

THE N-H, N-D AND C=S STRETCHING REGIONS IN THE INFRARED SPECTRUM OF THIOSACCHARIN : COMPARISON WITH THE SPECTRUM OF SACCHARIN

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The infrared spectra of the protiated and partially deuterated samples of 1,2-benzisothiazol-3(2H)-thione 1,1-dioxide (known as *thiosaccharin*) in the N-H, N-D and C=S stretching regions were studied. The spectral features were correlated with the structural data obtained by single crystal X-ray analysis.

1. INTRODUCTION

Continuing our studies [1-4] on the structural and spectral characteristics of some cyclic imides and thioimides and of their complexes with different metals we now report the results of the partial analysis of the infrared spectrum of thiosaccharin or, using its systematic name, 1,2-benzisothiazol-3(2H)-thione 1,1-dioxide.

Relatively little is known about either the spectra or the structure of thiosaccharin except for our own studies [1,4]. It was shown that two different polymorphic modifications (designated α and β) of thiosaccharin exist [1,4], the crystal structure of the more stable α modification was determined and the infrared spectra were partly analyzed [4].

In this paper we report the results of the analysis of the infrared spectra of protiated and partially deuterated samples of thiosaccharin in the N-H, N-D and C=S stretching regions as well as the comparison

with the spectrum of saccharin. Reported are also some results of the correlations of the spectral characteristics with the crystallographic data obtained by X-ray diffraction [4].

2. EXPERIMENTAL

The needle-shaped crystals of the stable modification (α thiosaccharin) were prepared by treating saccharin dissolved in xylene with portions of P_2S_5 [1,4]. Sometimes mixtures of the α and β modification were obtained during a given preparation.

The deuteration was carried out by dissolving thiosaccharin in dioxan and treating the solution with D_2O .

The infrared spectra were recorded (from KBr discs and CCl_4 solutions) on a Perkin Elmer 580 spectrophotometer. A VLT-2 variable-temperature cell (RIIC, London) cooled with liquid nitrogen was used for the low-temperature (LNT) measurements.

3. RESULTS AND DISCUSSION

3.1. N-H and N-D stretchings

The infrared spectrum of α -thiosaccharin in the 3500 - 2300 cm^{-1} region is shown in Fig. 1 (curve 1). Also given are the spectra (curves 2 and 3) of two samples of its partially deuterated analogue (prepared at two different occasions). The appearance of a sharp single bands in the N-H and N-D stretching regions (at 3340 and 2485 cm^{-1} , respectively), agrees well with the existence of only one type of N-H groups in the structure of α -thiosaccharin [4] and with the fact that these groups form weak hydrogen bonds, with $R(\text{N-H}\cdots\text{O}) = 299.9$ pm.

A closer look at curve 3, however, reveals the presence of two very weak (but real) bands on the low-frequency side of the band due to the N-D stretch and the corresponding side of the N-H band is broadened. These bands are due to the presence of small amounts of the less stable phase β .

It is interesting to compare the spectra of thiosaccharin with those of its oxo analogue - saccharin. As seen (cf. Fig. 2 a), the solid-state spectra of the two compounds are appreciably different, whereas the spectra recorded from CCl_4 solutions (Fig. 2 b) are almost identical.

The frequency difference between the sharp N-H stretching band in the spectrum of thiosaccharin and the centroid of the broad and complex feature in that of saccharin is easily understood if the considerable dissimilarity in the hydrogen bond strength is taken into account. In saccharin, namely, the $\text{N-H}\cdots\text{O}$ distance is around 279.5 pm (279,4 pm according to Bart [5] or 279.6 pm

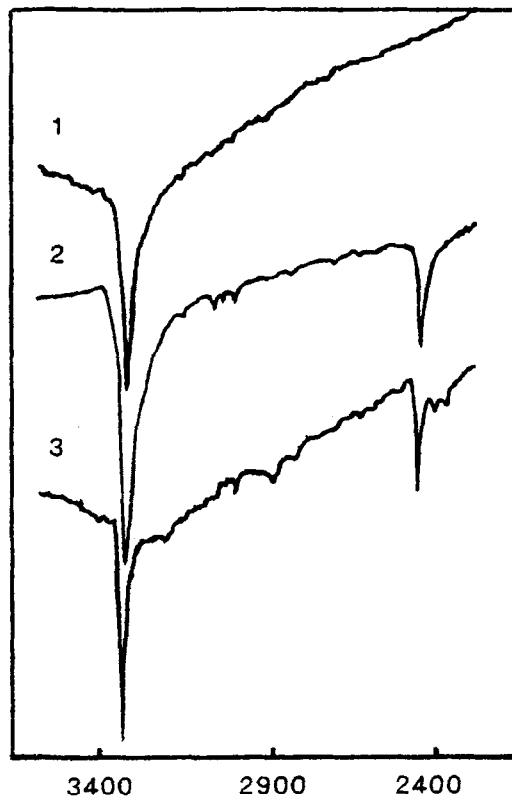


Fig. 1. The N-H and N-D stretching region in the spectra of thiosaccharin (1) and of two of its partially deuterated analogues (2 and 3)

