/gauche*, *gauche/cis*) and 2.32 kJ mol^{-1} (*gauche/gauche*). The difference between the energies of the minima corresponding to the *cis* and *gauche* forms is 1.60 kJ mol^{-1}.

Thus, in vinyl methyl selenide, the planar *s-cis* form is also the most favorable energetically, but the difference in the energies of the *s-cis* and *gauche* forms is small. Two quasi-degenerate nonplanar *gauche* forms are separated by a low but well-defined barrier of the order of *kT* (φ 180°).

The population of the *s-cis* form, calculated according to the Boltzmann distribution, is as follows (%): CH_2=CHOCH$_3$, 99 (25 and 50°C), 98 (100°C), 97 (150°C), and 94 (250°C); CH_2=CHSCH$_3$, 86 (25°C), 84 (50°C), 79 (100°C), 75 (150°C), and 67 (250°C); and CH_2=CHSeCH$_3$, 46 (25°C), 45 (50°C), 40 (100°C), 37 (150°C), and 31 (250°C). The experimental data obtained by various physicochemical methods for room temperature are as follows (%): CH_2=CHOCH$_3$, ~99% [13]; CH_2=CHSCH$_3$, 33 [25], 38 [11], 79–89 [26], or 94% [29].

Table 2. Bond angles (deg) and bond lengths (Å) in CH_2=CHXCH$_3$ molecules (X = O, S, Se) in the stationary points

φ, deg	∠CXC	$\angle C^{\beta}C^{\alpha}X$	$l(C^{Å}=C^{\beta})$	$l(C^{\alpha}–X)$	$l(X–C_{Me})$
		MP2(f)/6-31G*			
		CH_2=CHOCH$_3$			
0.002	112.32	128.19	1.339	1.361	1.423
74.743	113.39	123.63	1.334	1.381	1.428
158.149	113.76	121.91	1.334	1.368	1.424
180.000	114.14	121.87	1.335	1.367	1.424
		CH_2=CHSCH$_3$			
0.000	101.19	128.62	1.340	1.751	1.801
66.166	99.72	123.96	1.338	1.776	1.813
138.746	99.18	123.30	1.338	1.759	1.809
180.000	99.75	124.23	1.338	1.759	1.808
		CH_2=CHSeCH$_3$			
0.000	98.96	127.80	1.339	1.889	1.939
55.372	97.88	123.88	1.337	1.909	1.950
125.753	96.65	122.17	1.338	1.900	1.950
180.000	97.26	123.90	1.338	1.896	1.946
		MP2(fc)/6-311G**			
		CH_2=CHOCH$_3$			
0.000	114.77	128.27	1.342	1.354	1.418
75.157	112.69	123.69	1.336	1.375	1.424
158.000	113.11	122.26	1.337	1.361	1.420
180.000	113.57	122.28	1.337	1.360	1.420
		CH_2=CHSCH$_3$			
0.000	100.81	128.62	1.343	1.747	1.799
66.613	99.23	123.50	1.339	1.775	1.812
135.000	98.73	123.15	1.340	1.759	1.808
180.000	99.37	124.40	1.341	1.756	1.806

Geometries. The optimized bond angles and bond lengths in the CH_2=CHXCH$_3$ molecules are listed in Table 2. According to the gas-phase electron diffraction data, the COC and $C^{\beta}C^{\alpha}O$ bond angles in the planar *s-cis* form of the CH_2=CHOCH$_3$ molecule are 116.8(1.8)° and 127.3(1.8)°, respectively [13, 58]. Our ∠COC values differ from the experimental values by 4.48° in the MP2(f)/6-31G* approximation and by 2.03° in the MP2(fc)/6-311G** approximation. For $\angle C^{\beta}C^{\alpha}O$, the respective differences are 0.89° and 0.97°. The experimental bond lengths are as follows: $l(C^{\alpha}=C^{\beta})$ 1.337(20), $l(C^{\alpha}–O)$ 1.359(15), and $l(O–C_{Me})$ 1.427(7) Å [13, 58]. The calculation results differ

Table 3. Degrees of hybridization [$s(\pi_\sigma)$ and $s(n_\pi)$, %], energies [$E(n_\sigma)$ and $E(n_\pi)$, eV], and populations [$P(n_\sigma)$ and $P(n_\pi)$, *e*] of the lone electron pairs of the O, S, and Se atoms in CH_2=CHXCH_3 molecules

