UV, IR, AND PMR SPECTRA AND STRUCTURE OF 2-THIAINDAN AND 2,3-DITHIA-1,2,3,4-TETRAHYDRONAPHTHALENE

M. G. Voronkov, A. N. Pereferkovich,
V. A. Pestunovich, A. K. Grinval'd,
and I. V. Turovskii

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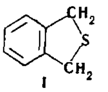
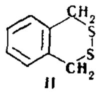
The UV, IR, and PMR spectra of 2-thiaindan (I) and 2,3-dithia-1,2,3,4-tetrahydronaphthalene (II) have been studied. In contrast to the spectra of dibenzyl sulfide (III) and dibenzyl disulfide (IV), the UV spectra of I and II show no gem conjugation between the unshared electrons of the sulfur atom and the aromatic ring. Also in favor of this are the PMR spectra of I and II, in which the values of τ_{CH_2} are lower than in III and IV. The low activation energy of the transformation of one conformation of the heterocycle into the other, particularly in the molecule of I, shows its almost planar structure, which is an obstacle to gem conjugation.

2-Thiaindan (phthalyl sulfide) (I) and 2,3-dithia-1,2,3,4-tetrahydronaphthalene (phthalyl disulfide) (II), which differ from their alicyclic analogs by their extremely high reactivity, have not hitherto been studied spectroscopically from all sides. The present paper gives the results of a study of their UV, IR, and PMR spectra.



I



II

UV SPECTRA

The UV spectrum of I in n-heptane (see Fig. 1) has a strong absorption band at the limit of the vacuum ultraviolet and three fairly weak maxima at 274 nm (2.88), narrow, 266 nm (2.86), narrow, and 258 nm (2.79), diffuse (the values of log ε_{max} are given in parentheses). In addition, there is a shoulder at 251 nm (2.72).* The spectrum of II in the same solvent has a maximum at 224 nm and a series of shoulders at, nm: 282 (2.67), 270 (2.76), 263 (2.82), 256 (2.87), and 247 (2.93).

The bands in the 200–230 nm region are difficult to interpret and they will not be discussed below.

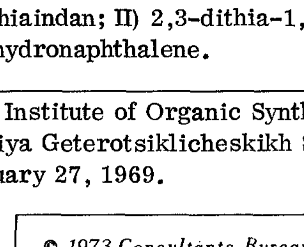


Fig. 1. UV spectra (in n-heptane): I) 2-thiaindan; II) 2,3-dithia-1,2,3,4-tetrahydronaphthalene.

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*The recently published [25] UV spectrum of I in isooctane has, in addition to the bands mentioned, a series of others (with log ε > 2) in the 370–290 nm region the presence of which is obviously due to impurities (these are apparently products of the polymerization, decomposition, or oxidation of I, which is extremely unstable on storage).

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TABLE 1. Maxima in the UV Spectra of I and II and Hydrocarbons of Analogous Structure

Compound	Solvent	λ_{max} (log ε_{max})
I	n-Heptane	274(2,88); 266(2,86); 258(2,79)
II	n-Heptane	sh 282(2,67); sh 270(2,76); sh 263(2,82); sh 256(2,87); sh 247(2,93)
Indan [1]	Isooctane	273,5(3,17); 267(3,08); 261(2,94)
1,4-Dihydronaphthalene [2]	n-Heptane	274(2,93); 267(2,90); infl. 262(2,70)
Tetralin [1]	Isooctane	273(2,80); 267(2,71); 261(2,57)
o-Xylene [1]	Isooctane	270,5(2,15); 265(2,30); 262,5(2,43)

In position and intensity the maxima in the spectrum of I practically coincide with the maxima of the hydrocarbons related to it (see Table 1).

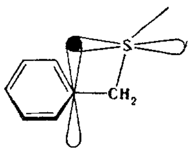
The figures given in Table 1 show that the spectrum of I reflects only the fine structure of the aromatic band at 260–270 nm in the variant appropriate to compounds with two condensed rings – benzene and nonaromatic rings – and also o-dialkylbenzenes. This band relates to the $\pi-\pi^*$ transition, and the $-\overset{..}{\underset{..}{S}}-$ chromophore has practically no effect on the spectrum. At the same time, in the UV spectrum of dibenzyl sulfide (III) in n-heptane, apart from the maximum close to 200 nm, there is only a shoulder at 244 nm (3.17) [3] while in ethanol there is a shoulder at 238 nm (2.90), a weak maximum at 260 nm (2.85), and a shoulder at 266 nm (2.66) [4], only the last two of which may be connected with the absorption of the benzene ring. In view of this, the question arises of the cause of the low intensity of the sulfur band in the spectrum of I and its masking by the aromatic band.

