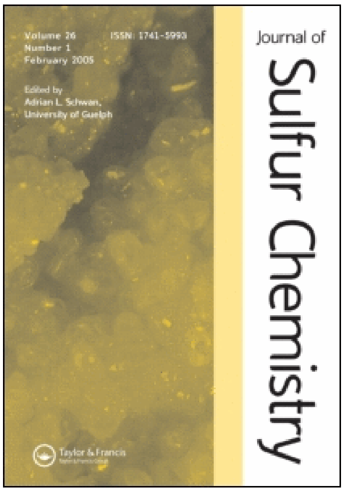

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ROTATIONAL ISOMERISM OF VINYL ETHERS AND SULFIDES

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The investigations of rotational isomerism of p,π-conjugated systems discussed in the present review have revealed unexpected and, in many respects, conspicuous features in their molecular and electronic structure.

The most stable conformation of ethenol, ethenethiol, methyl vinyl ether and methyl vinyl sulfide is the *s-cis* form exhibiting the largest steric strain. The stabilization of *s-cis* rotamers in these compounds is caused by not only the energy difference of p,π-interactions in planar *s-cis* and *s-trans* conformations, but also by a significant contribution to the potential of internal rotation about the C_{sp^2}–X bond (X = O, S) from a third-order barrier.

The molecules of compounds of a general formula $CH_2{=}CHXR$ and $CH_2{=}CHXCH{=}CH_2$ (X = O, S) show two stable conformers of quite different types. The conformers of the first type are characterized by a certain torsional angle and slight oscillations relative to the position with minimal potential energy. The conformers of the second type display motion of large amplitude and potential well with a wide flattened bottom. This motion may involve not one but several minima on the potential curve of internal rotation, and the number of stable conformers may exceed that obtained by considering only static rotamer forms.

Key words: Vinyl ethers, vinyl sulfides, rotational isomerism.

CONTENTS

I. INTRODUCTION

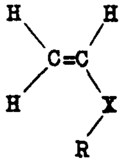
The interest in the electronic and conformational structure of simple p,π-conjugated systems of the type $CH_2{=}CHXR$ ($X = O, S$) arises from a number of features shown by rotational isomerism of this class of compounds. This includes, first of all, the possible existence of a greater number of specific rotamer forms than should be expected on the basis of canonical concepts of the nature of rotational isomers characterized by a certain value of torsional angles. Along with classical rotamers to which can be assigned an appropriate molecular structure and, consequently, one of widely accepted terms (*s-cis, s-trans*, etc.), the molecules of alkyl vinyl ethers and sulfides can be represented by rotameter forms distinguished by torsional intramolecular motion of large amplitude. The close interrelation and interconditionality of the electron distribution and conformation of the molecules in question lead to an unusual manifestation of their physical properties. A thorough investigation of these phenomena is necessary not only from the purely analytical aspect but also because of their great importance in physical organic chemistry.

Research on the conformational diversity of vinyl ethers and sulfides may hold particular promise for a better understanding of the reactivity of a variety of polyfunctional chemical compounds containing $-O-CH{=}CH_2$ and $-S-CH{=}CH_2$ structural units.

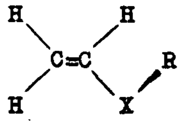
The investigation of compounds discussed in the present review, carried out over several decades by various physical methods both experimental and purely theoretical, now represents one of the fundamental sections of the theory of chemical structure and provides a comprehensive consideration of the problem of heteroatom/multiple bond interaction. There have been substantial achievements in solving the questions of the number and nature of rotational isomers, of the geometry of the most 'rigid' rotamer forms, of intercorrelated changes in the structural parameters upon internal rotation, of the character of the electronic distribution in various conformations, etc. However, the solution of these and other problems applied to selected compounds is impeded by the simplified concept of hindered internal rotation about the $C_{sp^2}-X$ bond ($X = O, S$) which rejects the idea of considering this rotation as a typically quantum-mechanical process. At the same time, the peculiar behaviour of these compounds in many cases can be explained only by consideration of the whole ensemble of steady states corresponding to the angular dependence of potential energy characteristic of each molecule. It goes without saying that it is this consideration that opens the way to the formulation of new problems which can be essential for not only theory, but for practical application as well.

The main object of the present review is the consideration of studies dealing with the conformational structure and electron distribution in vinyl ethers and sulfides. We have critically analysed the papers devoted to experimental and theoretical studies including quantum-chemical calculations. With the compounds studied, however, the latter fail to provide convincing results in certain cases. They are of greater importance as a reference point for further experimental and theoretical investigations. Besides, independently of improving these calculations for the investigation of the internal rotation potential, preference should be given, in our opinion, to methods based on experimental data of some kind or another.

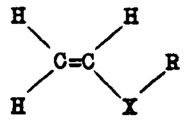
According to traditional concepts, when the internal rotation about the $C_{sp^2}-X$ bonds is hindered, the molecular system in question can exist in three conformations:



s-cis

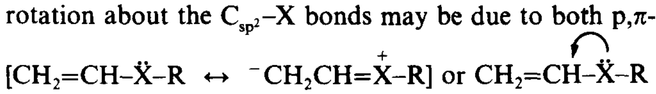


non-planar (gauche)



s-trans

The hindered rotation about the C_{sp^2}–X bonds may be due to both p,π-conjugation



$$[CH_2{=}CH{-}\ddot{X}{-}R \leftrightarrow {}^{-}CH_2CH{=}\overset{+}{X}{-}R] \text{ or } CH_2{=}CH{-}\ddot{X}{-}R$$

and solely steric interaction of R with hydrogen atoms of the vinyl group. In studying the conformational isomerism of these compounds it is very important to solve the question concerning the number and nature of stable conformers and their energies. This opens the way to a better understanding of the properties of the compounds studied on one hand and the character of the influence produced on these compounds by external factors such as electric and magnetic fields, environment, temperature, radiation, etc., on the other hand. The most complete information about the conformational isomerism of vinyl ethers and sulfides can be provided by the potential curve of internal rotation and (for divinyl and aryl vinyl compounds) the potential surface constructed as the function of rotation angles relative to C_{sp^2}–X bonds. The present state of this section of chemical structure theory is characterized by an intention to obtain potential curves and surfaces of internal rotation.

In alkyl vinyl ethers and sulfides, along with rotation about the C_{sp^2}–X bonds one can observe rotation around the C_{sp^3}–X bond and internal rotation in the alkyl substituent when $R \neq CH_3$. This increases the number of rotational states and hinders the applicability of many methods. This also accounts for an increasing interest in the simplest representatives of the series $CH_2{=}CHXR$, i.e., ethenol and ethenethiol.

II. VINYL ALCOHOLS AND THIOLS

II.1 Ethenol

Ethenol, the simplest representative of the enols, was for a long time unavailable for experimental studies and regarded as an unstable tautomeric form of acetaldehyde. Only in 1967 ethenol was detected by its mass spectrum during investigations of the products of deuteroacetylene oxidation.[1] In 1973 it became possible to take an NMR spectrum of ethenol, without isolating this compound, from the products of the photolysis of acetaldehyde and 2-hydroxybutan-3-one.[2] The data on the molecular structure of ethenol were obtained by microwave (MW) spectroscopy,[3] also without isolating it, from the products of the gas phase pyrolysis (~900 °C) of ethylene glycol at 0.02–0.04 torr. The rotation constants turned out to be in agreement with a planar *cis* conformation of the ethenol molecule (Fig. 1). The structural parameters of ethenol are less affected by non-bonded atoms than those of any other compounds containing a C=C–O moiety. The p,π-interaction in this molecule is manifested by shortening of the C–O bond (1.373 Å) as compared with saturated alcohols (1.43 Å) and by an increase of the C=C–O angle (126°) as compared to the normal C=C–X angle (ca. 120°). A refined *cis*-structure of ethenol has been obtained by MW spectroscopy of the pyrolysis products

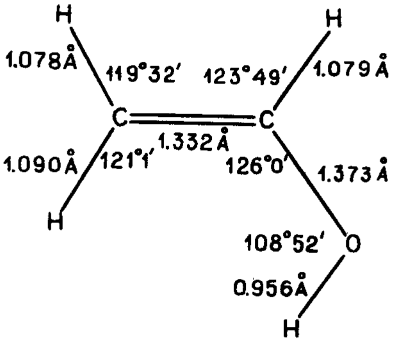


Figure 1 Molecular structure of *cis*-ethenol.[3]

of isotopically substituted cyclobutanols.[4] The C–O bond length and the C=C–O angle are the same as those found in.[3] The C=C bond length (1.326 Å) is slightly shorter than the corresponding bond lengths of ethenol (1.333 Å),[3] ethene (1.337 Å),[5] and propylene (1.336 Å).[6] The MW spectra of nine isotopic species of ethenol have been analysed.[4] The moments of inertia and small inertia defects for all the ethenol isotopic species suggest a planar *cis*-conformer structure.

Studies of the vibrational spectra of ethenol are rather scarce.[7] The IR data of ethenol are essential for the determination of this and other enolic compounds as chemical intermediates. A compound, found among the products of the atomic oxygen-ethene reaction in a solid argon matrix exposed to UV-irradiation, has been identified by IR spectroscopy as ethenol.[8] Ethenol, ethene, and acetaldehyde have been found among the products of the thermolysis of cyclobutanol in an argon matrix.[9] The analysis of the IR spectra of ethenol and its nine isotopic species and the calculation of the normal vibrations have allowed assignment of absorption bands of the *cis*-conformer of ethenol and all side products. The *cis*-conformer valence force field was determined using the centrifugal distortion constants obtained from the rotational spectra of the *cis*-structure and its isotopic species.[9] The force constant (6.14 mdyn/Å) of the C–O stretching vibration of ethenol is considerably greater than that for methanol (5.27–5.28 mdyn/Å)[10,11] which can be explained by the formation of a weak π-bond of the C–O fragment due to interaction of π-electrons of the double bond with lone electron pairs of the oxygen atom. This may also account for the appearance of ethenolic OH torsional vibration in a higher-frequency region as compared with methanol, 413 and 217 cm^{-1}, respectively. The corresponding force constants are 0.073 mdyn/Å in ethenol[9] and 0.027 mdyn/Å in methanol.[10,11]

Experimental evidence for the second, less stable *trans*-conformer was obtained by MW spectroscopy.[12] The analysis of the rotation constants of the *trans*-conformer of ethenol and its isotopic analog (*trans*-CH_2=CHOD) permitted the geometric parameters of the *trans*-conformer of ethenol to be determined: r (Å) = 1.378 (C–O), 1.323 (C=O), 0.957 (O–H); ∠CCO = 122°, ∠OCH = 109.6°, ∠CHO = 108.6°. Measurements of the relative intensities in the spectrum gave the energy difference between the vibrational states of *cis*- and *trans*-ethenol equal to 1.08 kcal/mol.[12]

Theoretical investigations of the conformational properties of ethenol have been carried out in.[13-17] In one of the first *ab initio* calculations of ethenol and its sulfur analog, ethenethiol, using an *spd* basis set and partial optimization it has been found that both compounds exist as a mixture of two rotational isomers, the *cis*-conformer being the

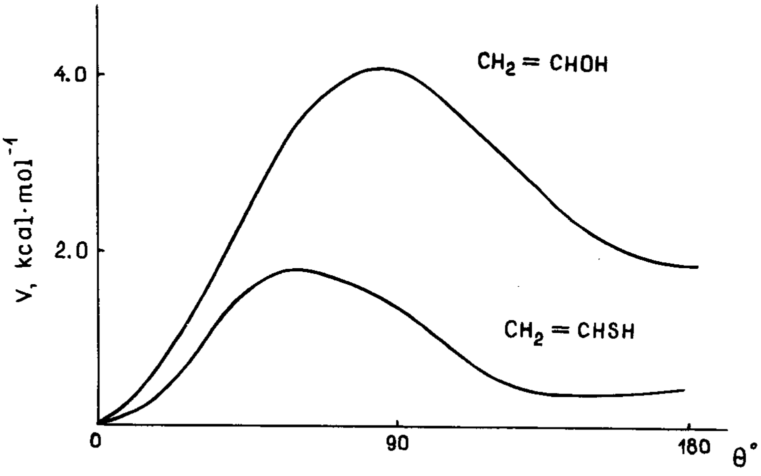


Figure 2 Calculated potential energy functions for internal rotation in ethenol and ethenethiol.[13]

most stable one.[13] For ethenol the energy maximum on the potential curve of internal rotation occurs at 90° whereas for ethenethiol it lies at 60°, the rotation barrier being for the former two times as high as for the latter (4.2 and 1.9 kcal/mol, respectively)[13] (Fig. 2). The second stable conformer of ethenethiol is *gauche* with a torsional angle of about 150° and a very low barrier *gauche* $\rightleftarrows$ *trans* ($\sim$0.07 kcal/mol), whereas *trans*-ethenol corresponds to a gently sloping portion of the curve with an energy maximum of 1.9 kcal/mol.[13] The difference in the rotational barrier values for these compounds indicates the difference in the π-population of the C–S and C–O bonds. In fact, *spd* calculations of the *cis*-form show a decrease in the π-population in going from C–O to C–S bonds (0.04 and 0.005, respectively).[13]

Ab initio calculations with geometry optimization of the ethenol molecule using Gaussian minimal (STO-3G) and split-valence (4-31G) basis sets have been carried out.[14,15] The optimized geometric parameters for two planar conformers, *cis* and *trans*, are given. The calculations with both basis sets lead to a conclusion of greater stability of *cis*-ethenol which is in agreement with the geometric parameters obtained from the MW spectra.[3,4] The calculated energy difference between the conformers has been found to be 2.24 (STO-3G) and 2.15 kcal/mol (4-31G),[15] consistent with the 1.9 kcal/mol[13] obtained by *ab initio* calculations with partial geometry optimization. The geometric parameters of *cis*-ethenol are predicted in[15] using a method allowing the correction of the experimental geometries of the molecules H_2O, CH_3OH, and $H_2C{=}CHX$ (X = H, CN, F, OCH_3) with those calculated using the STO-3G and 4-31G basis sets.

As seen from Fig. 3, the predicted CCO angle is the same as the value derived from the MW study whereas the C–O bond length (1.364 Å) is shorter (1.373 Å[3] and 1.372 Å[4]).