X	Parameter	φ, deg						
		0	30	60	90	120	150	180
O	$s(n_\sigma)$	41.31	40.36	37.63	45.05	39.79	41.28	41.97
S	$s(n_\sigma)$	65.77	65.80	66.27	68.11	66.45	66.26	66.68
Se	$s(n_\sigma)$	72.44	72.46	72.85	74.36	73.08	72.88	73.22
O	$s(n_\pi)$	0.00	1.51	6.14	0.33	5.16	1.85	0.00
S	$s(n_\pi)$	0.00	0.43	1.16	0.01	1.40	0.86	0.00
Se	$s(n_\pi)$	0.00	0.38	0.96	0.00	1.07	0.68	0.00
O	$-E(n_\sigma)$	21.60	21.30	21.52	21.86	21.01	21.42	21.59
S	$-E(n_\sigma)$	20.99	20.88	20.76	21.05	21.14	20.95	21.06
Se	$-E(n_\sigma)$	22.07	21.96	21.82	22.08	21.94	22.03	22.12
O	$-E(n_\pi)$	12.97	13.28	14.23	13.18	14.05	13.45	12.97
S	$-E(n_\pi)$	9.18	9.28	9.44	9.26	9.47	9.34	9.20
Se	$-E(n_\pi)$	8.61	8.70	8.84	8.67	8.85	8.75	8.62
O	$P(n_\sigma)$	1.9439	1.9423	1.9351	1.9236	–1.9345	–1.9406	–1.9435
S	$P(n_\sigma)$	1.9549	1.9547	1.9532	1.9508	1.9525	1.9547	1.9563
Se	$P(n_\sigma)$	1.9607	1.9607	1.9599	1.9582	1.9591	1.9607	1.9617
O	$P(n_\pi)$	1.8165	1.8335	1.8802	1.9080	1.8794	1.8484	1.8368
S	$P(n_\pi)$	1.8207	1.8417	1.8900	1.9069	1.8853	1.8537	1.8414
Se	$P(n_\pi)$	1.8440	1.8632	1.9047	1.9191	1.9015	1.8730	1.8607

from these values by 0.002 Å for $l(C^\alpha{=}C^\beta)$ and $l(C^\alpha{-}O)$ and by 0.004 Å for $l(O{-}C_{Me})$ in the MP2(f)/6-31G* approximation, and by 0.005 Å for $l(C^\alpha{=}C^\beta)$ and $l(C^\alpha{-}O)$ and by 0.009 Å for $l(O{-}C_{Me})$ in the MP2(fc)/6-311G** approximation.

The bond angles in the CH_2=CHSCH_3 molecule, determined by electron diffraction, are as follows: ∠CSC 102.1(5)° [27, 59] or 102.5(20)° [26, 59]; $\angle C^\beta C^\alpha S$ 127.5(7)° [27, 59] or 127.0(15)° [26, 59]. Our values differ from those given in [27] (with the smaller measurement errors) for ∠CSC by 0.91° in the MP2(f)/6-31G* approximation and by 1.29° in the MP2(fc)/6-311G** approximation, and for $\angle C^\beta C^\alpha S$, by 1.12° in both approximations. The experimental bond lengths are as follows: $l(C^\alpha{=}C^\beta)$ 1.343(1) [27, 59] or 1.342(7) Å [26, 59], $l(C^\alpha{-}S)$ 1.759(8) [27, 59] or 1.752(10) Å [26, 59], and $l(S{-}C_{Me})$ 1.795(8) [27, 59] or 1.794(12) Å [26, 59]. Our results differ from those given in [27] by 0.003 Å for $l(C^\alpha{=}C^\beta)$, 0.008 Å for $l(C^\alpha{-}O)$, and 0.006 Å for $l(O{-}C_{Me})$ in the MP2(f)/6-31G* approximation and by 0.000 Å for $l(C^\alpha{=}C^\beta)$, 0.012 Å for $l(C^\alpha{-}O)$, and 0.004 Å for $l(O{-}C_{Me})$ in the MP2(fc)/6-311G** approximation. The agreement is quite reasonable taking into account the experimental errors given in parentheses. To our knowledge, no experimental geometric parameters are available for CH_2=CHSeCH_3. Apart from the parameters listed in Table 2, the following geometric parameters should be noted. According to MP2(f)/6-31G* calculations, in the planar *s-cis* form $\angle C^\beta C^\alpha H$ 105.90°, $\angle C^\alpha C^\beta H$ 110.90° (*cis* and *trans*), $l(C^\alpha{-}H)$ 1.086 Å, $l(C^\beta{-}H)$ 1.082 Å (*cis* and *trans*), $l(C{-}H_{Me})$ 1.089 Å, 1.095 Å × 2 in CH_2=CHOCH_3; $\angle C^\beta C^\alpha H$ 106.92°, $\angle C^\alpha C^\beta H$ 111.10° (*cis* and *trans*), $l(C^\alpha{-}H)$ 1.087 Å, $l(C^\beta{-}H)$ 1.083 Å (*cis* and *trans*), $l(C{-}H_{Me})$ 1.091 Å, 1.092 Å × 2 in CH_2=CHSCH_3; $\angle C^\beta C^\alpha H$ 106.66°, $\angle C^\alpha C^\beta H$ 109.95° (*cis* and *trans*), $l(C^\alpha{-}H)$ 1.087 Å, $l(C^\beta{-}H)$ 1.084 Å (*cis* and *trans*), $l(C{-}H_{Me})$ 1.090 Å × 3 in CH_2=CHSeCH_3. These geometric parameters vary only slightly with the torsion angle φ and differ from those obtained in the MP2(fc)/6-311G** approximation insignificantly.

