

# Benzothiazole compounds

## XXI. The C=O stretching frequencies and structure of 3-substituted 2-oxobenzothiazoles

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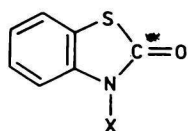
The C=O stretching frequencies in tetrachloromethane and chloroform and the structure of a series of thirty-five 3-substituted 2-oxobenzothiazoles were investigated. A good linear correlation has been found between the carbonyl stretching frequencies of 2-oxo group and Taft inductive  $\sigma^*$  constants of substituents in position 3. The mutual comparison of C=O stretching frequencies and results of the above correlation enables to determine or predict the conformation of several 3-substituted 2-oxobenzothiazoles.

Исследованы частоты валентных колебаний связи C=O в тетрахло-  
метане и хлороформе и структуры ряда тридцати пяти 3-замещенных  
2-оксобензотиазолов. Найдена хорошая линейная корреляция между час-  
тотами валентных колебаний карбонила 2-оксо группы и индукционными  
константами Тафта  $\sigma^*$  заместителей в положении 3. Взаимное сравнение  
частот валентных колебаний C=O и результатов проведенной кор-  
реляции позволяет определить или предсказать конформацию нескольких  
3-замещенных 2-оксобензотиазолов.

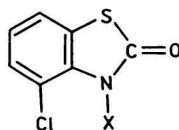
Our previous paper [1] dealt with the synthesis and investigation of infrared spectra (measured in solid state) of some 3-substituted 2-oxobenzothiazoles.

As the most of benzothiazole derivatives exhibit a significant biological activity, we decided to examine their structure more in detail, using infrared spectroscopy.

The present study concerns the C=O stretching frequencies of 3-X- and 3-X-4-chloro-2-oxobenzothiazoles I—XXXV as measured in dilute  $\text{CCl}_4$  and  $\text{CHCl}_3$  solutions; it is aimed to determine the conformation of the above-mentioned compounds.



I-XXXII



XXXIII-XXXV

A linear correlation between the carbonyl stretching frequencies and Taft inductive  $\sigma^*$  constants of substituents was also employed in this investigation.

### Experimental

The preparation, elemental analyses, physical properties, and biological activity of compounds I—XXXV will be described elsewhere [2].

The infrared spectra were taken on a Specord 75 IR spectrophotometer (Zeiss, Jena) in the 1800—1600  $\text{cm}^{-1}$  region. For compounds containing a hydroxyl group also the spectra in the range of 3700—3200  $\text{cm}^{-1}$  were recorded. The carbonyl stretching frequencies were measured at 25 °C in NaCl cells of 0.1, 1.0, and 10 mm thickness using  $\text{CCl}_4$  and  $\text{CHCl}_3$  as solvents. Concentrations of solutions were chosen to give maximal absorption between 70—75 %. The instrument calibration was verified using indene and atmospheric water vapour standard spectra. Peak positions were determined by averaging the results of three measurements and are believed to be accurate to  $\pm 0.5 \text{ cm}^{-1}$ . The hydroxyl stretching frequencies of some compounds were measured in  $\text{CCl}_4$  solutions in NaCl cells of 10 mm path length with an accuracy of  $\pm 2 \text{ cm}^{-1}$ .

### Results and discussion

The carbonyl stretching frequencies of compounds I—XXXV measured in tetrachloromethane are given in Table 1. To examine the origin of carbonyl vibrations also the C=O stretching frequencies of some compounds measured in chloroform are presented in Table 2.

3-Acyl-2-oxobenzothiazoles XVI—XVIII, XXXIII, and XXXIV exhibit two absorption bands in the region of C=O stretching vibrations. The lower frequency band belongs to the  $\nu(\text{C}=\text{O})$  of 2-oxo group in a five-membered heterocyclic ring and the higher frequency one was assigned to the  $\nu(\text{C}=\text{O})$  of 3-acyl group (i.e. of substituent X). The extraordinary high frequency of the last absorption band, similarly to other heterocyclic compounds [9], can be explained by a strong electron-withdrawing effect of 3-(2-oxobenzothiazolyl) residue having a tendency to acquire a more aromatic character. The position of this band is very sensitive to the effect of Cl substituent in position 4, as well as to the character of the acyl

