

Isothiocyanates and Their Synthetic Producers. XI.
Study of Infrared and Ultraviolet Spectra of 3-Substituted
2-Thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines and N-Substituted
O-(2-Methoxycarbonylphenyl)monothiourethanes

M. NOVOTNÁ, P. KRISTIAN, and J. BERNÁT

*Department of Organic Chemistry, Faculty of Natural Sciences,
P. J. Šafárik University, Košice*

Received March 9, 1971

Accepted for publication July 7, 1971

Infrared and ultraviolet spectra of ten 3-substituted 2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines and of fifteen N-substituted O-(2-methoxycarbonylphenyl)monothiourethanes as their direct intermediates are described. The obtained results make possible to distinguish simply the studied compounds from each other qualitatively. For the NCS group of monothiourethanes, two intensive absorption bands in the region ~ 1530 and $\sim 1380\text{ cm}^{-1}$ are typical. With the benzoxazine derivatives the first band is absent. In contrast to monothiourethanes, the benzoxazine derivatives are characterized in the u.v. region by two absorption bands at ~ 275 and $\sim 300\text{ nm}$. The nature and the position of absorption bands of the studied compounds in dependence on their structures are discussed in this work.

So far, no data have been published on i.r. and u.v. spectra of 2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines. In our previous works [1, 2] we dealt with the synthesis of the mentioned derivatives as new types of synthetic producers of isothiocyanates and worked out a method for their preparation. The appropriate N-aryl substituted O-(2-methoxycarbonylphenyl)monothiourethanes served as direct intermediates of benzoxazine derivatives. Results of the study on i.r. and u.v. spectra of monothiourethanes are discussed also in our previous work [3]. From the point of the structural study and properties of synthetic producers of isothiocyanates, the recognition of spectral properties of NCS group (typical for these compounds) is very important.

Infrared spectra of the compounds with thiocarbonyl groups bound to nitrogen were studied by Rao [4, 5] who did not achieve unambiguous results. The absorption of the mentioned groups was strongly dependent on the whole type of compound.

Besides the overall study of spectral properties of the mentioned compounds, in the present work we focused our attention mainly on the localization of absorption bands belonging to NCS group of 3-substituted 2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines and pointed out the possible differences between them and monothiourethanes.

The u.v. spectra were taken to learn more about the structure of the studied compounds and to obtain further physicochemical data for the investigation of relations between their structure and biological activity.

Table 1

Spectral data of *N*-R-*O*-(2-methoxycarbonylphenyl)monothiourethanes

No.	R	B.p. [°C]	$\tilde{\nu}(\text{NH})$	$\tilde{\nu}(\text{C}=\text{O})$	$\tilde{\nu}(\text{C}-\text{O}-\text{C})$ \parallel O	$\tilde{\nu}(\text{C}-\text{O}-\text{C})$	$\tilde{\nu}(\text{NH}-\text{C}=\text{S})$ <i>a</i>	$\tilde{\nu}(\text{NH}-\text{C}=\text{S})$ <i>b</i>	$\tilde{\nu}(\text{NH}-\text{C}=\text{S})$ <i>c</i>	λ_{max} log ϵ	λ_{max} log ϵ
I	phenyl-	112-114	3420 3398	1725	1303	1165	1530	1385 1365	932	282 4.30	—
II	4-tolyl-	141-143	3420 3398	1726	1302	1160	1530	1380 1368 sh	932	283 4.25	—
III	4-methoxy- phenyl-	114-115	3423 3399	1732	1306	1162	1530	1388 1372 sh	938	285 4.27	—
IV	4-dimethyl- aminophenyl-	110-111	3423 3398	1730	1305	1160	1536	1385 sh 1358	953	300 4.25	—
V	4-diphenyl-	139-141	3420 3395	1729	1305	1166	1532	1388 1370 sh	939	300 4.48	—
VI	4-bromophenyl-	145-147	3415 3399	1724	1302	1164	1520	1379 1358 sh	931	288 4.33	—
VII	4-methoxycar- bonylphenyl-	148-149	3420 3395	1731	1290	1170	1536	1378	938	302 4.33	—
VIII	4-nitrophenyl-	138-139	3420 3392	1735	1308	1172	1548	1378	936	329 4.15	—
IX	1-naphthyl-	119-120	3415 3390	1729	1306	1168	1520 sh	1385 1352	925	297 4.04	325 3.79
X	2-naphthyl-	106-108	3420 3398	1725	1302	1162	1539	1390 1355	938	274 4.49	302 4.30
XI	butyl-	90-92	3415	1732	1308	1167	1545	1420 1412 sh	—	248 4.04	—
XII	octyl-	63-65	3410	1728	1300	1168	1536	1415	—	247 4.10	—
XIII	cyclohexyl-	132-133	3402	1726	1301	1161	1522	1390 sh 1412	—	250 4.11	—
XIV	benzyl-	80-82	3410	1727	1302	1142	1528	1408 1390 sh	—	250 4.11	—
XV	furylmethyl-	68-70	3415	1729	1304	1150	1528	1410 1385 sh	—	250 4.28	—