Intramolecular interactions. Transformation in terms of the NBO approach of the canonical molecular orbitals obtained with the MP2/6-31G* geometry gives the following results. The degrees of hybridization, energies, and populations of the orbitals of the lone electron pairs of the heteroatoms are listed in Table 3. The two lone electron pairs of the O, S, and Se atoms are nonequivalent. One is a hybrid orbital (n_σ), and the other, a virtually pure *p* orbital (n_π). The *s* contribution to the orbital of the hybrid lone electron pair of the O atom (n_σ) varies from ~38 to ~42% depending on φ (in the orthogonal conforma-

Table 4. Energies of the n,σ^* and n,π^* interaction [$E(n,\sigma^*)$ and $E(n,\pi^*)$, kJ mol^{-1}] of the lone electron pairs of the O, S, and Se atoms with the antibonding orbitals of the double bond in CH_2=CHXCH_3 molecules

X	Parameter	φ, deg												
		0	15	30	45	60	75	90	105	120	135	150	165	180
O	$E(n_\pi,\pi^*)$	181.7	173.3	149.6	114.2	72.8	33.8	0.0	24.1	52.0	83.6	116.4	144.0	155.4
S	$E(n_\pi,\pi^*)$	139.5	130.1	104.4	68.2	32.8	8.6	0.0	8.8	29.2	55.7	84.0	108.6	119.6
Se	$E(n_\pi,\pi^*)$	109.0	101.3	80.2	51.4	24.2	6.4	0.0	6.5	22.6	44.1	67.3	86.7	94.9
O	$E(n_\sigma,\pi^*)$	0.0	0.0	0.0	4.9	9.6	20.0	35.9	22.1	12.9	7.5	3.7	0.0	0.0
S	$E(n_\sigma,\pi^*)$	0.0	0.0	0.0	2.4	4.2	6.7	8.1	6.9	4.8	3.0	0.0	0.0	0.0
Se	$E(n_\sigma,\pi^*)$	0.0	0.0	0.0	0.0	2.2	3.5	4.5	4.1	3.0	0.0	0.0	0.0	0.0
O	$E(n_\pi,\sigma^*)$	0.0	0.0	2.8	5.4	7.9	12.9	33.3	31.6	25.1	17.7	11.8	2.9	0.0
S	$E(n_\pi,\sigma^*)$	0.0	0.0	5.2	10.3	15.7	21.3	26.2	26.7	22.8	16.5	9.3	2.3	0.0
Se	$E(n_\pi,\sigma^*)$	0.0	0.0	4.4	8.5	12.7	16.6	17.5	20.3	17.5	12.7	7.1	2.1	0.0
O	$E(n_\sigma,\sigma^*)$	32.0	32.3	31.3	30.1	27.9	22.1	2.9	0.0	0.0	0.0	0.0	0.0	2.1
S	$E(n_\sigma,\sigma^*)$	22.5	22.5	20.7	18.3	14.9	10.3	5.4	2.3	0.0	0.0	0.0	0.0	0.0
Se	$E(n_\sigma,\sigma^*)$	17.1	17.1	15.4	13.5	10.9	7.8	4.6	2.3	0.0	0.0	0.0	0.0	0.0

tion it reaches 45%). Taking into account that the CH_2=CHOCH_3 molecule exists chiefly in the *s-cis* conformation, the *s* contribution to the n_σ orbital of the O atom is ~40–41%. The *s* contribution to the hybrid n_σ orbitals of the S and Se atoms is appreciably higher: 66–68 and 72–74%, respectively. In [60, 61], the orbitals of the lone electron pairs of the O and S atoms in the CH_2=CHXCH_3 molecules, obtained by MNDO calculations, were distinguished on going to the naturally hybridized basis according to [62]. The results of the calculations in [60, 61] also indicate that the lone electron pairs of the O and S atoms are nonequivalent. One of these orbitals is a virtually pure *p* orbital, but the *s* contribution to the other orbital, according to [60, 61], is similar for O and S (75 and 80%, respectively) and appreciably overestimated as compared to our results, especially for O. The different hybridization of the lone electron pairs of chalcogens is also confirmed by photoelectron spectroscopy [63, 64]; it explains the results of many physicochemical studies, e.g., of [65–70]. The hybrid lone electron pair n_σ lies considerably deeper on the energy scale than n_π. The n_π energy grows in the order O < S < Se, whereas the energy characteristics of n_σ are affected by the degree of hybridization more strongly than by the principal quantum number. The population of n_σ is higher than that of n_π. The populations of n_σ and n_π increase in the order O < S < Se. This trend is due to changes in the hybridization in the case of n_σ and to a decrease in the resonance interaction with the π system (and hence to greater localization of n_π on the heteroatom) in the case of n_π. In going from planar (φ 0° and 180°) to orthogonal (φ 90°) conformers, the n_π population, as expected, increases. The n_π population in the planar *s-cis* form is higher than that in the planar *s-trans* form. The parameter $P(n_\pi)$ varies with conformation in the following ranges: 0.0915 (O) > 0.0862 (S) > 0.0751 e (Se). The n_σ population is also sensitive to conformation, but, in contrast to $P(n_\pi)$, it decreases in going from planar to orthogonal conformations. In the ether, the n_σ population is similar in the *s-cis* and *s-trans* forms, whereas in the sulfide and selenide it is higher in the *s-trans* form. The n_π population is more sensitive to the molecular conformation than the n_σ population. The energy of the π orbital of the double bond in unsubstituted ethylene, calculated in the same approximation, is –10.05 eV. The XCH_3 groups decrease the energy of the π orbital of the double bond. With the OCH_3 group, it ranges from –10.15 to –10.37 eV, and with the SCH_3 and $SeCH_3$ groups, from –10.43 to –10.51 eV. The energy of the σ orbital of the double bond in unsubstituted ethylene is –26.46 eV. This parameter also decreases on substitution with XCH_3 groups. With the OCH_3 group, the energy of the σ orbital of the double bond ranges from –26.79 to –26.56 eV; with the SCH_3 group, from –26.92 to –27.09 eV; and with the $SeCH_3$ group, from –27.02 to –27.16 eV.

