

Spectral properties and thione-thiole tautomerism of benzothiazole, benzoxazole, and benzimidazole derivatives

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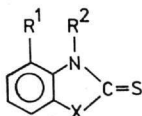
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Dedicated to Professor J. Kováč on his 50th birthday

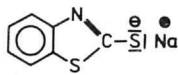
Infrared, Raman, and ultraviolet spectra of products of the reaction of *o*-substituted anilines with thiophosgene and of some model compounds are interpreted. The thione-thiole tautomerism of compounds in the crystalline state as well as in various solvents is discussed.

В работе дана интерпретация ИК спектров, спектров комбинационного рассеяния и УФ спектров продуктов реакции *o*-замещенных анилинов с тиофосгеном и некоторых модельных соединений. Обсуждается тион-тиоловая таутомерия в кристаллическом состоянии и различных растворителях.

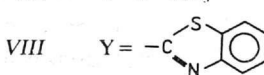
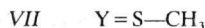
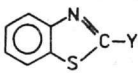
In papers [1, 2] dealing with bromination and alkylation of benzothiazole and benzoxazole 2-mercapto derivatives a possibility of thione-thiole tautomerism was considered. Paper [3] dealt with the structure and ultraviolet spectra of some *N*-alkyl and *S*-alkyl derivatives of mercaptobenzothiazole and six-membered nitrogen heterocycles. The reaction of *o*-aminothiophenol with methyl isothiocyanate had been reported by authors [4] who found that a relatively stable *S*-(*o*-aminophenyl)methyl dithiocarbamate first formed undergoes ring closure in 4 M hydrochloric acid giving benzothiazolidine-2-thione. The present work deals with the study of spectral properties of products of the reaction of *o*-substituted anilines with thiophosgene and thione-thiole tautomerism of compounds investigated is discussed. Eight compounds have been examined



I	$R^1 = R^2 = H$	$X = S$
II	$R^1 = R^2 = H$	$X = O$
III	$R^1 = R^2 = H$	$X = NH$
IV	$R^1 = CH_3, R^2 = H$	$X = S$
V	$R^1 = H, R^2 = CH_3$	$X = S$



VI



Experimental

o-Aminophenol, *o*-aminothiophenol, *o*-phenylenediamine, and *p*-chlorothiophenol were commercial chemicals, purified by crystallization, and their physical constants agreed with those in the literature. Compounds investigated were prepared as follows: 2-mercaptobenzothiazole (*I*) and 2-mercaptobenzimidazole (*III*) by the reaction of thiophosgene with *o*-aminothiophenol and *o*-phenylenediamine, respectively, and 2-mercaptobenzoxazole (*II*) by thiophosgenating *o*-aminophenol in 4 M hydrochloric acid.

4-Methyl benzothiazolidine-2-thione (*IV*) was prepared according to [5] by the reaction of *o*-toluidine with sulfur and CS₂ at 215°C; 3-methyl benzothiazolidine-2-thione (*V*) by thiophosgenating *o*-*N*-methyl aminothiophenol in chloroform at 0°C; 2-methyl thiobenzothiazole (*VII*) by alkylation of *I* with methyl iodide according to [6] and 2,2'-dibenzothiazolyl (*VIII*) from *o*-aminothiophenol and oxalyl chloride according to [7]. 2-Mercaptobenzothiazole sodium salt was prepared by dissolving *I* in 10% NaOH aqueous solution, followed by evaporating H₂O and drying the product. Bis(*o*-isothiocyanatophenyl)- and bis(*p*-isothiocyanatophenyl)disulfides were prepared by thiophosgenating corresponding amines.

Infrared spectra of compounds investigated were recorded with a Zeiss UR-20 instrument in the range 800—3600 cm⁻¹ (concentration 2.5 × 10⁻²—7.5 × 10⁻² M in CHCl₃; cell thickness 0.4 mm). Spectra were also recorded in CCl₄ and dioxan as well as in KBr discs and in suspension with nujol. The wavenumber calibration was checked against the spectrum of the polystyrene foil. The accuracy of the wavenumber reading was around ± 1 cm⁻¹.