sh — shoulder; $\tilde{\nu}$ [cm⁻¹]; λ_{max} [nm]; log ϵ (l mol⁻¹ cm⁻¹).

Table 2

Spectral data of 3-R-2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines

No.	R	B.p. [°C]	$\tilde{\nu}(\text{C}=\text{O})$	$\tilde{\nu}(\text{C}-\text{O}-\text{C})$	$\tilde{\nu}(\text{N}-\text{C}=\text{S})$ $_b$	λ_{max} $\log \epsilon$	λ_{max} $\log \epsilon$
XVI	phenyl-	218—219	1724	1184	1300	276 4.35	300 3.75
XVII	tolyl-	247—248	1720	1172	1300	276 4.36	300 3.77
XVIII	4-methoxyphenyl-	204—205	1730	1172	1306	275 4.21	300 3.62
XIX	4-dimethylaminophenyl-	283—284	1730	1160	1307	267 4.61	300 4.01
XX	4-diphenyl-yl-	256—257	1731	1185	1302	270 4.59	302 3.88
XXI	4-bromophenyl-	263—264	1724	1182	1300	275 4.40	300 3.81
XXII	4-methoxycarbonylphenyl-	247—248	1731	1188	1305	275 4.37	303 3.78
XXIII	4-nitrophenyl-	279—280	1738	1190	1295	274 4.41	303 4.02
XXIV	1-naphthyl-	240—241	1729	1171	1306	275 4.50	297 4.13
XXV	2-naphthyl-	254—255	1725	1164	1300	275 4.48	304 3.88

 $\tilde{\nu}$ [cm⁻¹]; λ_{max} [nm]; $\log \epsilon$ [l mol⁻¹ cm⁻¹].

Experimental

The preparation of the studied 3-substituted 2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines and of the appropriate monothiourethanes is described in our previous work [2].

Infrared spectra were taken with a double-beam UR-20 (Zeiss, Jena) spectrophotometer in the $700\text{--}3600\text{ cm}^{-1}$ range. The spectra were measured in NaCl cells of 0.17 mm thickness, concentration in chloroform was 0.05 M. Chloroform anal. grade was percolated through the column of silica gel to remove moisture and ethanol. Polystyrene foil was used for calibration of wave number.

Ultraviolet spectra were taken on a Perkin—Elmer 402 recording spectrophotometer using 10-mm cells. Concentrations of compounds in dioxan (Uvasol Merck Darmstadt) were $3\text{--}8 \times 10^{-5}$ M.

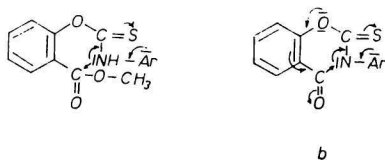
The characteristic data on i.r. spectra of *N*-substituted *O*-(2-methoxycarbonylphenyl)-monothiourethanes and 3-substituted 2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines are in Tables 1 and 2.

Discussion

Monothiourethanes (*I—XV*) showed an intensive absorption band of N—H vibration in the region $\sim 3400\text{ cm}^{-1}$. In the case of *N*-aryl substituents, this band showed a clear splitting (derivatives *I—X*) while with *N*-alkyl derivatives (*XI—XV*), the splitting was not observed. This finding is in agreement with the results of our previous work on monothiourethanes [3] and can help quickly determine the nature of the substituent on the nitrogen atom qualitatively.