The NBO analysis allows quantitative estimation of the interaction of the lone electron pairs of the O, S, and Se atoms with the antibonding σ* and π* orbitals of the double bond. The energies of these interactions are listed in Table 4. The nonhybridized lone electron pairs n_π interact most efficiently with the antibonding π* orbitals of the double bond in the planar conformations. In the *s-cis* form, the interaction

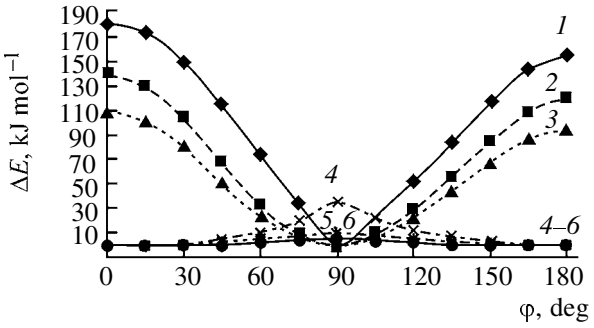


Fig. 2. Variation with the torsion angle φ of the energy of interaction of the lone electron pairs n_π and n_σ with the antibonding π* orbitals. (*1*) $E(n_\pi,\pi^*)$, CH_2=CHOCH$_3$; (*2*) $E(n_\pi,\pi^*)$, CH_2=CHSCH$_3$; (*3*) $E(n_\pi,\pi^*)$, CH_2=CHSeCH$_3$; (*4*) $E(n_\sigma,\pi^*)$, CH_2=CHOCH$_3$; (*5*) $E(n_\sigma,\pi^*)$, CH_2=CHSCH$_3$; and (*6*) $E(n_\sigma,\pi^*)$, CH_2=CHSeCH$_3$.

energy is estimated at ~182 (O), ~139 (S), and ~109 kJ mol^{-1} (Se). In the *s-trans* form, it is somewhat lower: 155 (O), 120 (S), and 95 kJ mol^{-1} (Se). As the torsion angle φ is varied from 0° to 90° and from 180° to 90°, the interaction of n_π with the antibonding π* orbitals of the double bond becomes weaker, and in the orthogonal form it fully disappears. Bond and Schleyer [71] estimated the energy of the interaction of n_π with the π* orbitals of the double bond in the planar conformations of CH_2=CHOH at 194 (*s-cis*) and 176 kJ mol^{-1} (*s-trans*). In $C_6H_5XCH_3$ (X = O, S, Se), in the planar conformation, the energy of the interaction of n_π with the antibonding π* orbitals of the aromatic ring are lower: 147 (O), 104 (S), and 81 kJ mol^{-1} (Se) [72]. Thus, the n_π orbitals of the O, S, and Se atoms in the planar conformation interact with the π system of the double bond more efficiently than with that of the aromatic ring. In some conformations, the hybrid lone electron pairs n_σ also interact with the antibonding π* orbitals of the double bond by the donor–acceptor mechanism. This interaction is the most efficient in the orthogonal form (φ 90°). Its energy is ~36 kJ mol^{-1} with O, 8 kJ mol^{-1} with S, and 4.5 kJ mol^{-1} with Se. Thus, in vinyl methyl ether, even in the orthogonal conformation, the O atom (via its n_σ) interacts fairly efficiently with the π system, whereas in the sulfide and selenide this interaction is considerably weaker. Figure 2 shows how the energies of the interaction of n_π and n_σ with the antibonding π* orbitals of the double bond vary with the torsion angle φ. The capability of the O atom to partially preserve the resonance interaction with the π system of the double bond in the orthogonal conformation is confirmed by the ^{13}C NMR spectra of CH_2=CHXAlk (X = O, S; Alk = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9) [73, 74].

Both lone electron pairs at the O, S, and Se atoms interact by the donor–acceptor mechanism with the antibonding σ* orbitals of the double bond. The nonhybridized lone electron pair n_π interacts with the σ* orbitals of the double bonds in all the conformations except planar or approximately planar ones (φ 0°, 15°, and 180°). The energy of this interaction is maximal in the conformations with φ 90°–105°: 33 (O), 27 (S), and 20 kJ mol^{-1} (Se). The hybrid lone electron pair n_σ interacts with the σ* orbitals of the double bond in the conformations with λ from 0° to 90° or 105°; the interaction is the most efficient in the planar *s-cis* form: 32 (O), 23 (S), and 17 kJ mol^{-1} (Se).

Electron density distribution. The natural charges obtained by the NBO method improve the description of the electron density in the molecule as compared to the traditional Mulliken analysis [75]. The natural atomic charges in CH_2=CHXCH$_3$ molecules in the conformations with φ 0°, 90°, and 180° are listed in Table 5.

As judged from the atomic charges, the double bond in the CH_2=CHOCH$_3$ molecule in any conformation is polarized toward the terminal atom (C^β). The difference between the charges on the C^α and C^β atoms is 0.7077 (0°), 0.6038 (90°), and 0.6464 e (180°). So large difference is primarily due to a considerable deficiency of the electron density on the C^α atom because of different electronegativities of the C and O atoms, although efficient *n*,π conjugation of the O atom with the double bond also makes a certain contribution. In the planar conformations of the CH_2=CHSCH$_3$ and CH_2=CHSeCH$_3$ molecules, the double bond is also polarized toward the C^β atom, but the difference between the charges on the C^α and C^β atoms is smaller than that in the ether: 0.0680 (0°) and 0.0484 e (180°) in the sulfide, and 0.0162 (0°) and 0.0040 e (180°) in the selenide. However, in the conformations with φ equal or close to 90°, the charge on the C^α atom in the sulfide and selenide is higher than that on C^β. The difference (at φ 90°) is 0.0078 e in the sulfide and 0.0485 e (90°) in the selenide.

