

Structural study of thiosaccharin by single crystal X-ray diffraction and infrared spectroscopy

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The structure of thiosaccharin (1,2-benzisothiazol-3(2H)-thione 1,1-dioxide) has been investigated by X-ray diffraction and infrared spectroscopic methods. The compound crystallizes in the orthorhombic space group *Fdd2* with $a = 26.591(3)$, $b = 25.058(3)$, $c = 4.934(5)$ Å, $Z = 16$. The structure consists of thiosaccharin molecules bonded to each other through $N-H \cdots O$ intermolecular hydrogen bonds. The infrared spectra of the thiosaccharin at room and liquid-nitrogen temperature were recorded. The spectral features in the $N-H$ stretching region were correlated with the crystallographic data on the geometry of the $N-H \cdots O$ hydrogen bonding. In an attempt to assign the bands due to the SO_2 stretching modes, the spectrum of thiosaccharin was compared with that of saccharin (1,2-benzisothiazole-3(2H)-one, 1,1-dioxide).

KEY WORDS: Thiosaccharin, infrared spectra, crystal structure polymorphs.

Introduction

In the course of our investigations of the structural characteristics of some cyclic imides and thioimides and their complexes with different metals, the thio analog of saccharin was prepared. Contrary to the numerous reports about structural characteristics of saccharin and its complexes with various metals¹⁻¹⁰ less seems to be known about the structural characteristics of thio-saccharin itself and related compounds.^{11,12}

Here we report the results of the single crystal X-ray study of thiosaccharin as well as the investigation of its infrared spectra in the region of $N-H$ and SO_2 stretching vibrations. Also we report the results of the correlation of the spectral characteristics with the crystallographically determined $N-H \cdots O$ and $O-S-O$ distances and angles.

Experimental

Preparation

Thiosaccharin was prepared by a modified general method for the thionation of organic compounds.¹³

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Namely, saccharin was dissolved in xylene and treated with several portions of P_2S_5 during 8 hr. Warm reaction mixture was filtered of waste products and cooled to room temperature yielding yellow transparent crystals. The single crystals were grown by recrystallization from ethanol.

Polymorphism in thiosaccharin

During recrystallization from ethanol two polymorphs were obtained and tentatively assigned as α - and β -thiosaccharin. The crystals of the α -modification were needle shaped while those of the β -phase were prismatic. Since, to the best of our knowledge, no evidence was found in the literature for the existence of more than one phase of thiosaccharin,¹⁴ we decided to characterize the two phases by analyzing their infrared spectra as well as their X-ray diffraction patterns.

The most noticeable differences between the infrared spectra of these two phases appear in the region of the bands originating from the $CSNHSO_2$ fragment of the thiosaccharin (see Fig. 1). This fact is probably related to the existence of different types of hydrogen bonds in the crystals of the two phases. The higher frequency of the band originating from the $N-H$ stretching vibrations in the α -phase (3340 cm^{-1}) compared

