Isothiocyanates. XXXVIII.
Ultraviolet spectra of isothiocyanatobenzoxazoles and isothiocyanatobenzothiazoles

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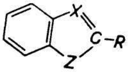
Characteristic ultraviolet spectral data of benzothiazolyl and benzoxazolyl isothiocyanates are presented. The possibility of ascribing the absorption bands to certain electron transitions of the studied systems and the interaction of the —NCS group with the mentioned systems are discussed. The effect of solvents and pH of the medium on the nature of the u.v. spectra of these systems is also studied.

There are several works available [1—4] dealing with the u.v. spectra of heterocyclic systems of the following types:



X = N, CH; Z = O, S; R = alkyl, aryl, H.

These works were valuable in elucidating important structural problems of the heterocyclic systems.

In the present work we study the effect of the —NCS group and the extent of its conjugation with 2-phenylbenzoxazole and 2-phenylbenzothiazole systems. The considered systems are compared with those without or with one substituent (R).

Experimental

The u.v. spectra of the mentioned benzothiazolyl and benzoxazolyl isothiocyanates were taken with a recording Specord UV VIS (Zeiss, Jena) spectrophotometer in the region of 210—400 nm in dioxan (concentration 2.5×10^{-5} M, cell thickness 1 cm, temperature 25 ± 0.2°C). The maxima of the obtained absorption bands and their intensities are given in Table 1. The u.v. spectra of the derivatives *I*, *VI*, *VIII*, and *IX* (Table 1) were measured also in cyclohexane, carbon tetrachloride, chloroform, methanol, water, and in 3, 1, 0.1, 0.01 N aqueous solutions of hydrochloric acid. The obtained values are given in Tables 2 and 3.

Results and discussion

As evident from [7] and from the data in Table 1, the skeletons of the benzoxazole and benzothiazole types have similar absorption spectra (Figs. 1 and 2). The u.v. spectra of these compounds showed 3 absorption bands (regions 210—230, 240—280, and 290 nm). Regarding the complicated conjugation systems, to which this absorption belonged, it was difficult to assign reliably the individual absorption bands to the corresponding electron transitions without a quantum-chemical calculation. But it is supposed that the absorption band in the region of 211 nm (*a* band) could be ascribed to ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of the benzene system. On the other hand, the absorption band of lower intensity (log $\varepsilon = 4.1$) in the region 250—280 nm (*b* band) could belong to the electron transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ [5, 6]. The effect and the interaction of the —NCS group with

Table 1

Characteristic ultraviolet spectral data

No.	Compound	λ_{max} (log ε) (band *a*)	λ_{max} (log ε) (band *b*)	λ_{max} (log ε) (band *c*)
I	2-Phenylbenzoxazole	215 (4.14)	265 (4.14)	301 (4.43)
II	5-Isothiocyanato-2-phenylbenzoxazole	217 (4.61)	266 (4.48)	316 (4.32)
III	2-(4-Isothiocyanatophenyl)benzoxazole	217 (4.29)		327 (4.70)
IV	2-(3-Isothiocyanatophenyl)benzoxazole	217 (4.63)	283 (4.52)	304 (4.43)
V	2-Phenylbenzothiazole	214 (4.53)	248 (4.08)	300 (4.43)
VI	5-Isothiocyanato-2-phenylbenzothiazole	215 (4.60)	278 (4.63)	291 (4.61)
VII	6-Isothiocyanato-2-phenylbenzothiazole	223 (4.65)	256 (4.10)	330 (4.49)
VIII	2-(4-Isothiocyanatophenyl)benzothiazole	216 (4.52)	230 (4.53)	335 (4.66)
IX	2-(3-Isothiocyanatophenyl)benzothiazole	224 (4.66)	254 (4.22)	284 (4.84)
X	5-Isothiocyanato-2-(4-chlorophenyl)benzothiazole	214 (4.54)	278 (4.58)	292 (4.60)
XI	5-Isothiocyanato-2-(4-bromophenyl)benzothiazole	217 (4.51)	279 (4.56)	292 (4.59)
XII	5-Isothiocyanato-2-(4-iodophenyl)benzothiazole	214 (4.52)	279 (4.57)	292 (4.63)
XIII	5-Isothiocyanato-2-(4-methylphenyl)benzothiazole	214 (4.54)	278 (4.63)	292 (4.62)
XIV	5-Isothiocyanato-2-(4-methoxyphenyl)benzothiazole	215 (4.55)	279 (4.54)	292 (4.56)
XV	2-(4-Isothiocyanato)-2-chlorophenylbenzothiazole	217 (4.64)	231 (4.51)	337 (4.46)
XVI	6-Methyl-2-(4-isothiocyanatophenyl)benzothiazole	217 (4.51)	258 (3.90)	337 (4.60)

Table 2

Ultraviolet spectral data of some 2-phenylbenzothiazoles and 2-phenylbenzoxazoles in different solvents