The charge on the carbon atoms in unsubstituted ethylene, calculated in the similar approximation, is –0.4231 e. The differences between the charges on the C atoms of the double bond in the CH_2=CHXCH$_3$ and ethylene molecules are listed in Table 5. The OCH_3 group is a strong electron acceptor with respect to the C^α atom, and the electron-acceptor effect of the SCH_3 group is appreciably weaker. The $SeCH_3$ group is an electron donor with respect to C^α. The OCH_3 group is an electron donor with respect to C^β in all the conformations, but the donor effect decreases with φ varied from 0° to 90° and from 180° to 90°. The SCH_3 and $SeCH_3$ groups are electron donors with re-

Table 5. Natural atomic charges (q, e) in the CH_2=CHXCH_3 molecules (X = O, S, Se)[a]

φ, deg	q(X)	$q(C^{\alpha})$	$q(C^{\beta})$	$q(H_A)$	$q(H_B)$	$q(H_C)$	$q(C_{Me})$	$\Sigma q(H_{Me})/3$
				CH_2=CHOCH_3				
0	–0.5334	0.1318 (0.5549)	–0.5759 (–0.1528)	0.2132	0.2317	0.2131	–0.3126	0.2090
90	–0.5782	0.1158 (0.5389)	–0.4880 (–0.0649)	0.1929	0.2232	0.2234	–0.2961	0.2012
180	–0.5466	0.1210 (0.5441)	–0.5254 (–0.1023)	0.1878	0.2233	0.2254	–0.3046	0.2064
				CH_2=CHSCH_3				
0	0.2998	–0.4092 (0.0139)	–0.4772 (–0.0541)	0.2464	0.2276	0.2118	–0.8416	0.2475
90	0.2263	–0.4072 (0.0159)	–0.3994 (0.0237)	0.2313	0.2207	0.2224	–0.8186	0.2415
180	0.2782	–0.4045 (0.0186)	–0.4529 (–0.0298)	0.2317	0.2240	0.2180	–0.8304	0.2455
				CH_2=CHSeCH_3				
0	0.3646	–0.4492 (–0.0261)	–0.4654 (–0.0423)	0.2459	0.2265	0.2117	–0.8856	0.2505
90	0.2980	–0.4489 (–0.0258)	–0.4004 (0.0227)	0.2363	0.2196	0.2233	–0.8629	0.2450
180	0.3462	–0.4440 (–0.0209)	–0.4480 (–0.0249)	0.2347	0.2237	0.2174	–0.8750	0.2486

[a] The differences between the charges on the carbon atoms of the double bond in the CH_2=CHXCH_3 and ethylene molecules are given in parentheses. The negative differences mean that the charge on the C^{α} and C^{b} atoms in the CH_2=CHXCH_3 molecules is higher than that in the ethylene molecule.

spect to C^{β} only at φ equal or close to 0°. The ^{13}C NMR chemical shifts of the C^{β} atoms are as follows (δ_C, ppm, reference TMS): 85.1 (ether), 107.7 (sulfide), and 114.2 (selenide). In unsubstituted ethylene, the ^{13}C chemical shift is 122.8 ppm [76]. Thus, according to the ^{13}C NMR spectra, the XCH_3 groups (X = O, S, Se) exert a shielding effect on the $^{13}C^{\beta}$ atoms, i.e., behave as electron donors. As shown above, the CH_2=CHOCH_3 molecule exists virtually exclusively in the planar *s-cis* conformation. Therefore, the large difference in the shielding of the $^{13}C^{\alpha}$ and $^{13}C^{\beta}$ nuclei in this molecule is determined by the large difference between the charges on the C^{α} and C^{β} atoms, which, in turn, is due both to different electronegativities of the O and C^{α} atoms and to the efficient n_{π},π^* interaction. In the CH_2=CHSCH_3 and CH_2=CHSeCH_3 molecules, along with the planar *s-cis* conformation, a significant contribution to the conformational equilibrium is made by two quasi-degenerate *gauche* forms separated by a low barrier and by the states lying above this maximum and characterized by a large amplitude of the mutual motion of the fragments about the center corresponding to the planar *s-trans* conformation. In the latter conformation, the n_{π},π^* interaction is also fairly efficient, though weaker than in the *s-cis* conformation. Therefore, the shielding of the $^{13}C^{\beta}$ nuclei reflects the averaged charge on the C^{β} atoms in these "conjugated" conformations.