Wave numbers of carbonyl groups of *O*-(2-methoxycarbonylphenyl)monothiourethanes were effected only insignificantly by the *N*-substituent. We supposed that the carbonyl group (4-oxo) of *N*-aryl substituted 2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazines would be in conjugation with the 3-aryl substituted nitrogen. However, it followed from the positions of absorption bands of carbonyl groups that the lone-pair electron on the nitrogen atom of the studied benzoxazines was in mesomeric interaction with the thio-carbonyl group of benzoxazine skeleton. This was also proved by comparison of the wave numbers of bands belonging to these carbonyl groups with those of carbonyl groups of monothiourethanes under investigation, in which case no differences were observed (Tables 1 and 2, derivatives *I—X* and *XVI—XXV*).

Contrary to unsubstituted *N*-phenyl derivative (*I*), all substituents on nitrogen atom shifted the absorption bands of carbonyl groups to higher wave numbers. We assume that in the case of *O*-(2-methoxycarbonylphenyl)monothiourethanes it was a spatial electrostatic interaction of nitrogen electrons with the carbon atom of carbonyl group (Scheme 1a), while in the case of the cyclic products (*XVI—XXV*), an inductive effect



Scheme 1

of nitrogen atom (Scheme 1b) was involved. The magnitude of both these effects will depend on the electron density on nitrogen which could be compensated by amido-imido tautomerism in the case of electron donor substituents (monothiourethanes), or by mesomeric interaction with *N*-aryl substituent and thione group of benzoxazines, respectively. Thus for instance the shift of $\tilde{\nu}(\text{C}=\text{O})$ of *N*-(4-dimethylaminophenyl) derivatives of both types of compounds (*III* and *XVIII*) regarding the basic derivatives *I* and *XVI* was 6 cm^{-1} and that of *N*-(4-methoxycarbonylphenyl) derivatives (*VII* and *XXII*) 7 cm^{-1} .

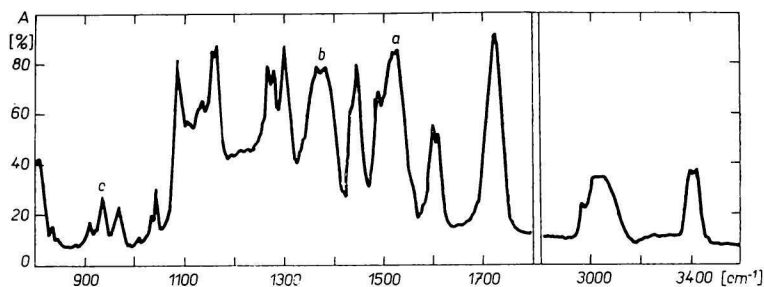


Fig. 1. Infrared spectrum of *N*-phenyl-*O*-(2-methoxycarbonylphenyl)monothiourethane *I* recorded in NaCl cells of 0.17 mm thickness; concentration 0.05 M in chloroform.

The studied monothiourethanes were characterized by two significant bands of ether and ester vibrations of C—O bonds ($\tilde{\nu}(\text{C}—\text{O}) \sim 1300$ and $\sim 1160\text{ cm}^{-1}$, respectively). The absorption band belonging to ester group of benzoxazine derivatives disappeared due to cyclization while the wave numbers of ether C—O bonds regarding the appropriate wave numbers of bonds in monothiourethanes were shifted by $\Delta\tilde{\nu}(\text{C}—\text{O}) \sim 15\text{ cm}^{-1}$. The wave numbers of ether C—O bonds of both types of compounds with electron acceptor substituents on nitrogen were shifted to higher values. This shift was especially significant with benzoxazines; the difference between *N*-(4-dimethylaminophenyl) derivative (*XIX* and *N*-(4-nitrophenyl) derivative (*XXIII*) was 30 cm^{-1} , while with monothiourethane (*V*, *IX*) only 12 cm^{-1} .