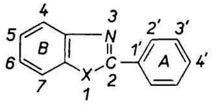
No.	$\lambda_{\max}$ [nm] (log ε)					
	dioxan	methanol	cyclohexane	CCl_4	$CHCl_3$	H_2O
I	301	298	300	301	301	290.7
	(4.43)	(4.46)	(4.48)	(4.46)	(4.46)	(4.36)
II	266	264	268	268	266	272
	(4.48)	(4.46)	(4.45)	(4.50)	(4.49)	(4.21)
III	327	324	326	328	328	308
	(4.70)	(4.68)	(4.52)	(4.68)	(4.70)	(4.11)
IV	283	281	284	285	284	280
	(4.50)	(4.48)	(4.42)	(4.48)	(4.39)	(4.03)
V	300	298	298	301	300	298
	(4.43)	(4.20)	(4.20)	(4.32)	(4.21)	(4.18)
VI	278	274	279	280	280	290
	(4.63)	(4.56)	(4.51)	(4.58)	(3.92)	(3.92)
VIII	335	331	335	337	335	317
	(4.66)	(4.67)	(4.61)	(4.62)	(4.60)	(4.24)
IX	284	281	284	286		295
	(4.84)	(4.39)	(4.36)	(4.56)		(4.00)

Table 3

Ultraviolet spectral data of some benzothiazole and benzoxazole derivatives in different acid medium

Solvent	Compound			
	I	*V*	*III*	*VIII*
Distilled water	291	298	308	317
	(4.36)	(4.18)	(4.18)	(4.40)
	300			
	(4.34)			
0.01 N-HCl	292	299	307	322
	(4.31)	(4.19)	(3.96)	(4.15)
	300.3			
	(4.36)			
0.1 N-HCl	292	309	307	326
	(4.31)	(4.13)	(4.146)	(4.11)
	300			
	(4.30)			
1.0 N-HCl	292	319	308	329
	(4.30)	(4.245)	(4.10)	(3.61)
	300.5			
	(4.29)			
3.0 N-HCl	304	322	327	353
	(4.39)	(4.283)	(4.38)	(4.11)

heterocyclic systems could be followed best by the shift of the absorption maxima in the region 290—330 nm (*c* band):



It was shown that when the —NCS group was bound in the benzene ring *A*, then the absorption band *c* was bathochromically shifted by 35 nm in the case of the benzothiazole derivative *VIII* due to the +M effect of the —NCS group. With the benzoxazole derivative *III* it was 26 nm. If this group was bound in the position 3′ of the benzene ring *A* then the absorption maximum (*c* band) was shifted to lower wavenumbers in the case of the benzothiazole derivative *IX* when compared with the basic derivative *V* With the 2-phenylbenzoxazole (derivative *IV*) the bathochromic shift was negligible. In this case the —NCS group was not in alternate position with the conjugated system. Only —I effect of the —NCS group was involved; therefore the interaction was insignificant.

When the —NCS group was in the 5 position of the benzene ring *B*, the position of the absorption maximum (*c* band) was influenced in a lower degree (Figs. 1 and 2). *E.g.*, the difference between *I* and *II* was $\Delta\lambda = 15$ nm and between *V* and *VI* $\Delta\lambda = {} = 9$ nm. In this substitution however, the shape of the absorption band changed which

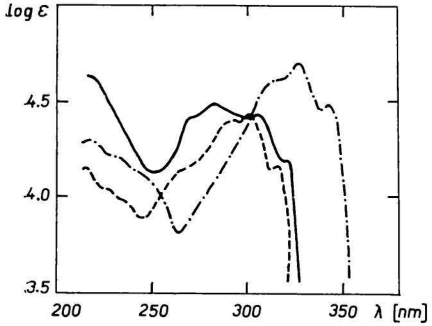


Fig. 1. Ultraviolet spectra of 2-phenylbenzoxazole derivatives in dioxan.
— — — 2-phenylbenzoxazole (*I*);
— . — . 2-(4-isothiocyanatophenyl)-benzoxazole (*III*);
——— 2-(3-isothiocyanatophenyl)-benzoxazole (*IV*).

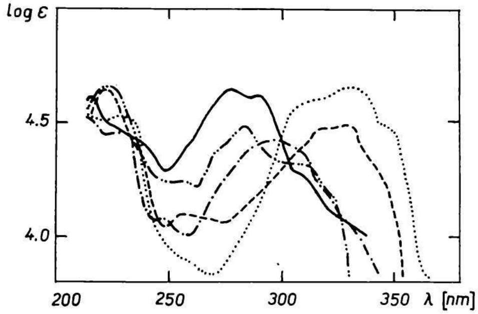
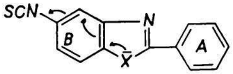