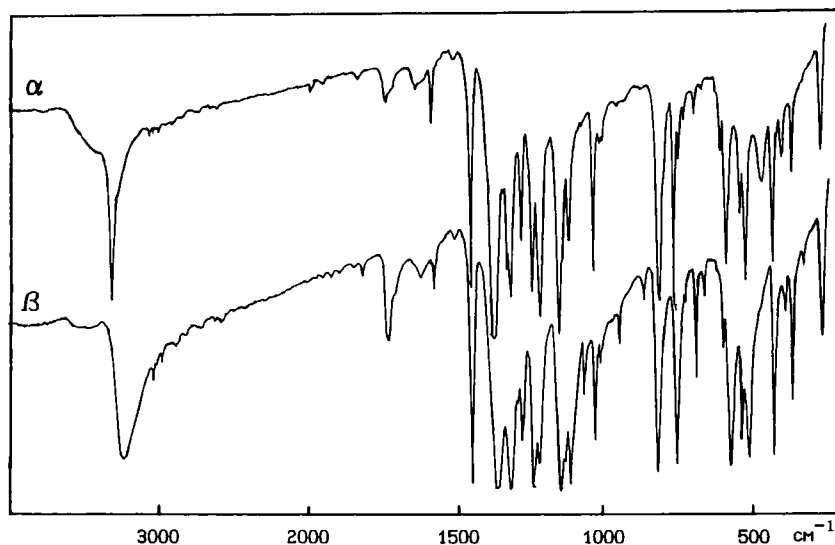


Fig. 1. The infrared spectra of α - and β -phase of thiosaccharin.

with the frequency of the analogous vibrations in the β -phase (3280 cm^{-1}) can be interpreted as an evidence of the existence of weaker intermolecular hydrogen bonds in the α -phase. This is not, however, in agreement with the stability of the phases. It was found, namely, that the β -phase is less stable and after a relatively short period transforms into the more stable α -phase (see Fig. 2).

The appearance of the X-ray diagrams of the two morphologically different types of crystals of thiosaccharin (see Fig. 3) confirms the conclusions made by

the infrared spectroscopy about the existence of polymorphism in thiosaccharin.

Since the crystals of the α -phase of thiosaccharin were of better quality and more stable, they were chosen for the determination of the crystal structure by X-ray diffraction.

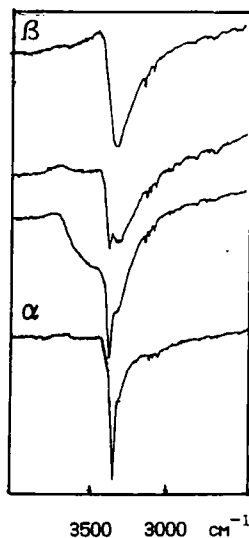


Fig. 2. The change of the $\nu(\text{N-H})$ band during the transition of the less stable β -phase of thiosaccharin into the more stable α -phase.

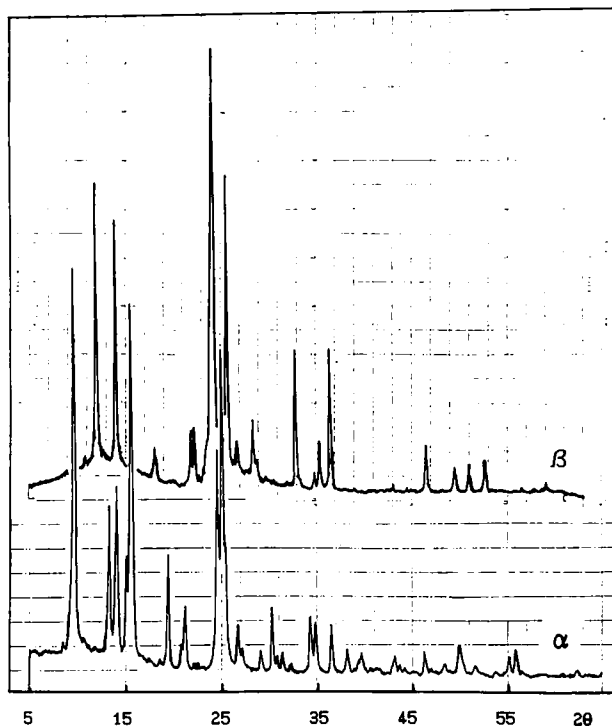


Fig. 3. The X-ray diagrams of α - and β -phase of thiosaccharin.

Data collection and processing

The infrared spectra were recorded at room and liquid nitrogen temperature (RT and LNT, respectively), on a Perkin-Elmer 580 infrared spectrophotometer using KBr pallets. For LNT infrared measurements a VLT-2 (RIIC) cell was used.