It has been shown previously [4-6] that the wavelength and extinction of the sulfur band depend on the possibility of the conjugation of the unshared electrons of the $-\overset{..}{\underset{..}{S}}-$ atom with the organic groups attached to it. From this point of view, organic sulfides can be divided into three main types.

1. Nonconjugated dialkyl sulfides, for example CH_3SCH_3, the spectrum of which has an inflection at 229 nm (2.14) – the $n \rightarrow \sigma^*$ transition. Saturated heterocyclic sulfides $\overline{S(CH_2)_nCH_2}$ with $n \geq 3$ also belong here. In their spectrum (in ethanol), when $n = 3$ there is a shoulder at 239 nm (1.73), and when $n = 4$ one at 229 nm (2.26).

2. Conjugated sulfides (α,β-unsaturated and aromatic sulfides), for example $CH_2=CH-S-CH=CH_2$ with λ_{max} (in ethanol) 255 nm (3.70) – the $n \rightarrow \pi^*$ transition. In the spectrum of $C_6H_5SC_6H_5$, the band of the $n \rightarrow \pi^*$ transition at 274 nm (3.74) is shifted so far in the long-wave direction that the benzene $\pi \rightarrow \pi^*$ band (also strengthened) appears beyond it – at 250 nm (4.08).

3. Sulfides of the allyl type (β,γ-unsaturated sulfides and those containing arylmethyl groups), for example, $CH_2=CHCH_2-S-CH_2CH=CH_2$ with λ_{max} (in ethanol) 221 nm (3.33). This type includes the above-mentioned dibenzyl sulfide (III). In the IR spectrum of the latter, the sulfur maximum is found close to the band of the benzene nucleus at 260 nm and is sufficiently strong to mask it either completely (in heptane) or almost completely (in ethanol). The strong absorption of the sulfides of this type suggests a geminal interaction ($n \rightarrow \pi^*$ transition) between the unshared electrons of the sulfur atom and the π electrons of the double bond [6] or the aromatic rings.



(1)

The gem conjugation* (homoconjugation [7]) of this type can be represented by the scheme (1) and in these circumstances the electron density on the sulfur atom must be lowered.

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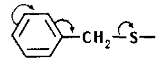
*The term "gem conjugation" has been proposed by one of us to indicate the conjugation of geminal substituents [9].

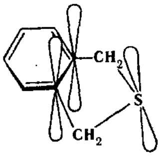
The possibility of $p_\pi - d_\pi$ interaction through the space between the π electrons of the aromatic nucleus and the vacant d orbitals of the sulfur atom, involving, conversely, an increase in the negative charge on the sulfur atom, is not excluded either.

In addition to the types of interactions mentioned, in the molecules of III $\sigma - \pi$ conjugation is also possible (2):



(2)

However, the UV spectra of benzyl chloride and fluoride [8] show that conjugation of this type does not affect the absorption. Because of the limited mobility of the sulfur atom in the nonplanar heterocycle I (see below), gem conjugation according to scheme (2) becomes impossible (3):



(3)

In the UV spectrum of diphenethyl sulfide, in the molecule of which, likewise, gem conjugation is impossible, there is only the band of the benzene rings [4], slightly enhanced because there are two aromatic nuclei in the molecule.

Compound II also has a relatively rigid ring condensed with an aromatic nucleus and, in addition, a $-S-S-$ chain which causes a red shift of the sulfur band, giving in the case of dibenzyl disulfide (in heptane) a shoulder at 258 nm (3.19) [3]. This shift is expressed particularly strongly in the spectra of heterocyclic disulfides in the molecules of which the $-S-S-$ group has the cis configuration: 1,2-dithiacyclohexane λ_{max} 292 nm (2.48) [6, 10]. In the spectrogram (see Fig. 1) it can be seen that absorption is greater than that of I in the 250 and 280 nm regions. It is most likely that the shoulder at 282 nm (2.67) belongs to the $-S-S-$ chain. Shoulders at 270, 263, and 257 nm relate to the benzene ring, and the question of the causes of the strong absorption at 247 nm remains open.