Fig. 2. Ultraviolet spectra of 2-phenylbenzothiazole derivatives in dioxan.
. — . — . 2-phenylbenzothiazole (*V*);
2-(4-isothiocyanatophenyl)-benzothiazole (*VIII*);
— . . . — 2-(3-isothiocyanatophenyl)-benzothiazole (*IX*);
——— 5-isothiocyanato-2-phenylbenzothiazole (*VI*);
— — — 6-isothiocyanato-2-phenylbenzothiazole (*VII*).

was manifested by great increase of log ε in the region of the absorption band *b*. On the basis of the obtained data we assumed that the —NCS group interacted with oxygen or sulfur whereas the benzylideneimine chromophore lost its priority. The absorption band *b* probably belonged to the absorption of the following group:



where the atom X was involved in conjugation more significantly. Therefore the interaction of the benzene ring *A* with the residual part of the molecule weakened. More marked involvement of the atom X in conjugation was observed with the benzothiazole derivative because in the excited state of the sulfur atom there were more favourable steric conditions for $p-\pi$ interaction. It is in accordance with the obtained values; the derivative *II* had $\lambda_{\max}$ at 266 nm (band *b*) while the derivative *VI* at 278 nm (band *b*).

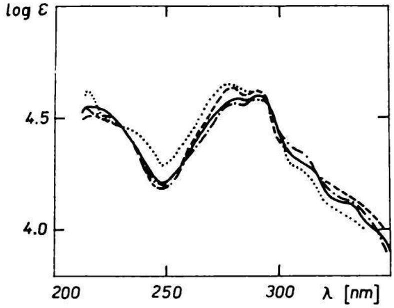


Fig. Ultraviolet spectrum of 5-isothiocyanato-2-(4-X-phenyl)benzothiazole in dioxan.

5-isothiocyanato-2-phenylbenzothiazole (*VI*);

— — — 5-isothiocyanato-2-(4-methylphenyl)benzothiazole (*XIII*);

——— 5-isothiocyanato-2-(4-chlorophenyl)benzothiazole (*X*);

. — . — . 5-isothiocyanato-2-(4-bromophenyl)benzothiazole (*XI*).

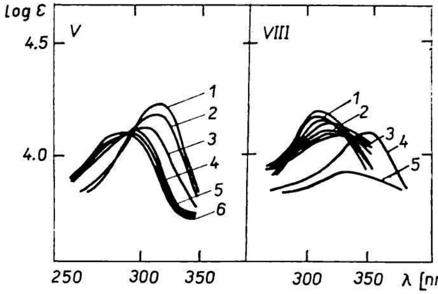


Fig. 4. Ultraviolet spectrum of 2-phenylbenzothiazole (*V*) and 2-(4-isothiocyanatophenyl)benzothiazole (*VIII*) in water solution acidified with HCl.

V: *1.* 3 N; *2.* 2 N; *3.* pH 1; *4.* pH 2; *5.* pH 3; *6.* pH 4—7.

VIII: *1.* pH 7, 6, 5; *2.* pH 2—4; *3.* pH 1; *4.* 3 N; *5.* 1 N.

The pronounced bathochromic shift of the absorption maximum (band *c*) in the derivative *VII* could be explained by conjugation of the *p*-positioned —NCS group with the benzene ring *A* [8, 9].

Comparison of the u.v. spectral data of the derivative *VI* with those of the derivatives *X*—*XIV* (Table 1, Fig. 3) showed that substituents in this position did not influence significantly the nature of the absorption band.

Table 2 contains the u.v. spectral data of some isothiocyanates of both heterocyclic systems where the effect of solvents was studied.

We attempted to follow the effect of solvents of different polarity on the change of both absorption band position and intensity. As evident from Table 2 the position of the absorption bands was only slightly influenced by solvents. The absorption maxima of the same compounds in different solvents fell into the interval of 6 nm. Exception was observed only with the spectra measured in water. Here the maxima of all the studied compounds were shifted to lower wavenumbers, the absorption bands were very broad and without fine structure.

More pronounced changes of the absorption band position were observed in acidified water solutions. With the derivatives *I* and *V* the absorption band *c* was shifted to higher wavenumbers (Table 3, Fig. 4). This shift was greater with 2-phenylbenzothiazole (*V*; 24 nm) than with 2-phenylbenzoxazole (*I*; 14 nm).

We assume that in the acid medium the studied heterocyclic systems are protonated. From several possible protonations in the heterocycle (oxygen, sulfur, nitrogen) the most probable seemed to be the attack of the free electron pair of the nitrogen atom by proton. In this case the nitrogen atom became more electropositive as a result of the more pronounced conjugation with benzene ring. These assumptions are in accordance with [10].

With the derivative *VIII*, the shift to higher wavenumbers was observed at low H^+ concentrations (pH 2) because of the +M effect of the —NCS group. The analogous shift with the derivatives of the benzoxazole types was observed only in strongly acid medium (3 N hydrochloric acid) because of the substantially lower electron density on the nitrogen atom caused by deactivation effect of the oxygen atom in the benzoxazole aromatic system.

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