From the atomic charges, we can determine the direction of the bond polarization and evaluate its polarity. The $C^{\alpha}\rightarrow O$ bonds are polarized toward the heteroatom, and the difference between the atomic charges is 0.6652 (0°), 0.6940 (90°), and 0.6676 e (180°). The $C^{\alpha}\leftarrow S$ and $C^{\alpha}\leftarrow Se$ bonds, on the contrary, are polarized toward the C^{α} atom. The difference between the charges on these atoms is 0.7090 (0°), 0.6335 (90°), and 0.6827 e (180°) in the sulfide and 0.8138 (0°), 0.7469 (90°), and 0.7902 e (180°) in the selenide. With increasing electronegativity of X (Se < S < O), the electron density on the C_{Me} atom decreases, and the degree of shielding of the $^{13}C_{Me}$ nuclei decreases in the same order [^{13}C NMR chemical shifts, δ_C, ppm: 4.2 (selenide), 13.4 (sulfide), and 54.5 (ether)]. The $C_{Me}\rightarrow O$ bonds are polarized toward the O atom; the difference between the atomic charges is 0.2208 (0°), 0.2821 (90°), and 0.2420 e (180°). The $C_{Me}\leftarrow S$ and $C_{Me}\leftarrow Se$ bonds are polarized toward the C_{Me} atom, and the difference between the atomic

charges is very large: 1.1414 (0°), 1.0449 (90°), and 1.1086 e (180°) in the sulfide and 1.2502 (0°), 1.1609 (90°), and 1.2212 e (180°) in the selenide. The C_{Me}←H bonds in all the three compounds are polarized toward the C_{Me} atom. The difference between the charges on these atoms in the ether (0.3632–0.3823 e) is smaller than that in the sulfide (0.8991–0.9241 e) and selenide (0.9446–0.9691 e).

Thus, the potential functions of internal rotation around the C_{sp^2}–X bonds in the CH_2=CHXCH_3 molecules (X = O, S, Se) exhibit a "sharp" potential well in the region of the planar *s-cis* conformation. This well corresponds to the deepest energy minimum, and the amplitude of the mutual motion of the fragments about the center is small. The second, less energetically favorable conformation of the ether has a broad shallow potential well, with a large amplitude of the mutual motion of the fragments about the center corresponding to the planar *s-trans* form. In the sulfide and selenide, the second conformation is a set of two quasi-degenerate nonplanar *gauche* forms separated by a rotation barrier at φ 180°. Since the potential barrier is low (of the order of *kT*), the motion of fragments can occur not only in the potential wells of the quasi-degenerate *gauche* forms, but also with mutual transformation of these forms, i.e., with a large amplitude about the center corresponding to the planar *s-trans* form. These results reasonably agree with experimental data [1–4]. The height of the *cis/gauche* and *gauche/cis* rotation barriers decreases in the order ether > sulfide > selenide. The difference between the energies of the minima in the potential function of internal rotation and the population of the planar *s-cis* form decrease in the same order. The quantitative estimates of the rotation barriers depend on the basis set used but, in principle, are mutually consistent. The NBO analysis shows that the lone electron pairs of the O, S, and Se atoms are nonequivalent. One of the pairs occupies a virtually pure *p* orbital (n_p), and the other, a hybrid orbital (n_σ) in which the s contribution increases in the order O << S < Se. The energy of the interaction of the n_π orbital of the X atoms with the antibonding π* orbitals of the double bond in the planar *s-cis* form is higher than that in the *s-trans* form. In the orthogonal conformation, there is no resonance interaction between n_π and the double bond, but n_σ interacts with the antibonding π* orbitals of the double bond; the extent of this interaction in the ether is greater than that in the sulfide and selenide. The electron density distribution in the molecules is governed by the electronegativity of X atoms and by their capability for n,π conjugation, which depends not only on the kind of the heteroatom, but also on the molecular conformation.

ACKNOWLEDGMENTS

The study was financially supported by the State Foundation for Basic Research of Ukraine (project no. F-7/334).

REFERENCES

1. Trofimov, B.A., *Geteroatomnye proizvodnye atsetilena* (Heteroatomic Acetylene Derivatives), Moscow: Nauka, 1981.
2. Trofimov, B.A. and Amosova, S.V., *Divinilsul'fid i ego proizvodnye* (Divinyl Sulfide and Its Derivatives), Novosibirsk: Nauka, 1983.
3. Sinegovskaya, L.M. and Trofimov, B.A., *Usp. Khim.,* 1996, vol. 65, no. 12, p. 1091.
4. Sinegovskaya, L.M., Keiko, V.V., and Trofimov, B.A., *Sulfur Rep.,* 1987, vol. 7, no. 5, p. 337.
5. Bzhezovskii, V.M. and Kapustin, E.G., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 3, p. 429.
6. Bzhezovskii, V.M. and Kapustin, E.G., *Zh. Obshch. Khim.,* 2000, vol. 70, no. 11, p. 1876.
7. Bzhezovskii, V.M. and Kapustin, E.G., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 1, p. 58.
8. Aroney, M.J., Le Fevre, R.J.W., Ritchie, G.L.D., and Saxby, J.D., *Aust. J. Chem.,* 1967, vol. 20, no. 2, p. 375.
9. Aroney, M.J., Le Fevre, R.J.W., Ritchie, G.L.D., and Saxby, J.D., *Aust. J. Chem.,* 1969, vol. 22, no. 7, p. 1539.
10. Owen, N.L. and Seip, H.M., *Chem. Phys. Lett.,* 1970, vol. 5, no. 3, p. 162.
11. Samdal, S. and Seip, H.M., *J. Mol. Struct.,* 1975, vol. 28, no. 1, p. 193.
12. Cahill, P., Cold, L.P., and Owen, N.L., *J. Chem. Phys.,* 1968, vol. 48, no. 4, p. 1620.
13. Pyckhout, W., Nuffel, P. van, Alsenoy, C. van, Enden L. van den, and Geise, H.J., *J. Mol. Struct.,* 1983, vol. 102, no. 3/4, p. 333.
14. Ignatyev, I.S., Lasarev, A.N., Smirnov, M.L., Alpert, M.L., and Trofimov, B.A., *J. Mol. Struct.,* 1981, vol. 72, no. 1/2, p. 25.
15. Cadioli, B., Gallinella, E., and Pincelli, U., *J. Mol. Struct.,* 1982, vol. 78, no. 3/4, p. 215.
16. Katritzky, A.R., Pinzelli, R.F., and Topsom, R.D., *Tetrahedron,* 1972, vol. 28, no. 13, p. 3441.
17. Gallinella, E. and Cadioli, B., *Chem. Phys. Lett.,* 1981, vol. 77, no. 3, p. 533.
18. Friege, H. and Klessinger, M., *Chem. Ber.,* 1979, vol. 112, no. 5, p. 1614.
19. Friege, H. and Klessinger, M., *J. Chem. Res. Synop.,* 1977, no. 8, p. 208.