The mentioned effects are in agreement with the structure of the derivatives under

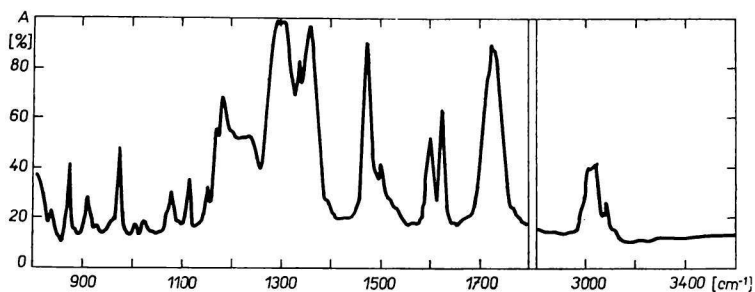


Fig. 2. Infrared spectrum of 3-phenyl-2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazine *XVI* recorded in NaCl cells of 0.17 mm thickness; concentration 0.05 M in chloroform.

investigation and point to higher electron acceptor effect of carbonyl group of the cyclic product.

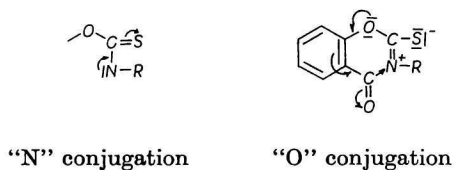
For monothiourethanes (*I*–*XV*) with $-\text{NH}-\text{C}=\text{S}$ group, mainly two absorption bands were typical; a significant absorption band of high intensity at $\sim 1530\text{ cm}^{-1}$, and in the case of *N*-aryl derivatives a further absorption band at $\sim 1380\text{ cm}^{-1}$ (Fig. 1). With the *N*-alkyl substituted compounds (*XI*–*XV*), this band was shifted to higher wave numbers ($\sim 1415\text{ cm}^{-1}$). In both cases it showed a splitting and a shoulder, respectively, and was considerably wide. The third absorption band of $-\text{NH}-\text{C}=\text{S}$ group was insignificant, untypical and appeared only with aromatic *N*-substituent containing derivatives in the $\sim 930\text{ cm}^{-1}$ range.

It is interesting that the benzoxazine derivatives (*XVI*–*XXV*) with the nitrogen inserted into the skeleton (does not bind hydrogen) did not show the typical absorption band of NCS group at $\sim 1530\text{ cm}^{-1}$ which could distinguish these derivatives from monothiourethanes.

The second absorption band of $>\text{N}-\text{C}=\text{S}$ group of benzoxazines was shifted to lower wave numbers in comparison with monothiourethanes (*I*–*XV*) and appeared as a wide, significant, and very intensive band at $\sim 1300\text{ cm}^{-1}$ without splitting (Fig. 2).

The position of the third absorption band of $>\text{N}-\text{C}=\text{S}$ group could not be proved with certainty on the spectra of benzoxazines (*XVI*–*XXV*).

The aryl substituted monothiourethanes (*I*–*X*) showed a significant absorption band at $280\text{--}300\text{ nm}$ ($\log \epsilon \sim 4.30$) while this absorption band with the *N*-alkyl derivatives (*XI*–*XV*) was shifted to lower wave numbers ($\lambda_{\text{max}} \sim 250\text{ nm}$, $\log \epsilon \sim 4.10$). This absorption is a result of $\pi \rightarrow \pi^*$ transition state conjugated with the electron transfer in consequence of $p-\pi$ conjugation of the lone-pair electron of nitrogen with the double bond of thione group. In our previous work [3] it was proved that an “N” conjugation was involved (Scheme 2).



Scheme 2

The totally different character of the absorption bands of 1-naphthyl and 2-naphthyl derivatives (*IX*, *X*) (Fig. 3) is interesting. The character and the intensity of the spectrum of 1-naphthyl derivative (*IX*) differed basically from that of the 2-naphthyl derivative (*X*) which was similar to the spectra of monothiourethanes. It can be explained by the significant conjugation of π -electrons of condensed aromatic rings with the lone-pair electron of nitrogen of 1-naphthyl derivative (*IX*), whereupon the spectrum is more complex and typical for naphthalene compounds. On the other hand, the naphthalene residue is withdrawn from the so-called “N” conjugation in the case of 2-naphthyl derivative (*X*) and so the structure of this spectrum was like that of the typical spectra of the other monothiourethanes (Figs. 3 and 4).