The *ab initio* method was used to calculate the potential functions of the internal rotation about the C_{sp^2}–O bond for ethenol[16] and a series of substituted ethenols XCH=CHOH (X = CN, H, F), with the substituent X located *trans* to the OH group.[17] Full optimization for two ethenol conformations was carried out using the molecular mechanics procedure as well as the 3-21G and 6-31G** basis sets with allowance for correlation energy in terms of the perturbation theory.[16] The molecular mechanics procedure turned out to be insensitive to variations in the HCCO dihedral angles and

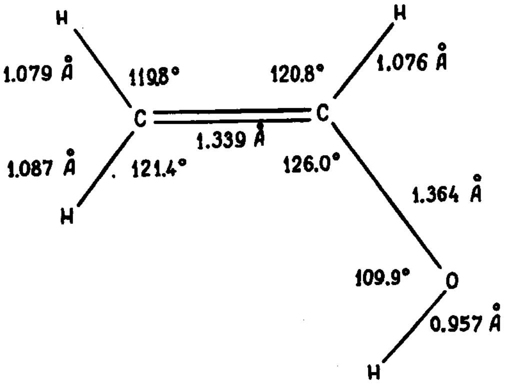


Figure 3 Predicted structure for *cis*-ethenol.[15]

the C–O bond length.[16] In this work the most stable conformer was found to be the *cis*-isomer whereas a less stable one is the planar trans-structure (θ = 180°) with an energy 1.7–1.9 kcal/mol higher than that of the *cis*-form. Also, the calculation was carried out using a 4-21G basis set.[17] For each torsional angle the optimization of all other parameters was undertaken. The internal rotation of the ethenol molecule is accompanied by changes in the CCO angle and the C–O bond length: θ = 0°, full

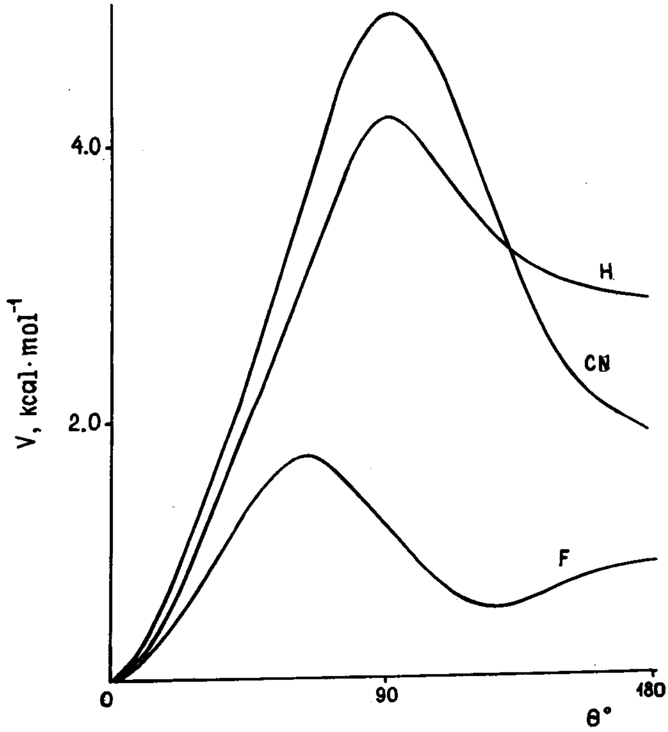


Figure 4 Potential functions for internal rotation in the ethenols scaled to the same zero as the *cis*-conformer.[17]

energy E = -152.54241 a.u., $\angle$CCO = 126.7°, r (C–O) = 1.387 Å; $\theta = 180°$, E = -152.53792 a.u., $\angle$CCO = 121.4°, r (C–O) = 1.396 Å, where θ is the torsional angle between the HCCH and COH planes. An analogous picture is observed for substituted ethenols, XCH=CHOH, where X = CN and F.[17] The potential curve of internal rotation in the molecules XCH=CHOH (X = H, CN, F) is influenced much by the nature of the substituent (Fig. 4).[17] The energy difference between the *cis*- and *trans*-conformers of ethenol is 2.81 kcal/mol.[17] The barrier separating these conformers is 4.14 kcal/mol[17] which is comparable with 4.2 kcal/mol[13] and 4.3 kcal/mol.[16]

II.2. Ethenethiol

A study of the IR and MW spectra of ethenethiol[18–21] shows this compound to exist as a mixture of two conformers, *cis* and *trans*. The *cis*-conformer is the most stable one. The IR spectrum of ethenethiol in the gas phase displays an intense band at 1603 cm^{-1}, corresponding to the C=C stretching mode and a number of other vibrational-rotational bands.[18] An analysis of the bands of non-planar deformational vibrations of the CH_2= group at 957 and 872 cm^{-1} showed the distance between the Q branch components to be 2.94 ± 0.05 cm^{-1}. A comparison with calculated data for two possible planar conformations of ethenethiol (2.89 cm^{-1} for *s-cis* and 3.14 cm^{-1} for *s-trans*) showed that the distance between the branch components was consistent with the planar *cis*-form.[18] Later these authors have carried out a more detailed analysis of the IR spectrum of ethenethiol in the gas phase, the crystalline state at 30 K and in Ar and N_2 matrixes.[19] Vibration assignments have been done based on an analysis of the IR band contours in the gas phase and by analogy with other vinyl derivatives. The band at 2599 cm^{-1} has been assigned to the S–H bond stretching mode in the gas phase. In an Ar matrix this band is split into two components at 2564 and 2548 cm^{-1}. At room temperature ethenethiol exists as two conformers, *cis* and *trans*, the *cis*-form being predominant. An intense band at 1602 cm^{-1} assigned to the C=C stretching mode is not split, neither in the gas phase, nor in the matrix or in the crystalline state. A calculation of frequencies and normal vibrations for the *cis*- and *trans*-forms has been carried out which shows the greatest band splitting for the C–S stretching, C=C–H deformational, and torsional modes.[19]

MW spectra in the gas phase of the *cis*-conformer of ethenethiol in the ground and three excited states and of its isotopic species (CH_2=CHSD) in the ground state have been obtained.[20] Rotational constants consistent with a planar structure of ethenethiol have been derived for these molecules (Fig. 5).

The C–S bond length of 1.776 Å calculated for ethenethiol is slightly longer than that of methyl vinyl sulfide (1.747 Å) determined in the gas phase by electron diffraction[13] and considerably shorter than in alkanethiols (1.80 Å).[21] The CCS angle in ethenethiol is the same (127°) as in methyl vinyl sulfide.[13] In the same work[20] the dipole moment components $\mu_a = 0.813$ D, $\mu_b = 0.376$ D and the full dipole moment $\mu = 0.896$ D have been measured for the *cis*-structure of ethenethiol.

In the MW spectrum of the *cis*-conformer of ethenethiol weak lines corresponding to transitions of the first and second excited states of the SH torsional vibration and the first excited state of the CCS bending mode are observed.[20] From measurements of the relative intensities of these lines the energy differences of the first two excited torsional

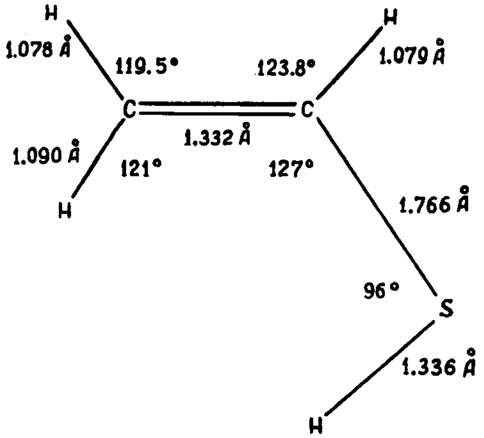


Figure 5 Structure of *cis*-ethenethiol.[20]

(SH) states at 155 and 334 cm^{-1} and the third excited state (CCS) at 346 cm^{-1} with respect to the ground state have been obtained.[20]

Using MW spectroscopy the *trans*-conformer of ethenethiol and its SD-isotopic species have been investigated.[22] The rotational constants for these molecules are found

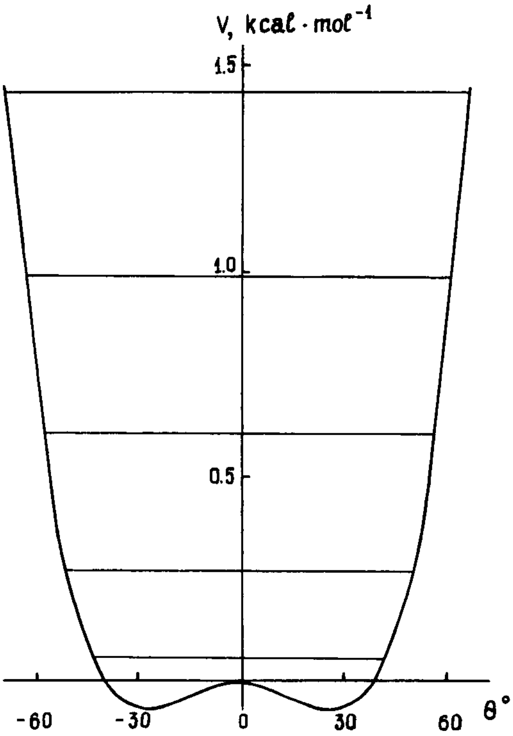


Figure 6 Potential function for the SH torsional vibration in the vicinity of the *trans*-conformation of ethenethiol.[22]

to be consistent with the following structural parameters: ∠CCS = 122°, ∠CSH = 98°. For the ground state of the *trans*-conformer of ethenethiol the dipole moment components $\mu_a = 0.425\,D$, $\mu_b = 1.033\,D$, and the full dipole moment $\mu = 1.117\,D$ have been determined.[22] These authors have derived a potential function for the SH torsional mode in the vicinity of the *trans* conformer (Fig. 6).[22] The potential function for the internal rotation can be calculated for a narrow range of angles and approximated by an equation $V(q) = -V_2q^2 + V_4q^4$. A small barrier height of $19\,cm^{-1}$ separating the two minima occurs at 26° relative to 0° for the planar conformation. The ground vibrational state of the *trans*-conformer lies above this barrier.[22]

MW spectroscopic data have been analysed[23] to give a potential function $V(\alpha) = \Sigma V_n/2\cdot[1\text{-}\cos n\alpha]$ for the torsional mode about the C–S bond in ethenethiol. In order to refine the molecular geometry the MW spectra of monodeutero- and dideuteroethenethiols have been measured.

The dipole moments for the *cis*- and *trans*-forms of ethenethiols have been calculated. There are considerable changes in μ_a and μ_b in both the ground and excited states in going from the *cis*- to the *trans*-conformer of ethenethiol.[23] Measurements of the relative band intensities have allowed the energy difference between the torsion states of ethenethiols to be determined (Table 1). The energy difference between the conformers is $50\,cm^{-1}$.

For the construction of the potential function of the internal rotation for ethenethiol an improved structure not identical with that obtained from MW spectra, but more consistent with the rotational constants of the *cis*-conformers was used. The potential function of the internal rotation about the C–S bond in ethenethiol is presented in Fig. 7.[23] The *cis*-form is by approximately $50\,cm^{-1}$ more stable than the *trans*-form. The rotation barrier between the *cis*- and the *trans*-conformer is $800\,cm^{-1}$. During the rotation the CCS angle decreases from 126.9° to 122.6° whilst the C–S bond length increases from 1.761 to 1.777 Å. The two quasi-planar *trans*-conformations with torsional angles of about 156° (0.87π) and 204° (1.13π) are separated by a barrier of approximately $12\,cm^{-1}$. A comparison of the experimental and theoretical potential curves is rather difficult. The theoretical potential function of the internal rotation around the C_{sp^2}–S bond in ethenethiol is obtained[24] by *ab initio* calculation using the 4-21G basis set for the first-row atoms and the 3-3-21G basis set for the sulfur atom, supplemented with

Table 1. Observed and calculated energy differences (cm^{-1}) between the SH torsional levels of ethenethiol[23]

Δv	ΔE	
	obs.	calc.
cis		
1–0	155 ± 20	158
2–0	179 ± 20	184
trans		
1–0	74 ± 30	76
2–1	112 ± 20	115
3–2	114 ± 20	115
	50 ± 25	49

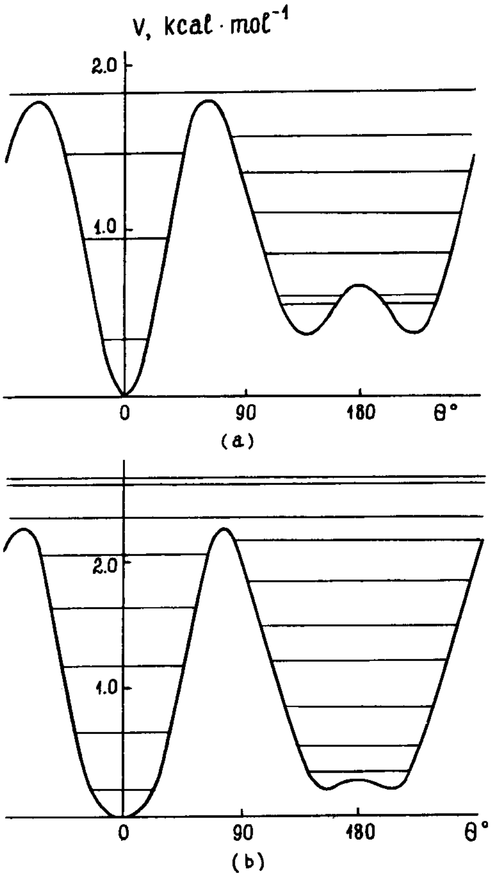


Figure 7 Calculated (a) and experimental (b) potential functions for internal rotation about the C_{sp^2}-S bond in ethenethiol.[24]

polarization functions.[24] The geometry parameters were optimized at every value of the torsional angle. The theoretical potential curve also gives two stable rotamers, the planar *cis*-form and the non-planar *gauche*-form, energetically less preferable by 120 cm^{-1} (Fig. 7).[24] The height of the barrier between the *cis*- and the *gauche*-form is 610 cm^{-1} and that for the *trans*-conformation is 105 cm^{-1}. The barrier computed[24] for the *cis*-conformer is 190 cm^{-1} lower whereas that for the *trans*-conformer is 95 cm^{-1} higher as compared to the experimental value.

