Structure-Stability Relationships in Vinyl Sulfides. I. On the Stable Conformations of Vinyl Sulfides

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A thermodynamic and ^{13}C NMR spectroscopic study of the structures of the less stable rotamers of alkyl vinyl sulfides have been performed. It has been shown that the less stable rotamer of methyl vinyl sulfide has the planar *s-trans* configuration and the proportion of this is about 20 %. The energy difference between the planar *s-cis* and *s-trans* is about 3.5 kJ mol^{-1} . Ethyl vinyl sulfide is almost an equimolar mixture of the planar *s-cis* and *s-trans* conformations. The ^{13}C NMR data showed that the p - π conjugation in the compounds that could not adopt any of the planar arrangements was decreased. In alkyl 1-propenyl sulfides, the stabilizing interaction between the methyl group and the S atom *cis* to each other was $\sim 1.8\text{ kJ mol}^{-1}$. The most probable choice for the most stable conformation of di-1-propenyl sulfides is the planar (or nearly planar) *s-trans,s-trans* one.

The question of the configurations of the stable rotamers of methyl vinyl sulfide is one of the most studied problems of vinyl sulfides. It has been studied using spectroscopic methods,^{1–5} electron diffraction,^{4,6–8} ultrasonic relaxation,⁹ dipole moment¹⁰ and theoretical calculations.^{11,12} All these studies agree in that the most stable has the planar *s-cis* conformation. However, the opinions concerning the arrangement of the less stable rotamer are contradictory. According to several studies it is nonplanar *gauche* with the rotation angle between 94° and 136° (calculated from the *s-cis* conformation).^{3,4,6–8,10,12} Planar *s-trans* has also been proposed⁵ and opinions suggesting the presence of only one stable conformation have been offered.^{1,11}

In the planar *s-cis* and *s-trans*, the lone pair of electrons of the sulfur atom conjugate with the π orbital of the double bond, which stabilizes the molecule (resonance structures 1 and 2),⁵ but in the nonplanar *gauche*, this conjugation is hindered.

The structures of the stable rotamers of methyl vinyl ether have also been extensively studied (see, e.g., Ref. 13, 14 and the references cited therein). The most stable rotamer has been established to have the *s-cis* conformation. The less stable rotamer was earlier thought to be nonplanar *gauche*, but now it has been shown that it is planar *s-trans*.^{15–17} In the present paper, a thermodynamic and ^{13}C NMR spectroscopic study have been performed to solve the problem of the conformation of the less stable rotamer of alkyl vinyl sulfides.

Results and discussion

In Fig. 1, the ^{13}C NMR chemical shifts of the β carbons of methyl vinyl sulfides are plotted against the shifts of the corresponding carbons of the corresponding olefins (a hydrogen atom in the place of the MeS group). The analogous plot for ethyl vinyl sulfides is seen in Fig. 2 (the ^{13}C shifts for these figures are summarized in Tables 1 and 2). With the aid of these figures, the relation between structure and the extent of conjugation can be studied. According to Fig. 1, the points for the compounds that cannot adopt any of the planar arrangements, i.e. compounds with both

Fig. 1. ^{13}C chemical shifts of the β carbons of methyl vinyl sulfides plotted against the shifts of the corresponding carbons of the corresponding olefins (a hydrogen atom in the place of the MeS group).

Fig. 2. ^{13}C chemical shifts of the β carbons of ethyl vinyl sulfides plotted against the shifts of the corresponding carbons of the corresponding olefins.

Table 1. ^{13}C chemical shifts of the MeS groups of some methyl vinyl sulfides, the shifts of the β carbons and the shifts of the corresponding carbons of the corresponding olefins (a hydrogen atom in the place of the MeS group). The shifts are in ppm from TMS. The values for compounds 7–10 and 12–14 are from the present study, for compound 11 from Ref. 18 and for the rest from Ref. 19

Compound	Isomer	$\delta(\text{MeS})$	$\delta(\text{C}_\beta)^{\text{SMe}}$	$\delta(\text{C}_\beta)^{\text{H}}$
1 $\text{MeSC}(\text{Me})=\text{CH}_2$		14.8	104.7	116.0 ⁵²
2 $\text{MeSC}(\text{Pr})=\text{CH}_2$		14.4	103.7	114.7 ⁵²
3 $\text{MeSC}(t\text{-Bu})=\text{CH}_2$		14.9	101.0	108.5 ⁵²
4 $\text{MeSC}(\text{Me})=\text{CHEt}$	<i>E</i>	14.6	124.2	132.4 ⁵³
5 $\text{MeSC}(\text{Et})=\text{CHMe}$	<i>E</i>	14.7	115.7	122.8 ⁵³
6 $\text{MeSC}(\text{Pr})=\text{CHEt}$	<i>E</i>	14.8	124.0	131.9 ⁵³
7 $\text{MeSCH}=\text{CHMe}$	<i>Z</i>	16.8	123.0	133.6 ⁵²
8 $\text{MeSCH}=\text{C}(\text{Me})_2$		17.2	133.0	141.8 ⁵²
9 $\text{MeSCH}=\text{CHEt}$	<i>Z</i>	17.0	130.5	140.5 ⁵²
10 $\text{MeSCH}=\text{CH}(i\text{-Pr})$	<i>Z</i>	17.1	136.3	145.9 ⁵²
11 $\text{MeSCH}=\text{CH}_2$		13.4	107.7	122.5 ^{52,54}
12 $\text{MeSCH}=\text{CHMe}$	<i>E</i>	15.2	122.4	133.6 ⁵²
13 $\text{MeSCH}=\text{CHEt}$	<i>E</i>	15.1	129.2	140.5 ⁵²
14 $\text{MeSCH}=\text{CH}(i\text{-Pr})$	<i>E</i>	15.0	134.3	145.9 ⁵²
15 $\text{MeSC}(\text{Me})=\text{CHEt}$	<i>Z</i>	14.6	130.4	133.2 ⁵³
16 $\text{MeSC}(\text{Et})=\text{CHMe}$	<i>Z</i>	14.9	123.2	123.6 ⁵³
17 $\text{MeSC}(\text{Me})=\text{C}(\text{Me})_2$		15.4	131.7	131.6 ⁵⁵
18 $\text{MeSC}(\text{Pr})=\text{CHEt}$	<i>Z</i>	14.8	132.1	132.4 ⁵³

Table 2. ^{13}C chemical shifts of the C_α atoms of the EtS groups of some ethyl vinyl sulfides, the shifts of the β carbons and the shifts of the corresponding carbons of the corresponding olefins. The shifts are in ppm from the TMS. The value for compound 9 is from Ref. 18, the rest from the present study