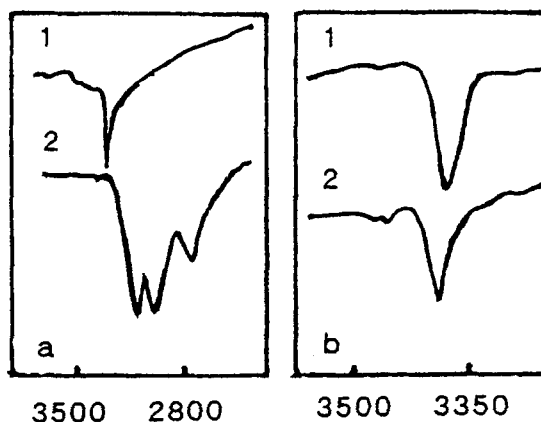


Fig. 2. The N-H stretching region in the spectra of thiosaccharin (1) and saccharin (2) in the solid state (a) and in a carbon tetrachloride solution (b)

according to Okaya [6]) as compared with 299.9 pm in thiosaccharin [4]. The substructure of the feature in the spectrum of saccharin has already been interpreted [7] as due to vibrational interactions of the fundamental N-H stretching vibration with second-order transitions.

More interesting is the frequency difference in the case of the spectra recorded from CCl_4 solutions (Fig. 2 b). Contrary to the solid-state case, here the frequency of the N-H stretch is for some 12 cm^{-1} lower in thiosaccharin than in saccharin. A tentative explanation for this fact can be given if the redistribution of the electronic density is taken (in qualitative terms) into account. The involvement of the N-H proton in strong hydrogen bonds (as are those in saccharin) is expected to lessen the electron density within the N-H bond and increase it in the neighbouring ones (N-C and N-S) so that these latter ones should be somewhat shorter than in thiosaccharin. The comparison of the structural data [4-6] shows that this is indeed so. The effects described above should disappear in solution and the distances and angles will take, so to say, their *normal* values. The lower N-H frequency in thiosaccharin implies a longer (and weaker) N-H bond, so that the values for the N-C and N-S distances are expected to be slightly lesser in "free" thiosaccharin than in its oxo analogue.

3.2. C=S stretchings

Although, as pointed out above, differences exist in the values for the interatomic distances and angles within the five-membered rings in the structures of thiosaccharin [4]

and saccharin [5,6], the differences are *small* (never exceeding 2 %) so that these rings are structurally quite similar.

This similarity could then be used in an attempt to assign the bands which, in the spectrum of thiosaccharin, are due to modes with C=S stretching character. It is well-known, namely, that the C=S stretch is not a good group vibration and the corresponding coordinate contri-

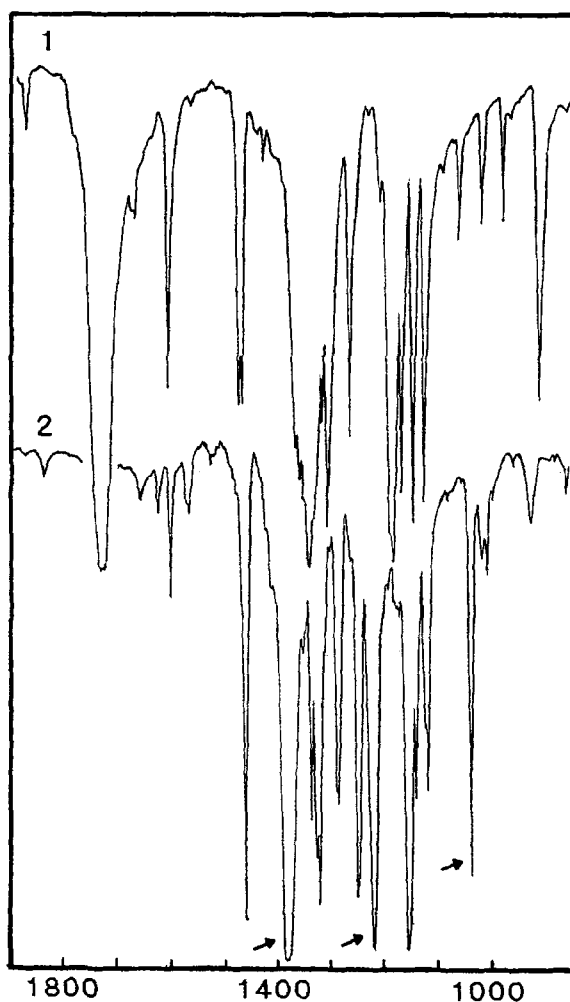


Fig. 3. The spectra of saccharin (1) and thiosaccharin (2) in the region of the C=S stretching frequencies

butes non-negligibly to a number of vibrations. Keeping this in mind, it is still reasonable to assume that the prominent bands which are present in the spectrum of thiosaccharin but absent in that of saccharin are a result of mixed modes with more or less pronounced C=S stretching character.

At least three such bands (appearing at ≈ 1380 , 1220 and 1040 cm^{-1}) can be detected and correspondingly assigned. They are marked by arrows in Fig. 3.

To be sure, differences between the spectra of thiosaccharin and saccharin exist in other spectral regions as well. This is an expected consequence of the different forms of all modes in the two cases. Still, we believe that the differences are more important for the modes with C=S stretching character than for those localized predominantly in the five-membered ring. Even less affected should be the modes which are best described as vibrations localized mainly in the aromatic six-membered ring.

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