Table 1

The C=O stretching frequencies (in  $\text{cm}^{-1}$ ) of 3-X- (I—XXXII) and 3-X-4-chloro-2-oxobenzothiazoles (XXXIII—XXXV) in  $\text{CCl}_4$  and Taft inductive  $\sigma^*$  constants of substituents X

Compound	X	$\nu(\text{C}=\text{O})^a$	$\sigma^*(\text{X})$	Ref.
I	$\text{CH}_3$	1692.5	0.00	[3]
II	$n\text{-C}_8\text{H}_{17}$	1690.5	-0.15	[3]
III	$\text{CH}_2(4\text{-NO}_2\text{C}_6\text{H}_4)$	1692.0	0.41	c
IV	$\text{CH}_2(3\text{-NO}_2\text{C}_6\text{H}_4)$	1692.0	0.39	c
V	$\text{CH}_2(3\text{-ClC}_6\text{H}_4)$	1691.0	0.31	c
VI	$\text{CH}_2(4\text{-BrC}_6\text{H}_4)$	1691.0	0.27	c
VII	$\text{CH}_2(4\text{-ClC}_6\text{H}_4)$	1691.0	0.33	c
VIII	$\text{CH}_2(4\text{-FC}_6\text{H}_4)$	1691.0	0.22	c
IX	$\text{CH}_2(4\text{-CNC}_6\text{H}_4)$	1692.0	0.38	c
X	$\text{CH}_2(3\text{-CH}_3\text{C}_6\text{H}_4)$	1692.0	0.20	[3]
XI	$\text{CH}_2\text{C}\equiv\text{CH}$	1698.0	0.76	[3]
XII	$\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	1694.0	0.17	c
XIII	$\text{CH}_2\text{COO}(\text{CH}_2)_2\text{Cl}$	1696.0, 1756.0 <sup>b</sup>	$\sim 0.72$	c
XIV	$\text{SO}_2\text{CH}_3$	1715.0	3.70	[7]
XV	$\text{SO}_2\text{C}_6\text{H}_5$	(1723.0)	3.28	[5]
XVI	$\text{COCH}_3$	(1700.0, 1733.5)	1.65	[5]
XVII	$\text{COC}_6\text{H}_5$	1708.0, 1742.5 <sup>b</sup>	2.20	[3]
XVIII	$\text{COCH}_2\text{Cl}$	1708.5, 1749.0 <sup>b</sup>	2.50	[3]
XIX	$\text{CONHCH}_3$	(1679.5) 1739.0 <sup>b</sup>	1.93	d
XX	$\text{CH}_2\text{Cl}$	(1710.5)	1.05	[5]
XXI	$(\text{CH}_2)_2\text{Cl}$	1693.0	0.38	c
XXII	$(\text{CH}_2)_2\text{CN}$	1693.5	0.47	c
XXIII	$\text{CH}_2\text{OH}$	1692.0 (1681.5)	0.49	[5]
XXIV	$\text{CH}_2\text{CH}_2\text{OH}$	1691.5 (1679.5, 1716.0)	0.21	[3]
XXV	$\text{CH}_2\text{CH}=\text{CH}_2$	1692.0	0.21	[5]
XXVI	$\text{CH}_2\text{OC}_6\text{H}_5$	1696.0	0.55	[5]
XXVII <sup>c</sup>	$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	1692.0	0.24	[3]
XXVIII	$\text{CH}_2\text{NHC}_6\text{H}_5$	1691.0 (1682.0)	0.05	d, e
XXIX	$\text{CH}_2\text{OCOOC}_6\text{H}_5$	(1708.8) 1751.0 <sup>b</sup> , 1768.5 <sup>b</sup>	$\sim 1.00$	d, e
XXX	$\text{CH}_2\text{OCOOC}_3\text{H}_7$	(1708.0) 1752.0 <sup>b</sup> , 1770.0 <sup>b</sup>	$\sim 1.00$	d, e
XXXI	$\text{CH}_2\text{OCOOC}(\text{CH}_3)_2$	(1708.5) 1751.0 <sup>b</sup> , 1770.0 <sup>b</sup>	$\sim 1.00$	d, e
XXXII	$\text{CH}_2\text{OCOO}(\text{CH}_2)_2\text{Cl}$	(1709.0) 1755.0 <sup>b</sup> , 1773.5 <sup>b</sup>	$\sim 1.00$	d, e
XXXIII	$\text{COCH}_3$	1716.0, 1775.0 <sup>b</sup>	—	—
XXXIV	$\text{COC}_6\text{H}_5$	1724.0, 1752.0 <sup>b</sup>	—	—
XXXV	$\text{CH}_2\text{CH}_2\text{OH}$	1692.0, 1680.5	—	—