Compound	Isomer	$\delta(\text{C}_\alpha)$	$\delta(\text{C}_\beta)^{\text{SEI}}$	$\delta(\text{C}_\beta)^{\text{H}}$
1 EtSC(Me)=CH ₂		25.3	106.3	116.0 ⁵²
2 EtSC(Me)=CHMe	<i>E</i>	25.2	121.4	124.2 ⁵³
3 EtSC(Et)=CHMe	<i>E</i>	25.3	120.3	122.8 ⁵³
4 EtSCH=CHMe	<i>Z</i>	27.7	123.8	133.6 ⁵²
5 EtSCH=CHEt	<i>Z</i>	27.8	131.4	140.5 ⁵²
6 EtSCH=C(Me) ₂		27.9	134.1	141.8 ⁵²
7 EtSCH=CH(<i>i</i> -Pr)	<i>Z</i>	27.7	136.8	145.9 ⁵²
8 EtSCH=C(Et) ₂		28.0	144.7	152.7 ⁵²
9 EtSCH=CH ₂		25.3	109.7	122.5 ^{52,54}
10 EtSCH=CHMe	<i>E</i>	26.8	125.7	133.6 ⁵²
11 EtSCH=CHEt	<i>E</i>	26.7	132.6	140.5 ⁵²
12 EtSCH=CH(<i>i</i> -Pr)	<i>E</i>	26.6	137.7	145.9 ⁵²
13 EtSC(Me)=CHMe	<i>Z</i>	24.9	125.5	125.4 ⁵³
14 EtSC(Me)=C(Me) ₂		25.9	134.3	131.6 ⁵⁵
15 EtSC(Et)=CHMe	<i>Z</i>	25.3	125.6	123.6 ⁵³

an α substituent and a β substituent *cis* to the methylthio group (compounds 15–18 in Table 1), are considerably above the other points. The points for the *Z* isomers in question in Fig. 1 are 6–8 ppm down field from the points for the corresponding *E* isomers, obviously because the former compounds must adopt the nonplanar *gauche* conformation. Consequently, the conjugation between the lone pair electrons of the sulfur atom and the π orbital of the double bond is diminished, the electron density around the β carbon is decreased and the ^{13}C signals of the β carbons are downfield from those of the *E* isomers. An effect of the same kind has been observed in corresponding ethyl vinyl sulfides (Fig. 2) and methyl vinyl ethers.²⁰

With the aid of Fig. 1, it can be proved that the conformation of the less stable rotamer of methyl vinyl sulfide is the planar *s-trans* and not the nonplanar *gauche*. If the less stable structure of methyl vinyl sulfide were the *gauche* structure, then those methyl vinyl sulfides which could not adopt the *s-cis* conformation, would adopt the *gauche* even in the cases where *s-trans* would be possible. The points for such compounds are denoted by $\odot$ in Fig. 1 (compounds 7–10 in Table 1). These points are, however, *ca.* 10 ppm more upfield than the points of those compounds for which the nonplanar *gauche* conformation is the only possible one. Thus, the conjugation in com-

pounds that can adopt the *s-trans* conformation is better than in the compounds that cannot adopt any of the planar patterns. It proves that *gauche* is out of the question if *s-trans* is possible. Hence the conformation of the less stable rotamer of methyl vinyl sulfide is concluded to be the planar *s-trans*.

According to Fig. 1, the points for the compounds, for which the *s-trans* conformation is the only possible planar arrangement (sulfides with no α substituent, but a β substituent *cis* to the methylthio group, i.e., compounds 7–10 in Table 1) form a straight line about 2 ppm above the line formed by the points for the compounds which can adopt either the *s-cis* or the *s-trans* configuration (sulfides with neither α substituent nor β substituent *cis* to the methylthio group i.e., compounds 11–14 in Table 1). The reason for this is obviously the fact that the methylthio group shields the β carbon in those compounds which adopt the *s-cis* conformation (Fig. 3) and this shielding moves the ^{13}C signals of the β carbons up field. The same effect can be seen in the corresponding vinyl ethers.²¹

In Fig. 2, the points for those ethyl vinyl sulfides, for which the *s-trans* is the only possible planar structure (compounds 4–8 in Table 2) and for those compounds which can adopt either the *s-cis* or the *s-trans* (compounds 9–12 in Table 2) fit into the same straight line, whereas there is a 2

Fig. 3. Distance of R from the β carbon in different conformations of vinyl sulfides.

ppm difference between the corresponding lines of the methyl vinyl sulfides. It indicates that the proportion of *s-trans* is larger in ethyl vinyl sulfides than in methyl vinyl sulfides.

The slope of the line for ethyl vinyl sulfides is 1.15 ± 0.05 ($r = 0.994$), which means that the β substituents in these compounds diminish the electron density around the β carbon more than in ordinary olefins. This is probably caused by the electron-releasing inductive effect of the β alkyl substituents, which opposes the $p-\pi$ conjugation in the molecule.

The ^{13}C shifts of the methylthio groups of the studied methyl vinyl sulfides are listed in Table 1. It can be seen from the table that the ^{13}C signals of the compounds, which adopt the planar *s-trans* conformation (compounds 7–10 in Table 1), are 16.8–17.2 ppm, whereas the shifts of the compounds, which adopt the planar *s-cis* (compounds 1–6 in Table 1), are between 14.4 and 14.9 ppm. The reason for this difference in the absorption regions of these two types of compounds is that in the *s-cis*, the β carbon shields the methyl group (γ effect). The MeS group of the compounds that are mixtures of the *s-cis* and *s-trans* (compounds 11–14 in Table 1) absorbs in the region 15.0–15.2 ppm (except the unsubstituted methyl vinyl sulfide, for which the ^{13}C shift of the methylthio group is 13.4 ppm), i.e., about 0.5 ppm down field from the *s-cis* compounds, and about 1.9 ppm up field from the *s-trans*. This shows that the proportion of the *s-cis* conformation is about 80 % in the cases where neither of the planar conformations is unfavoured by steric strains.

In ethyl vinyl sulfides, the ^{13}C signals of the C_1 of the ethylthio groups of the compounds which are mixtures of both of the planar conformations (compounds 9–12 in Table 2), are in the region 26.6–26.8 ppm (exception: the unsubstituted ethyl vinyl sulfide, for which the shift of the C_1 atom is 25.3 ppm). They are about 1.5 ppm down field from the signals of the *s-cis* compounds (be-

tween 25.2 and 25.3 ppm, compounds 1–3 in Table 2) and about 1.2 ppm up field from the signals of the *s-trans* (between 27.7 and 28.0 ppm, compounds 4–8 in Table 2). This means that the *s-trans* conformation is slightly more favoured than the *s-cis* the cases where neither one of the planar conformations is unfavoured by steric strains. The unsubstituted ethyl vinyl sulfide is almost an equimolar mixture of the *s-cis* and *s-trans*, from which can be concluded as follows: the ^{13}C shifts of the methylthio group of the unsubstituted methyl vinyl sulfide are 14.6–13.4 ppm = 1.2 ppm down field from the shifts of the methyl vinyl sulfides that adopt the *s-cis* form; the same kind of effect evidently exists in ethyl vinyl sulfide, too; when 1.2 ppm is added to the shift of the C_1 atom of the ethylthio group of the unsubstituted ethyl vinyl sulfide, the corrected value is $25.3 + 1.2 \text{ ppm} = 26.5 \text{ ppm}$, which is about 1.3 ppm down field from the signals of the compounds in the *s-cis* conformation and about 1.4 ppm up field from the signals of the *s-trans* compounds.