20. Planckaert, A.A., Doucet, J., and Sandorfy, C., *J. Chem. Phys.,* 1974, vol. 60, no. 12, p. 4846.
21. Sakakibara, M., Inagaki, F., Harada, I., and Shimanouchi, T., *Bull. Chem. Soc. Jpn.,* 1976, vol. 49, no. 1, p. 46.
22. Sullivan, J.F., Dickson, T.J., and Durig, J.R., *Spectrochim. Acta, Part A,* 1986, vol. 42, no. 2/3, p. 113.
23. Durig, J.R. and Compton, D.A.C., *J. Chem. Phys.,* 1978, vol. 69, no. 5, p. 2028.
24. Penn, R.E. and Curl, R.F., *J. Mol. Spectrosc.,* 1967, vol. 24, no. 2, p. 235.
25. Samdal, S. and Seip, H.M., *Acta Chem. Scand.,* 1971, vol. 25, no. 5, p. 1903.
26. Derissen, J.L. and Bijen, J.M., *J. Mol. Struct.,* 1973, vol. 16, no. 2, p. 289.
27. Samdal, S., Seip, H.M., and Torgrimsen, T., *J. Mol. Struct.,* 1979, vol. 57, no. 1, p. 105.
28. Bock, H., Wagner, C., Wittel, K., Sauer, J., and Seebach, D., *Chem. Ber.,* 1974, vol. 107, no. 6, p. 1869.
29. Muller, C., Schafer, W., Schweig, A., Thon, N., and Vermeer, H., *J. Am. Chem. Soc.,* 1976, vol. 98, no. 18, p. 5440.
30. Keiko, V.V., Sinegovskaya, L.M., Kalinina, N.A., Gusarova, N.K., Al'pert, M.L., and Trofimov, B.A., *Zh. Obshch. Khim.,* 1982, vol. 52, no. 4, p. 875.
31. Durig, J.R., Durig, D.T., Dickson, T.J., Jalilian, M., Jin, Y., and Sullivan, J.F., *J. Mol. Struct.,* 1998, vol. 442, no. 1/3, p. 71.
32. Surushkin, A.N., Sinegovskaya, L.M., Frolov, Yu.L., Gusarova, N.K., Potapov, V.A., and Trofimov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1987, no. 2, p. 1283.
33. Sinegovskaya, L.M., Frolov, Yu.L., Gusarova, N.K., Potapov, V.A., and Trofimov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1985, no. 1, p. 115.
34. Sinegovskaya, L.M. and Turchaninov, V.K., *Izv. Ross. Akad. Nauk, Ser. Khim.,* 1992, no. 9, p. 2080.
35. Sadioli, B. and Pincelli, U., *J. Chem. Soc., Faraday Trans. 2,* 1972, vol. 68, no. 6, p. 991.
36. Bernardi, F., Epiotis, N.D., Yates, R.L., and Schlegel, H.B., *J. Am. Chem. Soc.,* 1976, vol. 98, no. 9, p. 2385.
37. John, I.G. and Radom, L., *J. Mol. Struct.,* 1977, vol. 36, no. 1, p. 133.
38. Pyckhout, W., Alsenoy, C. van, Geise, H.J., Veken, B., and Pieters, G., *J. Mol. Struct.,* 1985, vol. 130, no. 3/4, p. 335.
39. Lister, D.G. and Palmieri, P., *J. Mol. Struct.,* 1976, vol. 32, no. 2, p. 355.
40. Nobes, R.H. and Radom, L., *J. Mol. Struct.,* 1981, vol. 85, no. 1/2, p. 185.
41. Osapay, K., Delhalle, J., Nsunda, K.M., Rolli, E., Houriet, R., and Hevesi, L., *J. Am. Chem. Soc.,* 1989, vol. 111, no. 14, p. 5028.
42. Kajimoto, O., Kobayashi, M., and Fueno, T., *Bull. Chem. Soc. Jpn.,* 1973, vol. 46, no. 8, p. 2316.
43. Mangini, A., *Atti Acad. Naz. Lincei, Mem., Cl, Sci. Fis. Mat. Nat., Sez. 2a,* 1977, vol. 14, no. 2, p. 31.
44. Kao, J., *J. Am. Chem. Soc.,* 1978, vol. 100, no. 15, p. 4685.
45. Kao, J., *J. Am. Chem. Soc.,* 1985, vol. 107, no. 19, p. 5323.
46. Frolov, Yu.L., *Khimiya organicheskikh soedinenii sery. Obshchie voprosy* (Chemistry of Organic Sulfur Compounds. General Problems), Belen'kii, L.I., Ed., Moscow: Khimiya, 1988, p. 238.
47. Gallinella, E. and Cadioli, B., *J. Mol. Struct.,* 1991, vol. 249, no. 3/4, p. 343.
48. Frolov, Yu.L., Chipanina, N.N., and Sapoznikov, Yu.M., *Main Group Chem.,* 1996, vol. 1, no. 4, p. 445.
49. Møller, Ch. and Plesset, M.S., *Phys. Rev.,* 1934, vol. 46, no. 4, p. 618.
50. Pople, J.A., Seeger, R., and Krishnan, R., *Int. J. Quantum Chem.,* 1977, symp. 11, p. 149.
51. Hehre, W.J., Radom, L., Schleyer, P.v.R., and Pople, J.A. *Ab initio Molecular Orbital Theory,* New York: Wiley, 1987.
52. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Adamo, C., Clifford, S., Ocherski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T.A., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B.G., Chen, W., Wong, M.W., Andres, J.L., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *GAUSSIAN 98W,* Rev. A.7, Pittsburgh: Gaussian, 1998.
53. Weinhold, F. and Carpenter, J.E., *The Structure of Small Molecules and Ions,* Naaman R. and Vager, Z., Eds., New York: Plenum, 1988, p. 227.
54. Reed, A.E., Curtiss, L.A., and Weinhold, F., *Chem. Rev.,* 1988, vol. 88, no. 6, p. 899.
55. Nemukhin, F.V. and Veinkhol'd, F., *Ross. Khim. Zh.,* 1994, vol. 38, no. 6, p. 5.

