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AMIDE AND THIOAMIDE BANDS OF BENZANILIDE AND THIOBENZANILIDE IN THE VIBRATIONAL SPECTRA

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ABSTRACT

It has been widely accepted that in secondary amides and secondary thioamides, in the spectral region between 1600 and 1200 cm^{-1} two characteristic bands could be recognized (Amide II and Amide III for amides and B and C bands for thioamides). Our spectra of benzanilide, $C_6H_5(C=O)NHC_6H_5$, and thiobenzanilide, $C_6H_5(C=S)NHC_6H_5$, show that in this region there are, at least, four prominent bands which shift on deuteration. That could indicate that all these bands are in connection with the vibrations of amide and/or thioamide groups. Some other amide and thioamide bands have been also discussed.

INTRODUCTION

The infrared spectra of amides and thioamides have been a subject of investigation of many authors (ref. 1-9). The assignements of the characteristic bands have been made, both empirically and by the use of normal coordinate calculations with various degree of sophistication.

The infrared spectrum of thiobenzanilide has been already reported and some assignments have been made (ref. 3,4). Our study (ref. 10) of the N-H stretching region in the infrared spectra of thiobenzanilide showed that thiobenzanilide crystallizes in four different modifications, which we designated as α, β, γ and δ phases. The structural differencies among these phases are related mainly to the differencies in the hydrogen bonding (ref. 10).

This paper is mainly concerned with infrared and Raman spectra of benzanilide and thiobenzanilide*,in the region below 1600 cm^{-1}. We examined this spectral region in hope that it might extend our

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*In this article,we will discuss only α phase, since similar behavior has been noticed in the spectra of the other thiobenzanilide polymorphs.

understanding of the nature of the characteristic amide and thioamide bands.

EXPERIMENTAL

Benzanilide was prepared from aniline and benzoylchloride and than by action of P_2S_5 converted to thiobenzanilide.

Benzanilide and thiobenzanilide were deuterated by dissolving them in dioxan, adding D_2O until precipitation occured and drying the separated crystals in vacuo.

The infrared spectra were recorded mainly as KBr discs on a Perkin-Elmer 580 IR Spectrophotometer and Raman spectra on a Jeol JRS-S1B Laser Raman Spectrophotometer. For recording the infrared spectra at liquid nitrogen temperature (LNT), the variable VLT-2 cell (RIIC) was used.

RESULTS AND DISCUSSIONS

In the infrared spectra of benzanilide and thiobenzanilide, it is expected that two bands should disappear in the region between 1600 and 1200 cm^{-1}, on deuteration. Instead of that, four prominent bands disappear. At the same time, in deuterated spectra of examined compounds, instead of one, two strong bands appear, in the region between 1500 and 1400 cm^{-1}(see Fig. 1 and 2).

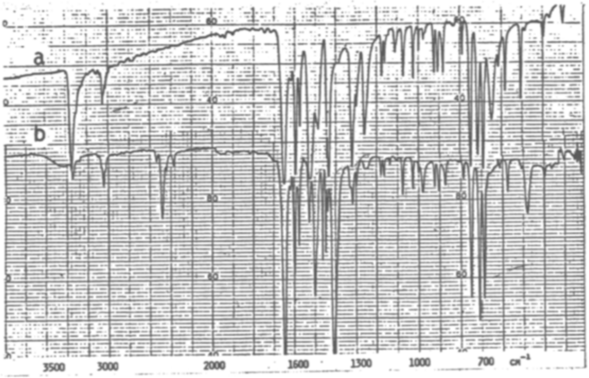

Fig. 1. Infrared spectrum of (a) protonated and (b) deuterated benzanilide

In the spectrum of D-benzanilide (see Fig. 1), in the lower frequency range, another band of medium intensity at 938 cm^{-1} can be seen, while in D- thiobenzanilide (see Fig. 2) there are three new bands in the same region.In the Raman spectra (see Fig. 3 and 4), the bands that occur in the region between 1600 and 1400 cm^{-1} are weak while the bands in the region between 1400 and 1200 cm^{-1} are quite strong, in both, benzanilide and thiobenzanilide.