The thermodynamic data for the $E \rightarrow Z$ isomerization of some 1-propenyl sulfides, (see scheme 1 in Table 9), are summarized in Table 3. In *t*-butyl vinyl sulfide,⁵ as well as in (*E*)- and (*Z*)-*t*-butyl 1-propenyl sulfides, the *s-cis* conformation is highly unfavourable because of steric strains, so that it can be assumed that the orientation of the *t*-BuS group remains unchanged in the $E \rightarrow Z$ isomerization of the latter compounds. Therefore, the ΔH° of the reaction reflects only the enthalpy change due to the altered position of the methyl group attached to the double bond. The enthalpy change of this reaction is -1.8 kJ mol^{-1} (Table 3), which can be ascribed to a stabilizing (attractive) interaction between the Me group and the S atom in the *Z* isomer (Me...S *cis* interaction). According to Taskinen, the corresponding interaction in alkyl 1-propenyl ethers (Me...O *cis* interaction) is -2.9 kJ mol^{-1} .²²

In Table 4, the ΔH° values for the $E \rightarrow Z$ isomerization reactions of some 1,2-disubstituted ethenes are summarized. In considering these ΔH° values it must be taken into account that the methoxy, ethoxy and ethylthio groups can assume the *s-cis* formation in the *E* isomer, while steric effects make this unfavourable in the *Z* isomer. Thus the $E \rightarrow Z$ isomerization involves some changes in the spatial orientation of the methoxy, ethoxy and ethylthio groups and these rotations

Table 3. Values for the thermodynamic functions ΔG° , ΔH° and ΔS° for the isomerization reaction in Scheme 1 (see Table 9) at 298 K. The values refer to the THF solution. The errors are twice the standard errors.

<i>R</i>	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J Mol ⁻¹ K ⁻¹)
CH ₃ -	0.67(9)	2.0(4)	4.6(9)
CH ₃ CH ₂ -	-0.41(7)	0.0(3)	1.2(6)
(CH ₃) ₂ CH-	-0.72(1)	0.2(1)	3.2(2)
(CH ₃) ₃ C-	-0.92(3)	-1.8(1)	-2.9(4)
C ₆ H ₅ -	-0.10(1)	-0.3(1)	-0.6(1)

Table 4. Values for the thermodynamic function ΔH° for the isomerization reaction (E)-XCH=CHY → (Z)-XCH=CHY. The values for reactions a–c refer to the THF solution, the rest to the gas phase. The errors in reactions a–c are twice the standard errors.

Reaction	X	Y	ΔH° (kJ mol ⁻¹)	Ref.
<i>a</i>	<i>t</i> -BuS-	Me-	-1.8(1)	
<i>b</i>	EtS-	EtO-	1.5(1)	
<i>c</i>	EtS-	EtS-	-2.9(2)	
<i>d</i>	MeO-	MeO-	-6.0(2)	23
<i>e</i>	F-	F-	-3.9	24
<i>f</i>	F-	Cl-	-3.3(1)	25
<i>g</i>	Cl-	Cl-	-2.7(3)	25

require energy. In the absence of these rotations, the enthalpy change of reaction *b* in Table 4 would also most likely be negative. The negative ΔH° values show that there is some attraction between the substituents *cis* to each other. Tureček and Procházka have also equilibrated the geometric isomers of 1-ethoxy-2-(ethylthio)ethene, but their results and the results of the present study are contradictory.²⁶ They reported that $\Delta H^\circ = 7.5$ kJ mol⁻¹ and $\Delta S^\circ = 13.9$ J K⁻¹ mol⁻¹ for the *E*→*Z* reaction, while the ΔH° and ΔS° are, respectively, 1.5 kJ mol⁻¹ and 0.5 J K⁻¹ mol⁻¹ according to the present study.

It can be seen from Table 3 that the ΔH° of Scheme 1 increases, as the size of the alkyl group decreases (except in the case where the alkyl group changes from isopropyl to ethyl group). This increase is caused by the rotation of the alkylthio group around the C(sp²)-S bond for small alkyl groups. An estimate of the energy needed for the rotation of a methylthio group

from the *s-cis* position to the *s-trans* is the difference in the ΔH° values of Scheme 1 between the cases *R* = Me and *R* = *t*-Bu. This difference (3.8 kJ mol⁻¹) is the minimum value for the energy needed for the rotation, because methyl vinyl sulfide exists as a mixture of two rotamers. This value can be compared with the value that can be calculated from the results acquired from the ¹³C data earlier in this paper. It was mentioned that the proportion of the *s-cis* form in methyl vinyl sulfide is about 80 %. This means that the energy difference between the planar structures at 298 K is about 3.4 kJ mol⁻¹. According to *ab initio* calculations, the energy difference between the two stable forms of methyl vinyl sulfide is 3 kJ mol⁻¹.¹² These three values are in reasonably good agreement with each other.

The difference in the ΔH° values between the cases *R* = Et and *R* = *t*-Bu is 1.8 kJ mol⁻¹, whereas the difference in the ΔH° values between the cases *R* = Me and *R* = Et is 2.0 kJ

mol^{-1} . Thus the energy needed for the rotation of an ethylthio group is 1.8 kJ mol^{-1} , while the energy needed for the corresponding rotation of a methylthio group is 3.8 kJ mol^{-1} . This confirms the conclusion that in ethyl vinyl sulfides the *s-trans* formation is slightly more favoured than the *s-cis*.

Sváta *et al.* have also equilibrated the geometric isomers of four alkyl 1-propenyl sulfides (the alkyl group was Me, Et, *i*-Pr or *t*-Bu).²⁷ The agreement between their results and the results of the present study is, however, poor. According to their study the ΔG° of the *E*→*Z* isomerization at 293 K increases from $-0.75 \text{ kJ mol}^{-1}$ ($R = \text{Me}$) to 2.15 kJ mol^{-1} ($R = t\text{-Bu}$), while according to the present study the ΔG° of the reaction under discussion decreases, when the size of the alkyl group increases. Furthermore, according to Sváta *et al.* the temperature dependence of *K* is surprisingly great in the cases $R = \text{Me}$ and $R = \text{Et}$.²⁷ In alkyl 1-propenyl ethers, the ΔH° of the *E*→*Z* isomerization also increases with decreasing size of the alkyl group, so that the $\Delta H^\circ(\text{g}) = (-2.9 \pm 0.3) \text{ kJ mol}^{-1}$ for $R = t\text{-Bu}$ and $\Delta H^\circ(\text{g}) = (0.4 \pm 0.3) \text{ kJ mol}^{-1}$ for $R = \text{Me}$.²²