56. Glendening, E.D., Reed, A.E., Carpenter, J.E., and Weinhold, F., *NBO Ver. 3.1*.

57. Scott, A.P. and Radom, L., *J. Phys. Chem.,* 1996, vol. 100, no. 41, p. 16502.

58. Naumov, V.A. and Kataeva, O.N., *Molekulyarnoe stroenie organicheskikh soedinenii kisloroda i sery v gazovoi faze* (Molecular Structure of Organic Oxygen and Sulfur Compounds in the Gas Phase), Moscow: Nauka, 1990.

59. Hargittai, I., *The Structure of Volatile Sulfur Compounds,* Budapest: Akad. Kiado, 1985.

60. Afonin, A.V., Vashchenko, A.V., Voronov, V.K., Danovich, D.K., and Zasyadko, O.A., *Zh. Org. Khim.,* 1989, vol. 25, no. 2, p. 240.

61. Afonin, A.V., Vashchenko, A.V., Danovich, D.K., and Andrianov, M.A., *Zh. Org. Khim.,* 1991, vol. 27, no. 1, p. 13.

62. Ruedenberg, K., *Rev. Mod. Phus.,* 1962, vol. 34, pp. 326–376.

63. Chmutova, G.A., *Stroenie i reaktsionnaya sposobnost' organicheskikh soedinenii* (Structure and Reactivity of Organic Compounds), Arbuzov, B.A., Ed., Moscow: Nauka, 1978, p. 227.

64. Tshmutova, G. and Bock, H., *Z. Naturforsch. B,* 1976, vol. 31, no. 12, p. 1611.

65. Gur'yanova, E.N., Gol'dshtein, I.P., and Romm, I.P., *Donorno-aktseptornaya svyaz'* (Donor–Acceptor Bond), Moscow: Khimiya, 1973.

66. Romm, I.P. and Gur'yanova, E.N., *Usp. Khim.,* 1986, vol. 55, no. 2, p. 225.

67. Bzhezovskii, V.M., Dolenko, G.N., Kalabin, G.A., Chmutova, G.A., and Trofimov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1977, no. 3, p. 586.

68. Schaefer, T., Salman, S.R., Wildman, T.A., and Clark, P.D., *Can. J. Chem.,* 1982, vol. 60, no. 3, p. 342.

69. Trofimov, B.A., Shergina, N.I., Atavin, A.S., Kositsyna, E.I., Gusarov, A.V., and Gavrilova, G.M., *Zh. Prikl. Spektrosk.,* 1971, vol. 14, no. 2, p. 282.

70. Glushko, G.N. and Krivdin, L.B., *Zh. Org. Khim.,* 1995, vol. 31, no. 11, p. 1623.

71. Bond, D. and Schleyer, P.v.R., *J. Org. Chem.,* 1990, vol. 55, no. 3, p. 1003.

72. Bzhezovskii, V.M. and Kapustin, E.G., *Zh. Org. Khim.,* 2002, vol. 38, no. 4, p. 591.

73. Kalabin, G.A., Trofimov, B.A., Bzhezovskii, V.M., Kushnarev, D.F., Amosova, S.V., Gusarova, N.K., and Al'pert, M.L., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1975, no. 3, p. 576.

74. Bzhezovskii, V.M., Kalabin, G.A., Trofimov, B.A., Efremova, G.A., and Gusarova, N.K., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1980, no. 5, p. 1007.

75. Reed, A.E., Weinstok, R.B., and Weinhold, F., *J. Chem. Phys.,* 1985, vol. 83, no. 2, p. 735.

76. Stothers, J.B., *Carbon-13 NMR Spectroscopy,* New York: Academic, 1972, p. 70.