A possible explanation for appearance of four appreciately strong bands in the range between 1600 and 1400 cm^{-1}, which shift on deuteration and have different intensities in the Raman and infrared spectra, may be that these bands are in connection with symmetrical and asymmetrical vibrational modes in which two non-equivalent C-N groups are involved. These modes probably couple strongly with δN-H mode giving rise to four bands. Thus, two strong bands which appear between 1500 and 1400 cm^{-1} in the spectra of deuterated compounds, may be due to the two stretching vibrations of the two nonequivalent C-N groups.

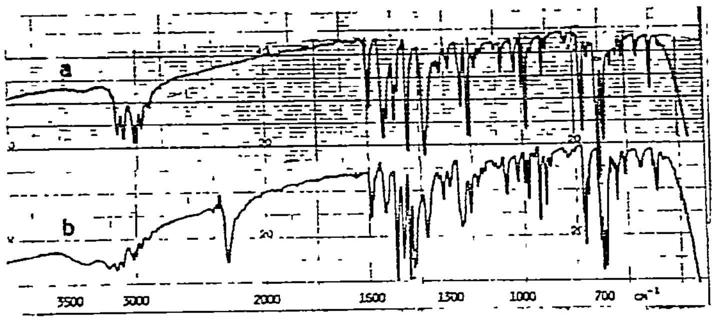

Fig. 2. Infrared spectrum of (a) protonated and (b) deuterated thiobenzanilide

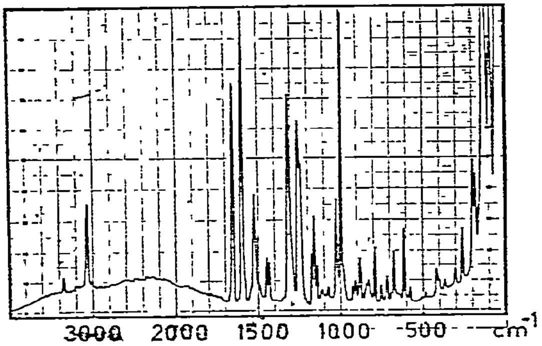

Fig. 3. Raman spectrum of benzanilide

A strong and sharp band at 985 cm^{-1}, in the infrared spectra of thiobenzanilide is considered to be localized νC=S vibration (ref. 3,4,9). However, Jensen and Nielsen (ref. 7) designated it as D band with major contribution of symmetrical stretching NCS vibration, which in most cases couples with N-H vibration. If this is so, then it should be expected that this band is rather strong in the Raman spectrum of thiobenzanilide. However, in our Raman spectrum this band appears as a very weak shoulder on the low frequency side of the very strong breathing band of the benzene ring, at 1000 cm^{-1} (see Fig. 4). We believe that the appearance of this band is mainly due to a contribution of νC=S. In deuterated thiobenzanilide δN-D mode probably couples extensively with this vibration to give rise to three new bands at 1250, 1070 and 940 cm^{-1}(see Fig. 2).

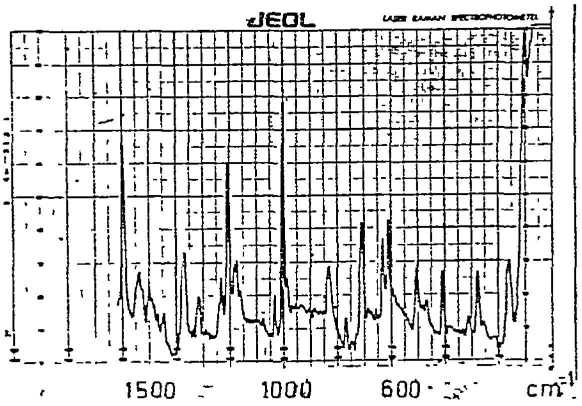

Fig. 4. Raman spectrum of thiobenzanilide

The infrared spectrum of benzanilide in the region below 900 cm^{-1} is very similar to that of the thiobenzanilide. In the range between 760 and 600 cm^{-1}, three strong bands could be seen in both of the examined compounds (see Fig. 1 and 2). Jensen and Nielsen (ref. 7) considered that 767/752 and 710 cm^{-1} bands of thiobenzanilide are due to mixed vibrations of the phenyl, C=S and N-H groups. We believe that the 760 cm^{-1} band almost certainly corresponds to γC-H of the phenyl ring. The 690 cm^{-1} band can also be assigned to phenyl bending mode. Therefore only the band at 710 cm^{-1}, which appear in the infrared spectra of both, benzanilide and thiobenzanilide, may partly belong to a vibration of the amide and/or thioamide group.

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