The conjugation in alkyl 1-propenyl sulfides can be studied with the aid of their ^{13}C NMR spectra. Trofimov *et al.*²⁸ and Kalabin *et al.*¹⁸ have studied the ^{13}C spectra of alkyl vinyl sulfides and alkyl vinyl ethers. They found that, in both cases, the ^{13}C signal of the β carbon shifts down field and the signal of the α carbon up field, when the size of the alkyl group increases. Trofimov *et al.* explained this effect as follows:²⁸ small alkyl groups adopt planar configurations, but when the size of the alkyl group increases, the group adopts the nonplanar *gauche*, to avoid steric strain. This diminishes the *p*– π conjugation in the molecule and the ^{13}C signal of the β carbon shifts down field and the signal of the α carbon up field. This reasoning is based on the assumption that the ^{13}C shifts can be used directly as a measure of the π electron density in the molecule, but using the ^{13}C shifts of alkyl 1-propenyl sulfides (Table 5) shows that the explanation given above is partly erroneous. Fig. 4 shows that quite a good linear relationship exists between the ^{13}C shifts of the α carbons of (*E*)- and (*Z*)-alkyl 1-propenyl sulfides (the slope is 1.52 ± 0.09 and $r = 0.996$). Thus, by varying the size of the alkyl group, the shift of the α carbon of the *Z* isomer changes somewhat more than the shift of the α

Table 5. ^{13}C shifts (ppm from the TMS) of the α and β carbons of alkyl 1-propenyl sulfides $\text{RSCH}=\text{CHMe}$

<i>R</i>	Isomer	$\delta(\text{C}_\alpha)$	$\delta(\text{C}_\beta)$
Me	<i>E</i>	124.7	122.4
	<i>Z</i>	127.8	123.0
Et	<i>E</i>	123.5	125.7
	<i>Z</i>	125.6	123.8
<i>i</i> -Pr	<i>E</i>	122.6	128.7
	<i>Z</i>	124.3	124.3
<i>t</i> -Bu	<i>E</i>	120.9	132.5
	<i>Z</i>	122.1	125.8

carbon of the *E* isomer. On the other hand, Fig. 5 shows that the shift of the β carbon of the *Z* isomer of alkyl 1-propenyl sulfides changes only about 3 ppm on going from $R = \text{Me}$ to $R = t\text{-Bu}$, while the corresponding change in the *E* isomer is about 10 ppm. Thus, according to the change in the ^{13}C shift of the α carbon of the *Z* isomer the extent of the *p*– π conjugation changes considerably with the bulkiness of *R*, whereas the shift of the β carbon of the *Z* isomer points only to a slight decrease in the conjugation on going from $R = \text{Me}$ to $R = t\text{-Bu}$. These observations show that it is erroneous to state that the ^{13}C chemical shifts of the α and β carbons of alkyl vinyl and alkyl 1-propenyl sulfides reflect only the *p*– π conjugation in the molecule. The explanation of Trofimov *et al.* concerning the ^{13}C spectra of the corresponding vinyl ethers²⁸ has been disproved by the same method.²⁹ A more appropriate explanation to the experimental results concerning alkyl

Fig. 4. $\delta(\text{C}_\alpha)^Z$ versus $\delta(\text{C}_\alpha)^E$ for alkyl 1-propenyl sulfides.

Fig. 5. $\delta(C_\beta)^Z$ versus $\delta(C_\beta)^E$ for alkyl 1-propenyl sulfides.

vinyl and alkyl 1-propenyl ethers has been offered and evidently the explanation is valid also for the corresponding sulfides.²⁹ According to this explanation the ^{13}C shifts of the carbons of the double bond do not reflect merely the conjugation in the molecule, but also the through-space shielding effect. Because the bond angles and bond lengths are about the same in different conformations,¹² the distance of R from the α carbon, and hence its shielding effect on the α carbon, does not depend greatly on the arrangement in the molecule (Fig. 3). Thus, the increase in the size of the alkyl group increases the shielding effect on the α carbon and the ^{13}C signal shifts up field. This is indeed the case both in *E* and *Z* isomers. On the other hand, the distance between R and the β carbon depends essentially on the structure of the molecule and hence also the shielding effect on the β carbon. In the *E* isomer small alkyl groups adopt the *s-cis*, but when the size of the alkyl group increases, the steric strains make this energetically unfavourable. Thus, the proportion of the *s-cis* decreases, the distance between the alkyl group and the β carbon increases and the shielding effect decreases when the size of the alkyl group increases. This causes the down field shift in the ^{13}C signals of the β carbons. On the other hand, in the *Z* isomer the *s-cis* conformation is energetically highly unfavoured because of steric strain even with small alkyl groups. Thus, the distance between the alkyl group and the β carbon is relatively long and it is reasonable to assume that the through-space shielding effect of R is small enough so that varying the size of R has no practical effect on the chemical shift of the β carbon. The slight down field trend of the shift of the β carbon of the *Z*

isomer, when the size of R increases, is not what would be expected on the basis of the inductive effect of R, because the electron-releasing effect of the *t*-Bu group is larger than that of the Me group³⁰ and thus the change from *R* = Me to *R* = *t*-Bu should increase the electron density in the β carbon and cause an upfield shift in the ^{13}C signal of the β carbon. The observed downfield shift is probably due to the deviation from planar *s-trans* for bulkier alkyl groups.

Di(1-propenyl) sulfides. The possible configurations of a divinyl sulfide system are presented in Fig. 6. There are three planar possibilities, where the lone pair electrons of the sulfur atom can conjugate with the π orbitals of both of the double bonds. In the nonplanar conformations (Fig. 6a, when $\alpha \neq 0^\circ$ and/or $\beta \neq 0^\circ$, $-180^\circ < \alpha, \beta < 180^\circ$) the conjugation is hindered at least to one direction. According to Remizov *et al.*³¹ and Trofimov *et al.*,³² divinyl sulfide has two stable forms in the liquid phase, the planar *s-trans,s-trans* being one of them. Remizov *et al.* did not solve the structure of the other stable rotamer, but according to Trofimov *et al.* it was nonplanar. Fortunato and Giorgini³³ came to the conclusion that divinyl sulfide has two stable arrangements, both of which are nonplanar. The results of the investigations of the most stable conformation of divinyl ether are also contradictory. Both planar (or almost planar)³⁴⁻³⁷ and nonplanar³⁸ patterns have been suggested. The planar *s-trans,s-trans* was reported to be the only stable conformation of (*Z,Z*)-di-1-propenyl ether.^{35,39}

When the values of the thermodynamic functions for Schemes 2 and 3, (see Table 9), are discussed, the fact that the *E,Z* isomer is statistically favoured by factor 2 must be taken into account. To eliminate the effect of this statistical factor,

Fig. 6. Possible conformations of divinyl sulfide system. a: planar *s-trans,s-trans* conformation ($\alpha = \beta = 0^\circ$) or nonplanar conformation ($\alpha \neq 0^\circ$ and/or $\beta \neq 0^\circ$, $-180^\circ < \alpha, \beta < 180^\circ$), b: planar *s-cis,s-trans* conformation and c: planar *s-cis,s-cis* conformation.