The potential function of the internal rotation about the C_{sp^2}–S bond depends much on the nature of the substituent in compounds of the type XCH=CHSH (X = CN, H, CH_3, F) with X located *trans* to the sulfur atom (Fig. 8).[24] As the electron-withdrawing character of the substituent increases a reduction in the population of *cis*-conformer occurs, and with X = F, only the *gauche*-conformer remains. The internal rotation in these molecules is shown to be accompanied by a decrease of the CCS angle and the C–S bond length, whereas the CSH angle and the S–H bond length are practically constant.[24]

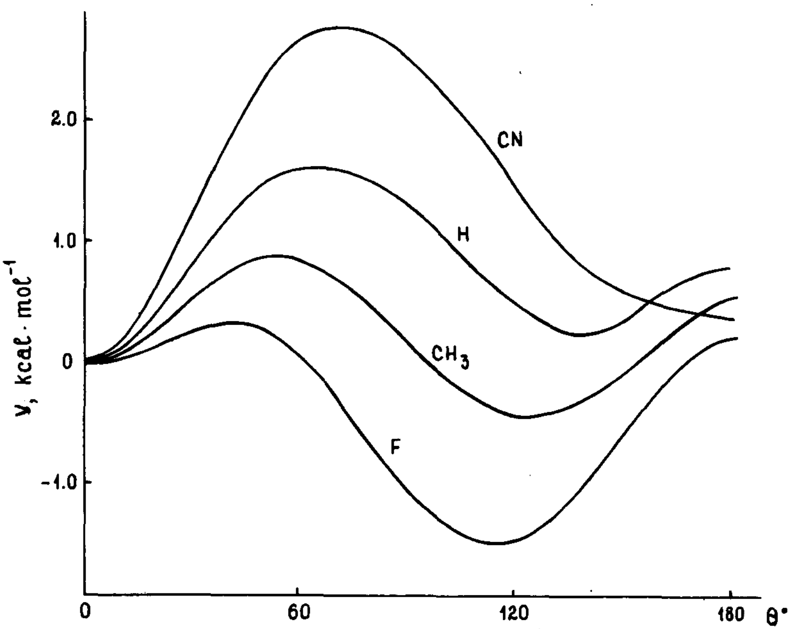


Figure 8 Potential functions for internal rotation in ethenethiols scaled to the same zero as the *cis*-conformation.[24]

In[25,26] a comparison is made of the potential curves of the internal rotation for ethenethiol obtained by *ab initio* (STO-3G, 3-21G, 44-31G, *spd*) methods and molecular mechanics. The molecular geometry is fully optimized with the exception of the C–H bond lengths taken as standards. In all the basis sets the *cis*-conformation of ethenethiol is found to be the most stable. A second, less stable conformation obtained with the minimal STO-3G basis set is planar *trans* (θ = 180°).[25,26] By 44-31G, 3-31G and *spd* basis sets the second, less stable form is represented as *gauche*-conformer, the minimum on the potential curve corresponding to a torsional angle of 120–135°. The energy maximum for this form on the potential curve is very low, therefore large amplitude vibrations are quite possible. The barrier to internal rotation in ethenethiol is 1.4 kcal/mol by 44-31G[25] and 1.9 kcal/mol by *spd*[13] as opposed to over 4 kcal/mol[25] by minimum STO-3G basis set which seems to be slightly overestimated and, therefore, in the latter case the prediction of the second, less stable conformation is incorrect. The calculation of ethenethiol by molecular mechanics gave a potential curve similar to that obtained by *ab initio* calculations, however, the rotational barrier is now 0.9 kcal/mol which is somewhat too low, the energy difference between the *cis*- and *gauche*-form being 0.6 kcal/mol.

III. ALKYL VINYL ETHERS AND SULFIDES

The investigation of rotational isomerism in vinyl ethers and sulfides is of considerable interest. The existence of rotational isomerism in vinyl ethers has been first established by Raman and IR spectra[27–33] and later confirmed by ultrasonic relaxation and MW spectral studies.[35] From the very beginning there were different opinions concerning the number and structure of stable conformations. From the temperature dependence of the optical densities of triplet components in the double bond stretching region the conclusion[31] has been drawn that the most stable of the two conformations is represented by two bands (1613 and 1650 cm^{-1}) whereas to the less stable a single peak at 1650 cm^{-1} is assigned. The appearance of a third, higher-frequency band in the vibrational spectra of alkyl vinyl ethers in the region 1600–1650 cm^{-1} is explained also by Fermi resonance between the $\nu_{C=C}$ and $\omega_{CH_2=}$ vibrations.[36] Temperature-induced changes in the integral intensity of the same triplet components in the Raman spectrum of butyl vinyl ether have allowed each of these components to be assigned to individual rotamers and their energy difference to be calculated.[32] On the assumption of the existence of three possible conformations (two planar, *cis* and *trans*, and one non-planar) the frequencies and normal vibration modes for methyl vinyl ether have been calculated, in good agreement with the experiment.[33] At the same time, the relaxation behaviour of methyl, ethyl, and 2-chloroethyl vinyl ethers indicates the existence of an equilibrium between the planar (*cis* and *trans*) conformations.[34] The vibrational spectra of methyl vinyl ether and its deutero derivatives have been studied and frequency assignments, on the basis of symmetry and mode of vibrations, suggested.[37] At room temperature this molecule exists presumably as a planar *cis*-form. At lower temperature, as the main bands in the spectrum become narrower, one can observe a number of new bands assigned to vibrations of another isomer exhibiting a planar *trans*- or very similar structure. From the analysis of the Raman and IR spectra of methyl vinyl ether[38–40] it follows that the second less stable rotamer is the *s-trans* conformation. The same is implied by photoelectron spectra of alkyl vinyl ethers.[41]

Owen and Sheppard,[36,42,43] analysing the rotational structure of the out-of-plane =CH$_2$ wagging mode (820 cm^{-1}) have found the most stable conformation of methyl and ethyl vinyl ether to have a planar sickle-shaped (*cis*) form. The other conformation should be, in their opinion, non-planar.[36,42] The conclusions[36,42,43] were further and independently supported by analysis of the MW spectrum of methyl vinyl ether[35] and its Raman and IR spectra.[44] Investigation of the vibrational spectra of gaseous methyl vinyl ether[44] allowed the energetically less prefered rotamer to be identified as '*skew*' with a torsional angle of 144°. The ratio of vinyl ether conformers may be judged by their IR spectra.

On the basis of the above experimental data the main characteristic bands of the vinyloxy group can be assigned to certain conformations.

The following main bands are assigned to the planar conformer: low-frequency component of the band at approximately 820 cm^{-1} ($\omega_{CH_2=}$, CH$_2$= out-of-plane wagging mode);[36,42,45,46] high-frequency component of the band at ~960 cm^{-1} ($\omega_{CH=}$, CH= out-of-plane wagging mode);[36,42,46] very strong broad band near 1200 cm^{-1} ($\nu_{C\text{–}O}$, C–O stretching mode);[31,36,42] narrow peak of medium intensity at 1320 cm^{-1} ($\delta_{CH=}$, CH= planar wagging mode);[36,42] low-frequency component of the triplet in the 1600 cm^{-1} region, usually at approximately 1620 cm^{-1} ($\nu_{C=C}$, C=C stretch).[31,32,36,42]

Non-planar conformer absorption: high-frequency shoulder of the band 820 cm^{-1};[36,42,45,46] low-frequency component of the $\omega_{CH=}$ doublet, usually at 950 cm^{-1};[46] weak bands in the 1150–1050 cm^{-1} region ($\nu_{C\text{–}O}$), 1138 cm^{-1} in methyl vinyl ether, for example,[36] 1143, 1100, 1081, 1048 cm^{-1} in ethyl vinyl ether;[42] center compoment of the $\nu_{C=C}$ triplet, normally at 1640 cm^{-1}.[31,32,36,42]

In[47,48] it was intended to trace, using the IR spectra of substituted vinyl ethers, in which way the substituent structure affects the relative intensity of bands of different conformations, without going into details of their molecular structure. A comparative analysis of the IR spectra of alkyl vinyl ethers (Table 2) shows the conformation ratio to depend much on the branching at the C_α-atom of the substituent R.[47] Thus, if in methyl vinyl and in vinyl ethers with unbranched substituents a planar conformer is dominating, judging by their IR spectra, then the relative intensity of its bands sharply drops and some of them even disappear with increasing R branching; at the same time the absorption bands of the non-planar conformer appear and grow stronger. *t*-Butyl and *t*-amyl vinyl ether exist mainly as one non-planar conformation. In fact, all the bands of the planar conformer in the spectra of these ethers almost or completely disappear. This is especially well expressed in the 1600 cm^{-1} region where instead of a very strong

Table 2. Fundamental frequencies* of the $CH_2{=}CHO$ group in the IR spectra of ethers $CH_2{=}CHOR$ with donor substituents R (Taft's $\sigma^* < 0$)[47]

R	Vibrational freqencies, cm^{-1}					
	$\omega_{CH_2=}$	$\omega_{CH=}$	$\nu_{C\text{-}O}$	$\delta_{CH=}$	$\delta_{CH_2=}$	$\nu_{C=C}$
CH_3	822 s	967 s	1210 s	1321 s	1391 w	1620 s 1653 m
C_2H_5	815 s	966 s	1117 m 1160 v w			
	850 w sh		1203 v w	1320 m	1390 w	1620 v s 1640 w sh
C_3H_7-*i*	821 s	950 m	1121 v w 1180 s 1202 v w	1317 s	1385 m	1626 w sh 1636 w sh
C_4H_9-*n*	820 v s	950 w sh 970 s	1130 m 1180 s 1200 s	1325 s	1380 s	1615 s 1640 m sh
C_4H_9-*i*	810 m 824 sh	943 sh 960 m 920 m 970 s	1140 m 1210 s	1305 w sh 1325 s	1390 m	1615 s 1640 m sh
C_4H_9-*t*	828 m 848 m	948 m	1161 vs 1197 w	1310 w	1395 m	1633 vs
C_5H_{11}-*t*	827 s		1160 vs			1630 vs
		945 s		1312 m sh	1385 m	
	840 m sh		1197 w			1650 m sh
Cyclohexyl	810 m sh	950 m	1130 s	1320 w		
	825 s		1158 s 1178 s 1190 m sh 1205 s		1380 s	1618 m sh 1635 vs
Decalyl	–	–	–	–	–	1636**

*C–H Stretching vibrations are not shown; s — strong, m — medium, w — weak, vs — very strong, vw — very weak, sh — shoulder, w sh — weak shoulder, m sh — medium shoulder.

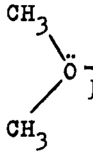
**Raman data.[49]

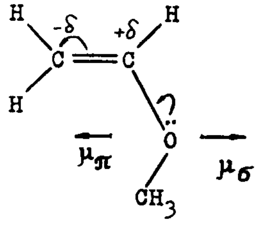
multiplet only its high-frequency component corresponding to the non-planar conformation is present.

The molecular structure of methy vinyl ether was also studied by electron diffraction.[13,50] In addition to the determination of the molecular geometry of the principal rotamer, the authors attempted to solve the problem of the conformation of the less energetically preferred form. In earlier work[50] preference was given to the *trans*-conformer in which a distortion of the coplanarity is allowed and the angle between the C=C–O and C–O–C planes is within 80–110°. Later on, under the influence of *ab initio* calculations implying a planar *s-trans* structure of the less stable conformer the authors reconsidered their experimental data and found them not to be in disagreement with the suggested planar structure of the second rotamer of methyl vinyl ether.[13]

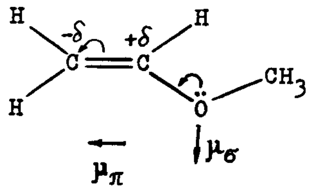
Essential data concerning the molecular and electronic structures of alkyl vinyl ethers have been obtained by studying their dipole moments. It is well known that the dielectric properties of most organic molecules are practically insensitive to electron transfers caused by mutual effects of intramolecular moieties. For alkyl vinyl ethers, $CH_2{=}CHOR$, however, an unprecedently strong dependence of the dipole moments on the structure of the alkyl group R[51] and the temperature[52] have been established. The reason for these peculiarities is a close relationship between p,π-conjugation and conformational isomerism.

A simple consideration of the dipole moment vector in dimethyl ether leads to the conclusion of dependence of the dipole moment on the internal rotation angle provided that the p,π-interaction involves polarization of the double bond:





s-cis



s-trans

This polarization is evident from the dipole moments of compounds $CH_2{=}CHOR$ with normal and branched alkyl substituents R (Table 3).[53] For comparison the dipole moments of some saturated ethers are also presented in Table 3.

In the *s-cis* conformer of methyl vinyl ether the π- and σ-components are opposite in direction. Therefore it is quite reasonable, in this case, to approximate the π-component by the difference (0.36 D) between the moment of dimethyl ether and the experimental moment for methyl vinyl ether (as in[56]). It is also necessary to bear in mind that the π-moment thus found includes the induced π-moment and the contribution from the difference of the moments of the C_{sp^2}–O and the C_{sp^3}–O bond. However, evaluation[56] of the dipole moments of other conformations by summing the π- and σ-vectors is basically unsound, since no variations in the degree of p,π-conjugation (and, hence, in the π-component) due to distortion of coplanarity are considered. In a non-planar (*gauche*) conformation with the angle between the C=C–O and the R–O–C plane equal 90° the π-component should be absent or, at least, much smaller than that in the planar

Table 3. Dipole moments of ethers

Ether	μ, D
$CH_2{=}CHOCH_3$	1.00,[53] 1.10[54]
$CH_2{=}CHOC_2H_5$	1.19,[53] 1.19[54]
$CH_2{=}CHOC_3H_7$-*n*	1.19[53]
$CH_2{=}CHOC_3H_7$-*i*	1.47[53]
$CH_2{=}CHOC_4H_9$-*n*	1.20,[53] 1.25[54]
$CH_2{=}CHOC_4H_9$-*i*	1.14,[53] 1.20[54]
$CH_2{=}CHOC_4H_9$-*t*	1.81[53]
$CH_2{=}CHOC_5H_{11}$-*n*	1.22[53]
$CH_2{=}CHOC_5H_{11}$-*t*	1.84[53]
$CH_2{=}CHOC_6H_{11}$-*cyclo*	1.64[53]
$CH_2{=}CHOC_6H_5$	1.41,[53] 1.10[55]
$CH_2{=}CHOCH{=}CH_2$	1.10,[53] 1.06[54]
$CH_2{=}CHO(CH_2)_2Cl$	1.85[53]
$(CH_3)_2O$	1.25,[55] 1.31[54]
$(C_2H_5)_2O$	1.27, 1.38,[54] 1.16, 1.22[55]
$(C_3H_7$-*n*$)_2O$	1.13[54]
$(C_3H_7$-*i*$)_2O$	1.26[54]
$C_2H_5OC_4H_9$-*n*	1.22,[55] 1.22[54]
$C_2H_5OC_4H_9$-*t*	1.29[53]

conformation. Inspection of a molecular model shows the σ-moment vector in this conformation to form an angle of approximately 55° with the double bond plane, the direction of its projection and that of the C_{sp^2}–O bond being coincident. For this model, in the presence of a π-component directed from the oxygen atom towards the terminal vinylic carbon the observed dipole moment will always be lower than the σ-vector (1.3 D) and equal to that in the absence of a π-component.