The data for the structure determination were collected on Philips PW 1100 automatic four-circle diffractometer, graphite monochromated $\text{CuK}\alpha$ radiation. Cell parameters were determined by the least-squares method of the setting angles (10 reflections in the range $12^\circ < \theta < 26^\circ$). Intensities of three standard reflections measured every 2 hr showed no evidence of crystal decay. Data were corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*.¹⁵ The structure was solved by direct methods¹⁶ and refined (on F) by full matrix least-squares. All H-atom positions were located from difference Fourier synthesis. The final least-squares refinement (including 109 variable parameters) assuming anisotropic thermal parameters for non-H-atoms and overall isotropic factors for all H-atoms gave the following discrepancy factors: $R = 0.036$, $R_w = 0.042$.

Results and discussion

Description of the structure

The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. Interatomic distances and angles are given in Table 3. A view of the structure showing the atom labeling scheme is presented in Fig. 4.¹⁷ Figure 5 shows the packing of the structural constituents in the unit cell.¹⁸

The structure consists of thiosaccharin molecules bonded to each other through the intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, the $\text{N} \cdots \text{O}$ distance being 2.999(4) Å. The $\text{N}-\text{H} \cdots \text{O}$ angle is $134.3(3)^\circ$. Interatomic distances and angles in the thiosaccharin molecule are in general close to the corresponding values found in the structure of saccharin,^{1,2} the differences being of the same order as those between the two sets of data for saccharin (see Table 2). It is apparently that the substitution of the O atom from the $\text{C}=\text{O}$ group in the saccharin molecule by the S atom in the analogous thiosaccharin molecule does not significantly affect the electron distribution in the five-membered ring of the title molecule.

The maximum deviation from the mean plane of the thiosaccharin molecule is 0.0500 Å for C5 atom,

Table 1. Crystal data, data collection, and refinement conditions

Formula	$\text{C}_7\text{H}_5\text{NO}_2\text{S}_2$
M_r	199.85
Crystal system	orthorhombic
Space group	$Fdd2$
$a/\text{Å}$	26.591(3)
$b/\text{Å}$	25.058(3)
$c/\text{Å}$	4.934(5)
$V/\text{Å}^3$	3287.6(3)
Z	16
$D_c/\text{g cm}^{-3}$	1.61
$\lambda (\text{CuK}\alpha)/\text{Å}$	1.5418
μ/cm^{-1}	54.5
$F(000)$	1642
Temperature/ $^\circ\text{C}$	20
Crystal dimensions/mm	$0.8 \times 0.14 \times 0.12$
Scan technique	$\omega - 2\theta$
2θ range/ $^\circ$	3 – 70
Scan speed/ $(^\circ\text{s}^{-1})$	0.04
Scan width/ $^\circ$	1.60
Number of standard reflections	3
Number of unique reflections	772
Number of reflections with $I < 2\sigma(I)$	744
Index range	$h = 0$ to 32 $k = 0$ to 28 $l = 0$ to 5
Number of parameters refined	109
$(\Delta/\sigma)_{\text{max}}$	0.17
Residual electron density (e Å^{-3})	
Max	0.19
Min	-0.29
w	$0.8375/[\sigma^2(F_o) + 0.002803 F_o^2]$
Final R	0.36
Final R_w	0.42

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters U_{eq} ($\text{Å}^2 \times 10^4$) for nonhydrogen atoms and U_{iso} ($\text{Å}^2 \times 10^3$) for H atoms

Atom	$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$			$U_{\text{eq}}/U_{\text{iso}}$
	x	y	z	
S1	8053(0.3)	4505(0.4)	1882(0)	404(3)
S2	9126(1)	5333(1)	-2525(4)	644(5)
O1	7802(1)	4785(1)	4016(9)	619(5)
O2	7777(1)	4102(1)	489(11)	649(14)
N	8289(1)	4943(1)	-311(10)	427(12)
C1	8651(1)	4281(2)	2830(11)	385(14)
C2	8755(2)	3894(2)	4744(13)	468(15)
C3	9258(2)	3764(2)	5132(14)	540(18)
C4	9627(2)	4015(2)	3608(16)	650(22)
C5	9515(2)	4401(2)	1686(16)	532(18)
C6	9012(1)	4541(2)	1338(12)	410(13)
C7	8808(1)	4944(2)	-533(12)	406(13)
H1	8001	5177	-1295	120(13)
H2	8402	3766	5613	120(13)
H3	9455	3487	6426	120(13)
H4	9971	3835	4323	120(13)
H5	9866	4527	786	120(13)