a) Values in parentheses were not included into the  $\nu(\text{C}=\text{O})$  vs.  $\sigma^*(\text{X})$  correlation. b) Carbonyl stretching frequencies belonging to the substituent X. c) Calculated using the equation  $\sigma^*(\text{X}) \equiv \sigma^*(\text{CH}_2\text{Y}) = 0.36 \sigma^*(\text{Y})$  [4] and  $\sigma^*(\text{Y})$  values taken from [3, 5, 6]. d) Calculated using the equation  $\sigma^*(\text{X}) = 6.23 \sigma_1(\text{X})$  [8] and  $\sigma_1(\text{X})$  values taken from [3, 5, 6]. e) Instead of  $\sigma_1(\text{CH}_2\text{OCOOR})$   $\sigma_1(\text{CH}_2\text{OAc}) = 0.16$  value taken from [6] was employed.

Table 2

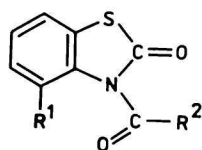
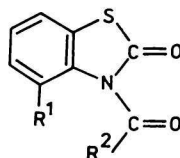
The C=O stretching frequencies (in  $\text{cm}^{-1}$ ) of some 3-X- and 3-X-4-chloro-2-oxobenzothiazoles in  $\text{CHCl}_3$

Compound	X	$\nu(\text{C}=\text{O})$
XIV	$\text{SO}_2\text{CH}_3$	1715.0
XV	$\text{SO}_2\text{C}_6\text{H}_5$	1707.0
XVI	$\text{COCH}_3$	1698.0, 1730.0
XVII	$\text{COC}_6\text{H}_5$	1699.0, 1742.5 <sup>a</sup>
XXXIII	$\text{COCH}_3$	1708.5, 1774.0 <sup>a</sup>
XXXIV	$\text{COC}_6\text{H}_5$	1698.0, 1753.0 <sup>a</sup>

a) Carbonyl stretching frequencies belonging to the substituent X.

group. On the other hand, the C=O stretching frequency of 2-oxo group is constantly raised by  $8\text{ cm}^{-1}$  in all compounds on passing the  $\text{COCH}_3$  to the  $\text{COC}_6\text{H}_5$  group.

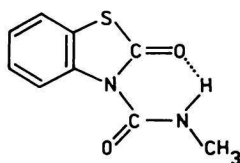
Generally, 3-acyl-2-oxobenzothiazoles can exist in two nearly planar conformations, *trans-cis* and *trans-trans* due to restricted rotation around the N—COR bond

*trans-cis* $\text{R}^1 = \text{H}, \text{Cl}$ *trans-trans* $\text{R}^2 = \text{CH}_3, \text{C}_6\text{H}_5, \text{CH}_2\text{Cl}$ 

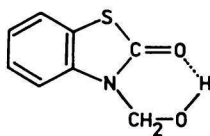
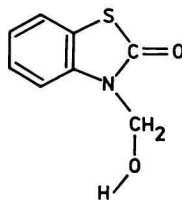
In compounds *XVII*, *XVIII*, *XXXIII*, and *XXXIV* the higher frequency carbonyl band is adequately affected by electronic effects of the moiety  $\text{R}^2$  attached to the exocyclic C=O group as well as by those of Cl substituent in position 4. The only exception is 3-acetyl-2-oxobenzothiazole *XVI*, which exhibits an anomalously low absorption of  $\text{COCH}_3$  group ( $1733.5\text{ cm}^{-1}$ ) with regard to the  $\text{COC}_6\text{H}_5$  group of the corresponding 3-benzoyl derivative *XVII* ( $1742.5\text{ cm}^{-1}$ ). On the basis of above results it is possible to assign the structure of compounds *XVII*, *XVIII*, *XXXIII*, and *XXXIV* to the *trans-cis* conformation and that of the compound *XVI* to the *trans-trans* conformation. Similarly as in the case of *trans-trans* acyclic imides of dicarboxylic acids [10], also in 3-acetyl-2-oxobenzothiazole *XVI* a vibrational coupling takes place between the C=O groups, which causes a significant change