The significant difference in the dipole moments of alkyl vinyl ether conformers could be explained by the electronegativity of the substituent R as well.[57] This suggestion is supported by a close linear dependence of the dipole moment on the inductive (σ^*) or steric (E_s°) constants of substituent R. The choice between the inductive and conformational nature of the differences in the dipole moments of alkyl vinyl ethers was made in favor of the latter hypothesis on the basis of the temperature dependence of the dipole moments (Table 4).[52]

The data of Table 4 reveal a difference in the dielectric behaviour of alkyl vinyl ethers with normal substituents from that of those with bulky branching substituents. In the former the dipole moment noticeably increases with the temperature whereas in the latter it decreases. For methyl vinyl ether the dipole moments measured over a wide temperature range are in good agreement with the idea of two rotamer forms being in equilibrium in octane and benzene solutions[52,58]

$$\mu_{\text{eff}}^2 = \mu_1^2 p_1 + \mu_2^2 p_2 \qquad (1)$$

where μ_{eff} is the dipole moment measured, μ_1 and μ_2 are the dipole moments of the stable rotamers, p_1 and p_2 represent their mole fractions defined by the equation

$$p_2/p_1 = g\cdot e - (\Delta E/RT)\cdot(p_1 + p_2) \qquad (2)$$

where ΔE is the energy difference between rotamers, g stands for the statistic factor taken to be equal to 2 on the assumption that the less stable rotamer is non-planar.

Table 4*. Temperature dependence of the dipole moments (D) of alkyl vinyl ethers (in octane)[52]

T, K	$CH_2{=}CHOAlk$				
	CH_3	C_2H_5	C_3H_7-*i*	C_4H_9-*t*	C_5H_{11}-*t*
223	0.93	1.08	1.56	1.91	1.95
233	0.94	1.11	1.55	1.90	1.94
243	0.96	1.13	1.54	1.90	1.93
253	0.98	1.15	1.53	1.89	1.91
263	1.00	1.15	1.52	1.88	1.89
273	1.04	1.16	1.50	1.87	1.87
283	1.05	1.17	1.49	1.86	1.86
293	1.07	1.18	1.48	1.82	1.85
303	1.10	1.19	1.46	1.82	1.84
313	1.11	1.20	1.44	1.81	1.82
323	1.12	1.24	1.42	1.80	1.79

*Condensed.

Thus, the following characteristics of the stable conformers of methyl vinyl ether were obtained:[52] $\Delta E = 1.55 \pm 0.01$ kcal/mol, $\mu_1 = 2.27 \pm 0.01$ D, $\mu_2 = 0.76 \pm 0.01$ D. An analogous interpretation of the temperature dependence of the dipole moment for *t*-butyl vinyl ether encounters considerable difficulties since the formally calculated μ_2 value of the less stable rotamer becomes negative in this case. The study of the dielectric properties of alkyl vinyl ethers thus clearly shows the inconsistency of the concept of their molecules, at least with $R = C_4H_9$-*t*, to exist as sufficiently rigid conformations which differ by a fixed torsional angle. The authors have concluded[52] that the decrease in the dipole moment with increasing temperature for $CH_2{=}CHOR$ with $R = C_3H_7$-*i*, C_4H_9-*t*, C_5H_{11}-*t* is caused not by the increase in population of the less polar form, but by coplanarity distortion of the molecular moiety $CH_2{=}CH{-}O{-}C$ upon torsional vibration. It is evident that the growing population of the excited torsional states may markedly affect the measured dipole moment only if the torsional motion is of rather large amplitude. The authors[52] have suggested a W-shaped potential curve of internal rotation which gives a qualitative explanation for the dielectric behaviour of all the alkyl vinyl ethers studied.

In one of the first *ab initio* calculations the potential curve of the internal rotation about the $C_{sp^2}{-}O$ bond in methyl vinyl ether was obtained.[59] The minima on the potential curve occur at $\theta = 0°$ (*s-cis* form) and $\theta = 180°$ (*s-trans* form). The calculated energy difference between the two conformers is 2.2 kcal/mol.[59] The barrier to internal rotation about the $C_{sp^2}{-}O$ bond of methyl vinyl ether is within the range of 5.7–6.6 kcal/mol.[59] In[60,61] the calculation of the potential function of the internal rotation of methyl vinyl ether was performed using the STO-3G and 4-31G basis sets. The potential curve obtained in[61] is shown in Fig. 9. The geometry optimization was carried out with the STO-3G basis sets. According to these calculations for methyl vinyl ether two stable conformations are predicted: planar *cis* ($\theta = 0°$) and planar *trans* ($\theta = 180°$). The calculated energy difference between the two conformers is satisfactorily consistent with the experimental values (1.15 kcal/mol):[13] 0.96, 1 kcal/mol (STO-3G),[60,61] 2.47, 2.3 kcal/mol (4-331G).[60,61] The barrier to internal rotation in methyl vinyl ether is 4.5 kcal/mol

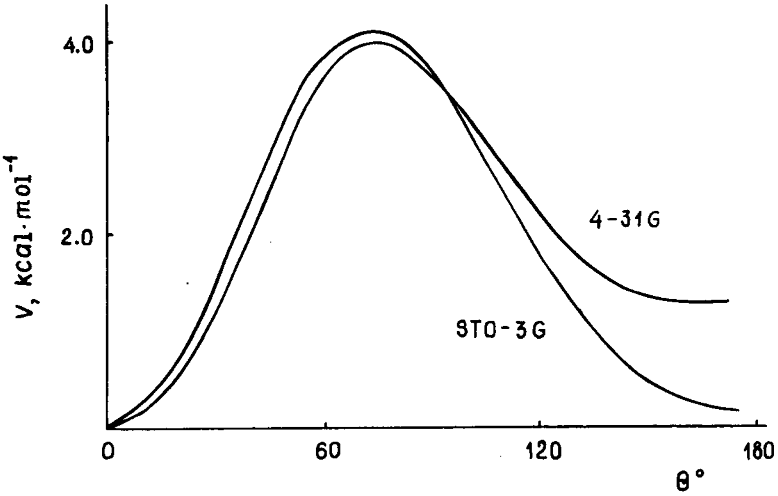


Figure 9 Potential functions (ab initio) for internal rotation about the C_{sp^2}-O bond in methyl vinyl ether.[61]

(STO-3G and 4-31G) at the torsional angle 74°.[61] An *ab initio* calculation of methyl vinyl ether using the 4-21G and full geometry optimization has provided detailed information concerning the structures of three conformers: an *s-cis* ($\theta = 0°$), an *s-trans* ($\theta = 180°$) and a *skew* conformer ($\theta = 168°$).[62] The population of the *skew* conformer is established to be 1–5%. The energy difference between the *s-cis* and the *s-trans* conformer is 2.97 kcal/mol.[62] However, other *ab initio* treatments of methyl vinyl ether predict stable states corresponding to torsional angles 0° (*s-cis*) and 150° (*gauche*), the former being 1.9–2.1 kcal/mol more stable.[16]

So, most work concerning rotational isomerism of vinyl ethers provides evidence for the existence of planar (*cis*) and non-planar (*gauche*) conformations. However, the question of the structure of the second, less stable conformer is still far from solved.

The molecular structure of methyl vinyl sulfide, the sulfur analog of methyl vinyl ether, has been studied by numerous methods.[13,63–67] According to the MW spectra,[63] methyl vinyl sulfide exists as a planar *cis* conformer: r (Å) = 1.33 (C=C), 1.77 (C_{sp^2}–S), 1.81 (C_{sp^3}–S), 1.07 (C–H); $\angle$CCS = 121°, $\angle C_{sp^2}SC_{sp^3}$ = 107°, $\angle SC_{sp^2}H$ = 119°, $\angle SC_{sp^3}H$ = 109.5°. According to gas electron diffraction methyl vinyl sulfide exists in two different conformations, energetically prefered planar *cis* and non-planar *gauche* with a dihedral rotational angle about the C_{sp^2}–S bond of 116–123°.[64–66] The most probable energy difference between the *cis* and the *gauche* conformer is found as 1.0–2.0 kcal/ mol.[66] This is well consistent with the number and position of fundamentals in the Raman and IR spectra of methyl vinyl sulfide.[66,67] The enthalpy difference of the conformers in the gas phase determined from the intensity ratio of the IR absorption bands at 680 and 705 cm^{-1} is 1.4 kcal/mol.[67] At the same time, analysis of the relative intensities of the rotational bands corresponding to different conformers in the MW spectrum of methyl vinyl sulfide reveals a quite small energy difference.[66] A detailed study of the vibrations of methyl vinyl sulfide and its deutero derivatives on the basis of IR and Raman spectra and mechanical model calculations has been carried out in.[69] Of

Table 5. Vinylthio group fundamentals* in the IR spectra of vinyl sulfides, $CH_2=CHSR$ (cm^{-1})[69]

R	$\nu_{=CH_2}$	$\nu_{C=C}$	$\delta_{=CH_2}$	$\delta_{=CH}$	ϱ_{CH_2}	τ_{CH_2}	ω_{CH_2}	ν_{CSC}	$\delta_{=CH_2}$
CH_3	3093 w 3033 w sh 3010 w	1584 s 1574 s sh	1388 m	1276 w	1036 s	960 s	885 s sh 860 s	742 m 735 m 699 w 678 s	596 m
C_2H_5	3092 w 3033 w sh 3010 w	1582 s 1574 s sh	1376 m	1260 m	1012 w	958 s	880 s sh 860 s	718 m 674 w 647 w	590 m
C_3H_7-*n*	3094 w 3020 w sh 3000 w	1584 s 1576 m sh	1376 m	1290 m 1275 m	1020 m	958 s	880 s sh 857 s	715 m 655 m	590 m
C_3H_7-*i*	3088 w 3020 w sh 3000 w	1584 s 1576 m sh	1366 m	1276 w	1022 m	958 s	880 s 860 s	726 m 707 m 648 w	592 s
C_4H_9-*n*	3105 w 3030 w sh 3000 w	1586 w 1574 m sh	1385 m	1275 m	1056 w 1024 s	964 s	880 s sh 860 s	744 m 716 m 696 w	595 s
C_4H_9-*s*	3097 w 3020 w sh 3002 w	1585 s	1388 m	1282 w	1061 w 1020 m	953 s	880 s sh 862 s	745 s 725 m 705 m 688 m	595 s
C_4H_9-*t*	3092 w 3028 w sh 3000 w	1587 s	1360 s	1270 w	1036 w 1017 w	959 s	890 s	728 s	590 m
C_5H_{11}-*t*	3088 w 3023 w	1585 s	1358 s 1368 s	1278 m	1056 m 1025 m	958 s	884 s	729 s	598 m 577 m
C_6H_{11}-*cyclo*	3105 3030 w sh 3003 w	1585 s	1382 m	1270 m	1025 m	963 s	888 s 865 s sh	742 m 722 m 694 m	594 m
$CH=CH_2$	3092 w 3025 w 3005	1592 s 1580 s 1560 m sh	1388 m 1380 s	1276 m 1268 m sh 1260 s	1038 m 1014 m	965 m sh 954 s	903 m sh 880 s	735 s 728 s 684 m	612 m 590 m 574 w
C_6H_5	3078 m 3063 m 3027 w 3008	1585 s	1382 m	1275 m	1069 m 1024 s	962 s	900 m 882 m	746 s 720 w 695 s 620 w	596 s

*C–H stretching vibrations are not shown since they do not depend much on the structure. The assignments are according to.[66]

interest is the comparison of the vibrational spectra of methyl vinyl sulfide and methyl vinyl ether. In the authors' opinion, the main differences in the vibrational spectra of these molecules are due to a change in the CSC and COC geometrical parameters, the different masses of sulfur and oxygen and their different electronegativities.[68] Some criteria allowing the prediction of the ratio and the nature of the conformers in vinyl sulfides with different substituents have been found and the major causes and tendencies for the change in the conformation ratio in this series have been recognized.[69] For this purpose the IR spectra of vinyl sulfides have been studied (Table 5).[69] The C=C double bond stretching is a doublet with the absorption maxima in the region 1575–1585 cm^{-1}. The low-frequency component of this doublet is assigned to a more stable *cis*-conformer, the high-frequency component to a non-planar *gauche*.[70] With increasing alkyl group branching the intensity of the low-frequency component drops and that of the high-frequency component rises. Non-planar CH_2 wagging ($\omega_{CH_{2=}}$) and C–S stretching ($\nu_{C\text{–}S}$) are represented, as a rule, by several bands, the number and intensity of which vary depending on the structure of R. According to the data,[67] the band at ~ 860 cm^{-1} should be assigned to a planar *cis*-conformer and the higher-frequency band (~ 880 cm^{-1}) to a *gauche*-conformer.

Judging by,[71] the rotational isomers of dialkyl sulfides are especially well displayed in the C–S–C vibration region (600–750 cm^{-1}). In the case of alkyl vinyl sulfides individual bands in this region will be those arising from rotamers relative to both C–S bonds (C_{sp^3}–S–C_{sp^2}). The ω_{CH_2} region is quite suitable for identifying the rotamers with respect to the double bond. It has been noted[69] that the band at 678 cm^{-1} ($\nu_{C\text{–}S\text{–}C}$ region) dominating in the spectrum of methyl vinyl sulfide, noticeably loses its intensity in the spectra of *n*-alkyl vinyl sulfides and disappears in the spectra of *s*- and *t*-alkyl vinyl sulfides. The latter show in this region only one band at ~ 730 cm^{-1} assigned to the *gauche* rotamer vibrations.[69] Comparing the relative intensities of bands in the region 650–750 and 890–900 cm^{-1} one can see that with increasing the R branching the planar *cis*-form population rapidly diminishes. *t*-Alkyl vinyl sulfides at ~ 20 °C exist mainly in the *gauche* conformation.

The investigation of the dipole moments of alkyl vinyl sulfides has shown their complete analogy to alkyl vinyl ethers. In the series CH_2=CHSR (R = CH_3, C_2H_5, C_3H_7-*i*, C_4H_9-*t*) a considerable increase of the dipole moment with the alkyl substituent branching is observed (Table 6).[72] However, the difference in the dipole moments of *t*-butyl vinyl sulfide and methyl vinyl sulfide at 25 °C is as small as 0.35 D which is less than half as much as the analogous difference for *t*-butyl vinyl ether and methyl vinyl ether (0.74 D). The deviation of the dipole moment of methyl vinyl sulfide from that of its saturated analog, methyl ethyl sulfide (μ = 1.60 D), towards lower values points to a CH_2=CH–O– fragment polarization in the same direction as that in vinyl ethers, induced by p,π-interaction.

