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## THE DIFFERENCES IN THE SPECTRA OF *cis* AND *trans* ISOMERS OF UNSATURATED SULPHIDES

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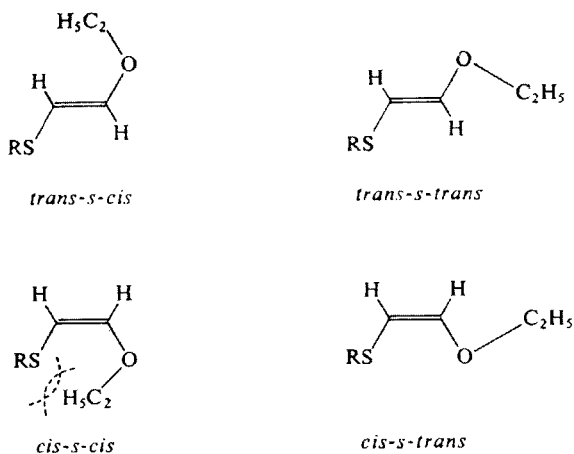
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The differences in the IR and UV absorption spectra of *cis*- and *trans*-1-ethoxy-2-alkylthioethenes (series *I*) and 1-chloro-2-alkylthioethenes (series *II*) are discussed. The spectra of the *trans*-isomers in the series *I* exhibit a doublet of the valence vibration  $\nu(\text{C}=\text{C})$  which has been ascribed to the conformational isomerism of the ethoxy group. In contrast to the *cis*-isomers, the *trans*-isomers of the series *II* exhibit a marked shift of the absorption bands in the UV region which depends on the nature of the alkyl group.

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In the course of our investigations concerning *cis-trans* isomerism of the unsaturated sulphides<sup>1</sup> we studied UV and IR spectra of these compounds. When identifying the products of the synthesis of *trans*-isomers of the series *I*, we observed a doublet (1605–1600, 1628–1622  $\text{cm}^{-1}$ ) in the region of the valence vibration  $\nu(\text{C}=\text{C})$ . Originally, we ascribed this doublet to an admixture of *cis*-isomer ( $\nu(\text{C}=\text{C})$  1629 to 1630  $\text{cm}^{-1}$ ) since the literature<sup>2</sup> reports for *trans*-1-ethoxy-2-ethylthioethene only one absorption band  $\nu(\text{C}=\text{C})$  at 1595  $\text{cm}^{-1}$ . However, according to gas-liquid chromatography and <sup>1</sup>H-NMR spectra, the purity of all the synthesized compounds was better than 99% and therefore we must regard the literature data as incorrect. The occurrence of several bands in the region of valence vibration  $\nu(\text{C}=\text{C})$  has been described<sup>3-7</sup> in the case of the  $\text{C}=\text{C}-\text{O}$  system of simple alkyl vinyl ethers, this phenomenon being explained either by conformational *s-cis*, *s-trans* isomerism<sup>5-7</sup> or by Fermi resonance of the second overtone of the out-of-plane deformation vibration  $\delta(\text{CH}_2=)$  at about 814  $\text{cm}^{-1}$  with the valence vibration of the double bond<sup>3-5</sup>. Soviet authors<sup>7</sup> have suggested to solve this problem by using a  $\beta$ -substituted vinyl alkyl ether,  $\text{R}_1-\text{CH}=\text{CH}-\text{OR}_2$ , which contains no terminal group  $\text{CH}_2=$ ; here the eventual occurrence of several bands  $\nu(\text{C}=\text{C})$  could be interpreted unequivocally as the result of *s-cis*, *s-trans* isomerism. The compounds of the series *I* represent similar suitable model because the influence of the alkylthio group manifests itself only by a hypsochromic shift of the band  $\nu(\text{C}=\text{C})$  for about 30  $\text{cm}^{-1}$  as compared with a simple alkyl vinyl ether. The wavenumbers are listed in Table I. The conclusion that this shift is also due to the conformational *s-cis*, *s-trans* isomerism, is supported

by the observation that *cis*-isomers, in which the *s-cis* conformation of the ethoxy group is unfavourable because of its steric interactions with alkylthio group (see Scheme 1), exhibit only one band due to  $\nu(\text{C}=\text{C})$  in the range  $1629-1631\text{ cm}^{-1}$ .



#### SCHEME 1

Conformational Isomers in Compounds Belonging to the Series *I* (Conformation of alkylthio and ethyl groups is not considered).

