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Spatial and electronic structure of vinyl and allenyl chalcogenides

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Abstract. Alkyl vinyl chalcogenides show a complex picture of rotational isomerism and are characterised by the presence of several qualitatively different types of stable conformers. The features of conformational structure of these compounds can be understood only by considering the stationary states altogether. Conformational analysis of divinyl chalcogenides indicates that the potential energy surface of internal rotation should be considered not as just a source of information on rotational isomerism; rather, it is a tool in a search for stationary states corresponding to definite intervals of variation of internal molecular coordinates. The principal details of the orbital structure of allenyl ethers and vinyl chalcogenides including a weak dependence of the structure and relative location of higher occupied π-MOs of alkyl vinyl chalcogenides on the nature of the heteroatom and the structure of the alkyl substituent are discussed. The common feature of chalcogenides is the presence of a low energy excited state of σ-symmetry. The excited states of π-symmetry are always located higher on the energy scale than the states of σ-symmetry. The bibliography includes 198 references.

I. Introduction

The interest in electronic and conformational structures of vinyl systems of the type $CH_2=CHXR$ (X = O, S, and Se, and Te, R = Alk, and $CH=CH_2$) stems from a number of important features specific to rotational isomerism in compounds of this class. First of all, the number of existing rotamers may exceed the number expected on the basis of canonical concepts about the nature of rotational isomers. In the majority of cases, the deviation of atoms from their equilibrium position are small, and the observed properties of the molecular system can be satisfactorily described in terms of the harmonic oscillator approximation. In the case of large deviations from equilibrium in molecules existing in several rotameric forms, quantum mechanical analysis leads to a revision of conclusions on the nature and the number of stable conformers.

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According to traditional concepts, hindered internal rotation about $C_{sp^2}-X$ (X = O, S, Se, and Te) bonds in molecular systems of alkyl vinyl chalcogenides provides three conformations, namely, *s-cis-*, *s-trans-*, and *gauche-* (non-planar).† The reason for hindered rotation about the $C_{sp^2}-X$ bonds can be both the interaction of the multiple bond π-electrons with the lone electron pair on the chalcogen atom (p,π-interaction) and purely steric interaction of substituent R with the hydrogen atoms of the vinyl group. For these types of molecules, the most important information on rotational isomerism is the number of stable conformers and their parameters. Mutual counterbalance between the changes in structural parameters in internal rotation and the electron distribution in different conformations opens the way to understanding both the properties of the compounds and the effect on them of external factors, such as electric and magnetic fields, medium, and temperature.

Typical of vinyl chalcogenides are rotameric forms characterised by torsional intramolecular motion of large amplitude. The peculiarities of the conformational structure of these compounds can be understood by considering the whole ensemble of stationary states. The most comprehensive information on rotational isomerism in alkyl vinyl chalcogenides can be gained from the internal rotation potential curve, and in divinyl chalcogenides, from the corresponding potential surface constructed as a function of rotational angles about $C_{sp^2}-X$ bonds. Alkyl vinyl chalcogenides are characterized by rotation about the $C_{sp^3}-X$ bond, in addition to the rotation about the $C_{sp^2}-X$ bond; for R other than Me, internal rotation in the alkyl substituent also takes place. This increases the number of rotational states and hampers the use of many methods of investigation. In this connection, an increased interest in the simplest analogues of compounds under study such as vinyl alcohol and ethenethiol is well understood.

The problem of the relationship between conformational isomerism, electronic structure, physicochemical properties, and reactivity in vinyl heteroatomic systems has first been formulated for vinyl ethers and sulfides in generalising papers.[1,2] In these studies, the main achievements in this field were summed up, and novel approaches (and solutions) were contemplated. These studies have stimulated systematic investigations in this field carried out in the last two decades[3–21] including also vinyl compounds of selenium,[9,11,13] tellurium,[4,9,11,13] and nitrogen.[16–20] A significant part of these investigations was performed by the NMR method on various nuclei. Large areas of this

† Hereinafter, the terms *cis-* and *trans*-conformers refer to *s-cis-* and *s-trans*-conformers of chalcogenides.

research are summarized in theses[9,13,16,18] and reviews.[3,4,6-8] However, recent results obtained by other methods have not been considered altogether except for a thesis,[21] in which the results of the study of the electronic and spatial structures of vinyl and allenyl chalcogenides by IR, Raman, UV, and PE spectroscopy methods, conformational analysis, quantum-chemical calculations, and normal coordinate analysis have been summarized.

The present review gives a systematic account and critical examination of investigations of the electronic and conformational structures of vinyl and allenyl chalcogenides carried out by complementary theoretical and experimental methods (gas electronography, microwave, vibrational, UV and PE spectroscopy, dipole moments).

II. Rotational isomerism in vinyl and allenyl chalcogenides

1. Vinyl alcohol and ethenethiol

For a long time, vinyl alcohol has not been available for experimental studies and has been considered as an unstable tautomeric form of acetaldehyde. Only in 1967 was vinyl alcohol identified by its mass spectrum in the analysis of the products of oxidation of dideuterioacetylene.[22] The NMR spectrum of vinyl alcohol (without its isolation from the products of photolysis of acetaldehyde) was reported.[23] The molecular structure of vinyl alcohol was elucidated from the MW spectra.[24,25] The analysis of the MW spectra favours the preferential planar *cis*-conformation of the molecule having the following geometric parameters: $r(C=C) = 1.33$ Å, $r(C-O) = 1.37$ Å, CCO bond angle is equal to 120°. Experimental parameters of the less stable *trans*-conformer of vinyl alcohol were obtained later by MW spectroscopy.[26] The analysis of rotational constants for the *trans*-rotamer and its deuterioisotopomer ($CH_2=CHOD$) gave the following geometry: $r(C=C) = 1.32$ Å, $r(C-O) = 1.38$ Å, the COD bond angle is 122°. The C=C bond distance in vinyl alcohol is somewhat shorter than the corresponding bond lengths in ethene[27] and propene.[28] Shortening of the C–O bond length and an increase in the CCO bond angle is observed in vinyl alcohol as compared to saturated alcohols (1.43 Å and 120°, respectively).[29] The energy difference of 4.5 kJ mol^{-1} was calculated for *cis*- and *trans*-conformers of vinyl alcohol from the variation of relative intensities in the MW spectrum.[26]

The characteristics of vinyl alcohol derived from IR, UV, and NMR spectra[30-32] are useful for the detection of this alcohol and other simple enol compounds among intermediates of chemical reactions. The absorption bands for the *cis*-rotamer and for all by-products formed in its synthesis were assigned based on the analysis of the IR spectra of vinyl alcohol and nine of its isotopomers and from normal coordinate analysis.[32] Five absorption bands are observed in the photoelectron spectrum of vinyl alcohol.[33,34] The low-energy band has a fine structure with a vibrational interval of 1400 cm^{-1}. The low-frequency component of this band is assigned to the *cis*- and the high-frequency component is assigned to the *trans*-conformer.[33]

According to the IR and MW spectra, the sulfur analogue of vinyl alcohol, ethenethiol, is also a mixture of two conformers.[35-40] A detailed analysis of the IR spectra of ethenethiol[36,37] in the gas phase, crystal state (at 300 K), and in argon and nitrogen matrices has shown that the molecule exists as *cis*- and *trans*-conformers, the *cis*-form being more favourable in energy, as in the case of vinyl alcohol. The normal coordinate analysis for *cis*- and *trans*-conformations indicates that the stretching C–S, bending C=C–H, and torsional S–H vibrations depend most of all on conformations.[37]

The planar *cis*- and 'quasi'-*trans*-conformers of ethenethiol and its deuterated isotopomers have been studied by MW spectroscopy.[35,36,38,40] The following geometric parameters were obtained for the most stable *cis*-conformer: $r(C=C) = 1.34$ Å, $r(C-S) = 1.76$ Å, bond angles CCS and CCH are equal to 126.9 and 95.8°, respectively.[40] Internal rotation about the

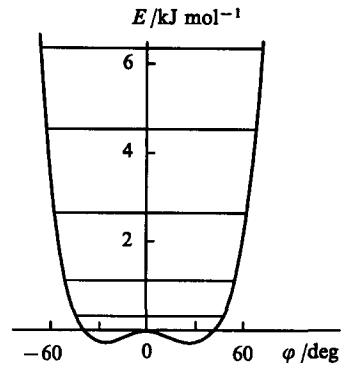


Figure 1. The potential function of internal rotation for the *trans*-conformer of vinylthiol.[39]

$C_{sp^2}-S$ bond results in a decrease in the CCS angle by 5° and in an increase in the C–S bond length by 0.02 Å. The characteristics of an ethenethiol rotamer and its SD-isotopomer differing from the *cis*-form in the ground and three excited vibrational states were also obtained from the MW spectra.[39] The dipole moments and rotational constants corresponding to the CCS and CSH bond angles equal to 122 and 98°, respectively, were determined. The potential curve of internal rotation for *trans*-ethenethiol was obtained in this work (Fig. 1). The ground vibrational state of this 'quasi'-*trans*-conformer (according to the authors' terminology) is above the barrier of 19 cm^{-1} at 26° separating the two minima relative to the zero of the planar conformation.

Considerable progress in studies of the conformational properties of α,β-unsaturated ethers and sulfides has been achieved with the use of *ab initio* calculations, which allow one to estimate the population of one conformation or another and the probability of the interaction of a lone electron pair of a heteroatom with the π-electron system.[41-46] One of the first theoretical studies of this type was the calculation on vinyl alcohol and ethenethiol,[42] which confirmed that both compounds have two rotational isomers, the *cis*-conformer being more stable. The maximum in the potential curve of internal rotation for vinyl alcohol corresponds to a dihedral angle (φ) of 90°, and for ethenethiol it corresponds to 60° (Fig. 2). The second minimum for ethenethiol corresponds to a torsional angle of 150°.

ab initio Calculations for vinyl alcohol have been performed with full optimization of the geometry of vinyl alcohol using STO-3G and 4-31G basis sets.[43-45] These calculations have also confirmed that the molecule exists in two planar conformations: *cis*- and *trans*-. For a series of substituted vinyl alcohols XCH=CHOH (X = H, CN, F),[46] the potential as a function of the internal rotation about the $C_{sp^2}-S$ bond calculated in the 4-21G basis set appeared to depend substantially on the nature of substituent X (Fig. 3) Internal rotation in these molecules is

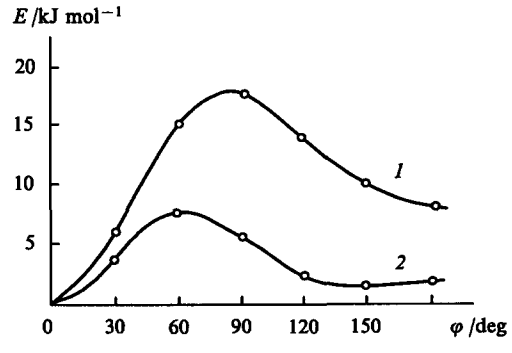


Figure 2. The potential functions of internal rotation for vinyl alcohol (*1*) and vinylthiol (*2*).[42]

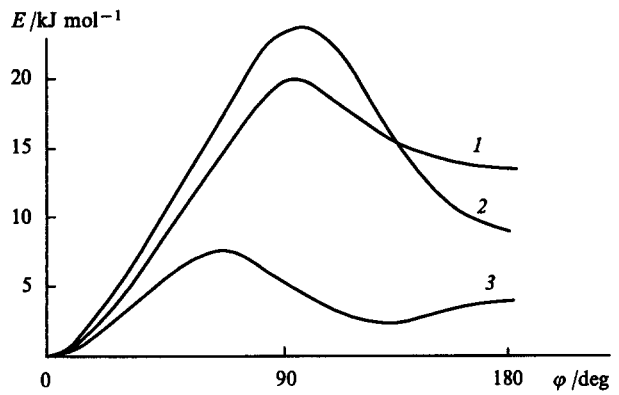


Figure 3. The potential functions of internal rotation for molecules XHC=CHOH.[46] X = H (*1*), CN (*2*), F (*3*).

accompanied by changes in the CCO angle and the C–O bond length.[45,46]

The energy difference between the conformers of vinyl alcohol is equal to 9.4 (STO-3G),[44] 9.0 (4-31G),[44] 7.1–7.9 (3-21G),[45] and 11.8 (4-21G)[46] kJ mol^{-1}, which agrees with the value of 7.9 kJ mol^{-1} (*spd*) obtained from the calculation using a partial geometry optimization.[42] The barrier to internal rotation separating the *cis*- and *trans*-forms of vinyl alcohol is equal to 17.3,[46] 17.6,[42] and 17.9 kJ mol^{-1}.[45]

The internal rotation potential curves for ethenethiol obtained by *ab initio* calculations in various basis sets (STO-3G, 3-21G, 44-31G, and *spd*) were compared with those obtained by molecular mechanics (MM) methods) (Fig. 4).[47,48] The *cis*-conformation is the most stable in all basis sets. The planar *trans*-form is the second stable conformer of ethenethiol in the STO-3G basis while in the 44-31G, 3-21G, and *spd* basis sets, the second stable conformer is a *gauche*-rotamer with a rotational angle about the C_{sp^2}–S bond of 120–135°. The rotational barrier obtained by the MM method (3.8 kJ mol^{-1}) is lower somewhat compared to those determined by other methods (5.9 (44-31G),[47] and 7.9 kJ mol^{-1} (*spd*).[42] The value of the barrier calculated using the STO-3G basis appeared to be significantly higher (16.7 kJ mol^{-1})[46] than those calculated in other basis sets. For this reason the prediction that the *trans*-form is the second stable conformation, most probably, cannot be considered to be correct.

Potential curves for internal rotation about the C_{sp^2}–S bond in ethenethiol obtained from the MW spectroscopy data[49] are presented in Fig. 5 *a*. In the region corresponding to the *trans*-conformation, there are two minima with torsional angles of about 156° (0.87π) and 204° (1.13π) separated by a barrier of about 0.14 kJ mol^{-1}. The ground vibrational state of the *trans*-conformer is above that small barrier. The *cis*-conformer of

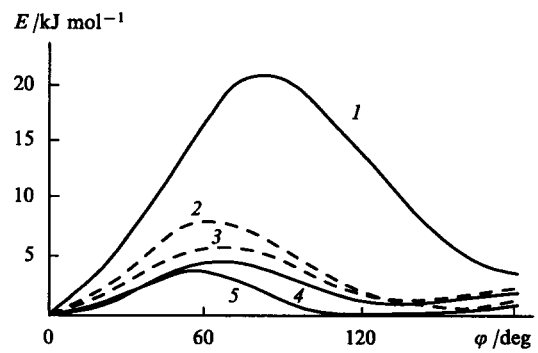


Figure 4. The potential functions of internal rotation for vinylthiol[47] obtained by different methods: (*1*) STO-3G, (*2*) *spd*, (*3*) MM, (*4*) 44-31 G, (*5*) 3-21 G.

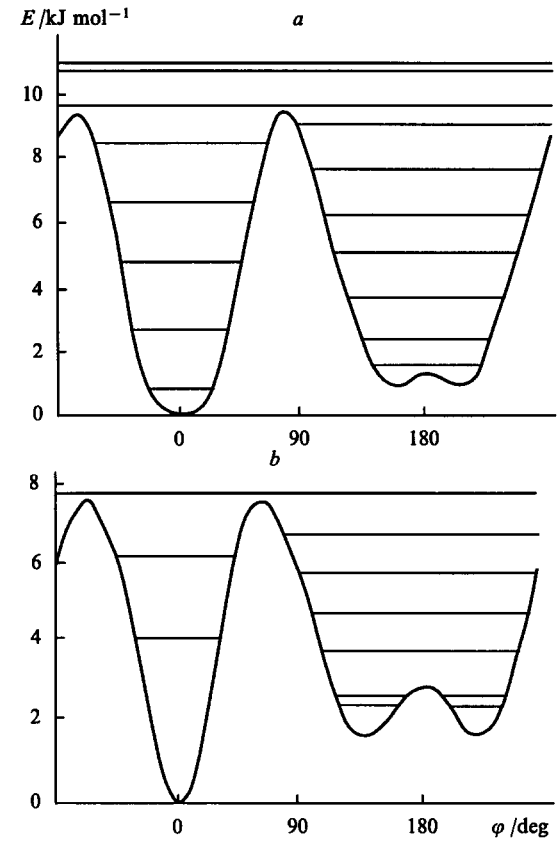


Figure 5. The experimental (*a*) and theoretical (*b*) functions of internal rotation for vinylthiol.[40]

vinylyhiol is 0.6 kJ mol^{-1} more stable, and the rotational barrier separating the *cis*- and *trans*-conformers is equal to 9.5 kJ mol^{-1}. The *ab initio* calculation in the 4-21G basis gave the internal rotation potential and the positions of stationary energy levels corresponding to the planar *cis*- and 'quasi'-*trans*-states as well as to the non-planar *gauche*-form (Fig. 5 *b*).[49]

The potential function for internal rotation about the C_{sp^2}–S bond in ethenethiols XCH=CHSH (X = H, CN, Me, F are *trans* oriented with respect to the sulfur atom) depends substantially on the nature of the substituent (Fig. 6).[49,50] The relative stability of the planar *cis*-conformer increases as the electron acceptor

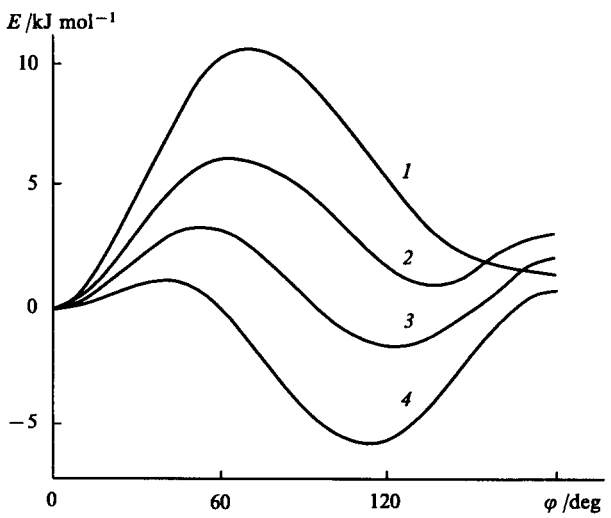


Figure 6. The potential functions of internal rotation for molecules XHC=CHSH.[49] X = H (*1*), CN (*2*), CH_3 (*3*), F (*4*).

properties of the substituent increase; for X = F, the acceptor properties of which are lowered due to the competitive p,π-interaction in the F–C=C system, only the *gauche*-rotamer exists in the system.

2. Alkyl vinyl ethers

The existence of rotational isomerism in vinyl ethers was first established from Raman and IR spectroscopy[1,52–59] and was confirmed later by studies of ultrasonic relaxation[51] and microwave spectroscopy.[60] From the very beginning, there were different opinions about the number and structure of stable conformers. The study of the temperature dependence of absorbance of triplet components in the range of double bond stretching vibrations allowed one to conclude[56] that the most stable conformation is characterised by two bands (1613 and 1650 cm^{-1}) whereas the less stable form is characterised by one maximum at 1642 cm^{-1}. The appearance of the third band in the 1600 cm^{-1} region (with the highest frequency) in the vibrational spectra of alkyl vinyl ethers is explained by Fermi resonance between the $\nu(C=C)$ and $\omega(CH_2=)$ vibrations.[61] The temperature dependences of integral intensities of the components of the same triplet in the Raman spectrum of n-butyl vinyl ether allowed one to assign each of the three components to a particular rotamer and to calculate the difference between their energies.[62] Assuming the existence of three possible conformations (two planar, *cis*- and *trans*-, and one non-planar, *gauche*-), one could calculate the frequencies and eigenvectors of the normal modes for methyl vinyl ether, which were in a satisfactory agreement with experimental data.[58] At the same time, the relaxational behaviour of methyl, ethyl, and 2-chloroethyl vinyl ethers indicates that there is an equilibrium between the planar conformations (*cis*- and *trans*-).[51] Vibrational spectra of methyl vinyl ether and its deuterio-isotopomers have been studied and the band assignment according to symmetry and eigen vectors has been proposed.[63] It is noted that this molecule exists at room temperature in the planar *cis*-form, and at lower temperature it exists in the planar *trans*-form (or nearly *trans*-), which follows from the appearance of a number of new bands in the spectra. From the analysis of Raman and IR spectra of methyl vinyl ether it also follows that the *s-trans*-conformation is less stable.[64–66] The same conclusions have been derived from the analysis of PE spectra of alkyl vinyl ethers[67–69] with normal alkyl substutuents.

Analysis of the rotational structure of $CH_2=$ out-of-plane bending modes (820 cm^{-1}) has led to a conclusion[61,70,71] that the most stable conformation in methyl and ethyl vinyl ethers has a sickle-like (*cis*-) form. It was suggested[61,70] that the other conformation should have a non-planar structure. These conclusions[61,70,71] have received additional and independent support from the analysis of MW,[60] Raman and IR[72–74] spectra of methyl vinyl ether. The study of vibrational spectra of methyl vinyl ether in the gas phase allowed the identification of a less preferred 'skew' rotamer with a torsional angle of 144°.[72]

The IR spectra of vinyl ethers are very useful in determining the conformer ratio. An analysis of extensive experimental data and literature assignments allowed the major bands of the vinyloxy group to be ascribed to particular conformations. For example, the following maxima correspond to the planar conformer: a low-frequency component of a band in the region of ~820 cm^{-1} [$\omega(CH_2=)$];[61,70,75,76] a high-frequency component of a band at ~960 cm^{-1} [$\omega(CH=)$];[61,70,76] a very strong broad band around 1200 cm^{-1} [$\nu(C-O)$];[56,61,70] a narrow band of medium intensity at 1320 cm^{-1} [$\delta(CH=)$];[61,70] a low-frequency component of a triplet in the 1600 cm^{-1} region (usually, ~1620 cm^{-1}) [$\nu(C=C)$].[56,61,62,70] The following peaks correspond to the non-planar conformer: a high-frequency shoulder on the band at 820 cm^{-1},[61,70,75,76] a low-frequency component of a doublet in the region of 950 cm^{-1} [$\omega(CH=)$];[66] weak peaks in the region of 1150–1050 cm^{-1} [$\nu(C-O)$] (for example, 1138 cm^{-1} in methyl vinyl ether[64] and 1143, 1100, 1081, 1048 cm^{-1} in ethyl vinyl ether[70]); the middle component of a triplet in the range of 1640 cm^{-1} [$\nu(C=C)$].[56,61,62,70]

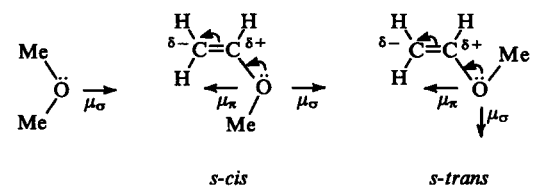
The aim of the studies[77–79] was to elucidate, using the IR spectra of alkyl vinyl ethers, the influence of the structure of alkyl substituent on the relative intensities of bands belonging to different conformations without going into details of their spatial structure. A comparative analysis of IR spectra of ethyl vinyl ether indicates that the conformation ratio depends very strongly on the degree of branching of the substituent at the α-carbon atom.[77] For methyl and alkyl vinyl ethers with normal substituents the planar conformers dominate, whereas the relative intensities of the bands of the planar conformer decrease abruptly with an increase in branching in the substituent up to the disappearance of some of them; simultaneously, the bands of the non-planar conformer appear and their intensiies increase. *tert*-Butyl and *tert*-pentyl vinyl ethers exist virtually as one non-planar conformer. Indeed, all the vibrational bands of the planar conformer in the spectra of these ethers decrease in intensity or disappear. This is most clearly illustrated in the 1600 cm^{-1} region, where only one high-frequency component of the very strong multiplet remains, which belongs to the non-planar conformation.