The correlation analysis of the dependence of the dipole moments of alkyl vinyl sulfides on the substituent constants indicates a close relationship between μ and the hyperconjugation constant Δn[72]

$$\mu = (1.95 \pm 0.08) - (0.21 \pm 0.04)\Delta n \qquad (3)$$

$$r = 0.98 \qquad s_o = 0.03$$

The same was obtained for alkyl vinyl ethers as well.[57] This dependence, as with alkyl vinyl ethers, seems to be of steric nature. If the steric effect in these series consists merely of inhibition of resonance, then the comparison of the regression coefficients (0.47 for

Table 6. Dipole moments of alkyl vinyl sulfides, CH_2=CHSR[72]

R	μ, D	R	μ, D
CH_3	1.35	C_4H_9-*i*	1.40
C_2H_5	1.47	C_4H_9-*s*	1.59
C_3H_7-*n*	1.44	C_4H_9-*t*	1.69
C_3H_7-*i*	1.58	C_5H_{11}-*t*	1.70
C_4H_9-*n*	1.41	C_6H_{11}-*cyclo*	1.60

Table 7. Temperature dependence of the dipole moments of alkyl vinyl sulfides (in octane)[52]

T, K	CH_2=CHSAlk			
	CH_3	C_2H_5	C_3H_7-i	C_4H_9-t
223	1.19	1.36	1.69	1.87
233	1.20	1.38	1.68	1.85
243	1.21	1.39	1.66	1.83
253	1.23	1.40	1.65	1.81
263	1.24	1.40	1.63	1.80
273	1.26	1.42	1.62	1.78
283	1.27	1.43	1.61	1.76
293	1.30	1.44	1.60	1.74
303	1.31	1.46	1.59	1.73
313	1.32	1.48	1.58	1.73
323	1.32	1.49	1.56	1.72

The data of the Table from[52] are given in condensed form.

ethers[57] and 0.21 for sulfides[72]) implies the π-component of the dipole moment in alkyl vinyl sulfides to be 0.45 of that in alkyl vinyl ethers.

The temperature dependence of the dipole moments of alkyl vinyl sulfides is analogous to that observed for alkyl vinyl ethers with the only difference that the dipole moments vary within a considerably narrower range (Table 7).[52] This does not permit quantitative treatment of the data of Table 7 on the assumption of the two rotamers being in equilibrium, even for methyl vinyl sulfide. The parameters obtained from this treatment for individual rotamers look quite unrealistic due to their uncertainty.[52] This difference between vinyl sulfides and vinyl ethers may be not only of purely quantitative, but of principal character related to the different shapes of the potential curves of internal rotation for the two compounds.

An investigation of the rotational isomerism of methyl vinyl sulfide was carried out by PE spectroscopy.[73] In the PE spectra recorded over the 20–600 °C temperature range the orbital ionization potentials were assigned on the basis of CNDO/2 calculated energies taking into account 3d-AO of the sulfur atom. The bands in the PE spectra corresponding to the *cis*- and the *trans*-isomer of methyl vinyl sulfide have been identified. The energy difference between the conformers obtained from the PE spectrum, $\Delta E = 2.3 \pm 0.2$ kcal/mol,[73] is in qualitative agreement with $\Delta E = 1.4$ kcal/mol obtained from IR spectra[67] and disagrees with the result of electron diffraction where $\Delta E \sim 0$.[13]

More research on the conformational transition energies of methyl vinyl sulfide is still needed. The potential curves of the internal rotation about the C_{sp^2}–S bond for methyl vinyl sulfide were obtained by *ab initio* calculations using the STO-3G, 44-31G,[25] 3-21G[26] basis sets (Fig. 10). There is also reported a rotational potential calculated for this molecule by molecular mechanics (Fig. 10). The energy values of methyl vinyl sulfide were determined for all torsional angles θ = 0, 30, 60, 90, 120, 150, 180°, the C_{sp^2}–S bond length and the corresponding valence angles being optimized in all the basis sets.

In all the basis sets the *cis*-conformation (0°) was found to be the most stable one. The next minimum on the potential curves of internal rotation is at 120° and corresponds to a *gauche*-conformation, whereas, when the minimal STO-3G basis set is used, a second

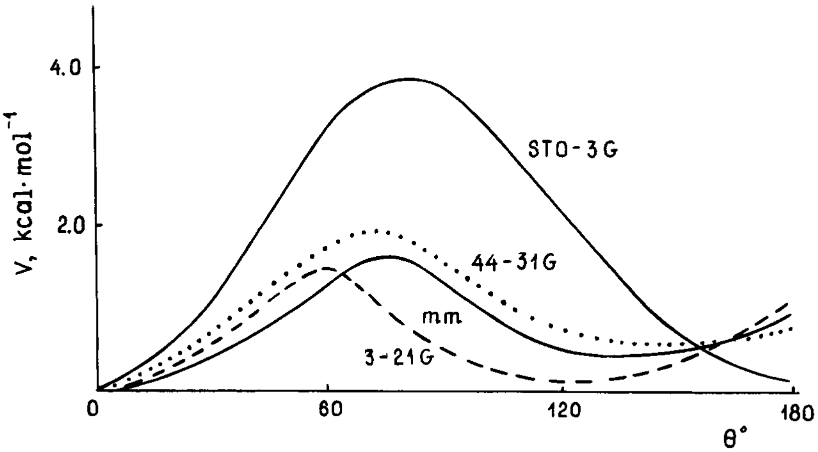


Figure 10 Calculated (ab initio) potential functions of internal rotation about the C_{sp^2}-S bond in methyl vinyl sulfide (mm = molecular mechanics).[26]

less stable conformation is found to be planar *trans* (θ = 180°).[25,26] The calculated energy difference between the conformers of 0.7 kcal/mol (44-31G),[25] 0.2 kcal/mol (3-21G)[26] is slightly lower than the experimental value. The potential curve of the internal rotation of methyl vinyl sulfide obtained by molecular mechanics is analogous to that calculated using the 44-31G and 3-21G basis sets, and the *cis*-conformer is by 0.4 kcal/mol more stable than the second non-planar (*gauche*). The energy maximum on the potential curve of internal rotation occurs at approximately 70° and the barrier to rotation in the 44-31G and 3-21G basis sets (1.4–2.1 kcal/mol) is $\frac{1}{2}$ to $\frac{1}{3}$ of that in the STO-31G basis set and close to the experimental data. The rotation of the methyl group in the *cis*- and the *trans*-conformation of methyl vinyl sulfide has also been discussed.[25,26] The rotational barrier for the *cis*-form (3.1 kcal/mol) is twice as large as that for the *gauche*.[25] The barriers to internal rotation in methyl vinyl sulfide calculated by molecular mechanics are ~2 kcal/mol for the *cis*-conformer and 3.3 and 1.7 kcal/mol for the methyl group in the *cis*- and the *trans*-conformation, respectively.[26] The rotational barrier for the methyl group in the *cis*-conformer is in agreement with the experimental value of 3.2 kcal/mol.[63]

Quantum chemical procedures including *ab initio* calculations applied to internal rotation of the molecule give ambiguous results, depending on many factors. Therefore, the potential energies of internal rotation obtained from experimental data on the structure and population of stable conformers are still of particular value.

A calculation of the main parameters of the potential of internal rotation in methyl vinyl sulfide, based on experimental values of enthalpy and entropy rotamerization has been carried out.[70] For the determination of the latter by temperature effects in the IR spectra it is necessary that the extinction ratio of the rotamers, $\varepsilon_2/\varepsilon_1$, is known since the replacement of the left-hand side of the equation $C_1/C_2 = \exp(-\Delta H/RT + \Delta S/RT)$ by I_1/I_2, introduces a considerable error into ΔS, whilst ΔH changes to a smaller extent only, owing to the temperature dependence of the ratio of the rotamer extinction (C_1 and C_2 are the mole fractions of the rotamers, I_1 and I_2 denote their band intensities in the IR spectrum). The stretching vibration of the double bond of vinyl sulfides is represented

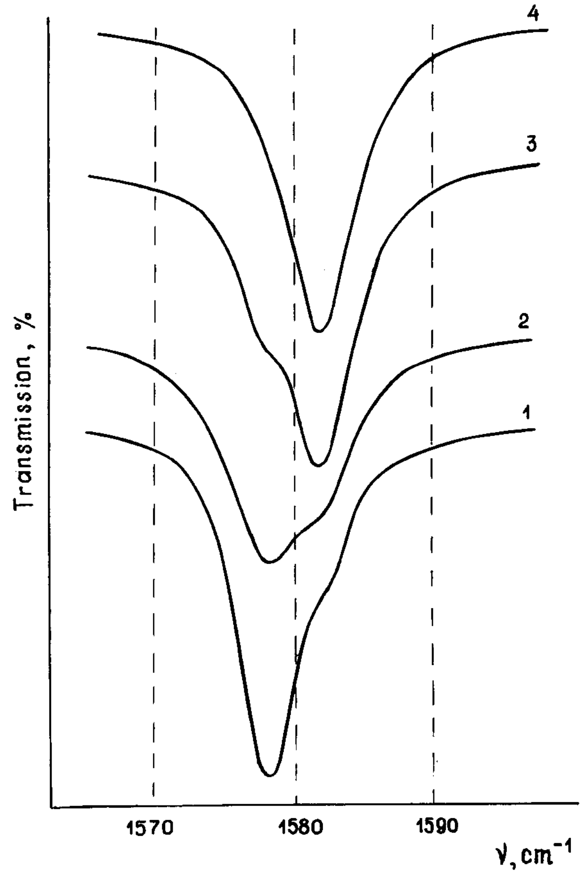


Figure 11 C=C Stretching mode in the IR spectra of compounds CH_2=CHSR, R = CH_3 (1), C_2H_5 (2), C_3H_7-*i* (3), C_4H_9-*t* (4) (in *n*-heptane).[70]

by a doublet (Fig. 11). The intensity of the higher-frequency component of this doublet increases with alkyl group branching as also observed in the IR spectra of vinyl ethers.[47] *t*-Butyl vinyl sulfide, like *t*-butyl vinyl ether,[47] displays no lower-frequency band. In the spectrum of methyl vinyl sulfide the relative intensity of the 1577 cm^{-1} band decreases with increasing temperature whereas that of the band at 1581 cm^{-1} increases. These regularities allow the doublet components to be assigned to individual conformations of the vinyl sulfides (in full agreement with the assignment[69] made previously by the analysis of doublet bands of alkyl vinyl sulfides occurring in the regions 650–750 and 850–900 cm^{-1}). As the double bond stretching intensity is mainly dependent upon the resonance effect of the substituent, the resonance constants of the alkyl substituent being nearly equal,[74] the double bond extinction in the *gauche*-conformation of methyl vinyl sulfide may be taken equal to that of *t*-butyl vinyl sulfide. Then the calculated extinctions for the *cis*- and the *gauche*-form of methyl vinyl sulfide, for 20° for example, are 482 and 356 cm^{-1} mol/degr., respectively.[70]

An analysis of the double bond band shape over a temperature range from −85 °C up to 60 °C has been performed by a special computer program. The experimental contours of the absorption bands in the region 1570–1590 cm^{-1} are approximated by the generalized Lorentz-Gaussian equation

$$\gamma = \sum_{i=1}^{k} \gamma_o^{(i)} \exp[-g_i^2(\nu - \nu_o^{(i)})^2]/[1 + h(\nu - \nu_o^{(i)})^2], \qquad (4)$$

where γ is the absorption at frequency ν, $\gamma_o^{(i)}$ is the absorption in the i-th band maximum, $\nu_o^{(i)}$ denotes the i-th band maximum position, g and h stand for the Gaussian and Lorentz coefficients, respectively, and k is the number of bands.

The conformity criterion of the calculated and experimental contours

$$P = 1/N \cdot \sum_{j=1}^{N} (\gamma_{\text{calc.}}^{(i)} - \gamma_{\text{exp.}}^{(i)})^2, \qquad (5)$$

where N is the number of measured contour ordinates was minimized by the steepest descent method. In all cases with k = 2 a P value of 0.4–0.6 is achieved which does not exceed the average noise of the spectrometer.

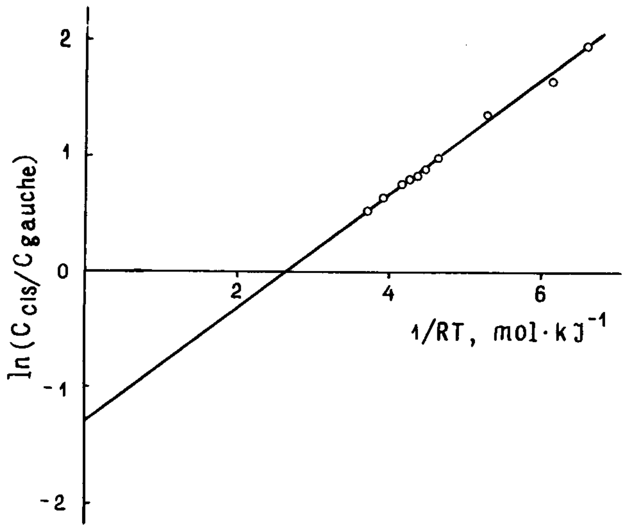


Figure 12 Temperature dependence of the *cis*/*gauche* concentration ratio in methyl vinyl sulfide.[70]

The ln C_{cis}/C_{gauche} value obtained with allowance for the temperature dependence of *t*-butyl vinyl sulfide extinction is presented in Fig. 12 as a function of the reciprocal absolute temperature. According to the plot the differences of the enthalpies and entropies of rotamers are $\Delta H = 1.45 \pm 0.04$ kcal/mol, $\Delta S = -1.74 \pm 0.08$ e.u.[70] This means that with $T \rightarrow \infty$ the mole fraction ratio $C_{cis}/C_{gauche} \rightarrow 1{:}5.7$, the less stable conformer dominating above 150 °C. A potential curve of interal rotation for which the number and energy of all the steady states fit the observed temperature change in the conformer ratio has been obtained.[70]