Ultraviolet spectra were recorded with a Zeiss Specord UV VIS instrument for dioxan, aqueous, and carbon tetrachloride (concentration 1.0 × 10⁻⁵—5.5 × 10⁻⁵ M) and methanolic (concentration 3 × 10⁻⁵—5 × 10⁻⁵ M) solutions; cell thickness 1.0 cm.

Raman spectra of pure solid compounds studied were recorded with a Spex Ramalog 4 spectrophotometer. A green line (λ 514 nm) of a Spectra Physics Model 164 argon ion laser was used to excite them. The wavenumber calibration was checked against the spectrum of CCl₄. Spectral grade CCl₄ and methanol were used. Anal. grade CHCl₃ was freed from ethanol by passing it several times through a column of silica gel; dioxan (anal. grade) was used without further purification.

Results and discussion

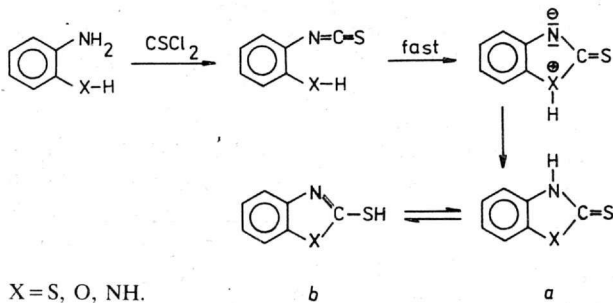
Thiophosgenation of *o*-aminothiophenol and *o*-phenylenediamine was performed in chloroform. With respect to insolubility of *o*-aminophenol in chloroform,

thiophosgenation was carried out in 4 M hydrochloric acid. The yields of cyclization products were $\sim 70\%$. Searching the reaction of *o*-aminothiophenol with thiophosgene spectroscopically it was found that in the reaction mixture, besides a cyclization product, *i.e.* 2-mercaptobenzothiazole, a free *o*-isothiocyanatothiophenol is also present.

By thiophosgenating bis(*o*-aminophenyl)disulfide in hydrochloric acid, besides a small amount of bis(*o*-isothiocyanatophenyl)disulfide 2-mercaptobenzothiazole (*I*) (25%) is also formed.

The formation of *I* can be explained by that the disulfidic bridge is cleaved by the action of acidic medium, which is also facilitated by an electron-withdrawing effect of the NCS group.

Spectral investigation of thiophosgenation suggests that isothiocyanates cyclizing to a more stable benzothiazole, benzoxazole, and benzimidazole derivatives, respectively, are formed first



Infrared spectral data of compounds investigated are summarized in Table 1. Relatively intense absorption bands, $\nu(\text{NH})$, in the region of $3100\text{--}3400\text{ cm}^{-1}$ and relatively weak bands, $\nu(\text{SH})$, in the region of $2500\text{--}2700\text{ cm}^{-1}$ are observed, indicating that in CCl_4 and CHCl_3 solutions these compounds exist mainly in the thione form *a*.