The possibility to apply *ab initio* calculations to analyse the vibrational spectra of methyl vinyl ether has been shown.[80] A theoretical force field has been composed and corrected by scaling factors, which have been either transferred from simpler molecules $CH_2=CHF$ and Me_2O or selected by calculation of the rotation about the $C_{sp^2}-O$ bond. The method of stepwise determination of scaling factors gave a satisfactory agreement between the calculated and experimental data.

The molecular structure of methyl vinyl ether was also studied by electron diffraction.[42,81] Along with the problem of the determination of the molecular geometry of the major rotamer, an attempt was made to solve the problem of the existence of a second less-preferable form. In an earlier paper[81], the *gauche*-conformer with an angle between the C=C–O and C–O–C planes between 80–110° has been favoured. Later, the results of *ab initio* calculations referring to the planar *s-trans*-structure of the second stable rotamer have convinced the authors to reconsider their experimental data and to conclude that these data do not contradict the supposition about the planar structure of the second rotamer in methyl vinyl ether.[42]

Important results concerning the spatial and electronic structure of alkyl vinyl ethers were obtained from the study of their dipole moments.[1] For alkyl vinyl ethers $CH_2=CHOR$, unprecedented dependences of dipole moments on the structure of the alkyl substituent[82] and temperature[83] were established. The reason for these features is a close relationship between p,π-interaction and conformational isomerism. Mere consideration of the dipole moment vectors for dimethyl and methyl vinyl ethers leads to the conclusion that the dipole moment of the latter depends on the torsional angle provided that the p,π-interaction is accompanied by polarisation of the double bond (Scheme 1):

Scheme 1



s-cis *s-trans*

The existence of this polarisation follows from the consideration of the dipole moment values of alkyl vinyl ethers with normal and branched alkyl substituents (Table 1).[84–86]

In methyl vinyl ether, which exists preferentially as the *s-cis*-conformer,[85] the directions of π and σ constituents are opposite. Therefore, in this case, it is worth estimating the π-constituent as the difference (0.36 D) between the moments of dimethyl ether and methyl vinyl ether (as in Ref. 87). Of course, one should bear

Table 1. Dipole moments of vinyl and dialkyl ethers.

Ether	μ /D	Ref.
$CH_2=CHOMe$	1.0	84
	1.1	85
$CH_2=CHOEt$	1.19	84
$CH_2=CHOPr^n$	1.19	84
$CH_2=CHOPr^i$	1.47	84
$CH_2=CHOBu^n$	1.20	84
	1.25	85
$CH_2=CHOBu^i$	1.14	84
	1.20	85
$CH_2=CHOBu^t$	1.81	84
$CH_2=CHOPent^n$	1.22	84
$CH_2=CHOPent^t$	1.84	84
$(CH_2=CH)_2O$	1.10	84
	1.06	85
Me_2O	1.31	85
	1.25	86
Et_2O	1.27	85
	1.22	86
$(Pr^n)_2O$	1.13	85
$EtOBu^t$	1.29	84

in mind that the π-moment value obtained in this way includes the induced π-moment and the contribution due to the difference in the moments of the $C_{sp^2}-O$ and $C_{sp^3}-O$ bonds. However, estimations of dipole moments of other conformations by the addition of π and σ vectors [87] are erroneous in principle, because they do not take into account the changes in the degree of p,π-interaction (and therefore, the π-constituent) due to violation of coplanarity. For a non-planar *gauche*-conformation (where the angle is 90°) the π-constituent should be absent or, at least, should be much less than that for the planar conformation. The consideration of the molecular model shows that for such a conformation, the σ-moment vector forms an angle of $\sim 55°$ with the double bond plane, and the directions of its projection to this plane and the $C_{sp^2}-O$ bond coincide.

A significant difference between the dipole moments of conformers of alkyl vinyl ethers could be rationalised in terms of electronegativity of a substituent R.[88] The validity of this supposition follows from a close linear dependence of the dipole moment on inductive (σ^*) and steric (E_s) constants of the substituent R. The study of temperature dependence of dipole moments [83] allowed one to choose between the inductive and conformational nature of the difference in dipole moments in the series of alkyl vinyl ethers in favour of the latter.

The dielectric behaviour of alkyl vinyl ethers with non-branched substituents was shown to differ substantially from that of vinyl ethers with bulky branched substituents. In the former case, the dipole moment increases markedly with temperature, and in the latter case it decreases. For methyl vinyl ether, the dipole moments measured in a broad temperature interval are in line with the concept about the equilibrium of two rotamers in octane and benzene solutions.[83,89] It was concluded [83] that a decrease in the dipole moments of alkyl vinyl ethers with Pr^i, Bu^t, $Pent^t$ substituents as temperature increases is caused, not by an increase in the population of the less polar form, but rather by violation of coplanarity of the molecular fragment $CH_2=CHO$ during torsional vibrations. It is evident that an increase in the population of excited torsional vibrational states can affect significantly the experimental dipole moment only if the torsional mode has a sufficiently large amplitude. A W-shaped potential curve of internal rotation has been proposed,[83] which can explain qualitatively the dielectric behaviour of all the alkyl vinyl ethers studied.

In addition to the experimental studies of rotational isomerism in vinyl ethers discussed, numerous publications concerning theoretical considerations [42,45,63,64,80,90–101] indicate that the planar *cis*-conformation is the most favourable in energy, while the structure of a second less stable conformer is still disputable. The potential curve of internal rotation for methyl vinyl ether was obtained in the CNDO/2 approximation; its shape depends significantly on the COC angle.[90,91] According to these calculations, the second less stable conformer has a non-planar *gauche*-structure. It is also possible that coplanarity in the *trans*-form is violated.[42,92]

One of the first *ab initio* calculations [94] yielded the potential curve of internal rotation for methyl vinyl ether. The minima of the potential function correspond to torsional angles of 0° (*s-cis*-form) and 180° (*s-trans*-form). The conformer energy difference was calculated as 2.2 kJ mol^{-1}.[94] The potential curve of internal rotation for methyl vinyl ether was calculated using the STO-3G and 4-31G basis sets.[95,96] The potential curve obtained is shown in Fig. 7.[96] The geometry optimization was performed in the STO-3G basis. The calculations predict two stable conformations for methyl vinyl ether: planar *cis*- and planar *trans*-. The conformer energy differences of 4.02 kJ mol^{-1} [95] and 4.2 kJ mol^{-1},[96] calculated in the STO-3G basis, are in satisfactory agreement with the experimental value (4.8 kJ mol^{-1}) obtained by gas electronography;[42] the values of 10.3 kJ mol^{-1} [95] and 9.6 kJ mol^{-1} [96] calculated in the 4-31G basis appeared to be twice as high.

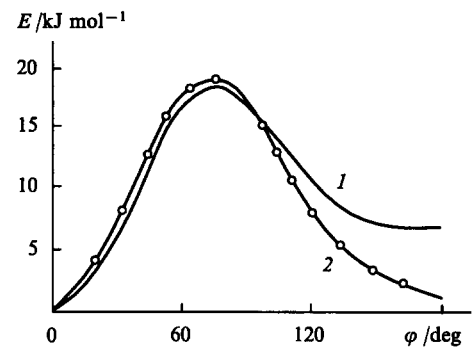


Figure 7. The potential function of internal rotation about the $C_{sp^2}-O$ bond in vinyl methyl ether.[96]
The method of calculation: (*1*) 4-31 G, (*2*) STO-3G.

The potential as a function of internal rotation for methyl vinyl ether was calculated in the 6-31G and 6-31G* basis sets with full geometry optimization.[97] A region in the potential curve with two flattened minima (torsional angle CCOC is 156.7–159.4°) and a barrier between them corresponds to a less favourable conformer (Fig. 8). The stationary state energies are located above the barrier; they are associated with the vibration of the Me group with large amplitude relative to the equilibrium position

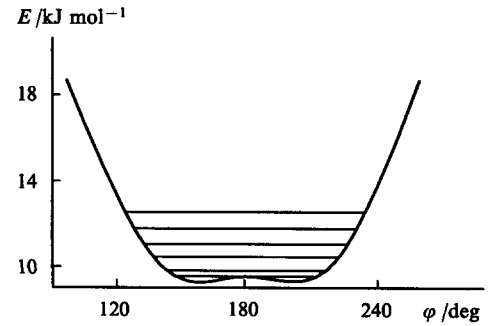


Figure 8. The potential function of internal rotation for vinyl methyl ether in the region of location of the *trans*-conformer and the positions of the steady energy levels (the calculation using the 6-31 G* basis set).[97]

corresponding to the planar *trans*-form. The energy difference between the lowest energy levels of the *cis*- and *trans*-forms, 8.3 kJ mol^{-1} (6-31G) and 9.9 kJ mol^{-1} (6-31G*), is in agreement with the experimental value (7.1 kJ mol^{-1}) obtained for the gas phase by IR spectroscopy.[74]

An *ab initio* calculation in the 4-21G basis with full geometry optimisation gave comprehensive data on the structure of three conformers, *s-cis*- (0°), *s-trans*- (180°), and skew (168°).[98] The population of the skew conformer is 1–5%, the energy difference between *s-cis*- and *s-trans*-rotamers is equal to 12.4 kJ mol^{-1}. However, according to other *ab initio* calculations for methyl vinyl ether,[45] torsional angles of 0° (*s-cis*-) and 150° (*gauche*-) correspond to the stable states, the first being more favourable by 7.9–8.8 kJ mol^{-1}.

Hence, most of the studies on rotational isomerism in vinyl ethers show that these ethers exist as two stable conformers. One of them is planar (*cis*-), the other is characterised by a relative motion with large amplitude of the molecular fragments and an effective non-coplanarity, which depends on the structure of the vinyl substituent.

3. Allenyl ethers

Allenyl ethers ($CH_2=C=CHOR$) are close analogues of vinyl ethers. Their unsaturated fragment is represented by two orthogonal π-systems. The spatial structure of allenyl methyl ether has been investigated by various physico-chemical methods.[102–112] The interest in allenyl ethers is easily understandable because they are both valuable initial substances for organic syntheses and convenient models for investigations of the relationship of, and mutual influence between, conformational isomerism and p,π-interaction. Experimental data obtained by gas electronography indicate that at room temperature allenyl methyl ether exists only in the planar *cis*-conformation; the second conformer was not detected.[102] This conclusion was confirmed by an analysis of coupling constants in the ^1H NMR spectrum of allenyl methyl ether.[103,104]

According to these data, alkyl allenyl ethers with non-branched substituents possess preferential planar *cis*-conformation, and homologues with branched substituents exist essentially in the planar *trans*-conformation. Conformational analysis of vinyl and phenyl allenyl ethers[104] allowed one to conclude that the planar *trans*-conformation predominated and the content of the *cis*-conformer was ~10%.

The molecular structure of allenyl methyl ether was also studied by MW spectroscopy.[105] The overall dipole moment was determined in the ground state ($\mu = 0.96$D). The barrier to internal rotation of the methyl group was obtained from the splitting of transitions in the excited state (V_3 = 11.86 kJ mol^{-1}). The values obtained were assigned to the planar *cis*-form. PE spectroscopic data and semiempirical MNDO/3 calculations showed that allenyl methyl ether exists as two conformers *s-cis*- and *s-trans*-, the former dominating.[106] Raman and IR spectra of allenyl methyl ether were studied using *ab initio* calculations within the 3-21G and 6-31G* basis sets. From the data obtained it was concluded that allenyl methyl ether has two conformers, viz, the planar *cis*-form and the non-planar *gauche*-form with a torsional angle of 140°. The energy difference of 11.2 kJ mol^{-1} for conformers was calculated from the temperature dependence of intensities of the bands sensitive to conformations. The potential curve of internal rotation for allenyl methyl ether was obtained[113] (Fig. 9). In the range of the second stable conformer, there are two small minima separated by a barrier of 1.42 kJ mol^{-1}, which correspond to enantiomeric forms. Large amplitude intramolecular motion of fragments of the molecule relative to the planar *trans*-form corresponds to the stationary energy states arranged above the barrier.

Rotational isomerism and the breakdown of local C_{3v} symmetry of the methyl group have been studied using vibrational spectra [IR (gas, liquid), Raman (liquid)] of allenyl methyl ether and its deuterio-isotopomer, $CH_2=C=CHOCD_3$.[114] Specific

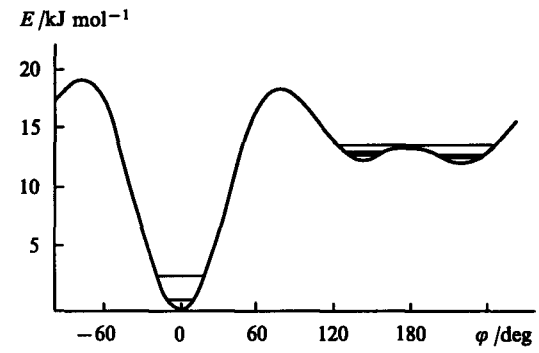


Figure 9. The potential function of internal rotation for allenyl methyl ether.[113]

interactions in the fragments $CH_2=C=$, $=CHO$ and COC can manifest themselves in vibrational spectra due to the orthogonal arrangement of the π-systems in allenyl methyl ether. It is difficult to estimate the coupling of these vibrations directly from experimental spectra. It became possible only by comparing experimental results and *ab initio* calculations.

The calculation of the equilibrium geometry and the force field was carried out by the gradient method using the 4-21G basis assuming the *cis*-conformer to be the most stable.[114] Scaling factors were transferred from simpler dimethyl ether and allene molecules, and for the rotation about the $C_{sp^2}-O$ bond these were selected from calculations. The scaling factors were determined by fragments, which gave a satisfactory agreement of calculated and experimental frequencies.[114]

Similar to Fermi resonance between $\nu_s(CH_3)$ and $2\delta_s(CH_3)$, there is a resonance between the $\nu_{as}(CH_3)$ and $2\,\delta_{as}(CH_3)$ modes. Comparative analysis of a splitting value of the degenerate $\nu_{as}(CH_3)$ mode of C_{3v} symmetry and the frequency shift for this mode upon isotopic substitution indicates that asymmetry of the C–H bond lengths in the methyl group of allenyl methyl ether is the same as in methyl vinyl ether.[115,116]

The antisymmetric stretching mode of the allenyl fragment $\nu_{as}(C=C=C)$ at 1960 cm^{-1} is not coupled and localised in double bonds, while the $\nu_s(C=C=C)$ mode at 1054 cm^{-1} is coupled with the vibrations of the COC and CH_3 groups. The frequencies of C=C=C bending modes occur in the low-frequency range at 270 and 170 cm^{-1}; the bending mode of the COC group contributes largely to the band at 170 cm^{-1}. The band responsible for the torsional motion relative to the CCC axis (612 cm^{-1}) is intense in the Raman spectrum and weak in the IR spectrum. This is explained by substantial changes in the molecular polarisability and a weak dependence of the dipole moment on the torsional motion of the allenyl fragment. Apparently, the perturbation introduced by the orthogonal π-system to the interaction of the lone pair electron with π-electrons of the double bond of the $=C=C(H)O$ fragment does not influence significantly the effects of electron density delocalisation.

Analysis of experimental spectra of allenyl methyl ether and its deuterio-isotopomer allowed one to identify the bands corresponding to the stretching modes of the CH and CH_2 groups. A band of medium intensity in the IR spectrum and a strong line in the Raman spectrum with a frequency of 3046 cm^{-1} were assigned to the stretching mode of the C–H bond.[114] It is identical in frequency and eigenvector with that of the analogous group in methyl vinyl ether.

The feature distinguishing allenyl methyl ether from methyl vinyl ether is an anomalous intensity ratio of the vibrational bands $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$. The intensity of $\nu_{as}(CH_2)$ in methyl vinyl ether is significantly higher than that of $\nu_s(CH_2)$, while, according to the calculation for allenyl methyl ether, confirmed by experimental results, the derivative of the dipole moment with respect to the normal coordinate is by an order of magnitude larger for

$\nu_s(CH_2)$ than for $\nu_{as}(CH_2)$. A similar picture is observed in the spectra of other molecules containing the allenyl group,[117] which might be rationalised in terms of peculiar features of the electronic structure of the allene framework.

In the IR spectrum of allenyl methyl ether in the gas phase, the A-type band with a frequency of 1430 cm^{-1} belongs to the bending mode $\delta(CH_2)$.[114] This assignment differs from the assignment[113] of this band to $\delta(CH_3)$, which has been made without analysis of the rotational structure of the deuterio-isotopomer. A low intensity δ_{CH2} bending mode at 1015 cm^{-1} manifests itself as a C-type band in the IR spectrum. According to calculation, it contains a contribution from a wagging mode, which features a departure of the α-hydrogen atom from the plane of the C=C–O fragment.[114]

Analysis of rotational contours in the IR spectrum of allenyl methyl ether allowed one to assign the bands in the 850–920 cm^{-1} range since in this range, the stretching COC mode gives rise to a band of the A type at 918 cm^{-1}, which is coupled with the wagging modes of the CH_2 group (895 cm^{-1}) and the bending mode of the allene framework.

In order to investigate rotational isomerism in allenyl methyl ether and in its deuterio-isotopomer, their IR spectra in various solvents (CCl_4, C_7H_{16}, C_4H_9Br, MeCN) were measured over a wide temperature range.[114] A normal coordinate analysis was carried out for various orientations of the COC and CCO fragments specified by the COCC torsional angle. The bands in the vibrational spectrum sensitive to conformations were identified by calculation. For allenyl methyl ether in the condensed state, two weak bands at 572 cm^{-1} (Raman) and 960 cm^{-1} (IR) were revealed, which, probably, belong to the modes of a second conformer differing from the *cis*-conformer in population and geometry. No features of the second conformer were detected in the gas-phase spectra. The splitting of the $\nu_s(C=C=C)$ and $\nu_{as}(C=C=C)$ bands cannot originate from conformational changes because it remains in the spectra of the gas phase, condensed and solid states. The bands observed on the high-frequency side of $\nu_{as}(C=C=C)$ and on the low-frequency side of $\nu_s(C=C=C)$ seem to belong to a series of so-called 'hot' transitions.

It follows from the above account that the planar *cis*-conformer with the methyl group of distorted C_{3v} local symmetry is the most preferable in energy for allenyl methyl ether. The splitting value of the degenerate $\nu_{as}CH_3$ mode of C_{3v} symmetry and the position of the low-frequency component of the Fermi resonance lead to the conclusion that the structures of methyl vinyl and allenyl methyl ethers are similar.

4. Alkyl vinyl sulfides

The molecular structure of the sulfur analogue of methyl vinyl ether, methyl vinyl sulfide, has been studied by both experimental and theoretical methods. The conclusions made from these investigations concerning the nature of possible stable conformers and their energy characteristics do not always coincide.[42,118–124] Thus the data of MW[120] and PE spectroscopy[125] indicate that methyl vinyl sulfide exists at room temperature only in the *cis*-conformation, whereas electronography shows that methyl vinyl sulfide exists as two conformers, *cis*- and *gauche*-, in the ratio of 33:66[121] and 38:62.[42] The content of the *gauche*-conformer was estimated as 11%–21%.[122] The electronographic data reported[42,121,122] and the MW and Raman spectra of methyl vinyl sulfide were analysed[123] using a static (considering small amplitude modes) and a dynamic (including large amplitude modes) models. The differences observed were explained by the fact that the use of the static model is incorrect because this model cannot be applied to high-temperature measurements as well as in the cases when the barrier separating the conformers is relatively high as is the case for methyl vinyl sulfide.

Dipole moments of alkyl vinyl sulfides appeared to be very much similar to those of alkyl vinyl ethers. In the series $CH_2=CHSR$ (R = Me, Et, Pr^i, Bu^t) a significant increase in dipole moments is observed with an increase in branching of alkyl substituent.[126]

R	Me	Et	Pr^n	Pr^i	Bu^n
μ, D	1.35	1.47	1.44	1.58	1.41
R	Bu^i	Bu^s	Bu^t	$Pent^t$	cyclo-C_6H_{11}
μ, D	1.40	1.59	1.69	1.70	1.60

However, the difference in dipole moments of *tert*-butyl vinyl sulfide and methyl vinyl sulfide at 298 K is only 0.35 D, which is more than twice as low as that of *tert*-butyl vinyl and methyl vinyl ethers (0.74 D). A smaller dipole moment value for methyl vinyl sulfide than that of the saturated analogue, ethyl methyl sulfide (1.60 D), as in methyl vinyl ether, indicates the same direction of polarization due to p,π-conjugation.

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 variation range is substantially narrower.[83] For alkyl vinyl sulfides with normal substituents, the temperature dependence originates from a change in the populations of *s-cis*- and *gauche*-conformations; for branched substituents, it is due to a change in the vibrational level populations of the *gauche*- conformation, i.e. the temperature dependence is determined by a different degree of deviation of the SR group from the equilibrium position as the planar form is approached.

Methyl vinyl sulfide was intensively studied by IR spectroscopy.[3,5,124,127–131] A detailed investigation of IR-active vibrations of the molecule has been given.[118,124,127] The bands sensitive to conformational changes were revealed. The results of these studies agree except for the assignment of the band at 1430 cm^{-1}, which has earlier been assigned to to the bending mode of the vinyl groups ($CH_2=$).[118] In more recent studies,[124,127] it was assigned to the out-of-plane bending vibration of the methyl group, and the $\delta(CH_2=)$ mode was associated with the bands in the range of 1360–1390 cm^{-1}.

Out-of-plane bending ($CH_2=$) (860–880 cm^{-1}) and C–S stretching (600–750 cm^{-1}) modes are sensitive to rotational isomerism and give rise to several bands, the number and intensity of which vary with the change in the structure of the alkyl substituent at the sulfur atom.[124,127,128] The band at 860 cm^{-1} was assigned[124] to the planar *cis*-conformer, and the higher-frequency band (~880 cm^{-1}), to the *gauche*-rotamer. A trend of increasing frequency of $\omega(CH_2=)$ (860 cm^{-1}) with increase in the electron-acceptor properties of the substituent was noted[131] in the spectra of substituted vinyl sulfides. Bearing in mind the IR spectra of vinyl ethers,[77–79] one can relate these changes to the increase in the population of the less conjugated non-planar conformer due to the shift of the lone electron pair of the sulfur atom toward the acceptor.