Table 6. Values for the thermodynamic functions ΔG° , ΔH° and ΔS° for reaction $(E)-RCH=CHMe \rightarrow (Z)-RCH=CHMe$ at 298 K. The values refer to the THF solution. The values for the first two reactions are statistically corrected. The errors are twice the standard errors.

R	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
(E)-MeCH=CHS-	0.31(2)	-0.8(1)	-1.8(3)
(Z)-MeCH=CHS-	-0.93(3)	-1.8(2)	-2.9(4)
Me ₃ CS-	-0.92(3)	-1.8(1)	-2.9(4)

the term $RT\ln 2$ (1.72 kJ mol⁻¹ at 298 K) and $-R\ln 2$ (-5.8 J mol⁻¹ K⁻¹) must be added, respectively, to the ΔG° and ΔS° values of the reaction in Scheme 2:

(E,E)-di-1-propenyl sulfide $\rightarrow$ (E,Z)-di-1-propenyl sulfide;

and the same factors must be subtracted from the ΔG° and ΔS° values of the reaction in Scheme 3:

(E,Z)-di-1-propenyl sulfide $\rightarrow$ (Z,Z)-di-1-propenyl sulfide.

The statistically corrected values are summarized in Table 6. Considering the planar conformations of di-1-propenyl sulfides as the possible stable ones, the planar *s-cis,s-cis* form (Fig. 6c) can be ruled out because of the steric strain between the two groups (or hydrogen atoms) *cis* to the sulfur atom (none of the investigators mentioned in this section noted the existence of this rotamer). The *s-cis,s-trans* forms (Fig. 6b) can be excluded by the following reasoning. If *E,E* and *E,Z* isomers exist in *s-cis,s-trans*, then the isomerization reactions *E,E* $\rightarrow$ *Z,Z* and *E,Z* $\rightarrow$ *Z,Z* in Fig. 7 involve changes in the spatial orientation of the C=C-S-C=C system, since the *s-cis,s-trans* structure in the *Z,Z* isomer would be energetically highly unfavourable due to the repulsive Me...H interaction shown in Fig. 8. Because of the assumed change in the spatial orientation of the C=C-S-C=C system in the *E,Z* $\rightarrow$ *Z,Z* reaction, the enthalpy change for the first step in Fig. 7 would be more negative than that of the second step. This is not, however, supported by the experimental evidence, since $\Delta H_2^\circ < \Delta H_1^\circ$ (Fig. 7). Hence, it can be concluded that the spatial orientation of the C=C-S-C=C system re-

mains unchanged in the *E,E* $\rightarrow$ *Z,Z* and *E,Z* $\rightarrow$ *Z,Z* reactions and the *s-cis,s-trans* form can be ruled out as the stable one for di-1-propenyl sulfide. The same kind of conclusions have been drawn for the corresponding vinyl ethers.⁴⁰

Earlier in this paper, it was concluded that the spatial orientation of the *t*-BuS group remains unchanged in the reaction in eq. (1) below. If the thermodynamic functions of this reaction are compared, respectively, with the statistically corrected ΔG° , ΔH° and ΔS° values of the reaction in eq. (2) (Table 6), it can be seen that they are equal within the experimental error.

Fig. 7. Isomerization of di-1-propenyl sulfide assuming that the most stable conformation of (*E,E*)-di-1-propenyl sulfide is the planar *s-cis,s-trans*.

Fig. 8. Repulsive Me...H interaction in the *s-cis,s-trans* conformation of (*Z,Z*)-di-1-propenyl sulfide.

This shows that there is no change in the spatial orientation of the C=C-S-C=C system of the reaction in eq. (2) either. Thus, the only possible planar conformation of di-1-propenyl sulfide is *s-trans,s-trans*. The ^{13}C shift of the β carbon of *t*-butyl vinyl sulfide is 115.7 ppm and the corresponding shift of divinyl sulfide is 114.3 ppm.¹⁸ Thus the π electron density around the β carbon of divinyl sulfide is about as large as around the β carbon of *t*-butyl vinyl sulfide. This suggests that the lone pair electrons of the sulfur atom can conjugate with the π orbitals of both of the double bonds in divinyl sulfide to approximately the same extent as with the π orbital of the double bond in *t*-butyl vinyl sulfide. This points to a planar pattern. Since it seems reasonable to assume that the most stable conformations of di-1-propenyl sulfides and divinyl sulfide are similar, the most reasonable choice for most stable is the planar (or nearly planar) *s-trans,s-trans*, i.e. the same as Trofimov *et al.*³² and Remizov *et al.*³¹ suggested for divinyl sulfide.

Experimental

Materials. *t*-Butyl 1-propenyl sulfides. *t*-Butyl 2-propenyl sulfide was prepared in a 45 % yield by the method described by Tarbell and Lovett.⁴¹ b.p. 417–418 K at 100 kPa. Potassium *t*-butoxide in a dimethyl sulfoxide solution isomerized the 2-propenyl sulfide almost quantitatively into the 1-propenyl sulfides. Yield 90 %, b.p. 416–417 K at 100 kPa, lit. b.p. 415 K at 100 kPa.²⁷

Phenyl 1-propenyl sulfides were obtained in a 74 % yield by the procedure given above; b.p. 383–386 K at 2.8 kPa, lit. b.p. 334–342 K at 0.17 kPa.⁴²

Di-1-propenyl sulfides were isomerized from di-2-propenyl sulfide in an 88 % yield by the method described above; b.p. 417–425 K at 100 kPa, lit. b.p. 333–334 K at 3.7 kPa.⁴³

α -Unsubstituted vinyl sulfides were prepared by the method described by Boonstra *et al.*⁴⁴ The products were: methyl 1-propenyl sulfides, yield 4.4 %, b.p. 373–376 K at 100 kPa, lit. b.p. 372–374 K at 100 kPa;²⁷ ethyl 1-propenyl sulfides, yield 11 %, b.p. 393–397 K at 100 kPa, lit. b.p. 392–394 K at 100 kPa;²⁷ isopropyl 1-propenyl sulfides, yield 20 %, b.p. 404–407 K at 100 kPa, lit. b.p. 403 K at 100 kPa;²⁷ 1-(methylthio)-1-butenes, yield 45 %, b.p. 390–394 K at 100 kPa; 1-(ethylthio)-1-butenes, yield 14 %, b.p. 332–338 K at 6.5 kPa; 3-methyl-1-(methylthio)-1-butenes, yield 51 %, b.p. 338–347 K at 10 kPa, lit. b.p. 407–409 K at 92 kPa;⁴⁵ 1-(ethylthio)-3-methyl-1-butenes, yield 22 %, b.p. 429–432 K at 100 kPa; 2-methyl-1-(methylthio)propene, yield 60 %, b.p. 396–397 K at 100 kPa, lit. b.p. 393 K at 100 kPa;⁴⁶ 1-(ethylthio)-2-methylpropene, yield 51 %, b.p. 413–415 K at 100 kPa and 2-ethyl-1-(ethylthio)-1-butene, yield 44 %, b.p. 335–337 K at 1.3 kPa.