Table 3. Interatomic distances (Å) and angles (°) in thiosaccharin compared with the corresponding values in saccharin^{1,2}

	Thiosaccharin	Saccharin	
		(Okaya, 1969) ²	(Bart, 1968) ¹
S1—O1	1.431(4)	1.421(4)	1.427
S1—O2	1.425(4)	1.409(4)	1.428
S1—N	1.664(4)	1.663(4)	1.663
S1—C1	1.750(3)	1.758(4)	1.761
S2—C7	1.622(6)	—	—
O3—C7	—	1.214(5)	1.220
N—C7	1.384(4)	1.363(5)	1.375
N—H1	1.08	—	—
C1—C2	1.382(8)	1.380(6)	1.383
C1—C6	1.374(6)	1.363(5)	1.385
C2—C3	1.389(8)	1.389(7)	1.365
C2—H2	1.08	—	—
C3—C4	1.387(8)	1.384(7)	1.391
C3—H3	1.08	—	—
C4—C5	1.387(9)	1.394(7)	1.382
C4—H4	1.08	—	—
C5—C6	1.393(6)	1.392(6)	1.368
C5—H5	1.08	—	—
C6—C7	1.472(7)	1.474(6)	1.480
N—S1—C1	92.5(1)	92.2	92.7
O2—S1—C1	111.7(2)	111.9	112.8
O2—S1—N	110.4(2)	110.2	109.1
O1—S1—C1	112.6(2)	112.8	111.8
O1—S1—N	109.3(1)	109.0	110.3
O1—S1—O2	117.5(2)	117.7	117.4
S1—N—C7	115.4(3)	115.1	115.0
S1—C1—C6	109.8(3)	110.1	109.8
S1—C1—C2	126.1(3)	126.9	128.1
C2—C1—C6	124.0(4)	123.1	122.1
C1—C2—C3	116.8(5)	116.0	116.7
C2—C3—C4	120.0(5)	121.8	121.7
C3—C4—C5	122.5(5)	120.8	121.0
C4—C5—C6	117.8(5)	117.7	117.7
C1—C6—C5	119.0(5)	120.6	120.8
C5—C6—C7	127.1(4)	126.5	126.6
C1—C6—C7	113.8(3)	112.9	112.6
N—C7—C6	108.5(3)	109.6	109.8
S2—C7—C6	126.9(2)	—	—
S2—C7—N	124.7(4)	—	—
O3—C7—C6	—	126.5	126.5
N—C7—O3	—	123.9	123.7

while the angle between the best planes through the five- and six-membered rings within the molecule is 2.21°.

Infrared studies

The infrared spectra of thiosaccharin and saccharin are shown in Fig. 6. Although, as it was mentioned above, the corresponding bond lengths and angles in both compounds are very similar (Table 2), their in-

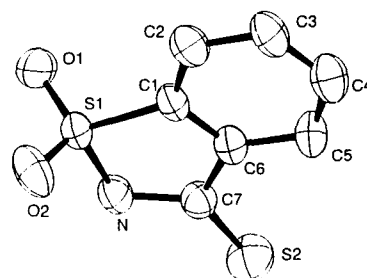


Fig. 4. A view of the title molecule showing the atom-numbering scheme.