It is noticed[128] that the band at 678 cm^{-1} [$\nu_s(C-S)$], which dominates in the spectra of alkyl vinyl sulfides with non-branched substituents, becomes less intense in the spectra of *sec*-alkyl vinyl sulfides and is absent in the spectra of *tert*-alkyl vinyl sulfides. The latter have the only band at 730 cm^{-1} assigned to *gauche*-rotamer modes.[128] A comparison of relative intensities of the bands in the ranges mentioned shows that vinyl sulfides are irregular as regards to conformation, and the proportion of the dominating stable *cis*-rotamer decreases with an increase in substituent branching. *tert*-Alkyl vinyl sulfides exist virtually completely in the *gauche*-conformation.

The band due to the double-bond stretching mode exhibits a doublet with absorption maxima in the range of 1575–1585 cm^{-1} (Fig. 10).[129] As the alkyl substituent branching increases, the intensity of the low-frequency component decreases and that of the high-frequency component increases. In the spectrum of *tert*-butyl vinyl sulfide, the low-frequency band is absent. A similar picture is observed in the IR spectra of vinyl ethers.[1,77] Hence, IR spectra of alkyl vinyl sulfides adequately reflect changes in the conformer ratio depending on the substituent structure.

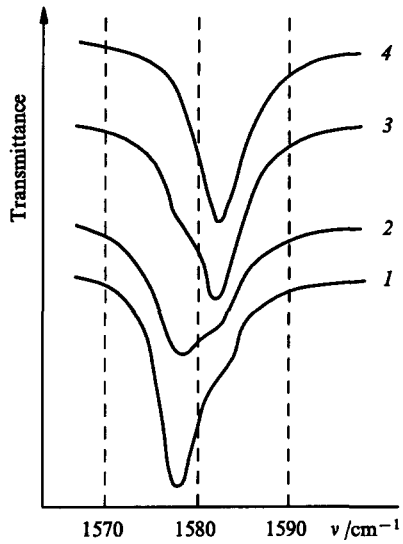


Figure 10. The band contour of the stretching vibration of the double bond in the IR spectra of compounds $CH_2=CHSAlk$.[129]
Alk = Me (*1*), Et (*2*), Pr^i (*3*), Bu^i (*4*).

IR spectroscopic data and quantum mechanical consideration of rotational isomerism gave the potential energy curve for internal rotation in methyl vinyl sulfide.[129] In the spectrum the doublet band of the double bond stretching mode has maxima at 1577 and 1581 cm^{-1}. The relative intensity of the low-frequency component decreases and that of the high-frequency component increases with temperature. The effect of alkyl substituent branching in a series of alkyl vinyl sulfides as well as the existence of a temperature dependence of relative intensities of the doublet components permitted their assignment to different conformations of the vinylthio group.[129] Since the intensity of the C=C bond stretching mode due to the substituent resonance effect is independent of the inductive effect influence and since the σ constants are equal in the substituent series AlkS,[130] the extinction for methyl vinyl sulfide in the *gauche*-conformation may be assumed to be equal to that for *tert*-butyl vinyl sulfide.

The temperature dependence of the ν(C=C) band contour has been analysed. The relationship between $\ln(c_{cis}/c_{gouche})$, obtained using the temperature dependence of *tert*-butyl vinyl sulfide, and 1/T gives the following enthalpy and entropy difference for the rotamers: $\Delta H = 6.1$ kJ mol^{-1}, $\Delta S = -1.74$ J K^{-1} mol^{-1}. The energy difference obtained for methyl vinyl sulfide conformers is close to those found earlier (kJ mol^{-1}): 9.63,[132] 5.86,[124] 7.95,[123] 3.3–3.7,[122] 7.9.[133]

Based on the quantum model of conformational isomerism, the internal rotation potential curve parameters were selected so as to correlate the number and energies of all the stationary states with the observed temperature behaviour of the conformer ratio (Fig. 11).[129] The stationary energy spectrum of the molecular rotation is found from the solution of the Schro:dinger equation:[129]

$$\left[-\frac{\hbar^2}{2J}\frac{\partial^2}{\partial\varphi^2}+U(\varphi)\right]\phi(\varphi)=\epsilon\phi(\varphi)$$

with the potential $U(\varphi)$ in the form:

$$U(\varphi)=U_n(\varphi)+\frac{1}{2}\sum_{k=1}^{3}V_k(1-\cos k\varphi),$$

where $U_n(\varphi)$ is the energy of steric hindrance, V_k is the characteristic internal rotation barrier about the $C_{sp^2}-S$ bond, J is the reducted moment of inertia of the molecule, and φ is the rotation angle.

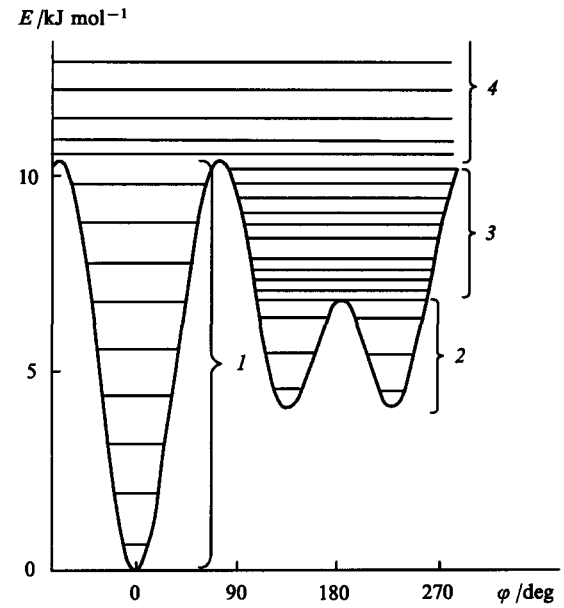


Figure 11. The potential function of internal rotation for vinyl methyl sulfide and the positions of the stationary energy levels.
States: *cis* (*1*), *gauche* (*2*), 'quasi'-*trans* (*3*), and free rotation (*4*).[129]

As is seen from Fig. 11, the methyl vinyl sulfide molecule is an ensemble of four types of rotamers corresponding to four types of stationary states, namely, planar *cis*-states (*1*), *gauche*-states with rotation angles about the $C_{sp^2}-S$ bond of 132±3° (*2*), the states above the *trans*-barrier ('quasi'-*trans*-states) associated with a large amplitude intramolecular mode having the equilibrium position in the planar *trans*-form (*3*), and the states of free rotation (*4*). The bands of the *gauche*- and 'quasi'-*trans*-states seem to differ somewhat in frequency, therefore, the width of the band at 1581 cm^{-1} is, on the average, 1.35 times larger than that of the band at 1571 cm^{-1}. A maximum in the potential curve corresponding to the planar *s-trans*-conformation is typical of the methyl vinyl sulfide molecule. The barrier separating the *gauche*-forms is equal to 2.5–2.9 kJ mol^{-1}.[129] There are two or three energy levels in the potential well of the *gauche*-conformer. The energy difference between lower *gauche*- and *cis*-levels (3.8–4.2 kJ mol^{-1}) differ substantially from the formal enthalpy difference of rotamers obtained on the basis of the static model of rotational isomerism (6.1 kJ mol^{-1}). The barrier to *cis-gauche*-transition is equal to 9.8–10.6 kJ mol^{-1}.

Optimal parameters of the potential V_k were obtained,[129] which correspond to the minimum of the fitness criterion F

$$F=\left\{\frac{1}{K}\sum_{i=1}^{2}\left[\ln\left(\frac{c_{cis}}{c_{gouche}}\right)_{calc}-\ln\left(\frac{c_{cis}}{c_{gouche}}\right)_{exp}\right]^2\right\}^{1/2}.$$

The value of $V_1 = 2.7\pm0.1$ kJ mol^{-1} means that the energy of the interaction between the lone electron pair on the sulfur atom and π-electrons of the double bond differs for planar *cis*- and *trans*-conformations. The interaction is more effective for the *cis*-form than that for the *trans*-rotamer. A value of $V_2 = 7.9\pm0.8$ kJ mol^{-1} is an average estimate of the interaction energy. The value of $V_3 = 6.3\pm0.4$ kJ mol^{-1} appeared to be unexpectedly high, probably, due to hybridisation intermediate between sp^2- and sp^3-hybridisations of the sulfur valence electrons.

The potential function for methyl vinyl sulfide (Fig. 11)[129] is qualitatively similar to that of ethenethiol (Fig. 5).[40] The barriers to *cis–gauche*-transitions are practically the same, while the barrier separating two *gauche*-forms is significantly higher for methyl vinyl sulfide (2.9 kJ mol^{-1}) than that for ethenethiol (0.14 kJ mol^{-1}). As a result, there are several (2 or 3) energy

levels in the potential well for the *gauche*-conformer of methyl vinyl sulfide.

The spatial structure of methyl vinyl sulfide was the subject of semiempirical and *ab initio* calculations. Semiempirical calculations were used for the analysis of the correlation between the structure of sulfur compounds and their various experimental characteristics such as electronic and PE spectra, and dipole moments. An analysis of publications[41] of this type leads to the conclusion that the interaction between the lone electron pair on the sulfur atom and the double bond π-electrons should be taken into account to interpret practically all the experimental data. CNDO/2 calculations of methyl vinyl and divinyl ethers and sulfides have been performed in *sp* and *spd* approximations in order to compare the electronic transfer effect through the hetero atom.[134] It was concluded that the transfer is more effective in the case of the sulfur atom due to $p\pi - d\pi$ interaction. Vacant orbitals were taken into consideration in the calculation though the question of whether it is necessary to include these into the basis set is still being debated.[135, 136] For vinyl sulfides, the passage from the *sp* to the *spd* approximation leads to a basically different conclusion on the nature of the sulfur atom: the sulfur atom is a π-donor within the *sp* basis, while it becomes a π-acceptor within the *spd* basis.[134] The CNDO/2 calculation in the *sp* approximation yielded the energies of *cis*- and *trans*-conformers for β-substituted methyl vinyl sulfides (XCH=CHSMe, X = Me, OMe, SMe)[137] with a fixed geometry.[121] It was shown that the *cis*-rotamer is more favourable in energy. The energy differences between conformers are as follows: 2.8, −3.6, and 2.4 kJ mol^{-1} for X = Me, OMe, and SMe, respectively. The corresponding enthalpy differences obtained from the equilibrium constants are 1.9 kJ mol^{-1}, 9.9 kJ mol^{-1}, and 2.8 kJ mol^{-1}.[137] An analysis of the interactions in XCH=CHX (X = OMe, SMe) has been carried out by the CNDO/2 method.[138] For these systems the *trans*-conformer appeared to be more favourable than *cis*-conformer. The calculated conformer energy differences are: 20.4 and 1.7 kJ mol^{-1} for X = SMe and OMe, respectively.

Considerable progress has been made in the analysis of conformational transitions in α,β-unsaturated sulfides using *ab initio* calculations. The efficiency of these calculations depends upon the approximation used, upon the type and set of the basis functions. *ab initio* Calculations are used for the analysis of the role of *nd*-AOs in the formation of chemical bonds by the sulfur atom in different valence states. It was concluded[135] that a meaningful, in quantitative terms, population of the 3*d*-AO is observed only for compounds with an increased coordination number of sulfur. The authors[135] believe that the 3*d*-AOs should be always taken into account as polarisation corrections in *ab initio* calculations; for compounds with a higher valence, they might play the role of real orbitals. The solution of a conformational problem requires that sulfur 3*d*-AOs should also be included in the basis for the correct representation of the wave function geometry.

Potential functions for internal rotation about the $C_{sp^2}-S$ bond for vinyl sulfides have been obtained by *ab initio* calculations.[47, 48, 92, 123, 139] The internal rotation potential for methyl vinyl sulfide was shown to depend strongly on the basis set used (Fig. 12).[47, 48] The *cis*-conformation was found to be the more stable regardless of the basis used, whereas the next conformation might be either *trans*- (STO-3G) or *gauche*-form with different values of the CCSC torsional angle (3-21G, 44-31G). The potential obtained by the MM method is analogous to that calculated within the 44-31G basis.[48] For a long time, the preference of the *cis*-conformer in methyl vinyl sulfide and in methyl vinyl ether was considered as an experimental fact. Later in theoretical studies,[95, 140, 141] it was suggested that the preference can result from the interaction between the σ-orbitals of two methyl hydrogen atoms and π-orbitals of the double bond. In the range of *trans*-conformation in the potential curve of methyl vinyl sulfide, there is a small maximum separating two *gauche*-forms (Fig. 12).[47] The barrier height is equal to 0.84 kJ mol^{-1}, which is

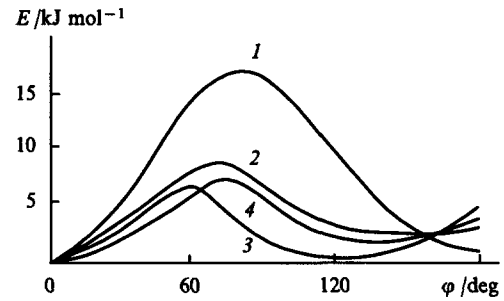


Figure 12. The potential functions of internal rotation about the C_{sp^2}-S bond in vinyl methyl sulfide.[48]
The method of calculation: (*1*) STO-3G, (*2*) 44-31 G, (*3*) 3-21 G, (*4*) MM.

insufficient for the existence of a stationary state of the *gauche*-type.

The energy differences calculated for methyl vinyl sulfide conformers, 2.9 kJ mol^{-1} (44-31G),[47] 0.8 kJ mol^{-1} (3-21G),[48] and 0.8 kJ mol^{-1} (MM),[48] are markedly lower than the experimental values obtained from the IR spectra (4.9 kJ mol^{-1} and 6.7 kJ mol^{-1}).[124, 129] A higher value (9.6 kJ mol^{-1}) is obtained from a temperature dependence study of the PE spectra of methyl vinyl sulfide.[132] Electronography[42, 121] gives the energy difference as close to zero.

5. Allenethiol and allenyl sulfides

ab initio Calculations for allenethiol and allenyl methyl sulfide have been performed.[47] The calculation for allenethiol within the STO-3G basis[47] revealed two stable forms, *cis* and *trans*. The potential curves of internal rotation for allenethiol and ethenethiol are similar. The conformer energy differences for these molecules are practically the same and are equal to ~4.6 kJ mol^{-1}.[47]

The calculations for allenyl methyl sulfide and methyl vinyl sulfide within the STO-3G and 44-31G basis sets give similar results.[47] Both calculations predict the greater stability of the *cis*-conformation for allenyl methyl sulfide. According to the calculation within the STO-3G basis, the next conformation is *trans*, while the calculation within the 44-31G basis gives a *gauche*-conformation as the next stable one (Fig. 13). The internal rotation potential curve for allenyl methyl sulfide is more flattened (44-31G, Fig. 13) than that for methyl vinyl sulfide (44-31G, Fig. 12), and the energy maximum corresponds to a dihedral angle of 65–70°. The rotational barrier for allenyl methyl sulfide is 5.5 kJ mol^{-1}, which is 3.3 kJ mol^{-1} lower than that for methyl vinyl sulfide (8.8 kJ mol^{-1}).

The corresponding barriers obtained in the STO-3G basis[47] are 12.6 kJ mol^{-1} for allenyl methyl sulfide and 16.4 kJ mol^{-1} for methyl vinyl sulfide.

The energy minimum in the potential curve for allenyl methyl sulfide corresponds to a torsional angle of ~120°. In the range of

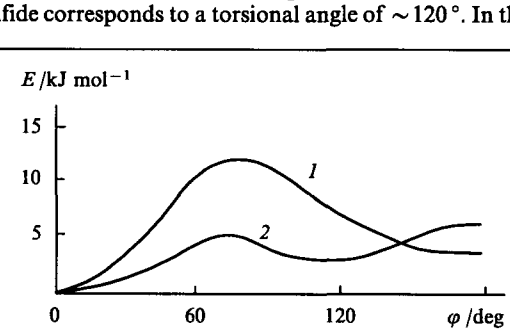


Figure 13. The potential functions of internal rotation for allenyl methyl sulfide.[47]
The method of calculation: (*1*) STO-3G, (*2*) 44-31G.

trans-conformation, there is a low barrier of 4.2 kJ mol^{-1} separating two *gauche*-forms. The energy difference between *cis*- and *trans*-conformers is higher for allenyl methyl sulfide than that for methyl vinyl sulfide (4.6 kJ mol^{-1} and 1.2 kJ mol^{-1} in the STO-3G basis and 7.5 kJ mol^{-1} and 3.8 kJ mol^{-1} in the 44-31G basis, respectively).[47] This seems to be due to the difference in spatial interaction between the Me group and the β-hydrogen, which is of a repulsive character in methyl vinyl sulfide and is absent in allenyl methyl sulfide.

ab initio Calculations[47] predict two stable conformers for allenyl methyl sulfide. PE spectroscopic data and semiempirical quantum calculations of allenyl methyl sulfide suggest two planar conformers, *cis* and *trans*.[106] At the same time, an electronographic investigation of allenyl methyl sulfide indicates only one planar *cis*-conformation.[102] The same follows from the ^{1}H NMR study of alkyl allenyl sulfides.[103]

6. Methyl vinyl selenide and methyl vinyl telluride

Analysis of vibrational spectra of methyl vinyl selenide and methyl vinyl tellurides suggests the presence of rotational isomers: it makes it possible to estimate the torsional angles between the CXC and XCC planes (X = Se, Te) and to assess the degree of interaction of the heteroatom with the double bond. Band assignments in the IR and Raman spectra of methyl vinyl selenide and methyl vinyl telluride were proposed based on a normal coordinate analysis.[142-144] The starting point for the discussion of the spectra of the molecules under study was a normal coordinate analysis of methyl vinyl sulfide and its deuterio-isotopomers.[127] The force fields of the vinyl and methyl groups of these molecules are mutually transferable, which indicates that their electronic structures are similar. While the force constant matrices are consistent, the frequencies of C–X modes differ significantly, which might be due to the difference in heteroatom masses, geometry and force constants of the C–S–C, C–Se–C, and C–Te–C groups. The C_{3v} local symmetry of the methyl group breaks down[127,142,143] in the case of methyl vinylchalcogenides. Analysis of the IR spectra of liquids and solutions in a temperature range of 193–353 K allowed one to suppose that methyl vinyl selenide[142,145,146] and methyl vinyl telluride[143,147,148] have rotational isomers.

Normal vibration frequencies calculated for various values of the CXCC torsional angle were correlated with the experimental frequencies.[142,143] The bending δ(XCC) and δ(CXC) modes are sensitive to changes in the torsional angle. Rotational isomers should manifest themselves most distinctly in the range of the stretching ν(CXC) modes. Unfortunately, in the case of methyl vinyl selenide,it was impossible to analyse the frequency changes in this region due to the overlap of bands of the stretching (CSeC) and out-of-plane bending (Se–C_{sp^2}–H) modes.[142]

According to the calculation for methyl vinyl telluride, the 500–600 cm^{-1} region should contain the bands due to out-of-plane bending modes of the vinyl group as well as the symmetric and antisymmetric stretching C–Te modes. Only one band is observed in the IR (at 519 cm^{-1}) and Raman spectra (at 530 cm^{-1}) of liquid methyl vinyl telluride at 298 K, whereas in the IR spectrum[143] of a CS_2 solution of methyl vinyl telluride at 193 K, this band is composed of three components at 512, 521, and 527 cm^{-1}. The band due to double bond stretching vibrations appears as a doublet with absorption maxima at 1582 cm^{-1} and 1585 cm^{-1} for methyl vinyl selenide and 1572 cm^{-1} and 1577 cm^{-1} for methyl vinyl telluride (in heptane solutions). The temperature dependence of the relative intensities of doublet components is analogous to that for methyl vinyl sulfide.[129] The intensity of the low-frequency band decreases, and that of the high-frequency band increases with a rise in temperature. Obviously, the doublet nature of the ν(C=C) band of methyl vinyl selenide and methyl vinyl telluride is due to the presence of several rotamers in solution.

The enthalpy and entropy differences have been calculated[147] for rotamers of methyl vinyl telluride: ΔH = 4.6 kJ mol^{-1}, ΔS = −11.1 J K^{-1} mol^{-1}. The ΔH value reflects the lowering of the rotational barrier from sulfur to tellurium. The high-frequency doublet component in the spectra of methyl vinyl selenide and methyl vinyl telluride corresponds, as for methyl vinyl sulfide, to several rotamers with large amplitude torsional motion or with above-barrier free rotation. A significant ΔS value indicates the presence of a large number of stationary energy levels coresponding to the high-frequency absorption band.

The data presented point to a similarity of the conformational structures of methyl vinylchalcogenides. It is reasonable to suppose that the low-frequency doublet component in the spectra of methyl vinyl selenide and methyl vinyl telluride, as in the case of the corresponding sulfide, belongs to the planar *s-cis*-form. This is confirmed by comparison of half-widths of the high-frequency doublet components.[129,142,147] The half-widths of the low-frequency components are virtually the same for all the chalcogenides considered, whereas the half-widths of the high-frequency doublet components are different: 5.5 cm^{-1} for methyl vinyl telluride, 8.0 cm^{-1} for methyl vinyl selenide, and 10.2 cm^{-1} for methyl vinyl sulfide. Evidently, the high-frequency doublet component of methyl vinyl telluride belongs preferentially to one type of stationary state. Apparently, the contribution of the p,π-interaction stabilising planar conformations is less, and the barrier separating two *gauche*-forms seems to be higher for methyl vinyl telluride than those for methyl vinyl sulfide.

In order to solve the problem of possible p,π-interaction in methyl vinyl telluride and methyl vinyl sulfide, the conformational energy has been calculated as a sum of energies of interaction between atoms separated by more than two bonds[147] and energies of bond angle strains.[149-151] The dependence of the conformational energy on the angle of rotation about C_{sp^2}–Te and C_{sp^2}–S bonds is presented in Fig. 14. It is seen that steric hindrance is practically absent in the *s-cis*-form of methyl vinyl telluride. The difference in the energies of steric hindrance between the planar *cis*- and *trans*-forms is 0.7 kJ mol^{-1} (for the sulfide it is 4.4 kJ mol^{-1}). The planar *s-cis*-form in methyl vinyl telluride is stabilised by electronic interactions of the same type as in the case of methyl vinyl sulfide, i.e. due to p,π-interaction. The energy of this interaction is 5.3 kJ mol^{-1}, which is twice as low as the energy of the same interaction in methyl vinyl sulfide (10.4 kJ mol^{-1}).

Thus, investigations of rotational isomerism in vinyl chalcogenides have revealed unexpected, and remarkable in many respects peculiarities of their molecular and electronic structure. Alkyl vinyl chalcogenides have two qualitatively different types of stable conformers. One of them is characterised by a definite torsional angle and small deviations from the global minimum of potential energy. The other is associated with a large amplitude relative motion of the fragments of the molecule within a flat-bottomed potential well. This motion can include more than one minimum in the internal rotation potential curve.