α -Alkyl substituted vinyl sulfides were prepared as follows: the acetal was first prepared by the method of House and Kramar,⁴⁷ converted into the thioacetal by adding ethanethiol (twice the molar ratio) to the solution, then cleaved into thiol and vinyl sulfide using *p*-toluenesulfonic acid as catalyst. The products were: 2-(ethylthio)-2-butenes + isom., yield 29 %, b.p. 409–417 K at 100 kPa; 2-(ethylthio)propene, yield 12 %, b.p. 383–388 K at 100 kPa, lit. b.p. 386–387 K at 100 kPa;⁴⁸ 2-(ethylthio)-3-methyl-2-butene + isom., yield 23 %, b.p. 431–438 K at 100 kPa and 3-(ethylthio)-2-pentenenes, yield 38 %, b.p. 429–431 K at 100 kPa.

1-Ethoxy-2-(ethylthio)ethenes. Sodium ethanethiolate was prepared from absolute ethanol, sodium and ethanethiol.²⁷ 2-Bromo-1,1-diethoxyethane was then slowly added into the solution to get 1,1-diethoxy-2-(ethylthio)ethane. After that, the acetal was cleaved into ethanol and 1-ethoxy-2-(ethylthio)ethenes using *p*-toluenesulfonic acid as catalyst. The product was obtained in a 21 % yield, b.p. 341–349 K at 2.4 kPa, lit. b.p. 341–344 K at 1.7 kPa.⁴⁹

1,2-Bis(ethylthio)ethenes. 1,1-Diethoxy-2-(ethylthio)ethane was converted into thioacetal (1,1,2-tris(ethylthio)ethane) by adding ethanethiol (twice the molar ratio) to the acetal. The thioacetal was cleaved into a mixture of ethanethiol and 1,2-bis(ethylthio)ethenes using *p*-toluenesulfonic acid as catalyst. Yield 14 %, b.p. 369–372 K

Table 7. Chemical shifts (ppm from TMS) from the ^1H NMR spectra recorded (the coupling constants are expressed in Hz)

Compound	Isom.	$\delta(\text{a})$	$\delta(\text{b})$	$\delta(\text{c})$	$\delta(\text{d})$	$\delta(\text{e})$	$\delta(\text{f})$	J(ab)	J(bc)	J(cd)	J(de)	J(ef)	others
$\text{CH}_3\text{SCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$	E	2.14	5.97	5.49	1.74				15.0	6.3			J(bd) = 0.8
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	Z	2.21	5.89	5.59	1.65				9.5	5.4			J(bd) = 0.9
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	E	1.27	2.60	5.93	5.65	1.76		7.3		14.9	5.2		J(ce) = 0
$(\text{CH}_3)_2\text{CHSCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	Z	1.26	2.62	5.92	5.62	1.68		7.4		9.1	5.4		J(ce) = 0.8
$(\text{CH}_3)_2\text{CHSCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	E	1.26	2.98	5.99	5.75	1.75		6.8		14.6	5.4		J(ce) = 0
$(\text{CH}_3)_3\text{CSCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$	Z	1.30	2.99	6.00	5.64	1.69		6.9		9.4	6.6		J(ce) = 0.9
$(\text{CH}_3)_3\text{CSCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$	E	1.29	6.09	5.90	1.79				14.6	4.4			J(bd) = 0
$\text{C}_6\text{H}_5\text{SCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$	Z	1.34	6.11	5.74	1.70				9.2	6.1			J(bd) = 0.8
$\text{C}_6\text{H}_5\text{SCH}=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$	E	7.0-7.3	6.05	5.88	1.8				14.8	5			
$\text{S}(\text{CH}=\text{CHCH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c}$	Z	7.0-7.3	6.15	5.78	1.8				9.3	5			
$\text{S}(\text{CH}=\text{CHCH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c}$	E/E	5.90	5.62	1.75				14.7	5.2				J(ac) = 0
$\text{S}(\text{CH}=\text{CHCH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c}$	Z/Z	5.89	5.72	1.69				9.4	6.4				J(ac) = 1.1
		1.77	5.61	5.92	5.93	5.61	1.71	5.2	14.7		9.2	6.4	J(df) = 1.2
$\text{CH}_3\text{SCH}=\text{C}(\text{CH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c}$		2.15	5.46	1.68					1.2				
$\text{CH}_3\text{SCH}=\text{CHCH}_2\text{CH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	E	2.06	5.1-6.0	1.74	1.94	1.00					7.4		
$\text{CH}_3\text{SCH}=\text{CHCH}_2\text{CH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	Z	2.19	5.1-5.8		1.94	1.00					7.4		
$\text{CH}_3\text{SCH}=\text{CHCH}(\text{CH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	E	2.15	5.84	5.30	2.3	1.01			14.9	6.8			J(bd) = 0.3
$\text{CH}_3\text{CH}_2\text{SC}(\text{CH}_3)=\text{CH}_2$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$	Z	2.20	5.65	5.27	2.6	0.99			9.0	9.4	6.6		J(bd) = 0.3
$\text{CH}_3\text{CH}_2\text{SC}(\text{CH}_3)=\text{CH}_2$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$		1.27	2.66	1.91	4.58 ^a			7.2					
$\text{CH}_3\text{CH}_2\text{SCH}=\text{C}(\text{CH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d}$		1.24	2.54	5.50	4.88 ^b								
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHCH}_2\text{CH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	E	1.25	2.61	5.87	5.57	2.08	0.99	7.3		1.2			
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHCH}_2\text{CH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	Z	1.26	2.63	5.85	5.49	2.08	0.98	7.2		0.8			
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHCH}(\text{CH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	E	1.27	2.59	5.81	5.51	2.3	1.01	7.3		15.1	6.7	7.4	
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHCH}(\text{CH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	Z	1.28	2.61	5.71	5.33	2.6	0.98	7.3		9.4	6.8	7.5	
$\text{CH}_3\text{CH}_2\text{SC}(\text{CH}_3)=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	E	1.22	2.60	1.84	5.37	1.68		7.4		15.7	6.4	6.6	J(ce) = 1.0
$\text{CH}_3\text{CH}_2\text{SC}(\text{CH}_3)=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$	Z	1.20	2.66	1.95	5.55	1.71		7.3		9.6	9.2	6.6	J(ce) = 0.4
$\text{CH}_3\text{CH}_2\text{SC}(\text{CH}_2\text{CH}_3)=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e} \quad \text{f}$	E	1.21	2.57	2.18	1.05	5.27	1.67	7.2		1.5	6.9		J(ce) = 0.7
$\text{CH}_3\text{CH}_2\text{SC}(\text{CH}_2\text{CH}_3)=\text{CHCH}_3$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e} \quad \text{f}$	Z	1.19	2.56	2.18	1.08	5.60	1.76	7.2		7.6		7.0	J(ce) = 0
$\text{CH}_3\text{CH}_2\text{SCH}=\text{C}(\text{CH}_2\text{CH}_3)_2$ $\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e}$		1.25	2.54	5.47	2.13	1.02		7.4		7.4		6.6	J(ce) = 0.5
					2.07	0.97					7.2		