In the UV spectra of the studied compounds we have found marked differences in position, shape and intensity of the bands of the corresponding *cis*- and *trans*-isomers (Fig. 1 and Table II). The spectra of both series of *cis*-isomers exhibit two overlapping bands above 200 nm, the position of which depends only very little on the alkyl group (the compound with tert-butyl in the series *I* being an exception) and on the polarity of the solvent. The band shape is formally similar to that of alkyl vinyl sulphides<sup>8,9</sup>. In the case of 1-ethoxy-2-tert-butylthioethene the stronger band is shifted to 205 nm. The shape and position of the bands of *trans*-isomers of the series *I* is also almost independent on the alkyl group and on the polarity of the solvent. The bands resemble formally that of alkyl vinyl ethers<sup>6</sup>, the bathochromic shift of about 60 nm being due to the extension of the conjugated system  $\text{C}=\text{C}-\text{OC}_2\text{H}_5$  by the alkylthio group. In contrast to the *trans*-isomers of the series *I*, *trans*-isomers of the series *II* exhibit a marked dependence of the intensity of the high frequency band on the alkyl group (Fig. 1). Interpretation of this phenomenon by conformational isomerism would mean that the steric requirements of the ground and excited state differ expressively only in the *trans*- and not in the *cis*-isomers. This conclusion is

TABLE I

Wavenumbers ( $\text{cm}^{-1}$ ) of the Valence Vibrations ( $\nu(\text{C}=\text{C})$ ) of Unsaturated Sulphides  $\text{A}-\text{CH}=\text{CH}-\text{B}$ 

	A	B	<i>cis</i>	<i>trans</i>
	$\text{CH}_3\text{S}$	$\text{OC}_2\text{H}_5$	1 630	1 605, 1 625
	$\text{C}_2\text{H}_5\text{S}$	$\text{OC}_2\text{H}_5$	1 630	1 605, 1 625
	$(\text{CH}_3)_2\text{CHS}$	$\text{OC}_2\text{H}_5$	1 632	1 602, 1 628
	$(\text{CH}_3)_3\text{CS}$	$\text{OC}_2\text{H}_5$	1 629	1 600, 1 622
	$\text{CH}_3\text{S}$	Cl	1 572	1 560 <sup>a</sup>
	$\text{C}_2\text{H}_5\text{S}$	Cl	1 574	1 564
	$(\text{CH}_3)_2\text{CHS}$	Cl	1 572	1 554
	$(\text{CH}_3)_3\text{CS}$	Cl	1 570	1 552

<sup>a</sup> Measured in a mixture with *cis*-isomer.

TABLE II

Ultraviolet Spectra ( $\lambda$ , nm and  $\epsilon$ ,  $\text{mol}^{-1} \text{l cm}^{-1}$ ) of Unsaturated Sulphides  $\text{A}-\text{CH}=\text{CH}-\text{B}$  in Solution