The steady-state energies (E) as eigenvalues of the Schrödinger wave equation

$$\left[-\frac{\hbar^2}{2J}\frac{\partial^2}{\partial\varphi^2} + U(\varphi)\right]\Psi = E\Psi, \tag{6}$$

where J is the reduced inertia moment of the torsional mode, are more conveniently calculated with the potential in the form

$$U(\varphi) = U_n(\varphi) + \frac{1}{2}\sum_{i=1}^{3} V_i(1 - \cos i\varphi), \tag{7}$$

where $U_n(\varphi)$ is the energy of steric hindrance calculated by theoretical conformation analysis,[75] V_i are the parameters of internal rotation barrier characteristic of the C_{sp^2}–S bond. The $U_n(\varphi)$ function is approximated by a cosine series in the form of the second term of equation (7) with $V_1 = -0.4$, $V_2 = -0.2$ and $V_3 = -0.2$ kcal/mol. The energies of the *cis*-states (and of the second rotamer states for potentials with a distinct minimum in the planar *trans*-form) were calculated in the anharmonic oscillator approximation using as the reduced moment of torsional vibration the following value

$$\langle J\rangle = \int\Psi^*(\varphi)J\Psi(\varphi)d\varphi,$$

where $\Psi(\varphi)$ is the solution of the wave equation for the inertia moment in the corresponding planar conformation. This is necessitated by a wide range of J (from 5.93 to 9.23 g·mol·A^2) in going from *trans* to *cis*. The energy of the steady *gauche*-states was calculated as described in[76] by approximating the wave function by the series

$$\Psi_i(\varphi) = \sum_n C_{in}\Phi_n(\varphi),$$

where $\Phi_n(\varphi)$ are the wave functions of the harmonic oscillator. Then the mole fraction ratio of the conformers may be written as

$$C_{cis}/C_{gauche} = g_{cis}\sum_{i=1}^{N_{cis}} \exp(-E_{i,cis}/RT)/g_{gauche}\sum_{i=1}^{N_{gauche}} \exp(-E_{i,gauche}/RT), \tag{8}$$

where g are the statistic sums of states and N the number of energy levels. A considerable contribution to g values can only be made by low-frequency vibrations ($\nu < 400\,cm^{-1}$). In this spectral region the greatest frequency difference between the *cis*- and the *gauche*-conformer was expected, by analogy with methyl vinyl ethers, for the CH_3 torsional mode, i.e., 200 cm^{-1} (*cis*) and 160 cm^{-1} (*gauche*).[63] No band at 160 cm^{-1}, however, was observed in the IR and Raman spectra, although, according to the conformational energy calculation,[70] a significant difference in the barriers to CH_3 group rotation in *cis* and *gauche* (or *trans*) conformations should only occur only in methyl vinyl ether due to the large steric strain of the molecule in the *cis*-form (1.51 kcal/mol). In methyl vinyl sulfide the planar *cis*-form strain is as small as 0.62 kcal/mol, and the frequency difference of the CH_3 torsional mode in the *cis*- and the *gauche*-conformation should not exceed 20 cm^{-1}. This means that the entropy of rotational isomerism for methyl vinyl sulfide is entirely due to the arrangement of the torsional mode energy levels relative to the C_{sp^2}–S bond, and in equation (8) $g_{cis}/g_{gauche} = 1$*.

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* Summing up in equation (8) is performed by a standard program of digital solution of the Schrödinger equation in which the degenerated levels are taken into consideration twice. Thus, all those factors included in the g values, have been accounted for and, therefore, the degeneration should not be taken into account twice, hence $g_{cis}/g_{gauche} = 1$ and not 0.5.

The optimal parameters of the potential V_i should correspond to the conformity criterion minimum, F:

$$F = (1/k \sum_{i=1}^{k} [\ln(C_{cis}/C_{gauche})_{calc.} - \ln(C_{cis}/C_{gauche})_{exp.}]^2)^{1/2} \tag{9}$$

where k is the number of temperature points.

The function F is interrupted when the V_i values correspond to variations in the number of steady states of one of the conformers. Therefore no gradient methods are applicable in the search for the function minimum. From the analysis of the F function sections determined with fixed V_i values it follows that at any V_1 values and $V_3 = 0$ the minimal $F = 0.39$ ($V_1 = 1.12$ kcal/mol, $V_2 = 3.0$ kcal/mol) which is by two powers of ten higher than the standard variance of the temperature dependence $\ln(C_{cis}/C_{gauche})$. Besides, with any V_i value adequate for the potential minimum of a planar *trans*-conformation, which is, with allowance for $U_n(\varphi)$ of equation (6), slightly different from $V_1 - 4V_2 + 9V_3 > 0$, the conformity criterion $F > 0.26$. The minimal F value within the range 0.055–0.065 is found for several nearly equivalent sets of V_i. Averaging of these values leads to $V_1 = 0.64 \pm 0.05$, $V_2 = 1.80 \pm 0.2$, $V_3 = 1.6 \pm 0.1$ kcal/mol. The shape of the potential function of the internal rotation of methyl vinyl sulfide and the position of the steady-state energy levels are depicted in Fig. 13. As seen from this Figure, methyl vinyl sulfide exists as an ensemble of four rotamer types corresponding

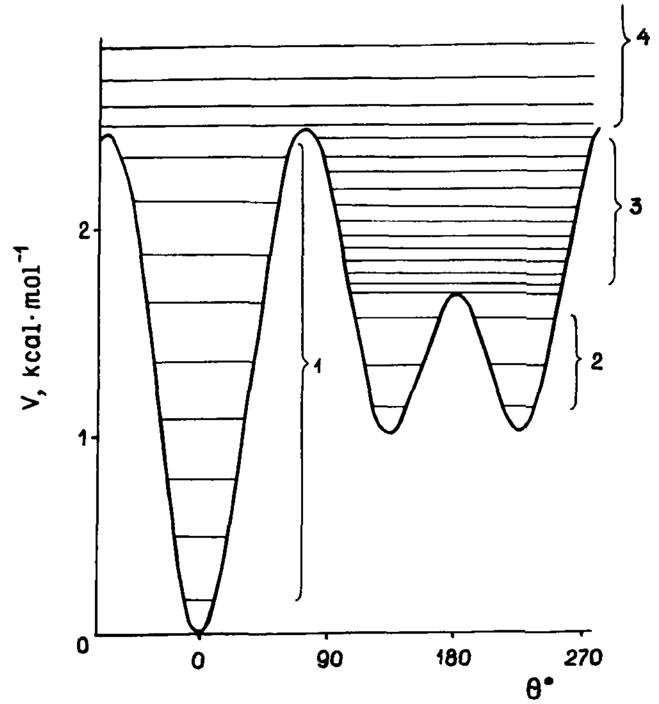


Figure 13 Potential function for internal rotation in methyl vinyl sulfide and the positions of the steady-state energy levels.[70]

to four steady states;[70] these are planar *cis* (1), *gauche* with a rotational angle 132 ± 3° about the C_{sp^2}–S (2), *gauche* (3) lying above the trans barrier (quasi-*trans*) associated with a large-amplitude motion of the CH_3 group with the equilibrium achieved in the planar *trans*-form, and the free rotational state (4). The population of the latter state remained extremely low in the experiment. The bands of *gauche* and quasi-*trans* states seem to differ slightly in frequency due to which the band 1581 cm^{-1} is on average 1.35 times as wide as the band 1577 cm^{-1}.

The energy difference between the lower *gauche* and *cis* levels is 0.9–1.0 kcal/mol which is considerably different from the formal enthalpy difference obtained by the statistic model of rotational isomerism (1.45 kcal/mol).[70] The barrier to the *cis*-*gauche* transition is 2.35–2.55 kcal/mol. Of great interest is the barrier value separating the *gauche*-forms. According to *ab initio* calculations using the 3-21G basis set[26] this value is 0.2 kcal/mol which is not enough for the *gauche* steady state to be achieved. For the potential reported[70] this value is 0.6–0.7 kcal/mol and there are 2–3 potential levels in the *gauche* potential well.

The V_i parameters obtained[70] are related to the rotational barrier due to electronic interactions. The value $V_1 = 0.64 \pm 0.04$ kcal/mol implies that in the planar *cis*- and *trans*-conformations the energies of conjugation between the sulfur lone pair and the double-bond π-electrons are not identical. The conjugation is more efficient in the *cis*-form than in the *trans*. The average energy conjugation value is $V_2 = 1.88 \pm 0.2$ kcal/mol. The V_3 value of 1.50 ± 0.1 kcal/mol turned out to be unexpectedly high. This appears to be due to an intermediate sp^2-sp^3-hybridization of the valence electrons of the sulfur atom. Thus, the *cis*-conformer (the sterically more strained molecular form) is energetically preferred owing to in-line effects governing the V_1 and V_2 values.[70]

IV. VINYL ETHERS AND SULFIDES WITH ELECTRON-WITHDRAWING SUBSTITUENTS

It is beyond doubt that the planar (or nearly planar) conformation is more favorable for p,π-conjugation to operate, whereas in the non-planar conformation this interaction is weakened to some extent. Disturbance of the conjugation in vinyloxy groups under the effect of a strong acceptor substituent was observed with the ether $CH_2{=}CHOCF_2CHFCl$, the IR spectrum of which contained only one band in the double-bond stretching region at 1653 cm^{-1}.[31] A $\nu_{C=C}$ band at 1667 cm^{-1} is present in the IR spectrum of trifluoromethyl vinyl ether as well.[77] Some shift of the $\omega_{CH_2=}$ band towards the higher-frequency region and a marked redistribution intensity in the $\omega_{CH=}$ (~950 cm_{-1}) and $\nu_{C\text{-}O}$ (1150–1200 cm^{-1}) regions in the IR spectra of 2-haloalkyl vinyl ethers have been reported.[78]

Therefore one may consider the conjugation in the vinyloxy group to be disturbed by a fairly strong acceptor substituent. The displacement of oxygen lone pairs in the direction opposite to the π-cloud of the double bond should lead to a weakening of the p,π-bonding and an increase in the population of the less hindered non-planar conformation. As seen from Table 8 the change in the electron-withdrawing power of the substituent (given in the Taft σ* scale) involves a marked redistribution of the relative intensities of bands caused by the planar and non-planar conformers. If in the IR spectra

Table 8. Fundamental frequencies of the $CH_2{=}CHO$ groups of vinyl ethers, $CH_2{=}CHOR$, with acceptor substituents[47]

No	R	Vibrational frequencies, cm^{-1}						
		$\omega_{CH_2=}$	$\omega_{CH=}$	$\nu_{C\text{-}O}$	$\delta_{CH=}$	$\delta_{CH_2=}$	$\nu_{C=C}$	σ^*
I[77]	CF_3	–	–	–	–	–	1667	+2.6
II[31]	CF_2CHFCl	–	–	–	–	–	1653	+2.82
III	$CHClCH_3$	852 s	940 m 965 m	1134 vs 1180 vs	1330 w	1375 s	1626 m sh 1640 vs	+0.95
IV	$CH_2OC_4H_9$	836 s	942 s	1136 s 1196 s	1320 m	1380 s	1625 s 1642 vs	+0.59[79]
V	$CH_2OC_6H_5$	846 s	940 s	1176 vs 1190 vs	1326 m	1385 m	1630 s 1648 vs	+0.85
VI	$CH_2SC_2H_5$	850 s	965 vs	1120 vs 1190 m	1320 vs	1365 s 1390 m	1620 m sh 1640 s	+0.47[79]
VII	$CH_2O(CH_2)_2Cl$	845 s	947 s	1185 vs	1323 m	1384 m	1625 s 1646 vs	+0.60
VIII	$(CH_2)_2OC_4H_9$	815 s 827 s sh 845 m sh	965 s	1173 m sh 1203 vs	1320 m sh	1360 s 1380 m	1620 vs 1635 s	+0.19
IX	$(CH_2)_2SC_4H_9$	820 s	964 s	1144 m 1196 vs	1320 s	1360 w sh 1378 m sh	1617 vs 1635 s	+0.12
X	$(CH_2)SH$	826 s 859 s	967 s	1170 m 1200 vs sh	1322 m	1380 s	1625 vs 1632 vs 1645 s	+0.23
XI	$(CH_2)CN$	830 s	970 s	1143 m 1170 w sh 1200 vs	1330 s	1360 w	1630 vs 1650 vs	+0.80
XII	$(CH_2)_2SCN$	830 vs	965 vs	1142 s 1188 s 1203 s	1322 s	1380 w	1642	+0.70
XIII	$(CH_2)_2S\underset{\underset{O}{\Vert}}{P}(OC_2H_5)_2$	815 m	973 vs	1140 vw 1165 m 1195 s	1320 m	1370 w 1390 m	1620 s 1640 s	–
XIV	$CH_2C{\equiv}CH$	827 s	934 s sh 960 m	1154 m 1200 s	1322 s	1361 s 1372 m sh	1624 s 1647 s	+0.76

of normal alkyl vinyl ethers the peak intensity of the band at 1620 cm^{-1} ($\nu_{C=C}$, planar conformation) is much higher than that of the band at 1640 cm^{-1} (non-planar form), the picture is inverted with increasing the substituent's electron-withdrawing power[47] till complete disappearance of the low-frequency component of the multiplet (ethers I, II, Table 8). The changes in other spectral regions are in full agreement with those observed with increasing the substituent branching in the series of vinyl ethers with electron-donating substituents. The only difference is that in the case of strong acceptors it is not only the characteristic absorption of the planar conformation that weakens or disappears completely, but the remaining bands of the non-planar form, especially $\nu_{C=C}$, $\omega_{CH_2=}$ and $\omega_{CH=}$, are noticeably shifted towards the higher-frequency region.

The unambiguous dependence of the conformational ratio upon the inductive effect of the substituent R is another indication that the rotational isomerism of vinyl ethers exists due to p,π-interaction rather than to purely conformational factors. However, as shown by a qualitative comparison of the peak intensities of the bands of certain conformers with the inductive constants of the corresponding substituents,[47] the effect of the structure on the conformer ratio in the series of ethers I-XIV is not free from steric effects. The ethers IV and VI ($\sigma^* = 0.59$ and 0.47, respectively), for example, are considerably richer in non-planar conformation than ethers XI and XII with stronger acceptor substituents ($\sigma^* = 0.80$ and 0.70). It is likely that such atoms as O, S, Cl, F in the α-position to the vinyloxy group create, apart from the inductive effect, some supplementary steric hindrance for the planar conformer. Besides, one should bear in mind, especially with α-halo substituted vinyl ethers, the possibility of weakening of the p,π-interaction in vinyloxy groups due to a competing resonance

$$[CH_2{=}CHOCHClCH_3 \leftrightarrow CH_2{=}CH{-}\overset{+}{O}{=}CH{-}CH_3] \atop \qquad\qquad\qquad Cl^-$$

When O, N, S, and Cl atoms are in the β-position relative to the vinyloxy group (ethers VIII, X, XII, XIII, Table 8) the conformer ratio does not differ much from that for normal alkyl vinyl ethers.