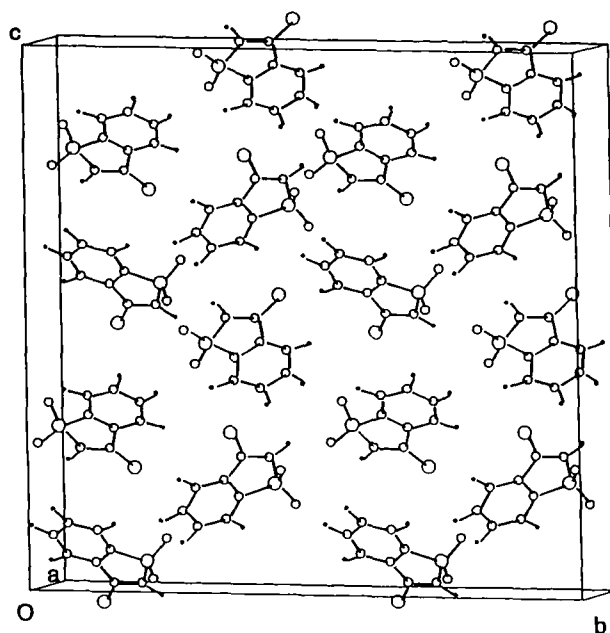


Fig. 5. Crystal structure viewed along the *c* axis.

frared spectra could be hardly compared. Besides the expected striking differences in the region of the CO (saccharin) and CS (thiosaccharin) stretchings, considerable differences are pronounced in the N—H and SO₂ stretching regions as well as almost in all other regions of the spectra.

N—H stretches. Contrary to the appearance of the wide complex band (with at least four submaxima) in the spectrum of saccharin (3100 to 2700 cm⁻¹), only one sharp and intense band at 3340 cm⁻¹ is present in the spectrum of thiosaccharin. The relatively high frequency (3340 cm⁻¹) of this band which is undoubtedly due to the N—H stretchings is in agreement with the existence of a rather weak (2.999 Å) hydrogen bond of the N—H···O type in the structure. The existence of the fairly bent (N—H···O angle is 134.3°) hydrogen

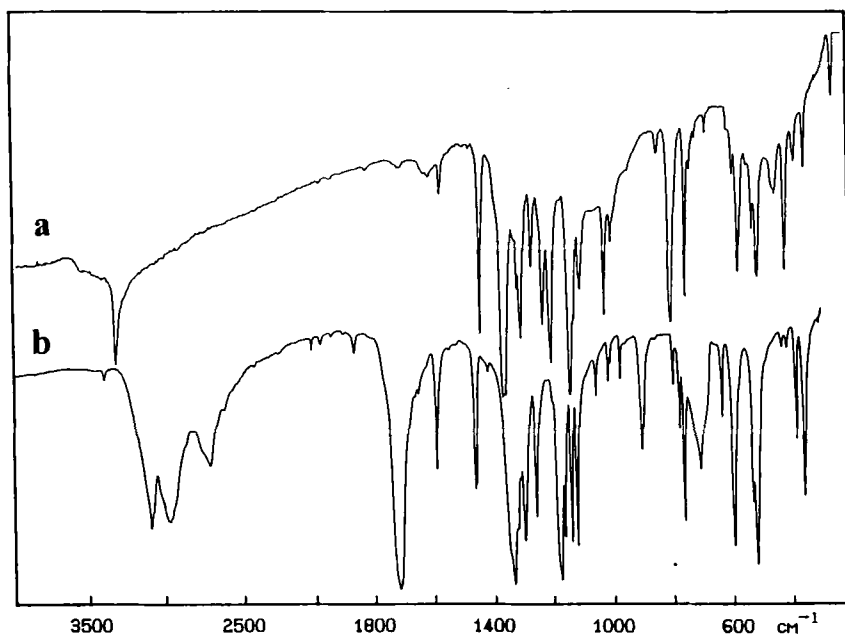


Fig. 6. The infrared spectra of thiosaccharin (a) and saccharin (b).

bond in the structure explains the unusual behavior of the band originating from the N—H stretching mode on lowering the temperature.¹⁹ The N—H stretching mode,

namely, shifts to higher frequencies when the temperature is lowered from RT (the uppermost curve in Fig. 7a) to LNT, which is opposite of what is considered as