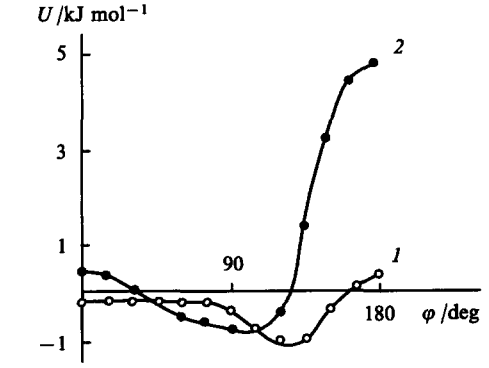


Figure 14. The dependence of the energy of steric strain on the angle of internal rotation for vinyl methyl telluride (*1*) and vinyl methyl sulfide (*2*).[147] For the planar *s-trans*-form φ = 0.

III. Rotational isomerism in divinyl chalcogenides

The presence of two unsaturated fragments in the immediate vicinity of the heteroatom in divinyl chalcogenides poses new problems of the competition in the interaction of the double bond π-electrons with the lone electron pair, of the possibility of a 'through' conjugation of the π-systems of the vinyl groups, and of a correlation between the barriers to internal rotation in alkyl vinyl and divinyl compounds. The most comprehensive information about rotational isomerism in divinyl chalcogenides can be gained from the potential surface composed as a function of angles of rotation about $C_{sp^2}-X$ bonds. In the case of divinyl chalcogenides, the internal rotation potential energy surface should be considered not only as source of information on rotational isomerism, but as a tool for a search for the stationary states corresponding to changes in the internal molecular coordinates.

A method of build up and analysis of potential energy maps was used to determine the number and the nature of rotational isomers of divinyl chalcogenides.[5] The most essential component of the potential energy, the energy of steric hindrance, was calculated by the MM method (Table 2).[5]

Table 2. The energies of steric strain U_n in various conformations for molecules $CH_2=CHXCH=CH_2$ (X = O, S, Se, Te).[5]

Conformation	U_n /kJ mol^{-1}			
	O	S	Se	Te
A (*trans–trans*)	3.8	2.5	2.0	1.8
B (*cis–trans*, planar)	14.5	12.9	8.4	5.1
C (*cis–trans*, deviation by 15°)	11.3	9.0	5.5	3.2
D (*cis–cis*, planar)	52.7	53.5	41.4	31.8
E (*cis–cis*, deviation by 38°)	9.4	5.3	2.7	1.0
F (*cis–cis*, deviation by 45°)	7.6	3.2	1.3	0.3

1. Divinyl ether

Electron diffraction study of the molecular structure of divinyl ether has led to the conclusion that the planes of the double bonds are turned by about 20° relative to the plane of the symmetrical *trans–trans*-conformation.[152] However, the analysis of MW spectroscopic data for divinyl ether [153–155] revealed a non-planar *cis–trans*-conformer. A deviation from the planar structure is supposed to be due to strong repulsion between the hydrogen atoms in the α- and β-positions of the *trans*- and *cis*-vinyl groups, respectively. The special feature of the *cis–trans*-conformation is the existence of a tunnel transition through an insignificant potential barrier, which manifests itself as a splitting of rotational transitions.[154] Taking into account tunnel splitting of rotational transitions made it possible to increase the accuracy of the calculation of frequencies of *cis*- and *trans*-conformers in the MW spectrum of divinyl ether.[155]

A study of the vibrational spectra of gaseous and liquid divinyl ether has provided evidence for the preferential planar *cis–trans*-conformation of C_s symmetry, however, the possibility of the existence of a second, less stable conformation having no symmetry elements (C_1) is also not ruled out.[156] Divinyl ether was shown [157] to exist as an equilibrium mixture of two conformers with an energy difference of 2.5 kJ mol^{-1}. Analysis of relative band intensities in the IR and Raman spectra and line polarisability in the Raman spectra leads to the conclusion that the planar *trans–trans*-conformer is the most stable, while the second conformer has no elements of symmetry.[157] An investigation of the band shapes of the COC stretching modes in the IR spectrum of gaseous divinyl ether has been performed [158] based on a theoretical simulation of profiles of these bands in different conformers. At 300 K, divinyl ether was shown to contain 80% of *cis–trans*-conformer with torsional angles of 13° and 145° and 20% of *trans–trans*-conformer.

ab initio Calculations have been carried out in order to investigate rotational isomerism in divinyl ether.[157–160] Two stable conformations have been predicted:[157] the first energy minimum corresponds to the *trans–trans*-form, and the second belongs to a non-planar conformation with torsional angles of 135° and 20°. A potential energy map has been constructed for divinyl ether,[159] and three stable conformations have been predicted corresponding to the potential energy minima of 0, 11.4, and 10.0 kJ mol^{-1} (Fig. 15). These conformations are non-planar *cis–trans*- (torsional angles 147.4° and −17.4°; C_1), planar *trans–trans*- (torsional angles 180°, 180°; C_{2v}), and near-planar *cis–cis*- (torsional angles 31.5° and 31.5°; C_2). The conformer geometry was optimised [159] within the STO-3G basis, relative energies were optimized within the basis 4-31G. The geometry of *cis–cis*-, *trans–trans*-, and *cis–cis*-conformers of divinyl ether were obtained by a gradient method within the 4-31G basis.[158] The difference in the conformer energy (0; 6.6, and 4.5 kJ mol^{-1}, respectively) differ from those obtained in another study.[159] The calculation of divinyl ether within the 6-31G** basis yielded two stable conformers:[160] a near-planar *cis–trans*-conformer as the most energy-favourable and the planar *trans–trans*-conformer with an energy difference of 1.5 kJ mol^{-1}.

A steric hindrance map for divinyl ether obtained by the MM method is given in Fig. 16.[3] The steric hindrance energy was calculated by varying φ_1 from 0° to 360° and φ_2 from 0° to φ_1 with a step of 15° (φ_1 and φ_2 are the rotation angles of the first and the second vinyl groups relative to the planar *cis–cis*-structure, respectively). A minimum of steric hindrance (−5.65 kJ mol^{-1}) belongs to a non-planar form, which results from the *trans–trans*-conformation by rotating two vinyl groups in opposite directions by an angle of about 75° (Fig. 16). Steric hindrance energies for other conformeations are listed in Table 2.

The potential energy for different conformations of divinyl ether was calculated as a sum of energies of steric hindrance and p,π-interaction. The values obtained from the *ab initio* calculation for methyl vinyl ether [94] were used as p,π-interaction energies for divinyl ether. Analysis of the potential energy map for divinyl ether (Fig. 17) shows that there are three different conformations corresponding to the minima of potential energy. In two non-planar quasi-degenerate *trans–trans*-forms, the vinyl groups deviate from the COC plane by $\varphi_1=130°$, $\varphi_2=130°$, and $\varphi_1=130°$, $\varphi_2=-130°$ (energy −26.1 kJ mol^{-1}). In a non-planar *cis-trans*-form, the rotational angle of one vinyl group is

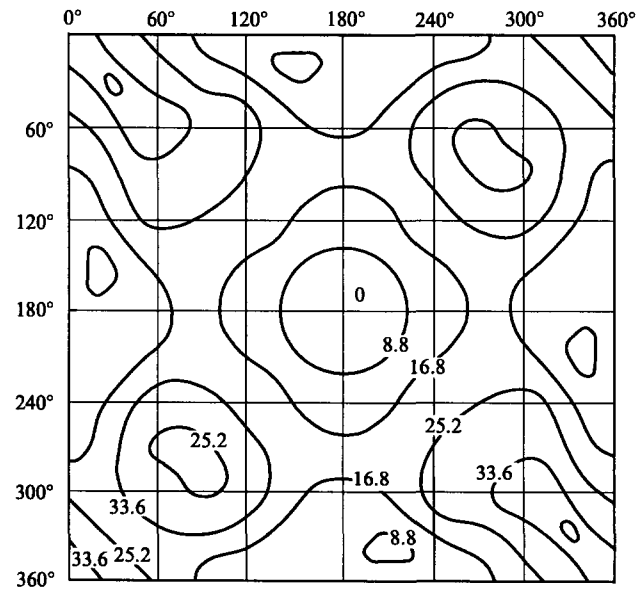


Figure 15. The map of the potential surface for the internal rotation in divinyl ether.[159]

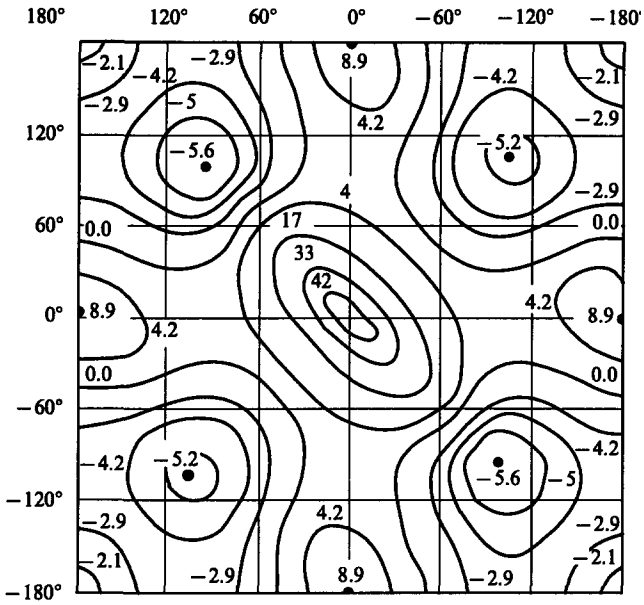


Figure 16. The map of steric hindrance energy for divinyl ether.[3]

about 10° and that of the other about 50° (energy −28.0 kJ mol^{-1}). These forms are separated by a barrier of −20.9 kJ mol^{-1}. The potential map (Fig. 17) does not take into consideration either effects connected with competition for the interaction of the double bond π-electrons with the lone electron pair of the oxygen atom or 'through' conjugation.

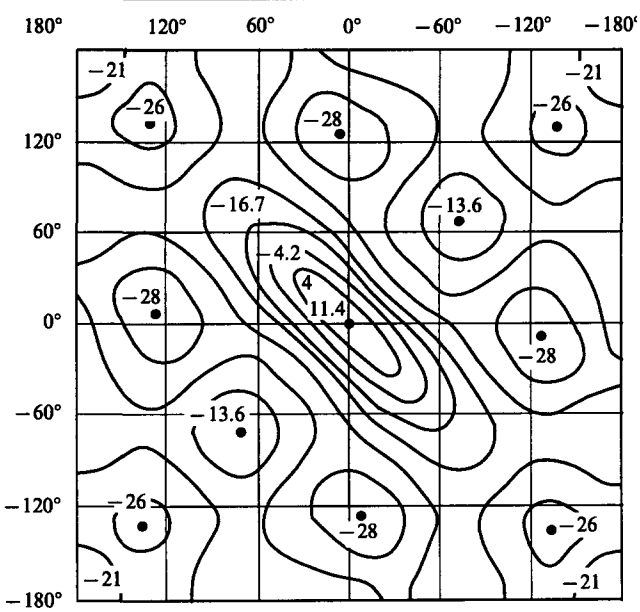


Figure 17. The map of potential energy for divinyl ether.[3]

2. Divinyl sulfide

The molecular structure of divinyl sulfide was studied by gas electronography.[161] Only one *cis*–*trans*-conformer with CSCC torsional angles of 32° and −148° having no elements of symmetry was detected in gaseous divinyl sulfide at room temperature. The basic structural parameters of the molecule are as follows: r(C–S) = 1.758 Å, r(C=C) = 1.342 Å; angles CSC 101.8°, SCC 123.7°. Similar torsional angles were obtained by the MM method (38°, 124°)[48] and by an *ab initio* calculation within the 3-21G basis (18° and 116°).[48] Low accuracy in the electronographic determination of some structural parameters for divinyl sulfide is probably due to large-amplitude intramolecular motion. Therefore the presence of a second (minor) conformer cannot be ruled out.

Rotational isomerism in divinyl sulfide was also studied by vibrational spectroscopy.[162–164] Analysis of the temperature dependence of intensities of the bands sensitive to conformations in the spectra of gaseous, liquid, and solid divinyl sulfide shows the presence of two conformers.[163] There is a dynamic equilibrium between the *cis*–*trans*- and *trans*–*trans*-conformations in liquid and solution, and in the crystal state only the planar *trans*–*trans*-conformation exists.[163] The conformer enthalpy difference is close to zero. Theoretical vibrational spectra of stable conformers of divinyl sulfide have been calculated[160] within the 6-31G** basis. The calculations showed that a non-planar *trans*–*trans*-conformer is the most favourable, a *cis*–*trans*-conformer is the next, in which the vinyl group deviates from the CSC plane by 20°; the energy difference between these conformers is 0.71 kJ mol^{-1}. The populations of the individual *trans*–*trans*-conformer at 300 K was calculated to be 57% and that of the *cis*–*trans*-conformer, 43% (Table 3).

Table 3. Calculated energy differences and populations for conformers of divinyl chalcogenides.[160]

Compound	ΔE, /kJ mol^{-1}	Statistical weight	Population at 300 K	
			calculation	experiment
$(CH_2CH)_2O$				
trans–*trans*	+1.46	1	22	20[a]
cis–*trans*	0.0	2	78	80
$(CH_2=CH)_2S$				
trans–*trans*	0.0	2	57	50[b]
cis–*trans*	+0.71	2	43	50
$(CH_2=CH)_2Se$				
trans–*trans*	0.0	2	60	
cis–*trans*	+0.1	2	40	
$(CH_2=CH)_2Te$				
trans–*trans*	0.0	2	71	
cis–*trans*	+2.26	2	29	

[a] The data of Ref. 158; [b] the data of Ref. 155.

The internal rotation potential curves for divinyl sulfide have been calculated within the STO-3G and 3-21G basis sets and by the MM method with a fixed *trans*–*trans*-conformation of one vinyl group (Fig. 18).[48] These potential functions differ significantly from those for ethenethiol (Fig. 4)[48] and methyl vinyl sulfide (Fig. 12).[48] The calculation in the STO-3G basis reveals the *trans*–*trans*-conformation to be the most stable. Two stable conformations, very similar in energy are obtained in the 3-21G basis and by the MM method: *cis*–*trans*- (0° and 120°, C_s symmetry) and *cis*–*cis*- (120° and 120°, C_2 symmetry).[48] ΔE values for the conformers calculated by these methods differ significantly: 5.0 kJ mol^{-1} (3-21G) and 1.3 kJ mol^{-1} (MM). The results obtained by the MM method are believed[48] to be more reliable because the dipole moment (1.48 D) calculated by the MM method fits better the experimental value of 1.07–1.2 D than that calculated within the 3-21G basis (1.9 D).

The conformational energy of divinyl sulfide was calculated[5,140] as the sum of contributions of the p,π-interaction stabilising the planar arrangement of each of the C–S–C=C fragments and the steric hindrance (Table 2). Minimum steric hindrance is unique to the non-planar *trans*–*trans*-form with a deviation of the vinyl groups to the both sides of the CSC plane by an angle of ~80° The planar *cis*–*cis*-form has a hindrance energy of 53.5 kJ mol^{-1} (Table 2). Rotation about the C–S bonds in the

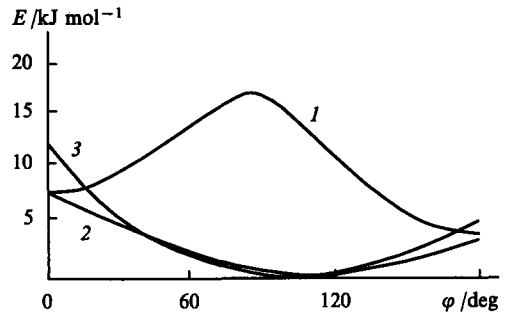


Figure 18. The potential functions of internal rotation for divinyl sulfide (φ_2 = 180°).[48]
The method of calculation : (*1*) STO-3G, (*2*) 3-21G, (*3*) MM.

opposite direction by less than 30° results in a conformation in which steric hindrance changes into stabilization due to Van der Waals interaction.

Quantitative estimation of the p,π-interaction energy in divinyl sulfide was determined[140] from the known internal rotation potential curve for methyl vinyl sulfide.[129] A part of the internal rotation potential of methyl vinyl sulfide was used in the calculation of the potential energy map for divinyl sulfide:

$$V(\varphi)= V_1\frac{1-\cos\varphi}{2}+V_2\frac{1-\cos2\varphi}{2}+V_3\frac{1-\cos3\varphi}{2},$$

where φ is the torsional angle of the rotation about the $C_{sp^2}-S$ bond for methyl vinyl sulfide; V_1 is the first-order barrier connected with the *cis*-preference; V_2 is the second-order barrier numerically equal to a half of the p,π-interaction energy; V_3 is the third-order barrier due to hybridisation of the lone electron pair of the sulfur atom, which is intermediate between sp^3- and sp^2-hybridisations. Since the *cis*-preference in divinyl sulfide molecules cannot take place, the p,π-interaction energy can be described by the equation:

$$V(\varphi_1,\varphi_2) = V_2\left(\frac{1-\cos2\varphi_1}{2}+\frac{1-\cos2\varphi_2}{2}\right)+$$

$$+V_3\left(\frac{1-\cos3\varphi_1}{2}+\frac{1-\cos3\varphi_2}{2}\right),$$

where V_2 = 7.9±0.8 kJ mol^{-1} and V_3 = 6.3± 0.4 kJ mol^{-1}.

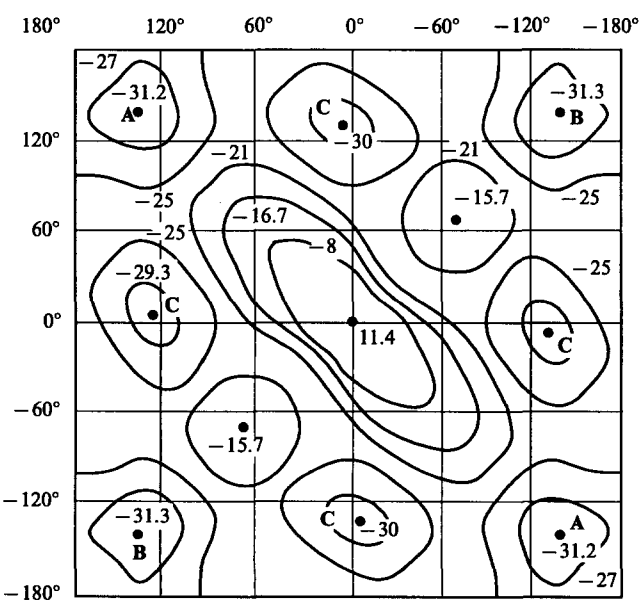


Figure 19. The map of potential energy for divinyl sulfide.[140]

The potential energy map for divinyl sulfide is presented in Fig. 19. The planar *trans*–*trans*-form corresponds to a local maximum rather than to the minimum of potential energy. Two more favourable quasi-degenerate forms have virtually the same energy and correspond to torsional angles $\varphi_1 = 137°$, $\varphi_2 = 137°$ (*trans*–*trans*-conformer **A**) and $\varphi_1 = 137°$, $\varphi_2 = -137°$ (*trans*–*trans*-conformer **B**). There is also a local minimum at $\varphi_1 = 125°$, $\varphi_2 \sim 0°$ (*cis*–*trans*-conformer **C**). The latter conformer is 0.84 kJ mol^{-1} less preferential than the former ones.

Complete understanding of rotational isomerism requires that excited states be taken into account. In the range of excitation energies up to 8 kJ mol^{-1}, there are states in the divinyl sulfide molecule in which torsional angle varies within the limits from −90° to +90° relative to the *trans*–*trans*-conformation.[140] The stationary state **D** includes simultaneously potential wells of both *trans*–*trans*-conformers **A** and **B**. Here, large-amplitude intramolecular motion takes place and the above-barrier states are

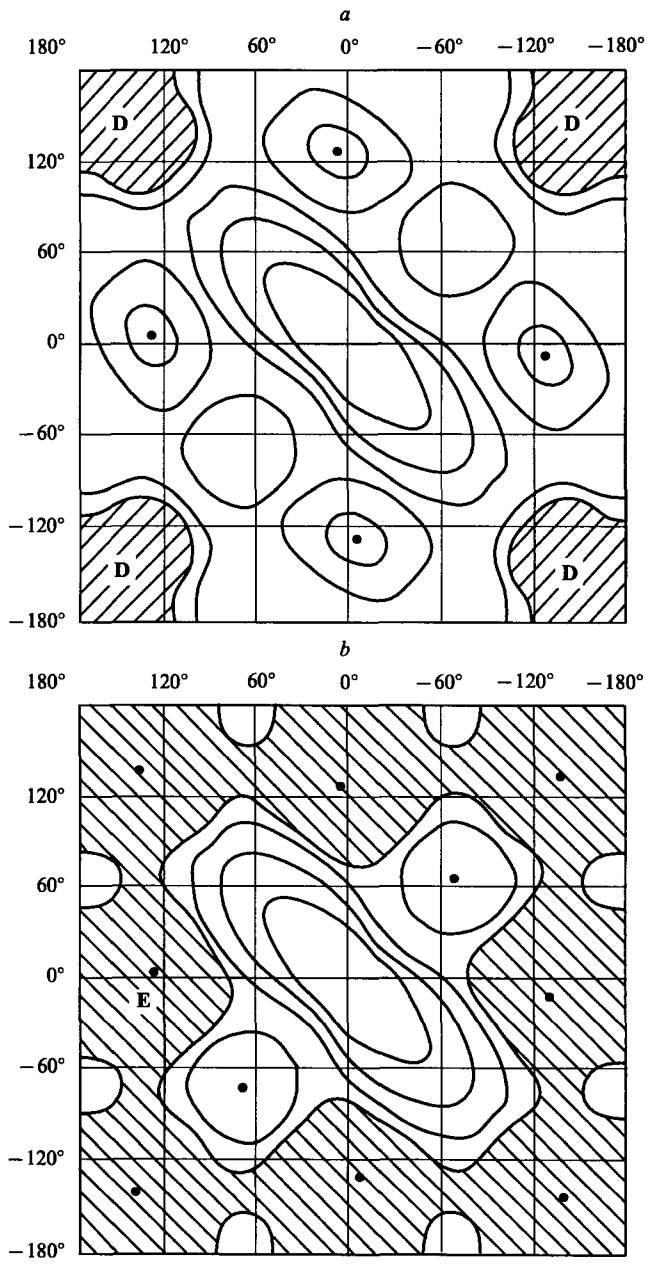


Figure 20. The stationary states of internal rotation[140] for divinyl sulfide: (*a*) type **D** with the energy to 8.0 kJ mol^{-1}, (*b*) type **E** with the energy above 8.0 kJ mol^{-1}.

becoming occupied. In this range of excitation energies, along with the stationary states of the D type (Fig. 20 *a*), excited states of the *cis*–*trans*-conformer C localised near the potential energy minimum are realised.

At excitation energies above 8 kJ mol^{-1}, the stationary state includes conformations that can have, with a few exceptions, practically any values of torsional angles φ_1 and φ_2 (stationary states of the E type, Fig. 20 *b*).[140] Complete equivalence of the double bonds is characteristic of all the stationary states, except for the *cis*–*trans*-conformer C in which one of the vinyl groups is practically not involved in the p,π-interaction.