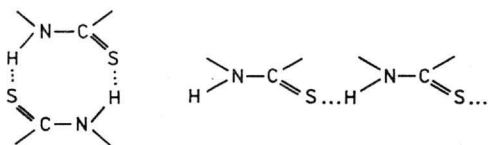
In the spectra recorded for dioxan solution, for KBr discs and for nujol, no bands, $\nu(\text{NH})$, are observed in the region of $3100\text{--}3400\text{ cm}^{-1}$, which can be explained by the $\text{N}\text{--}\text{H}\cdots\text{S}=\text{C}$ hydrogen bond formation and the consequent shift of $\nu(\text{NH})$ bands to the region of the $\text{C}\text{--}\text{H}$ bond vibration ($\sim 3100\text{ cm}^{-1}$). The $\nu(\text{NH})$ bands were found to be concentration dependent *e.g.* in the case of compound *I* the molar absorption coefficient of the $\nu(\text{NH})$ band decreased from the value of $\epsilon = 143$ to the value $\epsilon = 78\text{ l mol}^{-1}\text{ cm}^{-1}$ in the range $1.2 \times 10^{-4}\text{--}6.5 \times 10^{-3}\text{ M}$ concentration in CCl_4 . Similar dependence is also observed in the spectrum of compound *I* recorded for CHCl_3 solution ($\epsilon = 156 \rightarrow 75\text{ l mol}^{-1}\text{ cm}^{-1}$ in the range $3 \times 10^{-4}\text{--}4 \times 10^{-3}\text{ M}$ concentrations).

Table 1

Infrared (in CHCl_3) and Raman (for solids) spectral data of compounds studied

Compound	$\bar{\nu}$, cm^{-1}							
	Infrared				Raman			
	$\nu(\text{NH})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{NH}\dots)$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}-\text{S})$
<i>I</i>	3392	1609	1620	3075	1605	1620	1260	1080
<i>II</i>	3438		1628	3080	1620	1635	1235	
<i>III</i>	3248		1630	3090	1605	1630	1280	
<i>IV</i>	3390	1605	1625	3080	1607	1628	1260	1083
<i>V</i>			1630					
<i>VI</i>			1628					
<i>VII</i>			1629					
<i>VIII</i>		1600	1630		1575			1070

Evidently, association takes place with increasing concentration and thus "cyclic dimers" and "polymers" are formed [8, 9] *via* hydrogen bonds from the thione form of compound *I*



The formation of "polymer" chains of compound *I*, bonded by hydrogen bonds, has been determined by the X-ray diffraction analysis [10], and the length of hydrogen bonds was found to be 0.248 nm. In the spectra of *I* recorded for carbon tetrachloride solution at various temperatures an increase in the $\nu(\text{NH})$ band intensity has been observed, which can be explained by that on heating the cleavage of the hydrogen $\text{N}-\text{H}\dots\text{S}=\text{C}$ bonds takes place.

By studying the influence of concentration on the intensity of the $\nu(\text{NH})$ band it was found that in the range of concentrations (8×10^{-3} — 8×10^{-4} M in CCl_4) the molar absorption coefficient of the band is practically constant ($\epsilon = 198 \text{ l mol}^{-1} \text{ cm}^{-1}$, $c = 8 \times 10^{-3}$ M and $\epsilon = 199 \text{ l mol}^{-1} \text{ cm}^{-1}$, $c = 8 \times 10^{-4}$ M).

In the Raman spectra of compounds investigated (*I*—*IV*) (Table 1), recorded for solids, the $\nu(\text{SH})$ bands, usually very intense, are not observed. This fact suggests that in the solid state these compounds exist exclusively in the thione form.

Furthermore, the $\nu(\text{C}=\text{S})$ very strong bands are observed in the 1235—1280 cm^{-1} region while the $\nu(\text{CS})$ bands in the range 1070—1083 cm^{-1} . In consequence of hydrogen bond formation the $\nu(\text{NH})$ bands are shifted to the $\nu(\text{CH})$ aromatic region ($\sim 3100 \text{ cm}^{-1}$). In the Raman spectra of *p*-chlorothiophenol and *o*-aminothiophenol, both taken as model compounds, very strong $\nu(\text{SH})$ bands are observed at 2585 and 2536 cm^{-1} , respectively. The lower wavenumber of the $\nu(\text{SH})$ band in the spectrum of *o*-aminothiophenol compared with that of

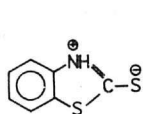
Table 2. Ultraviolet spectral data of compounds studied