Compound	Isom.	$\delta(a)$	$\delta(b)$	$\delta(c)$	$\delta(d)$	$\delta(e)$	$\delta(f)$	$J(ab)$	$J(bc)$	$J(cd)$	$J(de)$	$J(ef)$	others
$\text{CH}_3\text{CH}_2\text{SC}(\text{CH}_3)=\text{C}(\text{CH}_3)_2$ _{a b c d}		1.17	2.58	1.76	1.91			7.1					
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHOCH}_2\text{CH}_3$ _{a b c d e f}	<i>E</i>	1.27	2.44	5.20	6.65	3.79	1.20	7.4		12.0		7.2	
	<i>Z</i>	1.28	2.59	4.73	6.16	3.84	1.26	7.4		6.0		7.2	
$\text{CH}_3\text{CH}_2\text{SCH}=\text{CHSCH}_2\text{CH}_3$ _{a b c c b a}	<i>E</i>	1.29	2.65	6.06				7.4					
	<i>Z</i>	1.29	2.63	6.02				7.4					

^aShift for the proton *cis* to the ethylthio group.^bShift for the proton *trans* to the ethylthio group.at 1.9 kPa, lit. b.p. 378–381 K at 2.1 kPa.⁵⁰

¹H NMR spectra. The spectra were recorded with a 60 MHz spectrometer in 10–20 % CCl₄ solution with TMS as internal standard. The spectra of the 1-propenyl groups of 1-propenyl sulfides were rather complicated and to obtain the shifts of the vinylic protons, the spectra where the methyl groups were decoupled were recorded. Thus, the vinylic protons formed easily solvable AB quartets.⁵¹ The spectra of 1-(ethylthio)-1-butenes were solved using the same method. The ¹H NMR chemical shifts of the recorded spectra are summarized in Table 7.

¹³C NMR spectra. The spectra were recorded with a 15 MHz spectrometer in 10–20 % CDCl₃ solution with TMS as internal standard. The ¹³C NMR chemical shifts are summarized in Table 8.

Configurational assignments

Most of the geometric isomers were identified by their ¹H NMR spectra, but in some cases, other methods had to be used. The geometric isomers of 2-(ethylthio)-2-butene and 3-(ethylthio)-2-pentene were identified by their ¹³C NMR spectra using the arguments employed by Taskinen in the identification of the geometric isomers of related vinyl ethers.²⁰ Thus, the *Z* isomer is the one with the higher shift value (more down field) of the β carbon. Another basis for the above conclusion was the order of elution of the isomers in the column with XE-60 as stationary phase: all the (ethylthio)alkenes which could be identified with certainty, were eluted in the order *Z* isomer, *E* isomer.

Response ratio. To confirm that the relative peak areas represented the true isomer molar ratios, the response ratio for (*E*)- and (*Z*)-1-(ethylthio)-1-butenes was determined. It was found that the *Z* isomer gave a peak having an area 1–4 % larger than the area obtained from an equal amount of *E* isomer. The errors in the changes of the thermodynamic quantities in the reaction (*E*)-1-(ethylthio)-1-butene $\rightarrow$ (*Z*)-1-(ethylthio)-1-butene caused by the divergence of the response ratio from unity were thus negligible and it was considered justified to take the response ratio as unity in all isomeric compounds studied.

Equilibrations. The equilibration experiments were carried out in tetrahydrofuran solution with *p*-toluenesulfonic acid as catalyst. The solvent was first dried with metallic sodium for 12 h, then

^aShift for the carbon *trans* to the ethylthio group.
^bShift for the carbon *cis* to the ethylthio group.
^cShift for the carbon *cis* to the ethylthio group.
^dShift for the carbon *trans* to the ethylthio group.

Table 9. Equilibrium constants for the following isomerization reactions

Scheme 1

Scheme 3

1: R = Me, 2: R = Et, 3: R = *i*-Pr, 4: R = *t*-Bu, 5: R = Ph
 7: X = O, 8: X = S

Scheme 2

T/K	K(1b/1a)	K(2b/2a)	K(3b/3a)	K(4b/4a)	K(5b/5a)	K(6b/6a)	K(6c/6b)	K(7b/7a)	K(8b/8a)
446		1.17							
424	0.969	1.17		1.17					0.981
403	0.957	1.18	1.37	1.20	1.01	2.08	0.605	0.687	1.025
373	0.904	1.17	1.36	1.26	1.02	2.11	0.626	0.661	1.090
333	0.830		1.35	1.34	1.03	2.18	0.673	0.622	1.234
301					1.04				
299						2.27	0.729	0.590	

it was poured on calcium hydride and refluxed for one h. After distillation, the solvent was redistilled from lithium aluminum hydride. The substrate concentration of the samples was 5–25 vol. % and the catalyst concentration 0.1 mass %. The samples were sealed into glass ampoules and the ampoules kept in thermostated ovens at appropriate temperatures to establish equilibrium. The temperature in the ovens remained steady within 0.5 K. The isomerization was followed by analyzing a sample at suitable intervals by gas chromatography. The process lasted from 15 min to 1 h, depending on the vinyl sulfide used, the concentration of the substrate and the temperature. The time of equilibration of the last sample was 2–5 times longer than the time

necessary to attain equilibrium. The equilibrium state was, if possible, approached from two directions to make sure a true equilibrium state had been achieved. At each temperature, 2–4 samples from both sides were analyzed after the equilibrium state had been achieved and the mean value was calculated from the results. Usually, the results differed by less than 4% from each other. Each compound was equilibrated at 3–6 different temperatures. Before the sample was analyzed, it was made alkaline by adding diethylamine to the sample to prevent isomerization during the analysis. Columns with three different stationary phases (XE-60, Carbowax 20M or SE-30) were tested and XE-60 proved to be the best choice. The values of the thermodynamic par-

ameters were evaluated by linear least-squares treatment of $\ln K$ versus T^{-1} . The values of the equilibrium constant K for the reactions studied are given in Table 9.