Hence, the potential as a function of the internal rotation about the $C_{sp^2}-S$ bond for methyl vinyl sulfide was transferred (with some corrections) to the rotation about analogous bonds in the divinyl sulfide molecule.[140] Five types of stationary states have been characterised (A–E), two of which have no analogues among stable conformers in a classical sense.

3. Divinyl selenide and divinyl telluride

In this section, the published data on the structure of divinyl selenide and divinyl telluride are presented.[4,5,144,160,165] Theoretical vibrational spectra of these molecules have been obtained,[160] the analysis of which revealed two stable non-planar *trans*–*trans*- and *cis*–*trans*-conformations. The conformer energy differences and their populations at 300 K are listed in Table 3. A proportion of the more stable *trans*–*trans*-conformer increases with increase in the mass of chalcogenide. For divinyl sulfide and divinyl telluride, the *trans*–*trans*-conformer is preferential in energy. Recently the IR spectra of divinyl telluride in the gas, liquid, and solid states and the spectra at low temperatures in various matrices (argon, nitrogen, xenon, and krypton) have been measured and the bands sensitive to conformations have been found.[160]

It is interesting to compare the geometrical parameters of conformers for divinyl chalcogenides.[160] With an increase in the chalcogenide mass, the C–X bond length increases and the C–X–C angle decreases, the angle is somewhat less in the *trans*–*trans*-conformer than that in the *cis*–*trans*-conformer.

Potential energy maps were obtained for divinyl selenide and divinyl telluride: they were constructed as functions of rotational angles about $C_{sp^2}-X$ (X = Se, Te) bonds.[5] The steric hindrance energies calculated for different conformations by varying the angles φ_1 from 0° to 360° and φ_2 from 0° to φ_1 with a step of 15° are presented in Table 2.

For all the chalcogenide conformations, steric hindrance energies vary in the series O > S > Se > Te. Of the two structural factors, bond lengths and bond angles, exerting opposite influence on steric hindrance, the key role belongs to the increase in the C–X bond lengths. For all vinyl chalcogenides, the planar *cis*–*cis*-conformation (D) is the most sterically hindered (Table 2), the *trans*–*trans*-form (A) is the least hindered. The steric hindrance energy of the non-planar *cis*–*cis*-conformation (F) for divinyl sulfide, divinyl selenide and divinyl telluride is close to, or is lower than that of the *trans*–*trans*-conformer (A), and only for divinyl ether is it twice higher (Table 3). This conformation results from the planar *cis*–*cis*-form by rotating the vinyl groups to the opposite directions by an angle of 45°.

Thus, the potential energy maps for divinyl chalcogenides give a comprehensive idea of the steric structure. The potential of internal rotation about the $C_{sp^2}-X$ bonds (X = O and S) in alkyl vinyl chalcogenides can be transferred (with some corrections) to the rotation about analogous bonds in the corresponding divinyl chalcogenides. The latter exist as three non-planar stable conformers: two quasi-degenerate *trans*–*trans*- and one *cis*–*trans*-conformer. A complete picture of rotational isomerism in divinyl chalcogenides involves not only the ground, but also excited vibrational states, which are characterised by large-amplitude intramolecular motion encompassing more than one local minima in the potential energy map.

IV. Electronic structure of vinyl and allenyl chalcogenides

1. Photoionisation of vinyl ethers

Interesting and important regularities have been established on the basis of photoelectron investigations of organic compounds.[166] Ionisation potentials of organic molecules depend significantly on the structure of substituents at the atom ionised;[167,168] within one class compounds, these are dictated exclusively by the inductive effect.[168–171] However, ionisation processes should also be very sensitive to other intramolecular effects of the structure. In particular, considerable contributions to the ionisation energy might be expected from the interaction of a cation radical with neighbouring double bonds and heteroatoms. These contributions can be identified and measured as deviations from a regression line reflecting the relationship between the ionisation potential and inductive effect (for example, by sums of the substituent σ^* constants). Adiabatic ionisation potentials have been obtained for a series of vinyl ethers by the photoionisation method.[1,172] By analogy with alcohols and other classes of compounds[168–171] in which a linear dependence of the ionisation potential on the σ^* constants is quite unambiguous, a variation of ionisation potentials in the series of vinyl ethers can be supposed to originate primarily from the inductive effect. The correlation between the adiabatic ionisation potentials (I) and substituent inductive constants ($\Sigma\sigma^*$) is presented in Fig. 21; the correlation parameters are somewhat different for saturated (dialkyl and cyclic) (line 1) and divinyl (line 2) ethers.

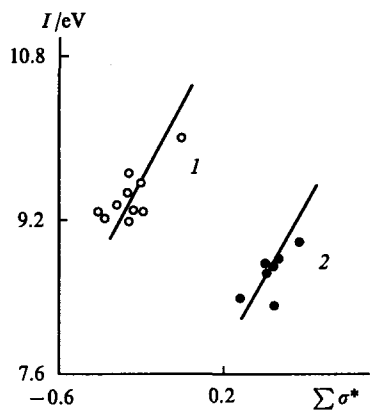


Figure 21. The correlation of ionisation potentials (I) of ethers with inductive constants of substituents ($\sum\sigma^*$).[172]
(1) aliphatic and cyclic ethers, (2) vinyl ethers.

The independent correlation for alkyl vinyl ethers can be explained[172] by p,π-conjugation in the radical cation. An energy gap separating lines *1* and *2* indicates an inequivalence in the coupling of the oxygen AOs with the orbitals of the sp^2- or sp^3-hybridised carbon atoms. Correlation processing points against multiple correlations with three arguments ($\Sigma\sigma^*$, Δn, and E_s) for diorganyl and vinyl ethers.[1,172] One of the reasons for the uncertainty of the regressions is a strong dependence between the arguments.

Analysis of the correlation $I = f(\Sigma\sigma^*)$ has shown[1,172] that other effects do not manifest themselves as distinctly as the inductive one. The deviation of the points exceeding significantly the accuracy of the ionisation potential measurement indicates a contribution of structural effects.[1,172] It cannot be ruled out that steric interactions might contribute. A linear dependence of the second ionisation potential (I_2) for alkyl vinyl ethers on the ionisation potentials of a standard series of alkyl iodides I_{RI}[173] and the existence of two different curves for compounds with linear (Me, Et, Bu^n) and branched (Pr^i, Bu^s, Bu^t) substituents has been found.[68] It was explained by a change in the conformational

state of the vinyl ether with the introduction of a bulky substituent.

2. PE spectra of alkyl allenyl ethers

PE spectra of alkyl allenyl ethers [106, 112, 174–176] have been studied and interpreted on the basis of the orbital energy values calculated by semiempirical and *ab initio* methods. The electronic structure of alkyl allenyl ethers was compared with that of alkyl vinyl ethers.[175] The latter are formal analogues of alkyl allenyl ethers except for the fact that the allenyl fragment comprises two orthogonal π-systems. The electronic structure of alkyl allenyl ethers is fully dictated by the interaction of the lone electron pair on the oxygen atom with the π-electrons of the double bond. The same interaction affects the steric configuration and, to some extent, the relative stability of the conformers.

The sequence of the π-type occupied molecular orbitals in alkyl allenyl ethers is considered [175] to be a result of the interaction between the fragmentary π- and *n*-MOs. According to the orbital correlation diagram (Fig. 22), four bands are expected to exist and observed in the low-energy range of the PE spectrum [87, 93, 174, 175] (Table 4). In the spectra of allenyl methyl and allenyl ethyl ethers, bands *1* and *2* have a fine structure, which corresponds to the stretching C=C=C modes of the radical cation and is therefore considered to be the vibrational structure.[112, 174] At the same time, the structure of band *1* in the PE spectrum of allenyl methyl ether is supposed [106] to be associated with the presence of *cis*- and *trans*-conformers. However, according to the gas electronography data,[102] the *cis*-conformation dominates at room temperature (other conformers were not detected).

The low-energy band (8.77 eV) is assigned to the MO which involves the *p*,π-interaction of the oxygen atom with the π-system of the $C_\alpha=C_\beta$ bond. The next band (10.33 eV) corresponds to the $\bar{\pi}$-MO of the $C_\beta=C_\gamma$ allenyl fragment. Consecutive replacement of the Me group by Et, Pr^n, Pr^i, Bu^n, and Bu^t groups leads to a low-energy shift of the first and second band maxima by 0.1–0.3 eV (Table 4).

The third band in the spectra of alkyl allenyl ethers (11.25–11.97 eV) belongs to the π_1-MO, which is a bonding combination of the oxygen lone electron pair and the π-MO of the $C_\alpha=C_\beta$ group.

The fourth band (12.28 eV) in the PE spectrum of allenyl methyl ether results from the ionisation of the π_1 and $n_O(\sigma)$ levels. The MNDO calculation shows [175] that a level deeper than that of the π_1-MO corresponds to the lone electron pair on the oxygen atom. For methyl vinyl ether, the band at 12.2 eV is assigned [69] to the $n_O(\sigma)$ level. For alkyl allenyl ether, this level is associated with the band in the range of 11.5–12.3 eV.[175] For allenyl methyl ether, this band (12.28 eV) originates from the ionisation of a nearly pure lone electron pair of the oxygen atom, whereas for compounds with R = Et, Pr^n, Pr^i, Bu^n, and Bu^t, a strong coupling between the $n_O(\sigma)$-MO and the σ_{CC}-MO is observed. As the substituent length and branching increase, the coupling efficiency between the $n_O(\sigma)$- and σ_{CC}-MOs increases.[175]

Table 4. Vertical ionisation potentials for compounds $H_2C=C=CHOR$.[175]

R	Ionisation energy[a] /eV			
	$I_1(\pi_3)$	$I_2(\bar{\pi}_2)$	$I_3(\pi_1)$	$I_4[n_O(\sigma)]$
Me	8.8	10.3	11.9	12.3
Et	8.7	10.2	11.7	11.9
Pr^n	8.6	10.2	11.5	see[b]
Bu^n	8.6	10.2	11.4	see[c]
Pr^i	8.6	10.1	11.4	11.6
Bu^t	8.6	9.9	11.25±0.1	11.5
$CH_2CH=CH_2$	8.8	10.0 10.4	11.9	12.4

[a] The band assignment is given in parentheses; [b] a system of overlapping bands with an overall maximum at 12.2 eV; [c] the same with a maximum at 12.3 eV.

Since the ionisation potential I_3 for alkyl allenyl ethers is analogous to I_2 for alkyl vinyl ethers,[69] the relationship between I_3 and the ionisation potentials for a standard series of alkyl iodides (I_{RI}) (I_{RI} values were found by PE spectroscopy [173]) is also true:[175] I_3 = 1.63 eV, I_{RI} = 3.60 eV. r = 0.994, s_0 = 0.03 (the standard deviation s_0 does not exceed the experimental error of ~0.05 eV). For compounds with R = Pr^i, and Bu^t, the points deviate from the regression line by a value approximately equal to s_0, therefore, there is no reason to set apart these compounds from the series of alkyl allenyl ethers (Table 4). The relationship $I_3 = f(I_{RI})$ is entirely determined by the inductive effect of the substituent. In this case, no conformational effects are revealed. Since the ionisation potentials of alkyl iodides are in turn linearly related to the substituent inductive constants (σ^*),[169–171] which have a more general character, the latter can be used for the correlation of orbital energies.

An MNDO calculation of the angular dependence of orbital energies ($-\varepsilon_i$) for allenyl methyl ether has been carried out (Fig. 23).[175] The $\varepsilon(\pi_1)$ value is rather sensitive to the departure from planarity and is practically the same for *s-cis*- and *s-trans*-conformations. Therefore, the existence of a common linear dependence $I_3 = f(I_{RI})$ indicates that all the alkyl allenyl ethers studied have a planar conformation. If for allenyl methyl ether it is definitely *s-cis*-, then the *s-trans*-conformation seems to be favoured for $CH_2=C=CHO\text{-}Bu^t$.

The comparison of total energies of possible conformers (*cis*-, *trans*-, and *gauche*-) for alkyl allenyl ethers obtained by the

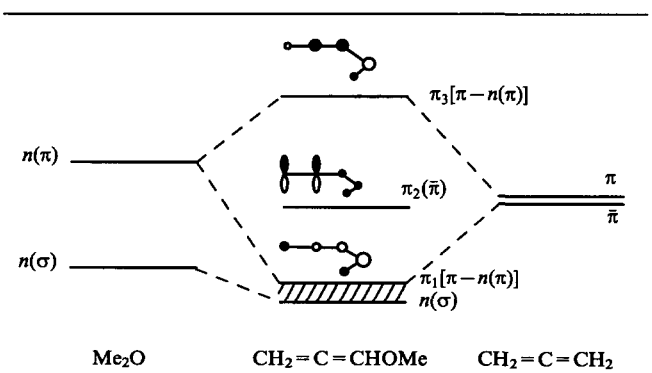


Figure 22. The correlational orbital diagram for the molecule $CH_2=C=CHOMe$.[175]

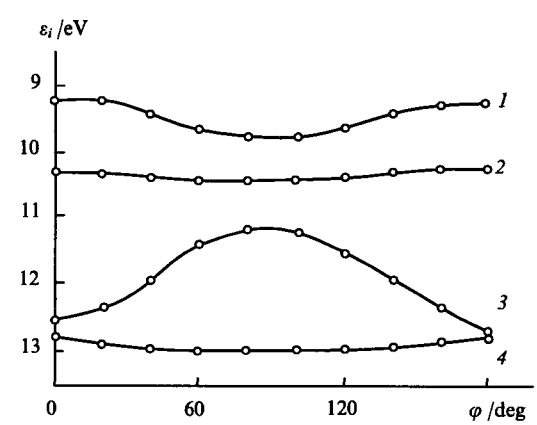


Figure 23. The angular dependence of orbital energies ($-\varepsilon_i$) for $CH_2=C=CHOMe$ (the MNDO method):[175] (*1*) $\varepsilon_1(\pi_3)$, (*2*) $\varepsilon_2(\pi_2)$, (*3*) $\varepsilon_3(\pi_1)$, (*4*) $\varepsilon_4(\sigma)$.

MNDO method[175] shows that the *s-cis*- form of the C=C=C−O−R fragment is the most stable in compounds with normal substituents. For compounds with branched substituents, the most stable conformation is the *s-trans*-form.

3. PE spectra of allenyl vinyl ethers

There are no published data on the electronic structure of allenyl vinyl ether $CH_2=C=CHOCH=CH_2$. In this connection, an empirical band assignment in its PE spectrum[177] was based on comparison of the spectrum with those of divinyl ether and allenyl methyl ether.[175] The spectrum of allenyl vinyl ether contains five well-resolved bands in the range of 8.0–16.0 eV (Table 5). The first two bands have fine structure. As in alkyl allenyl ethers,[112,174] the fine structure may be ascribed to the vibrational structure of corresponding states of the cation radical. The next band of allenyl vinyl ether has a distinct maximum at ~10.55 eV. The fourth broad band seems to result from the overlapping of several components with maxima at about 12.55 eV. The introduction of a Pr^n substituent into the α-position of the allene group leads to a shift of the band maxima by 0.3–0.4 eV.[177]

Table 5. Vertical ionisation potentials for allenyl vinyl ethers.[177]

R in compound	Ionisation potential[a] /eV				
$CH_2=C=C(R)OCH=CH_2$	$I_1(\pi_4)$	$I_2(\pi_3)$	$I_3(\bar{\pi}_2)$	$I_4[n_O(\sigma)]$	$I_5(\pi_1)$
H	8.7	10.2	10.6	12.5	12.5
cis–cis	8.9	10.3	10.3	12.8	14.1
trans–trans	8.9	10.2	10.3	12.9	14.0
Pr^n	8.4	9.9	10.2 (sh)	12.2	11.8 (sh)
$CH_2=CHOCH=CH_2$	9.0	10.5		12.4	12.6

[a] Band assignment is given in parentheses.

The orbital correlational diagram based on the interaction of the fragmentary π-orbitals of ethene and the hypothetical allenyl alcohol molecule was used for a quantitative analysis of the PE spectrum of allenyl vinyl ether[177] (Fig. 24). The sequence of one-electron levels for allenyl vinyl ether was determined from the MNDO data.[177] (Fig. 24). The first band (π_4-MO) corresponds to the HOMO composed of an antibonding combination of the lone electron pair of the oxygen atom, π-orbitals of the vinyl group (π_1-MO) and the $C_\alpha = C_\beta$ bond of the allene fragment (π-MO). The second band (10.22 eV) is associated with ionisation from the π_3-MO, which has a node at the oxygen atom and is antibonding. MOs of the vinyl (π_1-MO) and allenyl $C_\alpha = C_\beta$ (π-MO) groups contribute decisively to this orbital. A molecular orbital orthogonal to the rest of the π-system ($\bar{\pi}$-MO) gives rise to the third band (10.55 eV). The fourth band with a maximum at 12.54 eV results from ionisation from two MOs, a π-MO and an almost pure lone electron pair of the oxygen atom, $n_O(\sigma)$. The π_1-MO is a bonding combination of the lone electron pair of the oxygen and the fragmentary MOs of the vinyl and allenyl $C_\alpha=C_\beta$ groups. Thus, the structure and sequence of occupied π_4-, π_3-, and π_1-MOs are similar to those for divinyl ether[177] (Table 5).

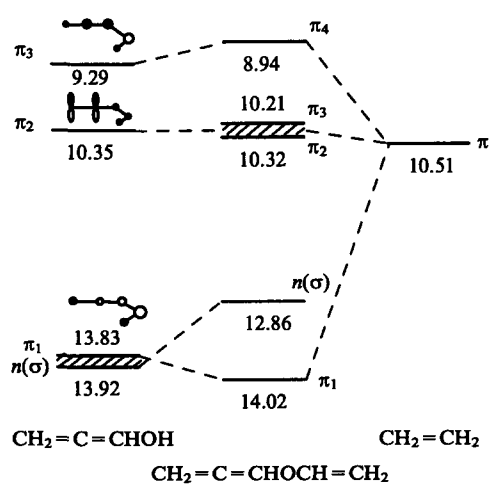


Figure 24. The orbital correlational diagram for hypothetical allenyl alcohol, ethylene, and $CH_2=C=CHOCH-CH_2$.[177]

An MNDO calculation of orbital energies for planar conformations[177] has shown that the bands in the PE spectrum of allenyl vinyl ether can be shifted by ~0.1 eV on transition from the *trans–trans*- to the *cis–cis*-conformation. The difference in the orbital energy values for the *cis–cis*- and *trans–trans*-conformations of allenyl vinyl ether is within the experimental errors of the PE spectroscopy method (0.1 eV for potential difference).

4. PE spectra of vinyl sulfides and selenides

The sequence of three higher occupied MOs of dialkyl sulfides and selenides does not depend on the nature of the chalcogenide:[178] $n_x(b_1) < \sigma_1(a_1) < \sigma_2(b_2)$. The effect of the heteroatom is reduced primarily to an increase in the energy of MOs and the contribution of atomic orbitals of the element (X) to these MOs with an increase in the element atomic number. Structural changes (chain length, branching) of the substituent in each series lead also to the expected effects.

The empirical approach to the low-energy range of PE spectra of vinyl derivatives allowed one to conclude that the relative arrangement of MOs in vinyl sulfides and selenides is practically independent of the nature of the heteroatom and the structure of the hydrocarbon substituent[179] (Table 6, Fig. 25): $\pi_2 < \pi_1 < \sigma_1 < \sigma_2$ ($CH_2=CH-X-Alk$), $\pi_3 < \sigma_1 < \pi_1 < \sigma_2$ ($CH_2=CH-X-CH=CH_2$). On going from dialkyl sulfides

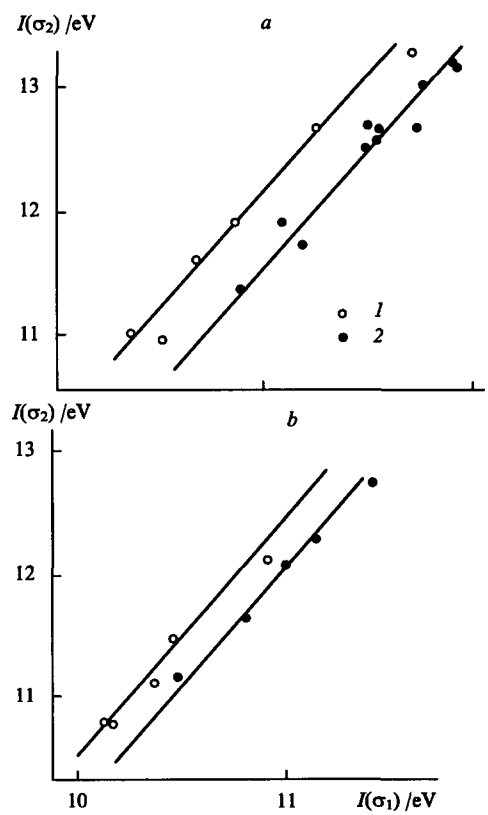
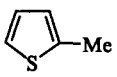
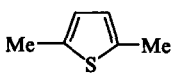
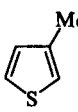
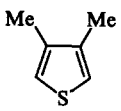
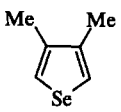
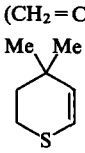


Figure 25. The correlation of σ-MO energies for diorganyl sulfides (*a*) and diorganyl selenides (*b*).[179]
(*1*) Saturated, (*2*) unsaturated.

Table 6. Vertical ionosation potentials for diorganyl sulfides and five-membered heterocyclic compounds.