in the region of carbonyl stretching frequencies. Passing from  $\text{CCl}_4$  to  $\text{CHCl}_3$ , a clear difference can be observed between the  $\nu(\text{C}=\text{O})$  values of compounds *XVII*, *XXXIII*, *XXXIV*, and that of *XVI*. The vibrationally coupled carbonyl stretching frequencies of *XVI* exhibit only a small solvent effect ( $\Delta\nu = 2.0 \text{ cm}^{-1}$ ) with regard to those of compounds *XVII*, *XXXIII*, and *XXXIV* ( $\Delta\nu = 9.0\text{--}26.0 \text{ cm}^{-1}$ ). Thus, the higher frequency band of compound *XVI* can be attributed to the in-phase and that of lower frequency to the out-of-phase vibration of coupled  $\text{CO}\text{--}\text{N}\text{--}\text{CO}$  system. It is evident from the above results that the existence of *trans-cis* or *trans-trans* conformation of 3-acyl-2-oxobenzothiazoles is determined mainly by steric interaction between the groups  $\text{R}^1$  and  $\text{R}^2$ . 3-Acetyl-2-oxobenzothiazole ( $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{CH}_3$ ) is practically lacking such an interaction, and consequently, the *trans-cis* conformation is preferred. In the remaining 3-acyl derivatives, where  $\text{R}^1 = \text{Cl}$  or  $\text{R}^2$  is bulkier than the methyl group, the *trans-trans* conformation will be favoured.

Compound *XIX* displayed an anomalously low frequency absorption band of 3-oxo group at  $1679.5 \text{ cm}^{-1}$ , practically independent of concentration. This can be explained by a strong intramolecular hydrogen bonding between the  $\text{NH}$  and  $\text{C}=\text{O}$  groups forming a six-membered ring of structure *XIXa*.

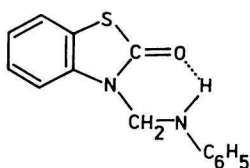
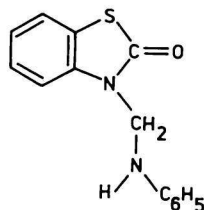
*XIXa*

In the case of 3-hydroxymethyl-2-oxobenzothiazole *XXIII* two absorption bands are observable in the region of carbonyl stretching vibrations. The lower frequency band at  $1681.5 \text{ cm}^{-1}$  can be assigned to the intramolecularly hydrogen-bonded 2-oxo group in structure *XXIIIa* and the higher frequency one at  $1692.0 \text{ cm}^{-1}$  probably belongs to the  $\text{C}=\text{O}$  stretching vibration of the free 2-oxo group in conformation *XXIIIb*.

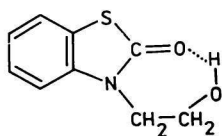
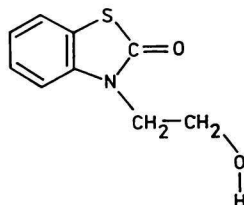
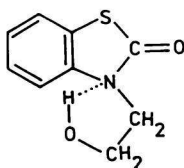
*XXIIIa**XXIIIb*

Similarly, two absorption bands in the region of hydroxyl stretching vibrations observed at  $3588\text{ cm}^{-1}$  and  $3604\text{ cm}^{-1}$  were ascribable to bonded and free OH groups, respectively.

An analogical structure can be suggested for 3-(phenylamino)methyl-2-oxo-benzothiazole *XXVIII*, in which the absorption of bonded 2-oxo group occurs at  $1682.0\text{ cm}^{-1}$  (*XXVIIIa*) and that of the free one at  $1691.0\text{ cm}^{-1}$  (*XXVIIIb*)

*XXVIIIa**XXVIIIb*

A little more complicated is the carbonyl stretching absorption of 3-(2-hydroxyethyl) derivative *XXIV*. The three well resolved bands at  $1679.5$ ,  $1691.5$ , and  $1716\text{ cm}^{-1}$  can be attributed to the  $\nu(\text{C}=\text{O})$  of 2-oxo group in structures *XXIVa*—*XXIVc*, respectively

*XXIVa**XXIVb**XXIVc*

The bands occurring at  $3584$ ,  $3630$ , and  $3395\text{ cm}^{-1}$  belong to the stretching vibration of OH groups in the structures *XXIVa*—*XXIVc*, respectively.