IR SPECTRA

The IR spectrum of I, which has also been published previously [11], and of II, obtained for the first time, are given in Table 2.

To explain the features of the spectra of I and II, they were compared with the IR spectra of compounds related to them: indan [12], tetralin [13], and 2-thia-1,2,3,4-tetrahydronaphthalene [14, 15]. It was found that the spectra of I and II have a comparatively weak but narrow band at 894 and 890 cm^{-1}, respectively, which is absent from the spectrum of indan. The spectra of tetralin and 2-thia-1,2,3,4-tetrahydronaphthalene have several bands in this region (807, 820, 867, and 901 cm^{-1} and 815, 853, 879, and 904 cm^{-1}, respectively), which complicates the comparison. The band at 890-894 cm^{-1} in the spectra of I and II may relate to the stretching vibrations of the heterocycle, since a band at 958-960 cm^{-1} corresponds to these vibrations in the spectrum of the related tetrahydrothiophene [10] (in condensed systems, it must be shifted in the low-frequency direction [10]).

The IR spectrum of II has a new strong band at 1399 cm^{-1}, the assignment of which is still not clear. Since the stretching vibrations of $-S-S-$ in the spectra of 1,2-dithiolanes are represented by absorption in the 500 cm^{-1} region [10], it is possible that the band at 438 cm^{-1} in the spectrum of II relates to them.

PMR SPECTRA

In the PMR spectra of I and II (in CH_2Cl_2), which are illustrated in Table 3, the resonance of the methylene protons is shown by a singlet right down to −80°C. This shows the lower activation energy of the transition of one conformation of the heterocyclic ring into the other. In the molecule of I, this ring is apparently almost planar, and in II the free enthalpy of activation has been evaluated as 8.5 kcal/mole [16].

The chemical shifts given in Table 3 show the following facts.

TABLE 2. IR Spectra of 2-Thiaindan (I) and 2,3-Dithia-1,2,3,4-tetrahydronaphthalene (II)

I				II		Assignment
this work		acc. to [11]†				
ν, cm^{-1}	intensity*	ν, cm^{-1}	intensity*	ν, cm^{-1}	intensity*	
3066	3			3060	3	ν CH ar
3028	3	3030	4	3020	3	ν CH ar
2918	4	2928	5	2948	3	ν_{as} CH al
2845	4	2833	3	2910	3	ν_s CH al
2352	1					
1920	2	1916	1	1900	2	
1808	2	1795	2			
1695	1	1684	1			
1590	2	1580	3	1578	4	ν C=C ar
1492	3	1497	5	1499	5	ν C=C ar
1460	3	1464	5	1478	5	ν C=C ar
1440	3	1441	5	1450	5	δ CH_2 (scissors)
		1355	2	1399	4	
1305	2	1300	3	1308	4	δ CH_2 (twisting)
1294	2	1288	3	1285	3	δ CH_2 (fanlike)
		1250	1	1260	4	
				1237	3	
		1198	3	1183	4	
1173	2	1166	4	1172	4	
		1107	3	1109	3	
		1091	2			
		1045	2	1050	3	
1032	2	1029	3			
		986	2	988	3	
949	2	942	4	960	3	
				900	3	
894	2	887	5	890	3	
				851	4	
				783	3	
752	4	743	5	765	4	δ CH (nonplanar)
		722	5	742	4	δ CH (nonplanar)
				708	2	
				690	2	
				583	2	
				438	3	
				424	2	
427	3			400	2	

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*According to a five-point scale (1 – lowest intensity of absorption).
† Calculated from the spectrogram.

TABLE 3. Chemical Shifts of the Protons in the PMR Spectra of 2-Thiaindan (I) and 2,3-Dithia-1,2,3,4-tetrahydronaphthalene (II) in CCl_4

Compound	τ_{CH_2}, ppm	$\tau_{C_6H_5}$, ppm
I	5,94	2,98
II*	6,06	3,0

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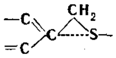
*According to the literature [17], in $CDCl_3$, τ_{CH_2} = 5.93 ppm and $\tau_{C_6H_5}$ = 2.87 ppm.