Compound	λ_{max} nm	$\log \epsilon$ $\text{l mol}^{-1} \text{cm}^{-1}$	λ_{max} nm	$\log \epsilon$ $\text{l mol}^{-1} \text{cm}^{-1}$	λ_{max} nm	$\log \epsilon$ $\text{l mol}^{-1} \text{cm}^{-1}$	Solvent
I	205	4.22	232	4.15	327	4.45	Methanol
	229	4.28	241	4.20	328	4.40	Dioxan
	204	4.30	229	4.14	323	4.39	Water
II	216	3.90	258	3.77	300	4.26	Methanol
	217	4.33	260	4.35	307	4.73	Dioxan
III	219	4.18	246	4.15	305	4.45	Methanol
	222	4.34	253	4.20	312	4.60	Dioxan
IV	228	4.01	243	3.96	325	4.27	Methanol
	230	4.12	246	4.07	330	4.38	Dioxan
V	229	4.18	240	4.13	324	4.37	Methanol
	204		234		320		Water
	198		231 ^a		322		<i>n</i> -Hexane
VI	205	4.30	231 ^b	4.18	321	4.41	Water
	223		241		298 ^c		Methanol
VII	199	4.26	235	3.94	280	4.11	Water
	228	4.27	245	3.90	289 ^d	4.08	Dioxan
VIII	224	4.49	253	3.86	330 ^e	4.38	Dioxan

Additional bands, λ_{max} ($\log \epsilon$): a) 247, b) 257 (3.82), c) 278 and 289, d) 298 (4.00), e) 341 (4.44).

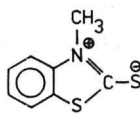
p-chlorothiophenol can be explained by hydrogen bonding of the S—H group with the nitrogen of the amino group.

In the ultraviolet spectra of compounds I, V, and VII (Table 2) three main absorption bands with shoulders and inflexes are observed. Intense long-wavelength bands can be assigned to intramolecular charge-transfer transition [11]



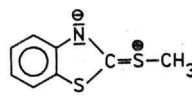
I

λ_{max} 323 nm
(H_2O)



V

320 nm



VII

298 nm

In their spectra, recorded for methanolic, ethanolic, and aqueous solutions, a hypsochromic shift of the longest-wavelength band is observed, which can be explained by the cleavage of the N—H...S=C hydrogen bond and the formation of the C=S...H—OR new hydrogen bond. On the other hand a bathochromic shift of the longest-wavelength band has been observed (λ_{\max} 230—276 nm) in their spectra, measured for proton-acceptor solvents (dioxan, acetone). Owing to the longer conjugated system, benzoheterocycles investigated absorb at longer wavelengths than do starting amines.

	<i>o</i> -Aminothiophenol	<i>o</i> -Aminophenol	<i>o</i> -Phenylenediamine
λ_{\max} (log ϵ)	219 (4.68)	215 (4.03)	216 (4.62)
	242 (4.39)	242 (3.96)	244 (4.01)
	303 (3.87)	292 (3.62)	298 (3.77)

In the u.v. spectra of bis(isothiocyanatophenyl)disulfides two absorption maxima are observed in the 223—288 nm region.

	λ_{\max} (log ϵ)	ν_s (NCS)	ν_{as} (NCS)
Bis(<i>p</i> -isothiocyanatophenyl)- disulfide	216 (4.64)	934	2116
	288 (4.58)		2189
Bis(<i>o</i> -isothiocyanatophenyl)- disulfide	232 (4.67)	942	2063
	273 (4.34)		2178

In the case of *o*-derivative, λ_{\max} of the band is observed at shorter wavelength as compared with that of *p*-derivative, which, owing to the steric hindrance, is due to the lesser conjugation of the π -electron system of aromatic rings with the NCS groups through disulfidic bonds. Infrared spectra of isothiocyanates studied show characteristic bands ν_s (NCS) and ν_{as} (NCS).

In infrared spectra of compounds I—IV the ν (SH) bands, which are relatively weak, are observed in the range 2575—2690 cm^{-1} .

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