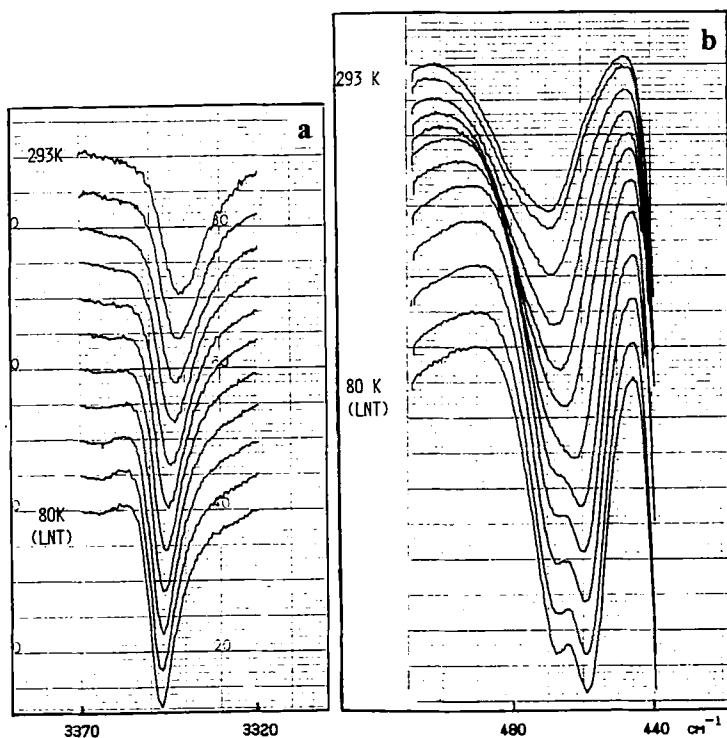


Fig. 7. The behavior of the $\nu(\text{N-H})$ (a) and $\gamma(\text{N-H})$ bands (b) by lowering of the temperature.

usual behavior.²⁰ Similar is the behavior of the $\gamma(\text{N-H})$ mode, which, instead to higher, shifts to lower frequencies by lowering the temperature (Fig. 7b).

SO₂ stretches. In the frequency region from 1500 to 1000 cm⁻¹ the bands originating from the CSNHSO₂ fragment of the thiosaccharin molecule are expected (e.g. the thioamide bands as well as the characteristic antisymmetric and symmetric SO₂ stretching modes). Since the thioamide modes appear as a result of various combinations between the $\nu(\text{CS})$, $\nu(\text{CN})$, and $\delta(\text{NH})$ modes and therefore are complex and rather complicated for interpretation we focused our attention on the assignment of the stretching SO₂ modes which are considered to be a rather good group vibrations.

The assignment of the SO₂ stretching bands, however, is not straight-forward. The number of strong bands in the corresponding region of the spectrum of thiosaccharin, namely, is considerably large since the bands due to modes with C=S stretching character appear in the same spectral region (see Fig. 6). The comparison with the spectrum of saccharin in the same spectral region, however, makes the assignment easier. The S—O distances and O—S—O angle in the presently investigated compound, namely, are very similar to the corresponding values in the structure of saccharin (see Table 2). Since the bands due to the $\nu(\text{C}=\text{S})$ modes in the spectrum of saccharin are absent, the assignment of the SO₂ stretching modes is relatively simple and possible solely on the bases of their intensities. As seen from Fig. 6, in the region of the SO₂ stretching vibrations of the spectrum of saccharin, only two bands (at 1335 and 1180 cm⁻¹) are strong enough to be assigned to such modes.

On the basis of such a comparison, namely, the bands appearing at 1320 and 1155 cm⁻¹ in the spectrum of thiosaccharin were attributed to the antisymmetric and to the symmetric SO₂ stretching vibrations, respectively.

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