R	Ionisation energy /eV					ΔI_σ	Ref.
	π (or n_X)	π_1	π_2	σ_1	σ_2		
Me_2S	8.7			11.3	12.7	1.4	178
	8.4			10.9	11.9	1.0	178
Et_2S	8.4			10.7	11.6	0.9	178
	8.4			10.6	11.0	0.4	178
$(Pr^i)_2S$	8.3			10.7	11.0	0.6	178
Me_2Se	8.4			11.0	12.0	1.0	178
	8.1			10.5	11.4	0.9	178
Et_2Se	8.2			10.4	11.1	0.7	179
$(Pr^i)_2Se$	8.0			10.2	10.8	0.6	179
$(Bu^n)_2Se$	8.0			10.2	10.8	0.6	179
	8.9	9.5	12.3	12.0	13.2	1.2	178
	8.3	9.0	12.4	11.8	13.0	1.2	179
	8.2	9.0	11.9	11.5	12.5	1.0	179
	8.5	9.1	12.5	11.9	13.1	1.2	179
	8.6	8.9	12.1	11.8	12.6	0.9	179
	8.8	8.9	12.1	11.5	12.7	1.2	179
	8.3	8.7	11.4	11.1	11.9	0.8	179
$CH_2=CHSMe$	8.4	11.0		11.6	12.6	1.0	179
$(CH_2=CH)_2S$	8.5	10.4	11.9	11.6	12.7	1.1	179
	8.1	10.9		11.2	11.7	0.1	69
$CH_2=CHSeMe$	8.3	10.8		11.2	12.2	1.0	179
$CH_2=CHSeEt$	8.2	10.7		10.9	11.6	0.7	179
$CH_2=CHSeBu^t$	7.9	9.7		10.5	11.1	0.6	179
$(CH_2=CH)_2Se$	8.3	10.3	11.5	11.0	12.0	1.0	179

and selenides to unsaturated derivatives with the same number of atoms, the stabilisation of the σ_1- and σ_2-MOs becomes non-equivalent, which indicates a different efficiency of coupling of the element (S, Se) AOs with the orbitals of the sp^2- and sp^3-hybridized carbon atoms. These differences lead to a splitting of the dependence $I(\sigma_2) = f[I(\sigma_1)]$ into two parts. One dependence includes saturated and the other includes unsaturated derivatives (Fig. 25). Analysis of the energies of the MOs of saturated and unsaturated organyl sulfides and selenides allowed one to state two general concepts, which facilitate the assignment of the 'σ'-bands in the PE spectra of alkyl vinyl and divinyl derivatives: i) the energy gap ΔI_σ separating the σ_1- and σ_2-MOs does not exceed a limiting value corresponding to the simplest representatives of the series and decreases with an increase in the substituent size (Table 6); ii) there is a linear correlation between the σ_1- and σ_2-MO energies, its parameters being somewhat different for saturated and unsaturated compounds of sulfur and selenium (Fig. 25).[179]

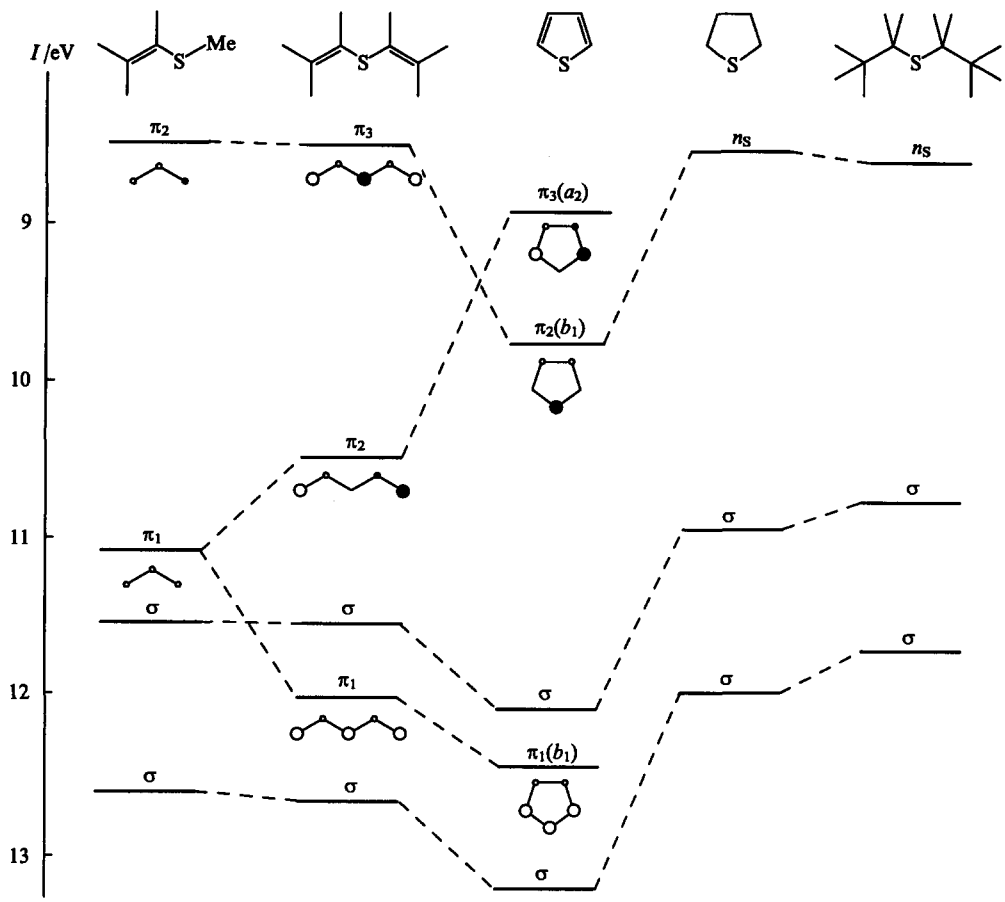


Figure 26. The orbital correlational diagrams for sulfur saturated and unsaturated derivatives.[179]

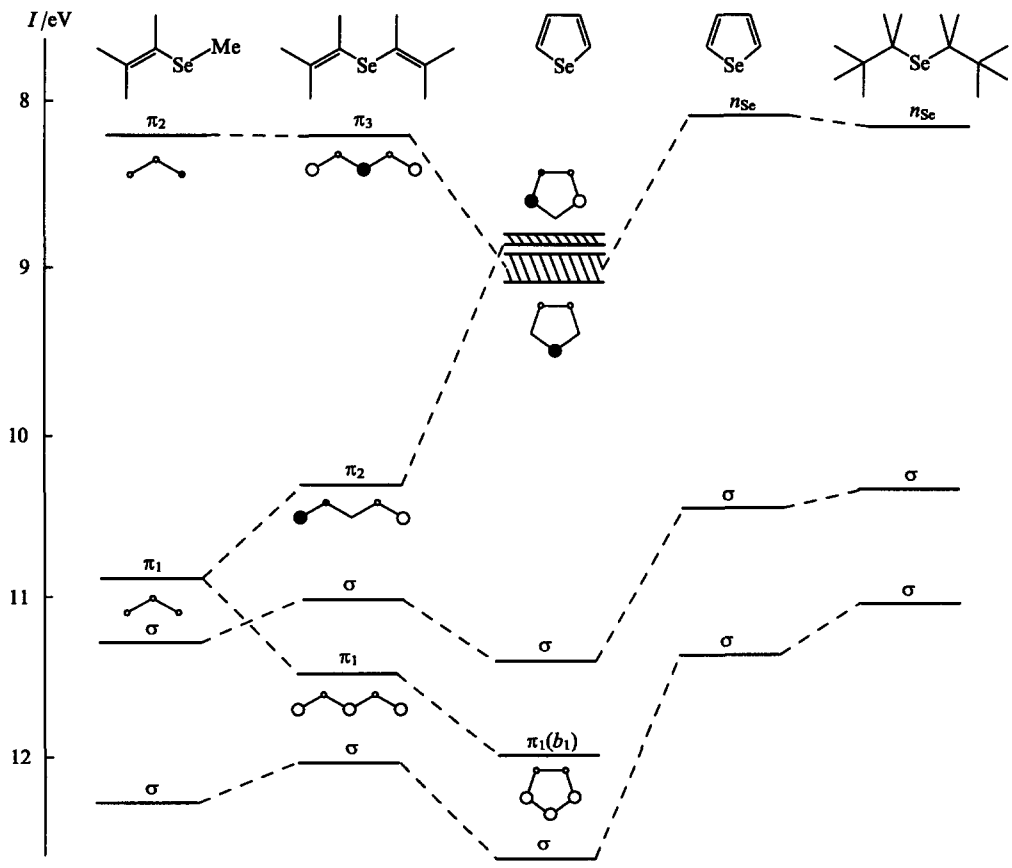


Figure 27. The orbital correlational diagrams for selenium saturated and unsaturated derivatives.[179]

The HOMOs also have common features. Comparison of dialkyl, alkyl vinyl, and divinyl sulfides and selenides shows that the first vertical ionisation potential I_1 (Table 6) practically does not change due to a rather weak coupling of p_z-AOs of a heteroatom with fragmentary π-MOs. The localisation of the orbital electron density mostly on the heteroatom and the terminal C_β atom is typical of HOMOs (I_1) of vinyl sulfides and selenides. This order of electron distribution gives reason to suppose that the transition from divinyl chalcogenides to saturated heterocyclic derivatives of sulfur and selenium will be accompanied by a strong stabilisation of the π_3-MO in the selenium derivatives. This is confirmed by the position of the first band in the PE spectra of divinyl sulfide and thiophene. The stabilisation of the π_3-MO leads to the inversion of the sequence of the two higher π-MOs. The PE spectra of divinyl selenide and selenophene consisting of a system of overlapping bands, are less indicative. Nevertheless, the mutual position of the first two bands makes it possible to state that the passage from divinyl selenide to selenophene results in, at least, quasi-degeneracy of the boundary π-MOs. The orbital correlational diagrams[179] for saturated and unsaturated sulfur and selenium derivatives indicate that the passage from saturated to unsaturated compounds of sulfur and selenium and to the corresponding cyclic structures leads to the stabilization of σ_1- and σ_2-MOs (Figs 26, 27).

For unsaturated sulfur compounds, comparison of results of the empirical approach to the estimation of their orbital structure with the results of the MNDO calculation (Table 7) shows that qualitative and quantitative agreement was obtained for each compound.[179] Calculations have been made for equilibrium planar *s-cis-*, *s-trans-*, *s-trans–s-trans-* (C_{2v}) forms and a non-planar *cis–trans*-form (C_1) of rotamers.[179] π-MO energy differences for these rotamers are extremely small, that is why the problem of rotational isomerism cannot be solved at the level of the first band in the PE spectrum. In the PE spectrum observed, the shape of the first band rules out the existence of a remarkable concentration of a less favourable rotamer differing from the major rotamer in torsional angles.

Adiabatic potentials for a series of diorganyl sulfides have been measured by the photoionisation method,[1,180] and conjugation energies in radical cations have been estimated by correlation analysis. Two-parameter approximation[180] yielded the plots (Fig. 28) showing that saturated and unsaturated representatives of the series correlate with the inductive Taft constants to form two independent regressions. The contributions of hyperconjugative and steric effects into the ionisation potential value were found with the requisite statistical accuracy: they make up ~20% of the contribution of the inductive effect.[180] At the same time, conjugation effects contribute significantly to the ionisation potentials, too (Fig. 28). The existence of independent linear dependences for saturated and unsaturated representatives of the series (Fig. 28, lines *1* and *2*, respectively) is due to the conjugation between the radical-cation centre and the adjacent double bond. The energy of this conjugation can be estimated[1,180] by deviations of the points for α,β-unsaturated sulfides from the basic correlational curve. For vinyl sulfides, it is equal to 1.0–1.3 eV.

Table 7. Theoretical and experimental assignment of bands in the PE spectra of divinyl sulfide and related compounds.[179]

Compound	Assignment				
	empirical		MNDO		
	MO	I_i/eV	MO	$-\varepsilon_i$/eV	
$CH_2=CHSMe$	π_2	8.4	π_2[a]	9.4[b];	9.3[c]
	π_1	11.0	π_1	11.8[b];	11.7[c]
	σ_1	11.6	σ_1	12.4[b];	12.1[c]
	σ_2	12.6	σ_2	12.9[b];	13.4[c]
$CH_2=C=CHSMe$	π_3	8.3	π_3	9.0[b];	9.0[c]
	π_2	9.7	π_2	10.2[b];	9.0[c]
	π_1	10.9	π_1	11.4[b];	11.4[c]
	σ_1	11.8	σ_1	12.0[b];	11.9[c]
	σ_2	13.3	σ_2	13.8[b];	14.0[c]
$(CH_2=CH)_2S$	π_3	8.5	π_3[e]	8.8[d];	8.7[e]
	π_2	10.4	π_2	10.7[d];	10.7[e]
	σ_1	11.6	σ_1	11.7[d];	11.6[e]
	π_1	11.9	π_1	12.4[d];	12.4[e]
	σ_2	12.7	σ_2	12.8[d];	13.0[e]
$CH_2=C=CHSCH=CH_2$	π_4	8.3	π_4[e]	8.7[b];	8.6[e]
	π_3	9.9	π_3	10.3[d];	10.2[e]
	π_2	10.3	π_2	10.6[d];	10.6[e]
	σ_1, π_1	12.0	σ_1	12.3[d];	12.3[e]
	σ_2	13.2	σ_2	13.8[d];	13.7[e]
	—	—	$\pi_3(1a_2)$		9.5
	—	—	$\pi_2(2b_1)$		10.0
	—	—	σ_1		12.8
	—	—	$\pi_1(1b_1)$		13.3

[a] The assignment based on the *ab initio* calculation;[69] [b] *s-cis*-form; [c] *s-trans*-form; [d] *cis–trans-* for $(CH_2=CH)_2S$ and $CH_2=C=CHSCH=CH_2$; [e] *s-trans–s-trans-* (C_{2v}) for $(CH_2=CH)_2S$ and $CH_2=C=CHSCH=CH_2$.

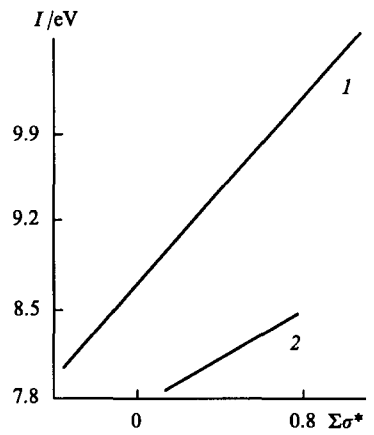


Figure 28. The dependence of ionisation potentials (*I*) of diorganyl selenides on inductive constants of substituents ($\Sigma\sigma^*$).[180]
(*1*) Unsaturated and cyclic organylthiols and sulfides, (*2*) vinyl sulfides.

5. Allenyl methyl sulfide and allenyl vinyl sulfide

Among unsaturated sulfides, allenyl methyl sulfide and allenyl vinyl sulfide occupy a somewhat unusual position (Table 7).[179] It might be expected that their orbitals, except for an additional π-MO localised at the $C_\beta=C_\gamma$ fragment (9.7 eV for allenyl methyl sulfide and 9.9 eV for allenyl vinyl sulfide) would follow the regularities found for vinyl sulfides. The similarity was, however, found only for allenyl vinyl sulfide (Fig. 25, Table 7). According to the data obtained by the MNDO method, which has shown a good performance in the case of other α,β-unsaturated sulfides, the energies of the σ_1- and σ_2-MOs of allenyl methyl sulfide fit the correlational curve of saturated sulfides (Fig. 25). The σ_2-MO energy for allenyl methyl sulfide is only 0.45 eV higher than the corresponding MO for methanethiol.[178] Unlike other analogous compounds, the σ_2-MO of allenyl methyl sulfide seems to be localised to a significantly greater extent within the $S-C_{sp^3}$ fragment. Other MOs of allenyl sulfides, except for the π-MO localised within the $C_\beta=C_\gamma$ fragment, are qualitatively the same as those for vinyl sulfides. The band assignment in the PE spectra of allenyl sulfides is given in Table 7.

6. PE spectra of vinyl tellurides

PE spectra of dimethyl telluride and some other dialkyl chalcogenides have been described.[181,182] An analysis of their orbital structure has been performed for model dimethyl derivatives of C_{2v} symmetry.[182] Three lowest-energy bands in the PE spectra of these compounds are associated with electron removal from the antibonding MO of the lone electron pair of the chalcogen atom and from two $\sigma_{1,2}$ bonds.

In the PE spectra of dialkyl tellurides in the range of 7.5–11.4 eV, as well as in the case of analogous sulfides and selenides, there are three bands (Table 8, Fig. 29 *a*). The lowest-energy and the narrowest band is unambiguously assigned to the MO with the major contribution of the tellurium p_z-AO. Two broader bands result from the ionisation of the σ-bonds (Fig. 29 *a*). Successive elongation of the hydrocarbon chain leads to a low-energy shift of all the bands. For saturated tellurides as well as for other dialkyl chalcogenides, there is a linear dependence between the higher σ-MO positions (Fig. 30).[183] An energy gap value ΔI_σ separating σ_1- and σ_2-MOs decreases systematically with an increase in alkyl substituent length and branching (Table 8). In other words, the behaviour of σ-MOs in dialkyl tellurides is completely similar to that of the corresponding sulfides and selenides.

Table 8. Vertical ionisation potentials for diorganyl tellurides.[183]

Compound	Ionisation energy /eV			
	$\pi(n_{Te})$	σ_1	π(C=C)	σ_2
Me_2Te[a]	7.9	10.3	—	11.3
$CH_2=CHTeMe$	7.9	10.3	10.6	11.4
Et_2Te	7.7	9.9	—	10.6
$(Pr^n)_2Te$	7.8	9.7	—	10.4
$(Pr^i)_2Te$	7.6	9.5	—	10.0
$CH_2=CHTePr^i$	7.8	9.7	10.5	10.4 (sh)
$(Bu^n)_2Te$	7.6	9.6	—	10.2
$CH_2=CHTeBu^n$	7.7	9.8	10.5	10.5
$(CH_2=CH)_2Te$	7.9	10.4	10.0, 11.0	11.4
	7.7	10.0	—	10.7
	8.4	10.8	8.9, 11.5	11.8

[a] The data of Ref. 178.

Analysis of PE spectra of vinyl tellurides has been carried out[183] using the empirical approach.[179] The PE spectra of vinyl tellurides contain four well-resolved bands (Table 8, Fig. 29 *b*, *c*). The low-energy band remains narrow. Moreover, for vinyl tellurides its position is practically the same as for dimethyl telluride. The replacement of an alkyl group by the vinyl group in the diorganyl telluride does not lead to a significant interaction of the fragmentary π-orbital with the p_z-AO of the tellurium atom, i.e. the first band relates to the MO localised primarily on the heteroatom. The second and the fourth bands belong to σ-MOs. Unlike saturated and unsaturated sulfur and selenium compounds, in tellurium compounds, the σ-MO energies correlate in the same manner (Fig. 30). The correlation extends also to the σ-MOs of divinyl telluride and tellurophene, thus indicating an equivalent coupling of the tellurium AOs with the orbitals of the sp^2- and sp^3-hybridized carbon atoms.[183] The third MO of vinyl tellurides is responsible for a slightly bonding combination of the π-MO of the vinyl fragment and the tellurium p_z-AO with a lesser contribution of the latter.

More detailed information on the structure of π-MOs in divinyl telluride can be obtained by comparing them with those of tellurophene. The π-MO of tellurophene can easily be composed from symmetry considerations.[183] The PE spectroscopic data (Table 8, Fig. 31) indicate that the passage from divinyl telluride to tellurophene leads to a remarkable increase in the first ionisation potential (0.5 eV). This is not due to the formation of the ordinary bond between the terminal carbon atoms of divinyl telluride, because the analogous structural variation for saturated compounds (tetrahydrotellurophene[184]) affects only slightly this

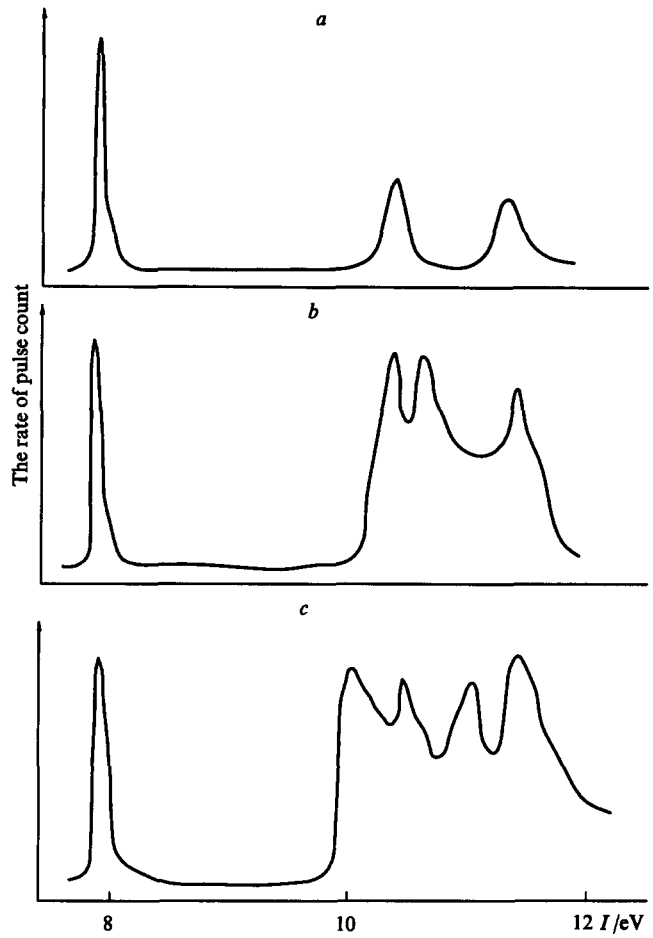


Figure 29. The PE spectra of dimethyl telluride (*a*),[182] vinyl methyl telluride (*b*), and divinyl telluride (*c*).[183]

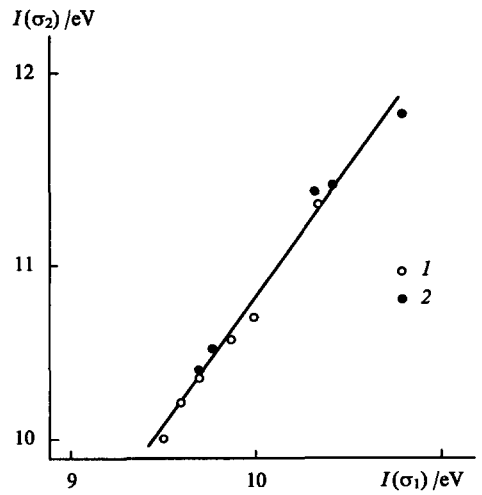


Figure 30. The correlation between the energies of σ-MOs for unsaturated (*1*) and saturated (*2*) organyl tellurides.[183]

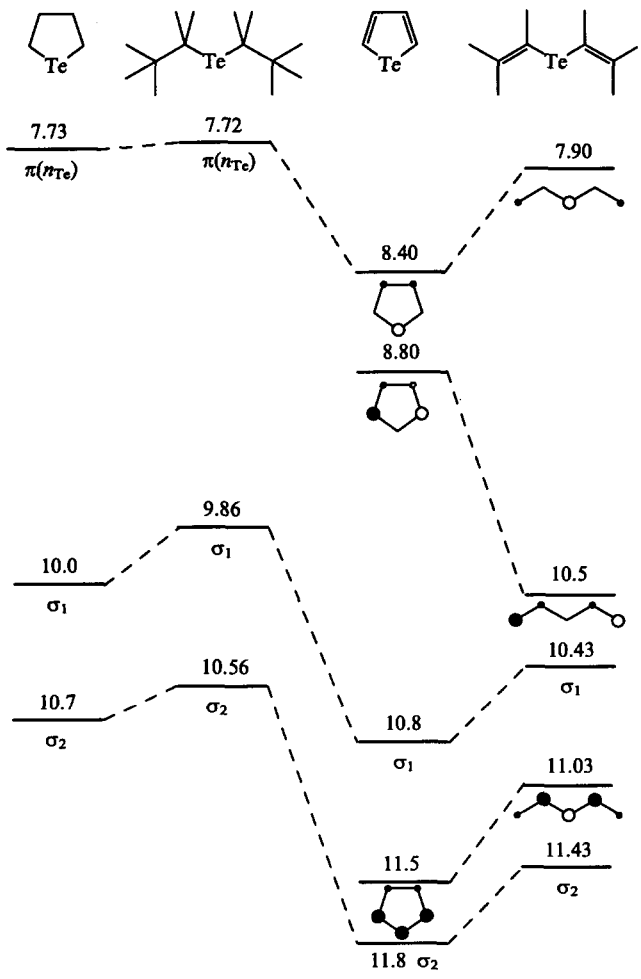


Figure 31. The orbital correlational diagrams for tellurium saturated and unsaturated derivatives.[183]

value. Apparently, stabilising interactions arise upon heterocyclisation. These interactions can be adequately rationalised only assuming that the HOMO structure for tellurophene is of the same type as that for the preferential rotamer of divinyl telluride. The correlation of the other π-MOs (Fig. 31) leads to the conclusion that the second occupied π-MO of divinyl telluride is an antibonding combination of orbitals of the vinyl fragment, and the lowest MO is, naturally, completely bonding.