The absorption bands of *N*-aryl derivatives (*I*–*X*) were found to be shifted bathochromically when compared with those of *N*-alkyl derivatives (*XI*–*XV*) due to conjugation of π -electrons of aromatic ring. This shift was most significant at aromatic

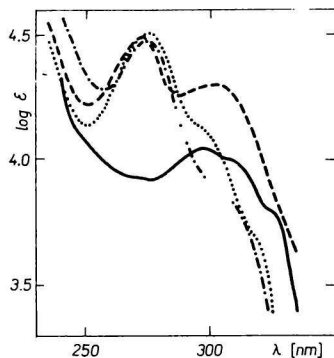


Fig. 3. Ultraviolet spectra.

- *N*-(1-naphthyl)-*O*-(2-methoxycarbonylphenyl)monothiourethane IX;
 --- *N*-(2-naphthyl)-*O*-(2-methoxycarbonylphenyl)monothiourethane X;
 -.-.- 3-(1-naphthyl)-2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazine XXIV;
 .-.-. 3-(2-naphthyl)-2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazine XXV.

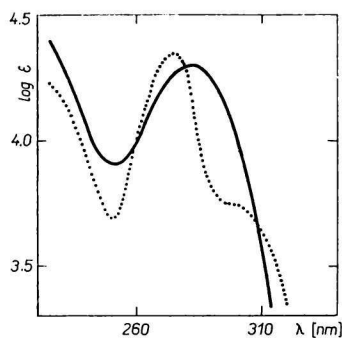


Fig. 4. Ultraviolet spectra.

- *N*-phenyl-*O*-(2-methoxycarbonylphenyl)monothiourethane I;
 3-phenyl-2-thioxo-4-oxo-3,4-dihydro-2H-1,3-benzoxazine XVI.

substituents with a strong +M effect. In the case of *N*-(4-nitrophenyl) derivative (VIII) we explain the particularly significant bathochromic shift by the strong electron acceptor NO₂ group which is capable to reverse the direction of conjugation of the lone-pair electron on nitrogen atom.

The ultraviolet absorption spectra of benzoxazine derivatives (XVI–XXV) were basically different from those of monothiourethanes (I–XV) (Figs. 3 and 4). As a consequence of cyclization, the electrons of nitrogen were partly withdrawn by carbonyl group and the so-called “N” conjugation showed a hypsochromic effect contrary to non-cyclized derivatives (e.g. derivative I λ_{\max} 282 nm, derivative XVI λ_{\max} 276 nm; Fig. 4). This shift however, was with all probability due to only a weak mesomeric interaction of electron pair on nitrogen with π -electrons of carbonyl group. On the other hand the amido group would be involved which should shift the wave numbers of stretching vibrations of carbonyl group to much lower values than the found ones ($\bar{\nu}(\text{C}=\text{O}) > 1710 \text{ cm}^{-1}$).

The absorption band at $\lambda_{\max} \sim 270 \text{ nm}$ was not very intensive and was not effected by substituents basically.

All the studied benzoxazine derivatives (XVI–XXV) showed another insignificant absorption band (rather a shoulder) at $\lambda_{\max} \sim 300 \text{ nm}$ of a lower intensity than that of the first band. We assume that this band belonged to the so-called “O” conjugation of carbonyl chromophore strengthened by –I effect of nitrogen atom. Due to that the mesomeric interaction of ether oxygen through aromatic ring with carbonyl group increased (Scheme 2).

This fact was proved also by the position of absorption bands belonging to stretching vibration of ether C—O bonds of benzoxazines (XVI—XXV) which were shifted to lower wave numbers in comparison with monothiourethanes (I—XV). Thus for instance, $\Delta\bar{\nu}(\text{C—O})$ with the *N*-phenyl derivatives (I, XVI) was 19 cm^{-1} .

Acknowledgements. We are grateful to Mrs V. Hain and Mr A. Dorčák for measuring the infrared and ultraviolet absorption spectra.

References

1. Bernát J., Kristian P., *Tetrahedron Lett.* **1971**, 1261.
2. Kristian P., Bernát J., Novotná M., *Collect. Czech. Chem. Commun.* **37**, 2972 (1972).
3. Bratovská A., Kristian P., *Chem. Zvesti* **23**, 736 (1969).
4. Rao C. N. R., Venkataraghavan R., *Spectrochim. Acta* **18**, 541 (1962).
5. Rao C. N. R., Venkataraghavan R., *Tetrahedron* (London) **18**, 531 (1962).

Translated by A. Kardošová