On passing from I to II, i.e., from a five-membered heterocycle to a six-membered one, τ of the proton adjacent to the sulfur atom rises, while on passing from III to IV it falls (τ_{CH_2} 6.58 and 6.49 ppm, respectively [18]). Thus, in the case of I and II the fall in the value of τ_{CH_2} with an increase in the number of sulfur atoms in the ring is masked by the stronger opposite effect. A similar effect is observed on passing from indan to tetralin (τ_{CH_2} 7.09 and 7.24 ppm, respectively [19]) and apparently has the same nature as the factors determining the dependence of the screening of the methylene protons in cycloalkanes [20].

The screening of the methylene protons in the molecules of I and II is considerably less than in the corresponding open-chain molecules (III and IV). A similar difference is observed in the case of alkanes and the corresponding cycloalkanes, but it is smaller (0.20-0.25 ppm) [21], the difference for I-III and II-

IV being 0.64 and 0.43 ppm, respectively. Such a large value of $\Delta\tau_{CH_2}$ cannot be explained by the introduction of corrections for the difference in the contributions of the diamagnetic anisotropy and of the electric field of the C−S and S−S bonds, the unshared electron pairs of the sulfur atom, and the ring current of the benzene nucleus. The combined effect of all the influences mentioned does not, according to our evaluation, exceed a value of the excess screening of 0.1–0.2 ppm for the acyclic molecules as compared with the corresponding cyclic molecules in which the bonds are more localized.

The contradiction arising can be explained in the following way: a three-membered ring is formed as the result of gem conjugation between the sulfur atom and the benzene ring in the molecules of III, IV, and dibenzyl polysulfides.



It may be assumed that anisotropy or ring currents of the deformed electron clouds in this ring are also the cause of the increased screening of the methylene protons in the molecules of III and IV, while in the molecules of I and II there is no gem conjugation effect.

The existence of gem conjugation – for example, in the molecules of enones – has hitherto been established only by changes in the UV spectra. This has given grounds for considering this interaction as a property only of excited molecules [7]. However, recently results have appeared showing the existence in certain cases of gem conjugation in the stationary state [9, 22]. The IR spectrum of III shows no changes connected with gem conjugation, but it must be taken into account that the absorption of the C−S band is very weak in any case and can be masked by the aromatic bands.

EXPERIMENTAL

2-Thiaindan (I). A solution of 26.4 g (0.1 mole) of o-xylylene bromide (obtained by the photochemical bromination of o-xylene) in 150 ml of benzene was added with vigorous stirring over 2 h in an atmosphere of nitrogen to a solution of 36.0 g (0.15 mole) of $Na_2S \cdot 9H_2O$ in 100 ml of water containing 0.5 g of OP-7 nonionic emulsifier heated to 40–50°C. Stirring was continued for another 6 h, and then the benzene layer was separated off and distilled with steam. The upper layer was separated off and dried over $MgSO_4$, and the benzene was distilled off from it. Vacuum distillation of the residue gave 5.8 g (47.7%) of I with mp 26°C, bp 77–78°C (5 mm). According to the literature [23], mp 26°C, bp 108°C (14 mm).

2,3-Dithia-1,2,3,4-tetrahydronaphthalene (II). The synthesis was performed similarly, but 4.8 g (0.15 g-atom) of sulfur was previously dissolved in the Na_2S solution. After the solvent had been distilled off, the residue was sublimed at 100°C and a pressure of 14 mm and was then recrystallized from ether. The yield of II with mp 80°C was 7.8 g (46.2%). According to the literature [24], mp 80°C.

The UV spectra of 10^{-4} M solutions of I and II in n-heptane were taken on a semiautomatic spectrophotometer constructed in the laboratory of physical organic chemistry of the Institute of Organic Synthesis, AS Latvian SSR.

The IR spectra were obtained on a UR-10 spectrometer – I in the form of a liquid film and II as mulls in paraffin oil (400–1800 cm^{-1}) and in hexachlorobutadiene (1800–3400 cm^{-1}).

The PMR spectra were obtained on a YaMR-5535-TsLA spectrometer with a working frequency of 40 MHz. The chemical shifts were measured on the τ scale by the side-band method as the arithmetic means of not less than ten measurements. Compounds I and II were investigated in the form of 0.5 M solutions in CCl_4 (with cyclohexane as internal standard) and in CH_2Cl_2.

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