Crystalline vinyl ethers with a charged ammonium group (vinyloxyalkylammonium salts) as a substituent

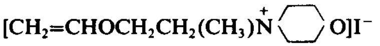
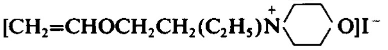
$$[CH_2{=}CHO(CH_2)_2\overset{+}{N}(R)_2R^1]X^-$$

(Table 9)[80] suggest the study of rotational isomerism to be reinforced by analysing the spectral changes responsible for the appearance of distant order in the system. The crystals are built, as a rule, of the most stable conformers.

The ion crystal lattice, however, due to its high energy and oriented electric field, sometimes may act as some sort of a matrix fixing less stable conformations.

In the IR spectra of vinyloxyalkylammonium salts in a region near 1600 cm^{-1} only one intense peak (1625–1630 cm^{-1}) corresponding to the low-frequency component of the normal triplet is present.[81] Other components occur in some spectra as very weak shoulders (1640 and 1655 cm^{-1}) on the principal band. The only exception is trimethyl(vinyloxyethyl)ammonium bromide the spectrum of which contains a central component of the multiplet (1643 cm^{-1}) only. This spectrum shows a very strong band near 1140 cm^{-1}, hardly seen in the other cases. In the spectra of liquid vinyl ethers a peak in the region 1140–1150 cm^{-1} is usually well defined. The presence of a characteristic doublet at 1620 and 1640 cm^{-1} in the latter permits the bands at 1140 and 1640 cm^{-1} to be assigned to the same rotational isomer and this is consistent with the data reported.[36,43] Consequently, unlike other vinyloxyalkylammonium salts, trimethyl(vinyloxyethyl)ammonium bromide crystallizes in another conformation. Since the absorption

Table 9. Trialkyl-*N*-(2-vinyloxyethyl)ammonium salts[80]

Formula	M.p., °C
$[CH_2{=}CHOCH_2CH_2\overset{+}{N}(CH_3)_3]I^-$	125 (with decomposition)
$[CH_2{=}CHOCH_2CH_2\overset{+}{N}(C_2H_5)_3]I^-$	79–83 (with decomposition)
$[CH_2{=}CHOCH_2CH_2\overset{+}{N}(C_2H_5)_2CH_3]I^-$	–
	122–129
	132 (with decomposition)
$[CH_2{=}CHOCH_2CH_2\overset{+}{N}(CH_3)_3]Br^-$	170–175

at 1140 cm^{-1} corresponds to one of the bands normally present in the spectra of saturated ethers and alkyl vinyl ethers with the conjugation disturbed by complex formation[82] this conformation is most likely to be less conjugated. In accord with this conclusion, the spectrum of trimethyl(vinyloxyethyl)ammonium bromide displays a lowering of the peak intensity at 1200 cm^{-1} and degeneration of this peak to a shoulder on a stronger band at 1175 cm^{-1} which may be interpreted as a consequence of the C_{sp^2}–O bond lengthening due to removal of the conjugation.

The correlations established here are confirmed by an analysis of the spectrum of 1-chloroethyl vinyl ether in which the population of the non-conjugated conformation should be significant due to competing resonance involving the α-chlorine atom. The spectrum of this ether (Table 8) differs much from the spectra of ethers enriched with 'conjugated' conformers, but in general corresponds to the spectrum of trimethyl(vinyloxyethyl)ammonium bromide: a strong band at 1641 cm^{-1}, with a small shoulder near 1620 cm^{-1}, an intense peak in the region 1134 cm^{-1}, considerable increase in the intensity and a low-frequency shift of the band at 1200 (1180 cm^{-1}); as with trimethyl(vinyloxyethyl)ammonium bromide, the CH_2= out-of-plane wagging frequency increases (850 cm^{-1}). The band intensity near 1320 cm^{-1} (=CH-planar wagging mode) markedly decreases which is in agreement with the assignment of this maximum to a planar sickle-shaped (*cis*) conformation.[36,42]

Thus, most crystalline vinyl ethers with an ammonium salt moiety in the β-position of the substituent exist predominantly as planar conformations in spite of the strong electron-withdrawing power of the substituent as a whole.

In the spectrum of substituted vinyl sulfides the $\omega_{CH_2=}$ frequency (860 cm^{-1}) shows the same tendency to be shifted up to higher values as the electron-withdrawing power of the substituent increases (Table 5).[69] On the basis of the IR spectral data for vinyl ethers these changes can reasonably be related to an increase in population of the less conjugated non-planar rotamer caused by displacement of the sulfur lone electron pairs towards the acceptor.

Thus, the analysis of the IR spectra of vinyl ethers and sulfides in which conformational inhomogeneity is quite evident can provide valuable information concerning the extent and character of p,π-conjugation in vinyloxy and vinylthio groups.[83] One of the most prominent features of the vibrational spectra of alkyl vinyl ethers and sulfides is the absorption multiplicity in the double-bond stretching region, two bands of the multiplet corresponding to different conformations.

V. DIVINYL AND ARYL VINYL ETHERS AND SULFIDES

The interest in the molecular and conformational structure of divinyl ether, divinyl sulfide, and aryl vinyl ethers and sulfides is not only caused by the close relation between the structure and the chemical behavior. The presence of two unsaturated units in the molecule in close vicinity to the heteroatom offers new problems such as those concerning the presence or absence of competition in the interaction with lone electron pairs, the transmission of barriers to internal rotation from alkyl vinyl to divinyl compounds, the possibility of 'through-conjugation' of π-systems of unsaturated units separated by the heteroatom.

Table 10. Fundamental frequencies of the vinyloxy group in divinyl and aryl vinyl ethers, $CH_2=CHOR$.[83]

No	R	Vibrational frequencies, cm^{-1}					
		$\omega_{CH_2=}$	$\omega_{CH=}$	ν_{C-O}	$\delta_{CH=}$	$\delta_{CH_2=}$	$\nu_{C=C}$
I[85]	$CH_2=CH$	838 sh	938* w sh				1619 vs
			944* m	1168 vs	1300 m	1378 m	1623 sh
			961* vw	1200 vs	1330 m	1392 vw	1641 s
							1672 vw
II[48]	C_6H_5	860 m	960 w sh	1165 s	1318 m	1395 m	1638 w sh
			970 s	1175 s	1343 w sh		1650 vs
III[87]	p-$CH_3OC_6H_4$						1622(I)**
							1638(10)**
IV[48,87]	p-$NO_2C_6H_4$	855 s	960 s	1110 m			1644(2)**
		865 s		1135 s	1335 w	1382 sh	1650 s
				1170 m	1340 s		
V	$CH_2=CHOCH_2$	840 s	940 s	1120 s	1310 w	1380 m	1625 s
			957 w	1139 m	1322 s		1642 vs
				1160 vs			
				1180 vs			
VI[48]	$CH_2=CHOCH(CH_3)$	840 s	945 s	1140 s	1315 w sh	[illegible]90 m	1640 w
		855 s sh	960 m	1175 s	1331 m		1650 s
			975 m	1200 s			
VII[48]	$CH_2=CHOCH(C_3H_7$-$i)$	844 s	944 s	1120 s	1300 m		1630 w sh
		860 w sh	966 w	1140 s	1312 m	1392 s	1641 vs
				1170 s	1330 w		
				1202 s			
VIII[48]	$CH_2=CHO(CH_2)_2$	821 s	950 w sh	1103 s	1320 s	1360 m	1623 vs
		850 w sh	965 s	1200 vs			1636 w sh
IX[48]	$CH_2=CHOCH(CH_3)CH_2$	826 vs	957 vs	1127 s	1325 s	1382 m	1620 vs
			967 m	1143 m			1640 vs
			985 m	1200 vs			

*In the original work[85] these frequencies are assigned to the $CH_2=$ torsional modes
**Raman data, the relative intensity is given in brackets

The structural study of divinyl ether by electron diffraction led to the conclusion that the double-bond planes were each rotated about 20° in opposite direction relative to the planar symmetric *trans-trans* conformation.[84] However, an analysis of the rotational structure and shape of the band at 837 cm^{-1} in the IR spectrum of divinyl ether provided some evidence in support of a planar *cis-trans* conformation of C_s symmetry (although the results do not seem to contradict the existence of an angle between the planes).[85] The lowest conformational repulsion should be common to non-planar conformations with the C–O–C plane normal to the plane of each double bond. One of this conformations may have a C_2 symmetry axis. According to,[85] divinyl ether exists at least as two conformers, one of which is represented by a non-planar conformation of C_1 symmetry. So, in the IR spectrum one should expect bands common in both planar and non-planar conformation of vinyl ethers to appear. In the non-planar conformation of C_1 symmetry (or in the planar *trans-trans*), owing to the symmetry of the inductive effect the oxygen lone electron pairs should, unlike those of other vinyl ethers, not be displaced towards any double bond. In the planar *cis-trans* conformation the double bonds are non-equivalent due to the absence of a symmetry axis and this should lead to splitting of the corresponding bands. The IR spectrum of divinyl ether (I, Table 10) supports this conclusion.[48] The low-frequency band in the double-bond stretching region is split, in fact, into two peaks (1619 and 1623 cm^{-1}). A distinct doublet character is also displayed by other bands belonging to the planar conformation. The non-planar conformer may be associated with a band at 1641 cm^{-1} whereas in[85] the bands at 1619 and 1641 cm^{-1} were assigned to one and the same planar conformer. A weak absorption at 1672 cm^{-1} is most likely to arise from the Fermi resonance involving the $\omega_{CH_2=}$ and one of the $\nu_{C=C}$ stretching modes.[48]

According to,[86] divinyl ether exists in the liquid phase as an equilibrium mixture of two conformers with an energy difference of 0.6 kcal/mol. An analysis of the relative intensities and the polarizability of the lines in the IR and Raman spectra suggests the planar *trans-trans* conformer to be the most stable one, the second conformer containing no symmetry elements.

Ab initio calculations[86] predicted two stable conformations for divinyl ether. The first energy minimum corresponds to a planar *trans-trans* form ($\theta_1 = \theta_2 = 0°$) and the second minimum belongs to a non-planar conformation ($\theta_1 = -20°$, $\theta_2 = 135°$). The calculated enthalpy difference between these conformations is 2 kcal/mol.

The conformational structure of divinyl ether was also studied by MW spectroscopy. A non-planar conformer structurally close to *cis-trans* has been identified.[88,89] It is suggested[89] that the non-planarity was caused by strong repulsion between the α- and β-hydrogen atoms of the *trans*- and *cis*-vinyl groups of divinyl ethers. A feature of the *cis-trans* conformation is tunneling through a rather low potential barrier which is observed as splitting of the rotational transition lines.[89]

Ab initio calculations of divinyl ether with the STO-3G and 4-31G basis sets indicate three stable conformers.[90] The potential surface calculated by the *ab initio* method for divinyl ether is shown in Fig. 14.[90] The most stable conformation is non-planar ($\theta_1 = 17.6°$, $\theta_2 = 212.6°$, C_1 symmetry) corresponding to a distorted *cis-trans* form. The other two minima correspond to a planar *trans-trans* form ($\theta_1 = \theta_2 = 180°$, C_{2v} symmetry) and a non-planar form close to *cis-cis* ($\theta_1 = 31.5°$, $\theta_2 = 31.5°$, C_2 symmetry). These conformations have energies 0.7 and 2.4 kcal/mol, respectively, higher than the preferred conformation.[90] According to *ab initio* calculations using the 4-21G basis set there are three stable conformers of divinyl ether. These are the non-planar conformer with C_1 symmetry (distorted *cis-trans*, $\theta_1 = 0°$, $\theta_2 = 120°$), the planar *cis-trans*, and the non-planar *cis-cis* ($\theta_1 = \theta_2 = 30°$) with relative energies of 0, 1.58, and 1.07 kcal/mol, respectively.[91]

Investigations of the rotational isomerism of divinyl sulfide are rather scarce. The IR spectrum of divinyl sulfide shows that two conformers exist in the liquid and the solution state and a *trans-trans* conformation to be achieved in the crystalline state.[92] According to[69] the twisted *trans-trans* conformation is also regarded as most favored. The existence of conformational isomerism for this compound is also in keeping with Raman and IR data for divinyl sulfide in the liquid and the solid phase.[93] For the isomer existing in the solid state a conformation with C_2 symmetry is suggested, whereas the second isomer seems to have no elements of symmetry. There are also two conformers in the liquid phase. The enthalpy difference between these conformers is negligible.

The rotational isomerism of divinyl sulfide was also studied by *ab initio* calculations

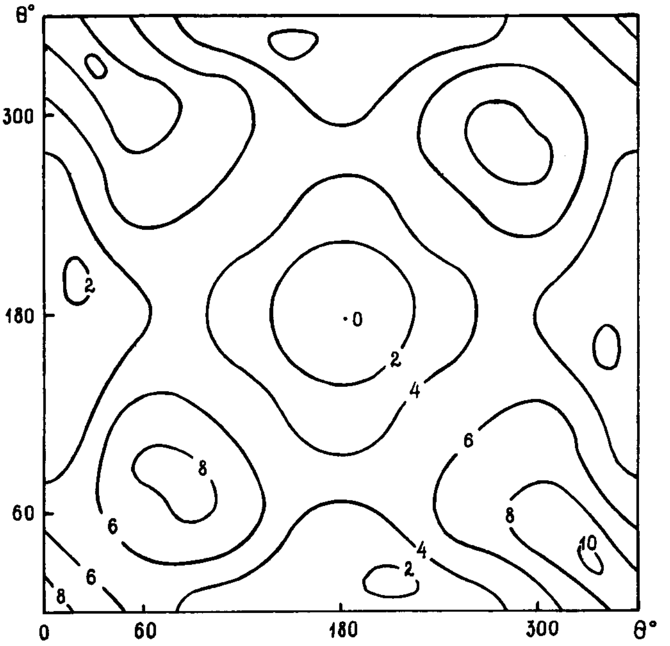


Figure 14 Map of the potential energy surface for internal rotation in divinyl ether, kcal·mol^{-1}.[90]

using the STO-3G, 3-21G basis sets and molecular mechanics.[26] The potential curve of the internal rotation for divinyl sulfide with a fixed *s-trans* conformation of one vinyl group, obtained by STO-3G (Fig. 15) differs much from the corresponding curves for ethenethiol and methyl vinyl sulfide.[25,26] The minimal energy on this curve corresponds to θ = 180°. According to STO-3G calculations the most stable conformation is *trans*-

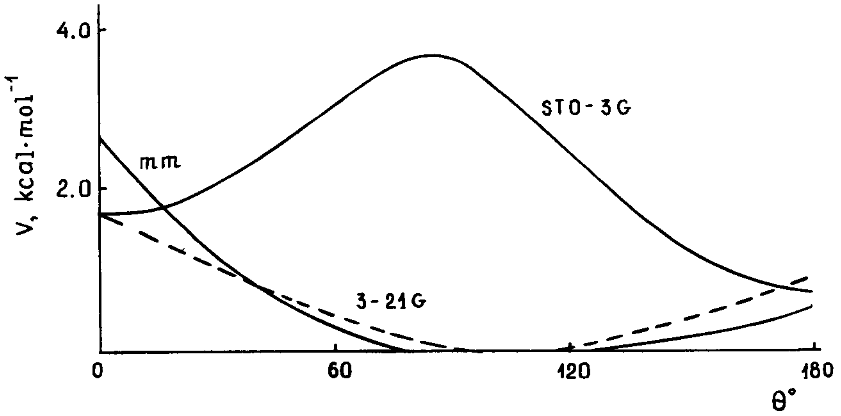


Figure 15 Calculated potential energy functions for internal rotation about the C–S bond in divinyl sulfide (mm = molecular mechanics).[26]

trans. The potential functions for divinyl sulfide calculated using the 3-21G basis set and molecular mechanics[26] are also quite different from those for ethenethiol and methyl vinyl sulfide. The 3-21G calculation predicts two stable, energetically very similar conformations, *cis-trans* ($\theta_1 = 0°$, $\theta_2 = 120°$, C_s symmetry) and *cis-cis* ($\theta_1 = \theta_2 = 120°$, C_1 symmetry).