References

- Penn, R. E. and Curl, R. F. *J. Mol. Spectrosc.* 24 (1967) 235.
- Fabian, J., Kröber, H. and Mayer, R. *Spectrochim. Acta A* 24 (1968) 727.
- Muller, C., Schäfer, W., Schweig, A., Thon, N. and Vermeer, H. *J. Am. Chem. Soc.* 98 (1976) 5440.
- Samdal, S., Seip, H. M. and Torgrimsen, T. *J. Mol. Struct.* 57 (1979) 105.
- Katritzky, A. R., Pinzelli, R. F. and Topsom, R. D. *Tetrahedron* 28 (1972) 3441.
- Samdal, S. and Seip, H. M. *Acta Chem. Scand.* 25 (1971) 1903.
- Derissen, J. L. and Bijen, J. M. *J. Mol. Struct.* 16 (1973) 289.
- Samdal, S. and Seip, H. M. *J. Mol. Struct.* 28 (1975) 193.
- Wyn-Jones, E., Crook, K. R. and Orville-Thomas, W. J. *Adv. Mol. Relaxation Processes* 4 (1972) 193.
- Trofimov, B. A., Modonov, V. B., Bazhenova, T. N., Istomin, B. I., Nedolya, N. A., Al'pert, M. L., Efremova, G. G. and Sitnikova, S. P. *Bull. Akad. Sci. USSR, Div. Chem. Sci.* (1979) 79.
- Lister, D. G. and Palmieri, P. *J. Mol. Struct.* 32 (1976) 355.
- Kao, J. *J. Am. Chem. Soc.* 100 (1978) 4685.
- Taskinen, E. *Kem. Kemi* 7 (1980) 808.
- Ignatyev, I. S., Lazarev, A. N., Smirnov, M. B., Al'pert, M. L. and Trofimov, B. A. *J. Mol. Struct.* 72 (1981) 25.
- Gallinella, E. and Cadioli, B. *Chem. Phys. Lett.* 77 (1981) 533.
- Friege, H. and Klessinger, M. *J. Chem. Res. Synop.* (1977) 208.
- Cadioli, B., Gallinella, E. and Pincelli, U. *J. Mol. Struct.* 78 (1982) 215.
- Kalabin, G. A., Trofimov, B. A., Bzhesovsky, V. M., Kushnarev, D. F., Amosova, S. V., Gusarova, N. K. and Al'pert, M. L. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (1975) 501.
- Barillier, D., Strobel, M. P., Morin, L. and Paquer, D. *Tetrahedron* 39 (1983) 767.
- Taskinen, E. *Tetrahedron* 34 (1978) 425.
- Rojas, A. C. and Crandall, J. K. *J. Org. Chem.* 40 (1975) 2225.
- Taskinen, E. and Liukas, P. *Acta Chem. Scand. B* 28 (1974) 114.
- Waldron, J. T. and Snyder, W. H. *J. Am. Chem. Soc.* 95 (1973) 5491.
- Craig, N. C. and Entemann, E. A. *J. Am. Chem. Soc.* 83 (1961) 3047.
- Craig, N. C., Piper, L. G. and Wheeler, V. L. *J. Phys. Chem.* 75 (1971) 1453.
- Tureček, F. and Procházka, M. *Collect. Czech. Chem. Commun.* 39 (1974) 2073.
- Sváta, V., Procházka, M. and Bakos, V. *Collect. Czech. Chem. Commun.* 43 (1978) 2619.
- Trofimov, B. A., Kalabin, G. A., Bzhesovsky, V. M., Gusarova, N. K., Kushnarev, D. F. and Amosova, S. V. *Org. React.* 11 (1974) 367.
- Taskinen, E. *Tetrahedron* 34 (1978) 353.
- Hine, J. *Structural effects on equilibria in organic chemistry*. John Wiley & Sons, New York 1975. p. 98.
- Remizov, A. B., Mannafov, T. G. and Tantasheva, F. R. *J. Gen. Chem. USSR* (1975) 1378.
- Trofimov, B. A., Frolov, Yu. L., Sinegovskaya, L. M., Modonov, V. B., Kositsyna, E. I., Amosova, S. V., Gusarova, N. K. and Efremova, G. G. *Bull. Akad. Sci. USSR, Div. Chem. Sci.* (1977) 302.
- Fortunato, B. and Giorgini, M. G. *Gazz. Chim. Ital.* 106 (1976) 1005.
- Cadioli, B., Fortunato, B., Gallinella, E., Mirone, P. and Pincelli, U. *Gazz. Chim. Ital.* 104 (1974) 369.
- Kimmel, H. and Snyder, W. H. *Spectrosc. Lett.* 4 (1971) 15.
- Barricelli, L. L. and Bastiansen, O. *Acta Chem. Scand.* 3 (1949) 201.
- Clague, A. D. and Danti, A. *J. Mol. Spectrosc.* 22 (1967) 371.
- Hirose, C. and Curl, R. F., Jr. *J. Mol. Spectrosc.* 38 (1971) 358.
- Hollein, H. C. and Snyder, W. H. *J. Mol. Struct.* 82 (1982) 187.
- Taskinen, E. and Virtanen, R. *J. Org. Chem.* 42 (1977) 1443.
- Tarbell, D. S. and Lovett, W. E. *J. Am. Chem. Soc.* 78 (1956) 2259.
- Tarbell, D. S. and McCall, M. A. *J. Am. Chem. Soc.* 74 (1952) 48.
- Price, C. C. and Snyder, W. H. *J. Org. Chem.* 27 (1962) 4639.
- Boonstra, H. J., Brandsma, L., Wiegman, A. M. and Arens, J. F. *Recl. Trav. Chim. Pays Bas* 78 (1959) 252.
- Pedersen, E. B. and Lawesson, S.-O. *Synthesis* (1969) 170.
- Vermeer, P., de Graaf, C. and Meijer, J. *Recl. Trav. Chim. Pays Bas* 93 (1974) 24.
- House, H. O. and Kramar, J. *J. Org. Chem.* 28 (1963) 3362.
- Mueller, W. H. and Griesbaum, K. *J. Org. Chem.* 32 (1967) 856.

49. Volger, H. C. and Arens, J. F. *Recl. Trav. Chim. Pays Bas* 76 (1957) 847.
50. Rinzema, L. C., Stoffelsma, J. and Arens, J. F. *Recl. Trav. Chim. Pays Bas* 78 (1959) 354.
51. Pople, J. A., Schneider, W. G. and Bernstein, H. J. *High-resolution nuclear magnetic resonance*. McGraw-Hill, New York 1959, Chapter 6-5.
52. De Haan, J. W., van de Ven, L. J., Wilson, A. R. and van der Hout-Lodder, A. E. *Org. Magn. Reson.* 8 (1976) 477.
53. De Haan, J. W. and van de Ven, L. J. *Org. Magn. Reson.* 5 (1973) 147.
54. van de Ven, L. J. and De Haan, J. W. *J. Chem. Soc. Chem. Commun.* (1978) 94.
55. Abruscato, G. J., Ellis, P. D. and Tidwell, T. T. *J. Chem. Soc. Chem. Commun.* (1972) 988.

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