The carbonyl stretching frequency decrease in *XXIVa* is caused by participation of 2-oxo group in the intramolecular hydrogen bonding, while the increase of that frequency in *XXIVc* can be accounted for a weakened electron-donating effect of nitrogen atom interacting with the OH group.

Since the structure of 3-(2-hydroxyethyl)-4-chloro-2-oxobenzothiazole (XXXV) analogical to XXIVc is sterically hindered by the bulky Cl atom in position 4, the higher frequency band is missing in the spectra.

The C=O stretching frequencies of twenty-four 3-X-2-oxobenzothiazoles (measured in  $\text{CCl}_4$ ) correlate reasonably good with Taft inductive  $\sigma^*$  constants of substituents X

$$\nu(\text{C}=\text{O}) = 7.02 (\pm 0.31) \sigma^*(\text{X}) + 1690.3 (\pm 1.0) \quad (1)$$

$$r = 0.979 \quad s = 1.3$$

where  $r$  is the correlation coefficient and  $s$  the standard deviation. The straight line of this correlation is illustrated in Fig. 1. The compounds and carbonyl stretching frequencies included into the correlation are evident from Table 1.

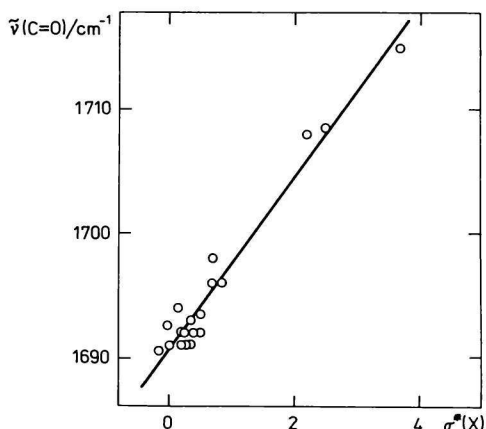


Fig. 1. The plot of  $\nu(\text{C}=\text{O})$  against  $\sigma^*(\text{X})$  for 3-X-2-oxobenzothiazoles.

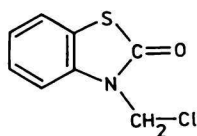
As the  $\sigma^*(\text{SO}_2\text{C}_6\text{H}_5)$  value discussed in [5] seemed to be rather uncertain, the compound XV has been excluded from the correlation.

The  $\nu(\text{C}=\text{O})$  values of compound XVI were also not employed in the correlation, because they originated from vibrational coupling of the CO—NH—CO system, as mentioned above.

The carbonyl stretching frequency of compound XIX does not fit eqn (1) due to the intramolecular hydrogen bonding (XIXa). On the other hand, the  $\nu(\text{C}=\text{O})$  values of the free 2-oxo group of compounds XXIII, XXIV, and XXVIII fit reasonably well the  $\nu(\text{C}=\text{O})$  vs.  $\sigma^*(\text{X})$  correlation.

A further exception from the linear trend of the above correlation is 3-chloromethyl-2-oxobenzothiazole XX, displaying an anomalously high  $\nu(\text{C}=\text{O})$  value. This phenomenon can be rationalized probably by more favourable steric conditions for the existence of conformation XXa, in which the frequency

of the C=O group is increased by a dipolar interaction between the C=O and Cl groups located in a close mutual proximity.



XXa

On the other hand, 3-(2-chloroethyl)-2-oxobenzothiazole XXI obeyed well eqn (1), and therefore we can suppose a conformation with the Cl atom to be far enough from the proximity of the C=O group.

Last exceptions, not included into the  $\nu(\text{C}=\text{O})$  vs.  $\sigma^*(\text{X})$  correlation, are 2-oxobenzothiazoles bearing substituents of the type  $\text{X} = \text{CH}_2\text{—O—CO—OR}$ , *i.e.* compounds XXIX—XXXII. The  $\nu(\text{C}=\text{O})$  values of these compounds are again anomalously high. This phenomenon is however not so easily explainable on account of a more complicated structure and shape of absorption in the region of 1800—1600  $\text{cm}^{-1}$ .

It can be concluded from the above results that the particular investigation of carbonyl stretching frequencies and deviations from the linearity of  $\nu(\text{C}=\text{O})$  vs.  $\sigma^*$  correlation enables to predict or determine the conformation of some 3-substituted 2-oxobenzothiazoles with a good deal of probability.

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