Con-figuration	A	B	$\lambda^a$	$\epsilon^a$	$\lambda^b$	$\epsilon^b$
<i>cis</i>	$\text{CH}_3\text{S}$	$\text{OC}_2\text{H}_5$	228, 256 <sup>c</sup>	6 430, 3 340 <sup>c</sup>	225, 251 <sup>c</sup>	6 550, 3 310 <sup>c</sup>
<i>cis</i>	$\text{C}_2\text{H}_5\text{S}$	$\text{OC}_2\text{H}_5$	224, 252 <sup>c</sup>	6 440, 3 820 <sup>c</sup>	224, 249 <sup>c</sup>	6 300, 3 420 <sup>c</sup>
<i>cis</i>	$(\text{CH}_3)_2\text{CHS}$	$\text{OC}_2\text{H}_5$	224, 252 <sup>c</sup>	9 200, 4 950 <sup>c</sup>	223, 249 <sup>c</sup>	9 440, 4 720 <sup>c</sup>
<i>cis</i>	$(\text{CH}_3)_3\text{CS}$	$\text{OC}_2\text{H}_5$	205, 252 <sup>c</sup>	9 630, 3 960 <sup>c</sup>	205, 248 <sup>c</sup>	9 370, 4 130 <sup>c</sup>
<i>trans</i>	$\text{CH}_3\text{S}$	$\text{OC}_2\text{H}_5$	252	5 480	250	5 270
<i>trans</i>	$\text{C}_2\text{H}_5\text{S}$	$\text{OC}_2\text{H}_5$	251	3 250	249	2 950
<i>trans</i>	$(\text{CH}_3)_2\text{CHS}$	$\text{OC}_2\text{H}_5$	250	3 380	246	3 770
<i>trans</i>	$(\text{CH}_3)_3\text{CS}$	$\text{OC}_2\text{H}_5$	252	4 360	248	4 520
<i>cis</i>	$\text{CH}_3\text{S}$	Cl	236, 246 <sup>c</sup>	8 560, 5 770 <sup>c</sup>	233, 246 <sup>c</sup>	8 280, 5 680 <sup>c</sup>
<i>cis</i>	$\text{C}_2\text{H}_5\text{S}$	Cl	235, 246 <sup>c</sup>	8 360, 5 750 <sup>c</sup>	233, 245 <sup>c</sup>	7 500, 5 110 <sup>c</sup>
<i>cis</i>	$(\text{CH}_3)_2\text{CHS}$	Cl	234, 246 <sup>c</sup>	7 810, 5 290 <sup>c</sup>	233, 245 <sup>c</sup>	7 750, 5 040 <sup>c</sup>
<i>cis</i>	$(\text{CH}_3)_3\text{CS}$	Cl	233, 245 <sup>c</sup>	7 840, 5 530 <sup>c</sup>	231, 246 <sup>c</sup>	8 000, 5 680 <sup>c</sup>
<i>trans</i>	$\text{C}_2\text{H}_5\text{S}$	Cl	237, 256	4 880, 5 860	236, 254	4 830, 5 650
<i>trans</i>	$(\text{CH}_3)_2\text{CHS}$	Cl	239 <sup>c</sup> , 258	3 330 <sup>c</sup> , 5 750	239 <sup>c</sup> , 256	3 900 <sup>c</sup> , 5 970
<i>trans</i>	$(\text{CH}_3)_3\text{CS}$	Cl	260	5 380	258	5 280

<sup>a</sup> In cyclohexane; <sup>b</sup> in methanol; <sup>c</sup> incompletely separated bands, both values correspond to shoulders.

surprising also in view of the fact that the *cis*-isomers are in the ground state more stable and that the difference of the internal energies increases from methyl to tert-butyl<sup>1</sup>.

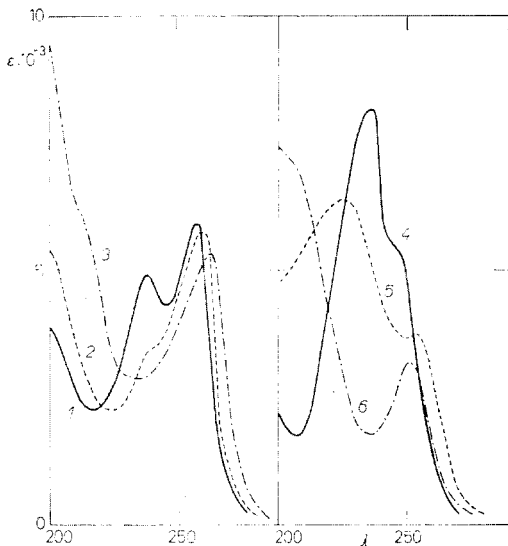


FIG. 1

Ultraviolet Spectra ( $\epsilon$ ,  $\text{mol}^{-1} \text{l cm}^{-1}$  and  $\lambda$ , nm) of Substituted Alkythioethenes in Cyclohexane Solution

1 *trans*-1-Chloro-2-ethylthioethene; 2 *trans*-1-chloro-2-isopropylthioethene; 3 *trans*-1-chloro-2-tert-butylthioethene; 4 *cis*-1-chloro-2-ethylthioethene; 5 *cis*-1-ethoxy-2-ethylthioethene; 6 *trans*-1-ethoxy-2-ethylthioethene.

## EXPERIMENTAL

The UV absorption spectra were taken on a Unicam SP-700 instrument, in cyclohexane and methanol (Merck, Uvasol) (Carlo Erba, spectrophotometric grade) solutions at 23°C, using 1 mm cells. The IR spectra were measured on a Zeiss (Jena) UR-20 spectrophotometer in liquid film. The measured compounds were prepared according to the literature<sup>1</sup> and purified by preparative gas-liquid chromatography.

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