In determining the number and the nature of the rotational isomers of divinyl sulfide quite reliable information can be provided by molecular mechanics, since steric strain plays a decisive role in molecular planar forms most essential for conjugation. The steric strain energies of divinyl ether and divinyl sulfide calculated by this method[94] are presented in Fig. 16. The steric hindrance energy was calculated by a 15° tracing of the θ_1 angles from 0° to 360° and the θ_2 angle from 0° to θ_1 (θ_1 and θ_2 are the rotation angles of one and the other vinyl groups, respectively, from the planar *cis-cis* structure). Repulsive interaction of non-bonded atoms completely prevents the existence of stable planar *cis-cis* structures for both compounds. The minimal steric hindrance is typical of a non-planar form derived from the *trans-trans* conformer by rotation of the two vinyl groups in opposite directions by an angle of about 75° in divinyl ether and 90° in divinyl sulfide. The steric hindrance energies of other conformations relative to these optimal forms are given in Table 11. It is seen from Table 11 that the decrease in the steric hindrance energy due to the X–C bond lengthening is a factor influencing the shape of the potential energy map. Thus, in divinyl ether in the *trans-trans* form (**A**) a clearly defined increase in the steric hindrance energy is observed whereas in divinyl sulfide the increase is considerably smaller. Mutual compensation of the influence of a greater C–S bond length and a smaller C–S–C angle as compared to the oxygen analog occurs only in the *cis-cis* conformation (**D**). The steric hindrance energy of 1 kcal/mol corresponds to the following angles of deviation of the planar *cis-cis* form: 57° for divinyl ether, 42° for divinyl sulfide.[94] The strain in the *trans-trans* conformation does not exceed 1 kcal/mol. One cannot but pay attention to the fact of the existence of conformation **F** in which the steric hindrance energy for divinyl sulfide is similar to that in the *trans-trans* conformer and ~ 1 kcal/mol higher for divinyl ether. This conformation is achieved when the vinyl groups of the *cis-cis* form are each rotated about 45° in opposite

Table 11. Steric hindrance energy in different conformations of divinyl ether and divinyl sulfide, kcal/mol[94]

Designation	Conformation	Divinyl ether	Divinyl sulfide
A	*trans-trans*	0.90	0.61
B	*cis-trans* (planar)	3.47	3.08
C	*cis-trans* (15° deviation)	2.71	2.15
D	*cis-cis* (planar)	12.60	12.80
E	*cis-cis* (38° deviation)	2.25	1.26
F	*cis-cis* (45° deviation)	1.81	0.77

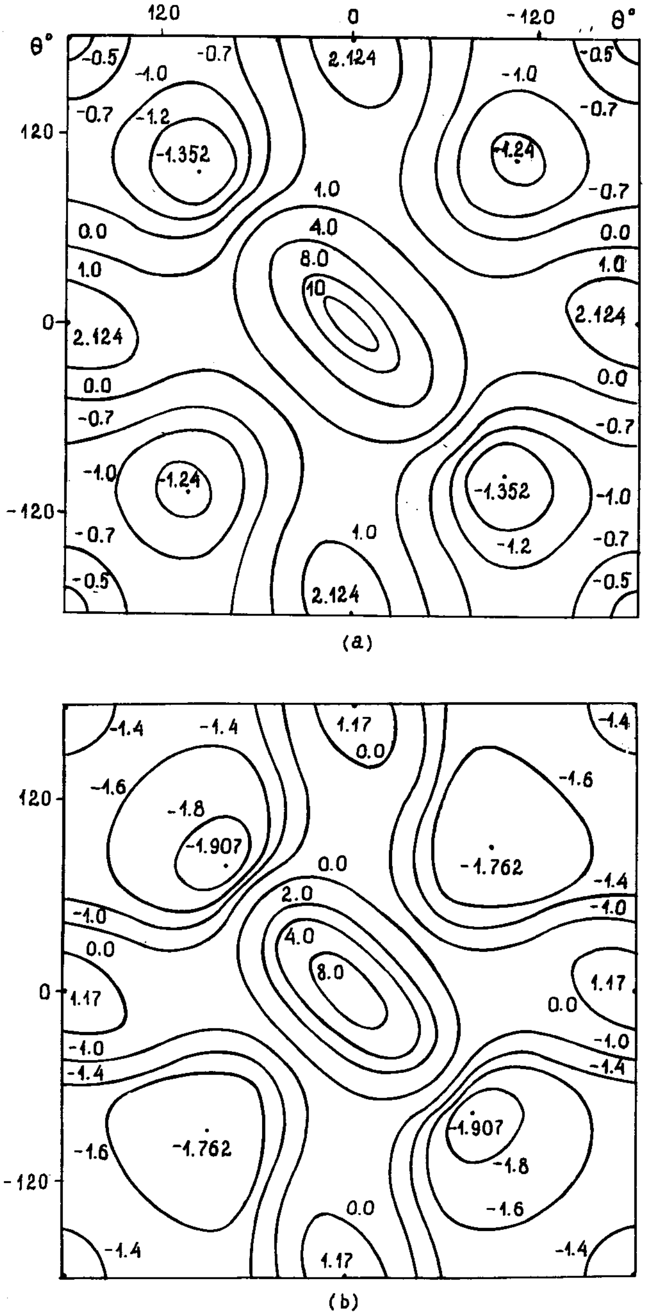


Figure 16 Maps of the steric hindrance energy surface of divinyl ether (a) and divinyl sulfide (b), kcal·mol.$^{-1}$ [94]

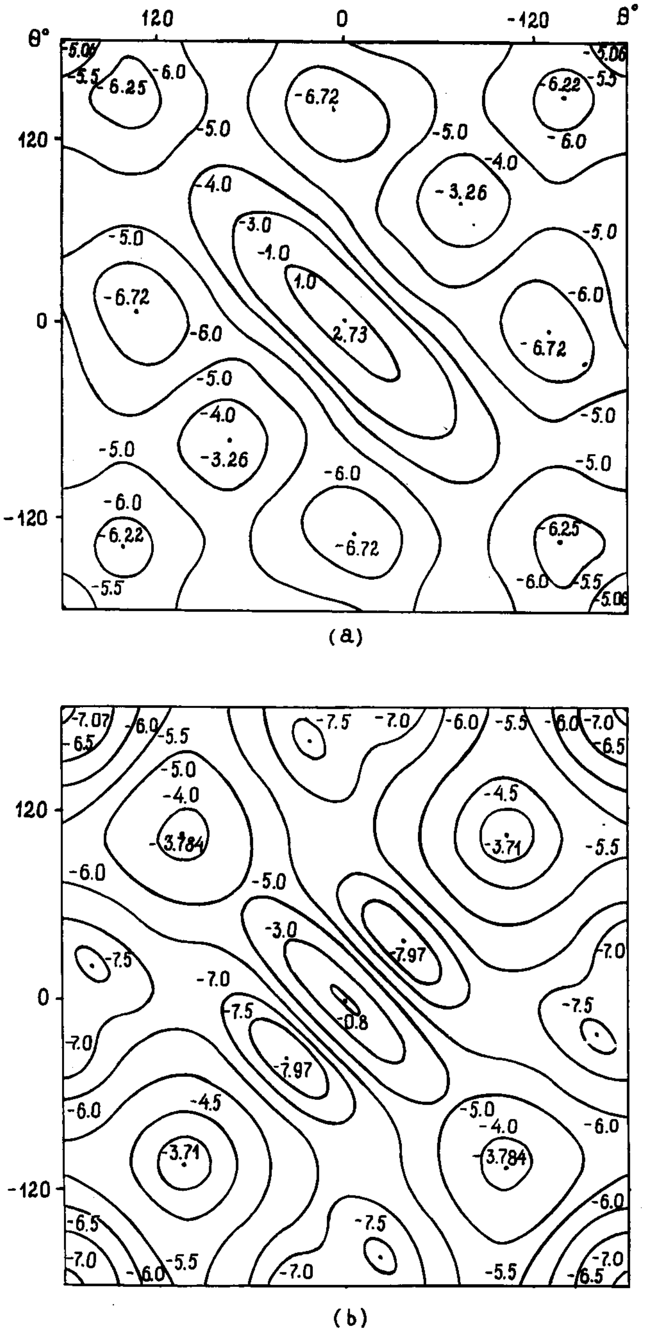


Figure 17 Maps of the potential energy surface of divinyl ether (a) ($V_1 = -2.8$, $V_2 = -3.3$ kcal·mol^{-1})[94] and divinyl sulfide (b) ($V_1 = 0.71$, $V_2 = 1.88$, $V_3 = 1.5$ kcal·mol^{-1}).

directions. It is likely that close to real energy ratios in different conformations of divinyl ether and divinyl sulfide have been obtained by summing up the energies of steric hindrance and p,π-interaction[94] borrowed from the data for methyl vinyl ether and methyl vinyl sulfide (Fig. 17). In the case of divinyl ether the V_1 and V_2 values -2.8 and -3.3 kcal/mol, respectively, obtained by *ab initio* calculations,[59] are taken as p,π-conjugation energies. For divinyl sulfide the potential barrier parameters for methyl vinyl sulfide obtained by IR spectroscopy ($V_1 = 0.71$, $V_2 = 1.88$ and $V_3 = 1.50$ kcal/mol)[70] are employed. So, on the maps shown in Fig. 17 only the effects due to the competition of the ethylenic bonds for interaction with the heteroatom lone pair and through conjugation are ignored. The absolute energy minima for divinyl ether and divinyl sulfide turn out to be quite different in this case. With divinyl sulfide the most preferable conformation is deformed *cis-cis* whereas with divinyl sulfide it is planar *trans-trans*. It should be noted that a relatively deep potential well can only be associated with the planar *trans-trans* conformation. Other possible stable conformations are characterized by shallow troughs on the potential energy surface owing to which they should display motions of large amplitude even in the torsional-vibrational ground state. This is also the case with distorted *cis-trans* forms.

The analysis of potential energy maps shows that divinyl ether and divinyl sulfide can exist in only three forms, i.e. planar *trans-trans* (**A**), the *cis-trans* (**C**) with a 15° deviation of vinyl groups from the C–X–C plane, and form **E** (or **F**) with a 30–55° deviation of the vinyl groups from the C–X–C plane.[94]

The population ratio of certain conformers of divinyl ether and divinyl sulfide has been calculated from their energies.[94]

The electronic and molecular structures of aryl vinyl ethers have been studied.[48,95,96] In studying the Raman and IR spectra of vinyl phenyl ether usually either one band corresponding to the vinyloxy group stretching vibration at ~1645 cm^{-1} with no question concerning conformational isomerism[49,87] or two bands at 1638 and 1650 cm^{-1} were discussed.[48] The appearance of the doublet[48] was explained by the existence of vinyl phenyl ether as two conformers (II, Table 10). In aryl vinyl ethers two principal conformers are possible. These are non-planar (the phenyl and vinyloxy groups lie in mutually perpendicular planes) and nearly planar. The dependence of the conformational composition in aryl vinyl ethers on the nature and position of substituents and of the temperature has been studied.[95]

The introduction of ortho-substituents into the phenyl ring of aryl vinyl ethers reduces the double-bond line intensity and splits the characteristic frequencies at 1640 and 1310 cm^{-1} of the vinyl group vibrations in the Raman spectra.[96] This effect can be explained by the existence of two rotational isomers formed upon distortion of the coplanarity of the system by rotation of both the vinyl group and the phenyl ring relative to the C–O–C plane.

The nature and ratio of the conformations in the case of aryl vinyl ethers are determined by the extent of competing p,π-interaction in the aryloxy group (IV, Table 10).[48] A decrease in integral intensity of a band corresponding to the $\nu_{CH_2=CHO}$ vibration is caused by weakening of the p,π-conjugation in the vinyloxy groups: the stronger the acceptor, the greater is the p,π-interaction betwen the ether oxygen and the aromatic moiety and the more difficult the ring displacement out of the C–O–C plane. In this connection, *p*-nitrophenyl vinyl ether exists evidently as a conformer near to planar.[48,95]

In the case of a OCH_3 substituent in the *p*-position of the phenyl ring the p,π-conjugation, on the contrary, between the vinyl group and the ether oxygen is increased owing to a competing interaction between the donor substituent and the phenyl ring.

Of great interest in aryl vinyl ethers are the θ_1 and θ_2 angles characterizing the rotations of the phenyl ring and the vinyl groups relative to the C–O–C plane. For an objective determination of the θ_1 and θ_2 values an X-ray diffraction analysis has been applied to *p*-$NO_2C_6H_4OCH{=}CH_2$.[97] The angle between the vinyloxy group and phenyl ring planes is 53.8°. The θ_1 and θ_2 angles are 27.3° and 36.6°, respectively. In this case the planes of the phenyl ring and of the double bond are turned in different directions relative to the C–O–C group. The θ_1 and θ_2 values provide for an effective overlapping of 2p-AO of atoms of the C–O–C moiety due to which the decrease in the conjugation energy relative to a planar conformation with $\theta_1 = \theta_2 = 0°$ should be small. In the IR spectrum of *p*-nitrophenyl vinyl ether in solution and the crystalline state the double-bond stretching turned out to be identical ($1649\,cm^{-1}$).[97] The position of other bands of the IR spectrum in the region $400–1700\,cm^{-1}$ does not change much either. The molecular and conformational structure of *p*-nitrophenyl vinyl ether does not seem to undergo any considerable change in going from the crystalline to the solution state in indifferent solvents.

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