Thus, the analysis of the PE spectral features of dialkyl, alkyl vinyl, and divinyl tellurides altogether gave the rationale for the nature of their MOs and allowed the empirical assignment to be made: the low-energy band for alkyl vinyl tellurides results from the ionisation of the MO with the dominating contribution of the tellurium p_z-AO, the second and the fourth bands correspond to the σ-MOs, the third band belongs to the π-MO. The orbital structures of divinyl telluride and tellurophene are of the same type.

7. UV absorption spectra of alkyl vinyl sulfides

UV absorption spectra are the subject of a large number of studies.[69, 132, 185–191] Nevertheless up to now, there is no unequivocal understanding of the nature of electronic transitions observed in liquid and in the gas phase. A discussion[69, 132, 185–191] about the band assignment in the near UV range for methyl vinyl sulfide is remarkable. The most long-wave transition was assigned to the first transition of the Rydberg series $\pi \rightarrow n_s$, and the next to the $\pi \rightarrow \pi^*$-type.[69] However, according to other data[191] the first long-wave band originates from the $n \rightarrow \sigma$ or $\sigma \rightarrow \sigma^*$ excitation, and the second band is associated with the $\pi \rightarrow \pi^*$ transition. Both transitions are considered[133, 190] to belong formally to the same ($\pi \rightarrow \pi^*$) type, but to correspond to two rotamers. Experimental data accumulated to date allowed one to perform systematic analysis of UV spectra of alkyl vinyl sulfides.[192] An empirical analysis of the full spectrum of gaseous methyl vinyl sulfide has been carried out.[69] In addition to the $\pi \rightarrow \pi^*$ transition, the spectrum of methyl vinyl sulfide is represented by three Rydberg series: $\pi \rightarrow ns$, $\pi \rightarrow np$, and $\pi \rightarrow nd$. Rydberg transitions fall primarily in the vacuum ultraviolet range and are inaccessible for comparative investigations in solutions. In the near UV range there are $\pi \rightarrow \pi^*$, $\pi \rightarrow 4p$, and $\pi \rightarrow ns$ transitions, the latter is believed[69] to be of the lowest energy in the series. Comparison (cf. with[193]) of the UV spectrum of methyl vinyl sulfide in the gas phase with those of solutions[189, 191] in hexane, dioxane, and ethanol, in which no narrow peaks of sufficient intensity were found at 204 nm, indicates that the most short-wave transition is largely of the Rydberg character. The quantum defect δ for this transition is relatively low, $\delta \sim \pm 0.59$ where

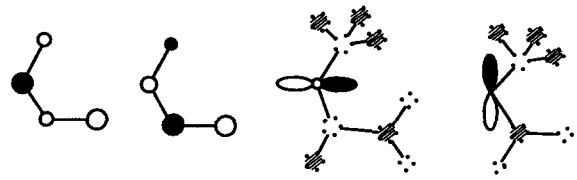
$$\delta = n - \left(\frac{R}{T}\right)^{1/2},$$

here R is the Rydberg constant, $T = I_1 - n$, n is a quantum number. Therefore, indeed, this transition can be assigned to the Rydberg transition of the $\pi \rightarrow 4p$ type.[192] An interesting feature of this transition is a dependence of the relative intensity of the corresponding band on the substituent structure, which decreases as the length of a hydrocarbon substituent and branching increase (Fig. 32); for compounds with R = *tert*-butyl and *tert*-pentyl, Rydberg transitions cannot be reliably assigned.[194]

The most long-wave band of methyl vinyl sulfide broadens on passage from the gaseous state to solution. It also broadens upon substitution of the methyl group for another alkyl substituent. Bulky substituents increase its absolute intensity (in solution). Sometimes even a slightly pronounced fine structure appears (Fig. 32, Table 9). For R = *tert*-butyl and *tert*-pentyl the intensity of this band increases, and a separate peak is observed (Fig. 32). An isotope effect was quite unexpected. In the case of methyl vinyl sulfide and its deuterio-isotopomer $CD_2=CDSMe$, the absorbance ratio of the maxima of the long-wave band and the neighbouring 'π' band (D_{244}/D_{225}) in the gas phase is 0.225, while in the spectrum of $CH_2=CHSCD_3$ this ratio is 1.35 times larger. The band half-width also increases (from 1540 cm^{-1} to 2130 cm^{-1}). Data on the deuteration effect also show that the methyl group orbitals (σ-symmetry) take part in the first excited state of methyl vinyl sulfide. The long-wave band of methyl vinyl sulfide might therefore be supposed to belong to the $\pi \rightarrow \sigma^*$ transition.

CNDO/C calculations indicate that yet another $\pi \rightarrow \sigma^*$-transition should exist in the UV range separated from the first one by an interval of ~1300 cm^{-1} (Scheme 2; *s*-AOs are marked with a dotted line). The band at ~196 nm in the spectrum of methyl vinyl sulfide in solution corresponds to the second $\pi \rightarrow s^*$-transition (Fig. 32, Table 10). In the spectrum of gaseous methyl vinyl sulfide, the band corresponding to this transition coincides with the components of a vibrational progression of the Rydberg $\pi \rightarrow 4p$ transition. A complex contour of the short-wave absorption band in gaseous methyl vinyl sulfide does not allow vibrational modes of this transition to be reliably identified.[192]

Scheme 2



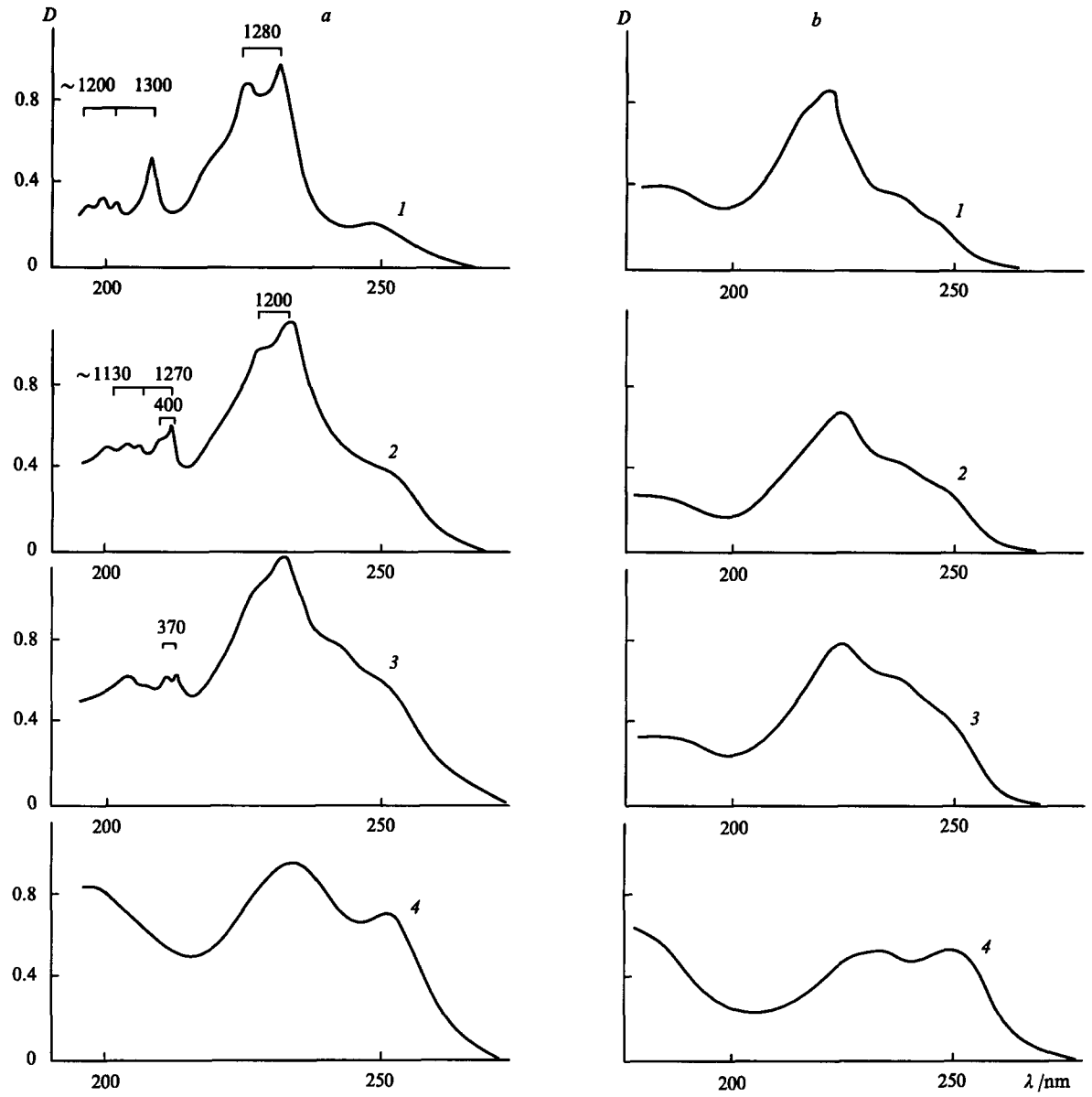


Figure 32. The UV absorption spectra of sulfides $CH_2=CHSR$, where R = Me (*1*), Et (*2*), Bu^i (*3*), Pent^t (*4*), in the gaseous state (*a*) and in a hexane solution (*b*).[192]

The $\pi\rightarrow\pi^*$ transition band with peaks in the range of 225–236 nm in the spectrum of gaseous methyl vinyl sulfide has a fine structure (the distance between the components is $\sim$1000–1300 cm^{-1}), which disappears in the solution spectra.[192]

Thus, the following energy sequence of transitions is observed in the UV spectra of alkyl vinyl sulfides:[192] $\pi\rightarrow\sigma^* < \pi\rightarrow\pi^* < < \pi\rightarrow np < \pi\rightarrow\sigma^*$.

8. UV absorption spectra of alkyl vinyl selenides

UV spectra of vinyl selenides have been studied.[191,192] The type and the sequence of electronic transitions have been determined (Fig. 33). Comparison of UV spectra of methyl and ethyl vinyl selenides in the gaseous and condensed state identifies the Rydberg transition at $\lambda=202$ nm and 204 nm, respectively. A relatively low magnitude of the quantum defect (0.48) makes it possible to assign these bands to the $\pi\rightarrow 5p$ type (Table 9). $\pi\rightarrow\sigma^*$-Transitions in alkyl vinyl selenide are red-shifted as compared to those in the corresponding sulfides, on the average, by 4600 cm^{-1} and occur in the range of 265–270 nm and at 220 nm (Table 10). In the spectrum of methyl vinyl selenide (Fig. 33), the band corresponding to the $\pi\rightarrow\pi^*$ transition has fine structure (1000, 600, $\sim$600 cm^{-1}), which differs from that for the analogous sulfur compounds (Fig. 32). Moreover, substitution of the methyl group for the ethyl group leads to a change in the Franck–Condon contour of the absorption band (Fig. 33). This gives grounds to suppose that the 'π' band of methyl vinyl selenide coincides with the band of the Rydberg transition ($\lambda=$ 236 nm), which distorts the profile of the absorption band in the gas phase. In solution, the Rydberg band disappears or decreases in intensity (Fig. 33, Table 10). The quantum defect of the Rydberg transition (0.88) corresponding to the band at 236 nm allowing one to assign it to the $\pi\rightarrow 5s$ type.

This assignment has further support. The first ionisation potentials for dimethyl and methyl vinyl selenides (to which Rydberg series converge) are close: 8.33 eV and 8.29 eV, respectively.[179] Therefore, their Rydberg $n_{Se}\rightarrow 5s$ and $\pi\rightarrow 5s$ transitions will also be close. In the spectrum of gaseous Me_2Se there is a narrow peak at $\lambda=236$ nm, which is not registered in solution.[191] Its quantum defect ($\delta=0.94$) is in full accord with the Rydberg transition from the series $n_{Se}\rightarrow ns$.[196] The following sequence of electronic transitions was found for alkyl vinyl selenides:[192] $\pi\rightarrow\sigma^* < \pi\rightarrow\pi^* \sim \pi\rightarrow ns < \pi\rightarrow\sigma^* < \pi\rightarrow np$ (Tables 9, 10).

Table 9. Rydberg ($np \rightarrow \pi$) transitions for organyl chalcogenides (gaseous phase).[192]

Compound	I_1 [a] /cm^{-1}	Transition (ν /cm^{-1}) [b]	λ /nm	δ [c]
H_2S	84451	65963 [d]	152	0.56
Me_2S	76304	57250 [d]	175	0.60
Et_2S	74933	56000 [e]	178	0.59
$(Bu^t)_2S$	72836	54000 [e]	185	0.585
Me_2S	70013	51165 (287; 698; 1004; 1316)[d]	195	0.59
Et_2S	68077	49000 (~600; 1160)	204	0.60
$EtSPr^i$	67400	48600 (~550; 1110)	206	0.585
$CH_2=CHSMe$	68077 [e]	49200 (1300; ~1200)	203	0.59
$CH_2=CHSEt$	67840 [f]	48480 (400; 1270; ~1150)	206	0.62
$CH_2=CHSPr^n$	67430 [f]	48000 (~400; 1280)	208	0.625
$CH_2=CHSPr^i$	67350 [f]	48520 (1240)	206	0.585
$CH_2=CHSBu^n$		47800	209	
$CH_2=CHSBu^s$		48160 (~1200)	208	
$CH_2=CHSBu^i$	67350 [f]	48270 (370)	260	0.60
$CH_2=CHSBu^t$	66710 [f]	–	—	
$CH_2=CHSPent^t$		~48000 (very weak)	~206	
$CH_2=CHSCD_3$		49240 (1210; ~1200)	203	
$CD_2=CDSMe$		49200 (1000; 1200)	203	
H_2Se	79692	60600[d]	165	0.60
Me_2Se	67432	49200 (~233; ~595; 981; 129)[d]	203	0.55
$CH_2=CHSeMe$	66867	~49000	~204	0.48
$CH_2=CHSeEt$	66141	48900	205	0.48
H_2Te	73723	55000 [c]	182	0.58
Me_2Te	63641	46240 (180; ~530; 898; 1252)[d]	216	0.49
$CH_2=CHTeMe$	63398	46700 (~200)	~214	0.44

[a] The data of Ref. 178; [b] the vibrational quantum number is given in parentheses; [c] while estimating, the major quantum number was decreased by 1, 2, 3 for S, Se, and Te, respectively; [d] an analysis of the vibrational structure see in Ref. 195; [e] the data of Ref. 195; [f] calculated from the data of Ref. 180: $I_i = I_1 + 0.2$ /eV.

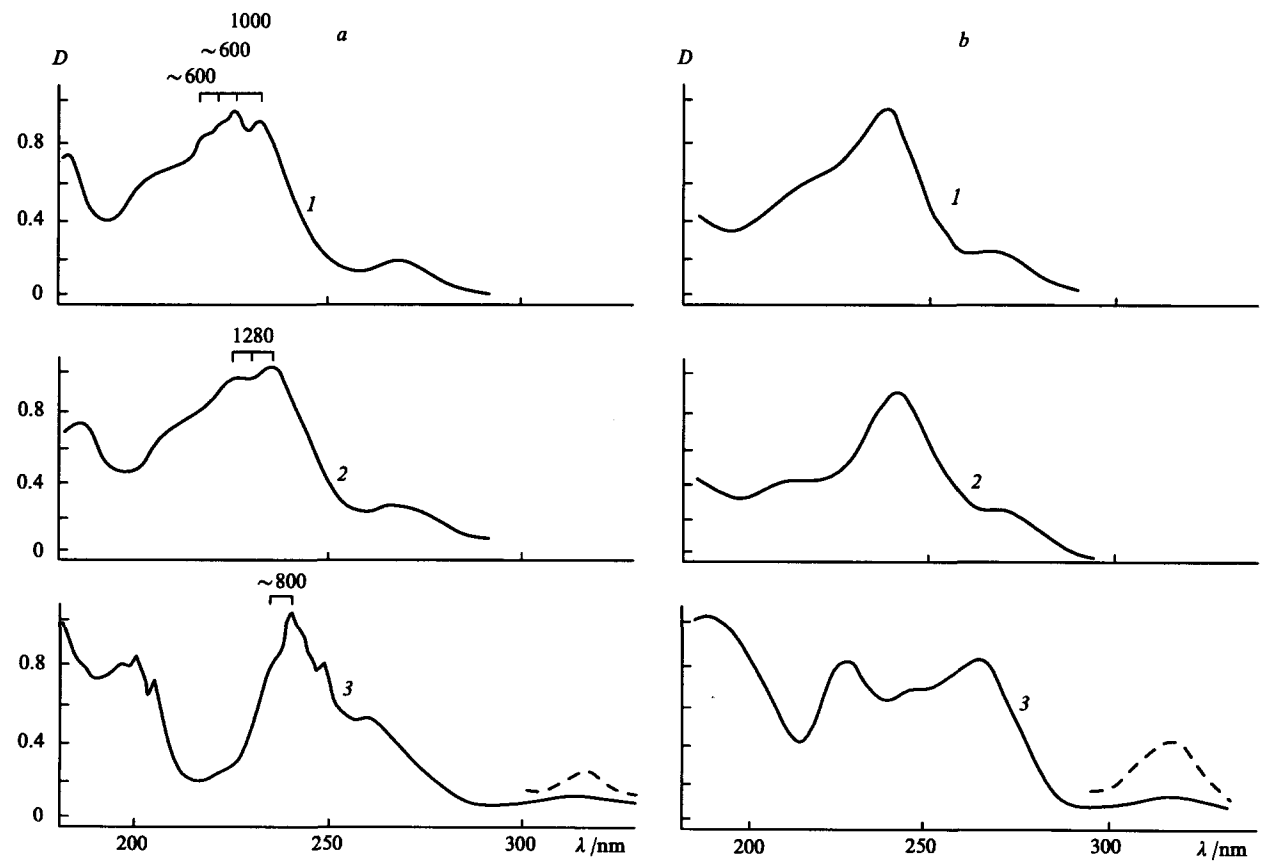


Figure 33. The UV absorption spectra of vinyl selenides $CH_2=CHSeMe$ (*1*), $CH_2=CHSeEt$ (*2*), and vinyl methyl telluride $CH_2=CHTeMe$ (*3*) in the gaseous state (*a*) and in a heptane solution (*b*).[192]

Table 10. Electronic transitions in the near UV region for vinyl chalcogenides.[192]

Compound	Medium[a]	Transition (λ /nm)		
		$\pi \rightarrow \sigma^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \sigma^*$
$CH_2=CHSMe$	GP	243	225 (1280; ~1300)[b]	196
	HX	238–250	227 (~1000)	<198
$CH_2=CHSEt$	GP	241–246	226 (1200)	199
	HX	247–253	229	<194
		238–244		
$CH_2=CHSPr^n$	GP	240–246	226 (~1150)	200
	HX	244–250	228	<198
		~238		
$CH_2=CHSBu^n$	GP	238–247	226	<199
	HX	244–250	230	~198
		~238 (sh)		
$CH_2=CHSBu^i$	GP	~244 (sh)	230 (~1150)	200
		232–238		
	HX	~250 (sh)	228	<196
		239		
$CH_2=CHSBu^s$	GP	247	227	199
	HX	~250 (sh)	231	<194
		235–241		
$CH_2=CHSPr^i$	GP	247	227 (~1250)	197
		235–238		
	HX	~252 (sh)	231	
		~240 (sh)		
$CH_2=CHSBu^t$	GP	249	229	
	HX	251	235	<199
$CH_2=CHSPent^t$	GP	249	229	198
	HX	251	235	<192
$CH_2=CHSCD_3$	GP	241	225 (1260; 1300)	196
$CD_2=CDSMe$	GP	244	225 (1160; ~1150)	196
$CH_2=CHSeMe$	GP	266	230 (~600; ~600)	~220
	HP	268	240	<220
$CH_2=CHSeEt$	GP	267	238 (~640)	~221
	HP	271	242	218
$CH_2=CHSePr^i$	HP	272	243	~219
$CH_2=CHSeBu^t$	HX	273	244	~219
$CH_2=CHTeMe$	GP	330	243	259
	HP	331	232	266
$CH_2=CHTeEt$	HP	332	230	267
$CH_2=CHTePr^n$	HP	329	229	268
$CH_2=CHTePr^i$	HP	333	229	268
$CH_2=CHTeBu^n$	HP	328	228	267

[a] Accepted notations: GP — gaseous phase, HX — hexane, HP — heptane; [b] the vibrational quantum number is given in parentheses.

9. UV absorption spectra of alkyl vinyl tellurides

Alkyl vinyl tellurides absorb in the range of 200–330 nm (Table 9, 10, Fig. 34).[192] The $\pi \rightarrow \sigma^*$ transitions in the UV spectrum of methyl vinyl telluride are strongly (by ~7100 cm^{-1}) red-shifted even in comparison with those in methyl vinyl selenide, and are located at 259 and 329 nm in the gas phase. For methyl vinyl sulfide band intensities of $\pi \rightarrow \sigma^*$ transitions are of the same order (~10^3), whereas dramatic redistribution takes place on going to vinyl telluride, i.e. with an increase in the mass of the heteroatom (Fig. 33). In the spectrum of a heptane solution of methyl vinyl telluride, the extinction ratio of long-wave and short-wave bands of $\pi \rightarrow \sigma^*$ transitions is $\sim 6 \times 10^{-2}$. This is probably due to localisation of the MOs of methyl vinyl telluride within the CTeC fragment having high symmetry (C_2 or C_{2v}). For the ground state of methyl vinyl telluride such a supposition is confirmed by PE spectroscopic data. In contrast to sulfides, the higher occupied π-MO in unsaturated tellurides contains a dominating contribution from the tellurium *pz*-AO (I_1 values are the same for Me_2Te and $CH_2=CHTeMe$).[183] UV spectra show that it is true of the excited state with an electron in the σ_1^*-MO and the vacant π-MO.

As was already noted, the long-wave σ band profile in the spectra of vinyl sulfides is dictated by the phase state and the structure of the alkyl substituents. In the spectra of alkyl vinyl tellurides, the contours of both σ-bands depend on none of these. Irreducible representations b_1, a_1, and b_2 correspond to the HOMO of the π-type and to two low-lying vacant σ^*-orbitals of the ground state of methyl vinyl telluride. Hence, it follows that the transitions will be one-configurational, and one of them [$^1A_1 \rightarrow {}^1B_1$ ($^1b_1{}^1a_1^*$) or $^1A_1 \rightarrow {}^1A_2$ ($^1b_1{}^1b_2^*$)] is symmetry-forbidden (in the absence of electronic-vibrational interactions).

A transition of the $\pi \rightarrow \pi^*$-type is responsible for the band at $\lambda = 243$ nm (gas) with a vibrational splitting of ~800 cm^{-1} in the UV spectrum of methyl vinyl telluride. The splitting is significantly higher than the frequency of the CTeC stretching mode in the ground state,[143] thus indicating that the bond becomes stronger upon excitation. The passage from gas to solution causes a red shift (1000 cm^{-1}) in the respective spectra.

It is known that in the UV spectrum of Me_2Te, the first Rydberg transitions of the series $n_{Te} \rightarrow 6s$ and $n_{Te} \rightarrow 6p$ are observed at 250 nm and 216 nm. Comparison of the spectra of methyl vinyl telluride in the gas phase and in solution and the fact that the first

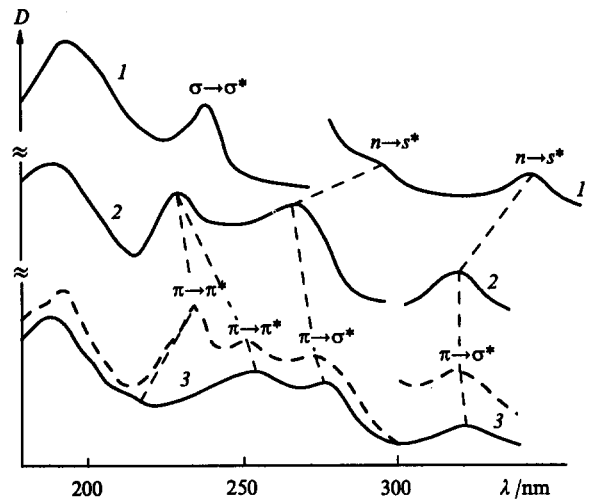


Figure 34. The UV absorption spectra of diorganyltellurides Et_2Te (*1*), $CH_2=CHTeEt$ (*2*), and $(CH_2=CH)_2Te$ (*3*) in a heptane solution. The spectrum of $(CH_2=CH)_2Te$ in the gaseous phase is shown in a dotted line.[197]

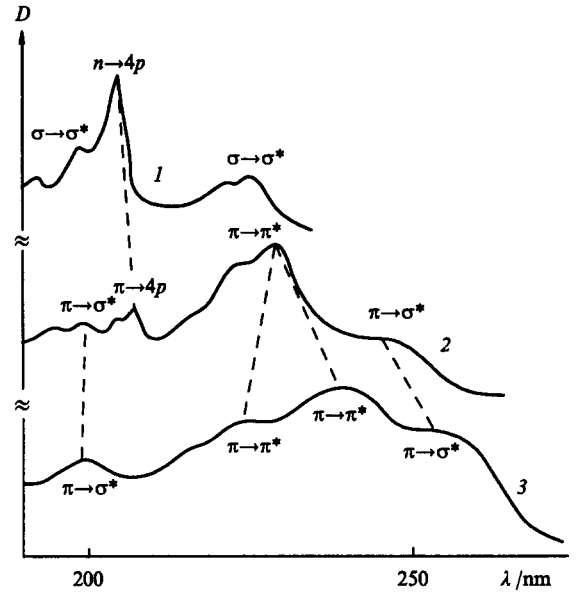


Figure 35. The UV absorption spectra of diorganylsulfides Et_2S (*1*), $CH_2=CHSEt$ (*2*), and $(CH_2=CH)_2S$ (*3*) in the gaseous phase.[197]

ionisation potentials of this compound[183] and Me_2Te are practically the same (7.90 and 7.89 eV) made it posible[192] to assign the bands at 250 nm and 214 nm to the $\pi\rightarrow 6s$ and $\pi\rightarrow 6p$ Rydberg transitions, respectively.

Hence, the following sequence of electronic transitions is observed in the UV spectra of alkyl vinyl tellurides:[192] $\pi\rightarrow\sigma^* < \pi\rightarrow\sigma^* < \pi\rightarrow ns < \pi\rightarrow\pi^* < \pi\rightarrow np$.

Thus, the common feature of the simplest unsaturated compounds of S, Se, and Te is the of presence a low-energy excited state[192] in which an electron occupies the σ_1^*-MO, and a vacancy arises on the π-MO. From the practical point of view, it is important that in the UV spectra of alkyl vinyl chalcogenides, the energies of $\pi\rightarrow\sigma_i^*$ transitions are approximately constant: for sulfides it is 9970 cm^{-1} in the gas phase, for selenides and tellurides it is ~8000 cm^{-1}. Quite different behaviour is typical of two higher occupied σ-MOs of the ground state: an energy gap between the transitions decreases with complication of the structure.[179,183] With the increase in the atomic number of the chalcogen, the $\pi\rightarrow\sigma^*$ and $\pi\rightarrow\pi^*$ transitions exhibit a systematic red shift, the former being more sensitive to the nature of the element than the latter.[192]

10. UV absorption spectra of divinyl chalcogenides

The following concepts[179,183] were used in the assignment of electronic transitions in the UV spectra of divinyl chalcogenides (Figs 34, 35):[197] a) the energy gap between the σ band maxima is practically independent of the alkyl substituent length and branching and somewhat decreases with an increase in the heteroatom atomic number; and b) the energies of two higher occupied σ-MOs of organyl chalcogenides are linearly related. These properties of $\pi\rightarrow\sigma^*$ transitions could make the band assignment in the absorption spectra of divinyl chalcogenides substantially easier if data were available on similar transitions in the series $CH_3-CH_2XCH_2-CH_3$, $CH_2=CHXCH_2-CH_3$, $CH_2=CHXCH=CH_2$ (for saturated compounds, the $\pi\rightarrow\sigma^*$ transitions are actually identical to the $n_X\rightarrow\sigma^*$ ones). Unfortunately, only long-wave $n_s\rightarrow\sigma^*$ transitions are known for saturated cyclic sulfides, which have an extremely low intensity because they are symmetry-forbidden.[194] For dialkyl sulfides, these bands overlap with an intense band associated with the $\sigma\rightarrow\sigma^*$ excitation.[194] For dialkyl sulfides in the gas phase and in solution, both $n_{Te}\rightarrow\sigma^*$ transitions are shown[197] to have an intensity quite sufficient for reliable detection, and are located in a more long-wave region than the transition of the $\sigma\rightarrow\sigma^*$ type (Table 11, Fig. 34). It can be seen from Table 11 that the Δ_σ^* values for saturated and unsaturated tellurides differ insignificantly.

The energies of two higher occupied σ-MOs of diorganyl chalcogenides are known[179,183] to be linearly interrelated. Similar relationship can also be true of two low-lying vacant σ*-MOs because in the molecules of high symmetry they are rearrange by the same irreducible representations as the higher occupied σ-MOs do. Analysis of UV spectra of diorganyl chalcogenides in which both $\pi\rightarrow\sigma^*$-transitions are satisfactorily resolved (Table 11), reveals indeed a linear correlation of their energies, which is true for all the compounds considered regardless of the chalcogen type and the number of unsaturated fragments (Fig. 36).[197] Taking this into account, the following energy sequence was obtained for electronic transitions in the UV absorption spectra of divinyl chalcogenides:[197]

for Te: $\pi\rightarrow\sigma^* < \pi\rightarrow\sigma^* < \pi\rightarrow\pi^* < \pi\rightarrow\pi^*$;

for S and Se: $\pi\rightarrow\sigma^* < < \pi\rightarrow\pi^* < \pi\rightarrow\pi^* < \pi\rightarrow\sigma^*$.

Changes in the Franck–Condon absorption profile for divinyl telluride with regard to the phase state (Fig. 34) indicate

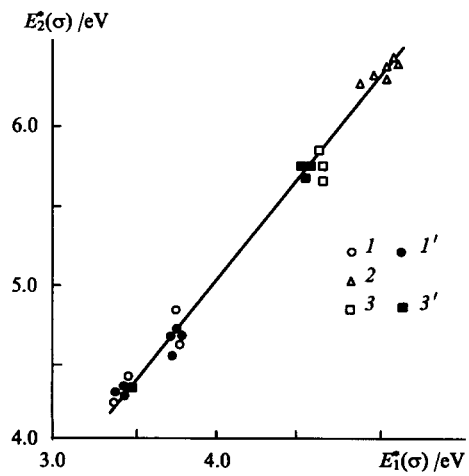


Figure 36. The correlation between the energies of the $\pi(n)\rightarrow\sigma^*$ transitions for tellurides (*1*,*1'*), selenides (*2*), and sulfides (*3*,*3'*) in the gaseous state (*1*–*3*) and in a heptane solution (*1'*, *3'*).[197]

Table 11. Characteristics of electronic transitions for diorganyl chalcogenides.[197]

Compound	$\pi \rightarrow \sigma^*$ transition[a]			$\sigma \rightarrow \sigma^*$ transition[a]
	E_1^* /eV	E_1^* /eV	Δ_σ^*	E_1^* /eV
Heptane				
Me_2Te	3.38 (1.9)	4.24 (2.2)	0.86	5.18 (3.8)
$CH_2=CHTeMe$	3.75 (2.5)	4.67 (3.7)	0.92	—
EtTeMe	3.42 (1.9)	4.29 (2.6)	0.87	5.24 (3.8)
$CH_2=CHTeEt$	3.72 (2.6)	4.64 (3.6)	0.91	—
$(Pr^n)_2Te$	3.41 (2.1)	4.25 (2.3)	0.84	5.21 (3.8)
$CH_2=CHTePr^i$	3.72 (2.5)	4.63 (3.5)	0.91	—
$(Bu^n)_2Te$	2.46 (1.9)	4.30 (2.6)	0.84	5.27 (3.8)
$CH_2=CHTeBu^n$	3.77 (2.6)	4.64 (3.6)	0.87	—
$(CH_2=CH)_2Te$	3.72 (2.6)	4.49 (3.7)	0.77	—
$CH_2=CHSeEt$	4.58 (3.3)	5.70 (3.3)	~1.10	—
$CH_2=CHSePr^i$	4.56 (3.3)	5.66 (3.4)	1.10	—
$CH_2=CHSeBu^t$	4.54 (3.4)	5.70 (3.5)	~1.20	—
Gaseous phase				
Me_2Te	3.36	4.23	0.87	see[b]
$CH_2=CHTeMe$	3.76	4.79	1.03	—
Et_2Te	3.43	4.30	0.87	see[b]
$(CH_2=CH)_2Te$	3.77	4.58	0.81	—
$CH_2CHSeMe$	4.66	5.70	~1.10	—
$CH_2=CHSeEt$	4.65	5.60	~0.90	—
$(CH_2=CH)_2Se$	4.64	5.80	~1.20	—
$CH_2=CHSMe$	5.10	6.33	1.23	—
$CH_2=CHSCD_3$	5.13	6.33	1.20	—
$CD_2=CDSMe$	5.08	6.32	1.24	—
$CH_2=CHSAm^t$	4.98	6.27	1.29	—
$(CH_2=CH)_2S$	4.90	6.22	1.32	—

[a] Extinction coefficient ($\lg \varepsilon$) is given in parentheses; [b] the bands of the $\sigma \rightarrow \sigma^*$ transition and the Rydberg transition overlap.

that in the gas phase the short-wave $\pi \rightarrow \pi^*$ transition overlaps with the Rydberg $\pi \rightarrow ns$ transition. Among $\pi \rightarrow \pi^*$ transitions in divinyl chalcogenides, the most short-wave transition is the least intense. A great difference in intensities of the σ-bands for divinyl telluride (Fig. 34) can be easily rationalised on the assumption of its planar conformation (C_{2v}). For a non-planar form (C_2) of divinyl chalcogenides, an $^1A < {}^1B$ sequence corresponds to π^* excited states. The ^1B state is associated with the electronic configuration $a^2b^1b^*a^1$, and the position of the a-symmetry orbitals depends slightly on the central atom, therefore, there is a near-linear correlation between the energy (E^*) of the $^1A \rightarrow {}^1B$ transition in divinyl chalcogenides and their first ionisation potentials (Fig. 37).[197]

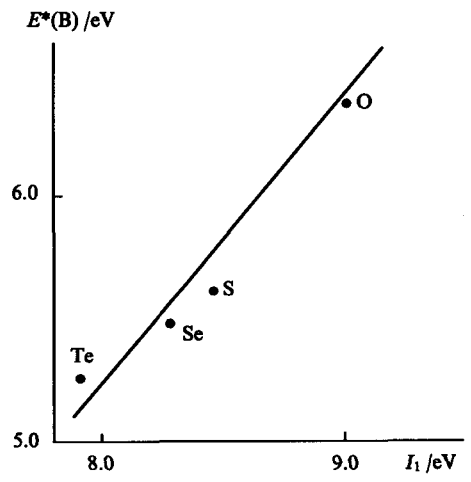


Figure 37. The dependence of the energies of $^1A \rightarrow {}^1B$ transitions for divinyl chalcogenides in the gaseous phase on the first ionisation potential (I_1). Points are the experimental values of E^*(B) in the gaseous phase.[197]

11. UV absorption spectra of allenyl ethers

Electronic transitions in the UV spectra of alkyl allenyl and allenyl vinyl ethers have been analyzed.[175,177] Two bands were observed in the spectra of heptane solutions, which had a tendency for a blue shift (~2–3 nm) on going to a polar solvent (Table 12). The bands of alkyl allenyl ethers belong to the $\pi \rightarrow \bar{\pi}^*$ and $\bar{\pi} \rightarrow \pi^*$ transitions partially allowed due to electronic-vibrational interaction in the allene group.[175] In allenyl vinyl ethers, the long-wave band corresponds to the transition localised within the allene fragment, and the short-wave band belongs to the $\pi \rightarrow \pi^*$ transition.[177]

In a series of alkyl allenyl ethers, the most significant changes in the UV spectra were observed for $CH_2=C=CHOBu^t$.[175] The electronic transition corresponding to the long-wave band appeared to be the most sensitive. In addition to a blue shift of this band by ~16 nm relative to its position in allenyl methyl ether, its half-width nearly doubles.

In order to study the possible influence of stereoisomerism in alkyl allenyl ethers on the nature and position of electronic transitions, CNDO/C calculations for the molecules $CH_2=C=CHOMe$ and $CH_2=C=CHOBu^t$ have been carried out.[175] The one-configurational long-wave transition appeared to be symmetry-forbidden (it belongs to the $\pi \rightarrow \bar{\pi}^*$ type). The next $\bar{\pi} \rightarrow \pi^*$ transition occurs at 4.83–4.86 eV. The energy gap between the bands observed in the ranges of 255–275 nm and 208–213 nm in the spectra of alkyl allenyl ethers corresponds to the difference in the calculated energies of the $\pi \rightarrow \bar{\pi}^*$ and $\bar{\pi} \rightarrow \pi^*$ transitions. A blue shift of the long-wave band in $CH_2=C=CHOBu^t$ as compared to that in allenyl methyl ether can be explained by a difference in the conformations of these

Table 12. The UV absorption spectra of allenyl ethers.[175,177]

Compound	Solvent	λ /nm (lg ε)	
$CH_2=C=CHOMe$	C_7H_{16}	274 (2.0);	212 sh (3.3)
	EtOH	270 (1.9);	210 sh (3.4)
	MeCN	269 (2.0);	210 sh (2.5)
$CH_2=C=CHOEt$	C_7H_{16}	272 (2.0);	211 sh (3.2)
	EtOH	269 (2.0);	210 sh (3.3)
	MeCN	268 (2.0);	210 sh (3.3)
$CH_2=C=CHOPr^n$	C_7H_{16}	272 (1.9);	211 sh (3.2)
	EtOH	270 (1.9);	211 sh (3.1)
$CH_2=C=CHOPr^i$	C_7H_{16}	271 (2.0);	211 sh (3.3)
	EtOH	268 (1.9);	211 sh (3.2)
$CH_2=C=CHOBu^n$	C_7H_{16}	272 (1.9);	211 sh (3.3)
	EtOH	269 (1.9);	211 sh (3.2)
$CH_2=C=CHOBu^i$	C_7H_{16}	271 (1.9);	211 sh (3.2)
	EtOH	269 (1.9);	211 sh (3.1)
$CH_2=C=CHOBu^t$	C_7H_{16}	258 (2.0);	208 sh (3.5)
	EtOH	257 (1.9);	208 sh (3.5)
$CH_2=C=CHOCH_2CH=CH_2$	C_7H_{16}	272 (1.9);	213 sh (3.5)
	EtOH	270 (1.8);	213 sh (3.3)
$CH_2=C=CHOCH=CH_2$	C_7H_{16}	265 (2.4);	213 (4.1)
	EtOH	263 (2.5);	211 (4.3)
	MeCN	261 (2.4);	210 (4.2)
$CH_2=C=C(Me)OCH=CH_2$	C_7H_{16}	267 (2.4);	216 (4.0)
	EtOH	266 (2.4);	214 (4.0)
$CH_2=C=C(Pr^i)OCH=CH_2$	C_7H_{16}	269 (2.3);	216 (4.2)
	EtOH	267 (2.4);	215 (4.3)
$CH_2=C=C(Pr^n)OCH=CH_2$	C_7H_{16}	270 (2.4);	215 (10940)
	EtOH	269 (2.4);	214 (10775)
$(CH_2=CH)_2O$	C_7H_{16}	—	210 (14430)
	EtOH	—	209 (19880)

molecules. However, the calculations for *cis*- and *trans*-rotamers in allenyl methyl ether show that the electronic transition energies depend little on the nature of the planar conformation. Violation of the orthogonal character of the π-systems of the allene fragment does not substantially affect spectral characteristics as well.[175] The calculated electronic spectrum of $CH_2=C=CHOBu^t$, in which the *tert.* butyl substituent is rotated relative to the $C_{sp^2}-O$ bond by 30–60° (from the planar *s-trans*-form), indicates that the long-wave band is 3–9 nm blue-shifted. It should be borne in mind that for this compound C_s symmetry might break if there is the only minimum in the internal rotation potential curve corresponding to the *s-trans*-rotamer. Presumably, the shape of the internal rotation potential ensures significant population of the excited torsional-vibrational states, for which large-amplitude motion is typical. It explains a larger width of the long-wave band in $CH_2=C=CHOBu^t$ as compared to that in allenyl methyl ether but does not explain a spectral shift because a vibration amplitude of 60° can hardly be supposed.

Another possible reason is the presence of a non-planar *gauche*- or near-*gauche*-form along with the planar *s-trans*-form. In this case, however, the extinction for the *gauche*-conformer should be, at least, two orders of magnitude higher than that for the planar one. This situation does not seem probable since the long-wave transition is symmetry-forbidden for alkylallenes. Thus, the reason for a blue shift of the long-wave band in $CH_2=C=CHOBu^t$ as compared to that in the spectrum of allenyl methyl ether remains obscure.

The most short-wave electronic transition was calculated[175] to have an energy > 6 eV and corresponds to the $\pi\rightarrow\pi^*$ transition observed for alkyl vinyl ethers in the range of 190–200 nm.[198]

According to CNDO/C calculations for allenyl vinyl ether,[177] the long-wave transition is located at 308.6 eV ($f=0$) and belongs to the $\pi\rightarrow\bar{\pi}^*$ type. The next transition belongs to the $\bar{\pi}\rightarrow\pi^*$ type of the allene fragment. Unlike the corresponding transitions in allenyl methyl ether, the long-wave transitions in allenyl vinyl ether are two-configurational (Table 13).[177] The short-wave transition in allenyl vinyl ether is mostly one-configurational. The calculation shows that the corresponding band is located in the range of 210–215 nm and originates from the $\pi\rightarrow\pi^*$ excitation.

V. Conclusion

The investigations of rotational isomerism in vinyl and allenyl chalcogenides summarised in the present review have revealed remarkable peculiarities of the molecular and electronic structure of this group of compounds. Two qualitatively different types of stable conformers exist. One of them is characterised by a definite torsional angle and small deviations from the global minimum of potential energy. The other is associated with large-amplitude relative motion of molecular fragments encompassing not one, but several local minima in the internal rotation potential curve. Methyl vinylchalcogenides represent an ensemble of stationary

Table 13. The UV absorption spectra of allenyl methyl, allenyl vinyl, and divinyl ethers.[177]

Molecule (rotamer)	λ_{exp} /nm	lg ε	λ_{calc} /nm	f_i	Transition	Dominating conformation (contribution)
$CH_2=C=CHOMe$ (*s-cis*)	274	2.0	316.6	0.0000	$\pi\rightarrow\bar{\pi}^*$	1–2* (1.00)
			255.3	0.0002	$\bar{\pi}\rightarrow\pi^*$	2–1* (1.00)
	212 (sh)	3.3	204.1	0.9680	$\pi\rightarrow\bar{\pi}^*$	1–1* (0.83)
						2–2* (0.53)
$CH_2=C=CHOCH=CH_2$ (*trans–trans*)	265	2.4	308.6	0.0000	$\pi\rightarrow\bar{\pi}^*$	1–3* (0.89)
						3–3* (0.45)
			260.0	0.0001	$\bar{\pi}\rightarrow\pi^*$	2–1* (0.65)
						2–2* (0.75)
	213	4.1	212.7	1.0820	$\pi\rightarrow\pi^*$	1–1* (0.88)
						2–3* (0.37)
			189.4	0.0800	$\pi\rightarrow\pi^*$	1–2* (0.89)
						1–1* (0.36)
$(CH_2=CH)_2O$ (*trans–trans*)	210	4.2	196.4	0.6520	$\pi\rightarrow\pi^*$	1–1* (0.99)
			181.5	0.0258	$\pi\rightarrow\pi^*$	1–2* (0.03)

states corresponding to planar *cis*-, *gauche*-, free rotational, and 'quasi'-*trans*-states, in which large-amplitude molecular motion occurs relative to the planar *trans*-form. The existence of three non-planar stable forms, viz, two quasi-degenerate *trans*–*trans*- and one *cis*–*trans*-, as well as large amplitude intramolecular motion at high temperatures and, occupancy of above-barrier states under these conditions are typical of internal rotation in divinyl chalcogenides.

The following features are typical of the ground state of alkyl vinyl chalcogenides: a) a weak dependence of the structure and the relative arrangement of higher occupied π-MOs on the nature of the heteroatom and the structure of substituent; b) the existence of a linear correlation between the energies of higher occupied σ-MOs, the parameters of which are dictated by the nature of the heteroatom and the number of unsaturated groups. For alkyl vinyl and divinyl chalcogenides, the lowest energy corresponds to the state, in which an electron migrates to the σ*-MO and a vacancy arises in the π-MO. Excited states of π-symmetry are located higher on the energy scale as compared to those of σ-symmetry. The latter are more sensitive to the nature of the heteroatom.

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