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INFRARED SPECTRA AND POLYMORPHISM OF THIOBENZANILIDE

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ABSTRACT

The infrared spectra of thiobenzanilide, $C_6H_5C(=S)NHC_6H_5$, and it's deuterated analogue have been recorded between 4000 and 300 cm^{-1}, at room and liquid nitrogen temperature. Depending on crystallization conditions, thiobenzanilide can give, at least four different spectra, which belong to four polymorphic modifications.

INTRODUCTION

In our laboratories, many thioamides derived from phenilendiamines or benzendicarboxylic acids, have been synthetized (1,2). When these thioamides were recrystallized from different solvents, they showed, very often, different vibrational spectra. In an attemp to understand the origin of these differencies, it seems desirable to look more closely into the spectra of thiobenzanilide, the simplest of the compounds of this type.

EXPERIMENTAL

Benzanilide was prepared from anilide and benzoylchloride and then, by action of P_2S_5 converted to thiobenzanilide. The thiobenzanilide crystals obtained by recrystallization, in different experimental conditions (different solvents, temperature and pressure), gave four different types of spectra. This showed that thiobenzanilide crystallizes in four different crystal modifications, which we designated as α, β, γ and δ.

α and β thiobenzanilide were deuterated by dissolving them in dioxan, adding D_2O until precipitation occured and drying the separated crystals in vacuo. We were unable to obtain deuterated analogues of γ and δ phases, because during the procedure of deuteration they were converted to other, more stable phases.

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.

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For recording the infrared spectra at liquid nitrogen temperature (LNT), the cell VLT-2 (RIIC) was used.

RESULTS AND DISCUSSIONS

The differencies in the infrared spectra of the different crystal phases were especially evident in the N-H stretching region, (see fig. 1). This fact suggested that the polymorphism of the thiobenzanilide crystals is due to the differencies in the hydrogen bonding. Some differencies were also observed in the region below 1600 cm^{-1}, mainly with the bands whose origin is connected with the vibrations of the thioamide group.

A high temperature phase, designated as α, is the most stable one. All other polymorphs, on heating above 333K convert into α phase. It's N-H stretching band is located between 3200 and 2850 cm^{-1} and consists of numerous subbands. The intensities of the subbands decrease with the extension of their frequency distances from most intense subbands at 3160 cm^{-1}. On the other hand, in the low temperature spectrum, the maxima of the subbands are moved to lower frequency, but the minima are nearly in the same positions as in the room temperature spectra. In the spectrum of the deuterated analogue, νN-D band appears as a strong band at 2315 cm^{-1}and a very weak one, on 2370 cm^{-1}. On the basis of these observations, it could be concluded that the structure of the N-H stretching band is due to the Evans type Fermi resonance (3). Namely, the broad N-H stretching band overlaps the overtones and combinations of some internal vibrations and Fermi resonance modifies the band shape which manifests itself by the appearance of transmission holes that are the minima of absorption on the band (4). The overtones and combinations giving rise to such Fermi resonance are given in Table I.

TABLE I

The minima on the N-H stretching bands and overtones or/and combinations of α and β thiobenzanilide

α thiobenzanilide		β thiobenzanilide	
minima	overtones/combinations	minima	overtones/combinations
3125	1535 + 1505	3190	2 x 1595
3065	2 x 1535	3140	1595 + 1545
2980	1535 + 1450	3080	2 x 1545
2910	1535 + 1370	2990	1545 + 1445
-	- -	2920	1545 + 1365

All frequencies are in cm^{-1}

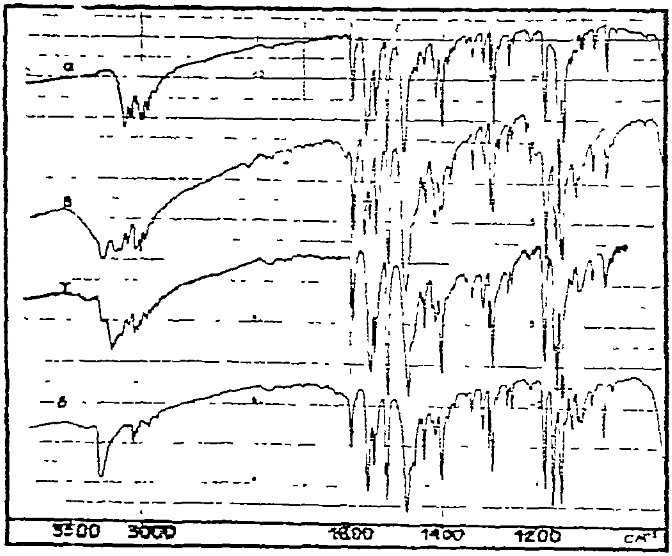

Fig. 1. Infrared spectra of α, β, γ and δ phases of thiobenzanilide, at room temperature.

The β phase of thiobenzanilide could be obtained on recrystallization from different solvents at room temperature, in the refrigerator and at temperature up to 313 K. It is relatively stable below 333K, but on higher pressure converts fast, to α phase.

In it's infrared spectrum there is very broad and structured N-H stretching band, between 3350 and 2850 cm^{-1}. At first, we thought that this spectrum arises as a result of the mixture of the α and δ phases. The careful inspection of the spectra of the mixture and of the β phase, however, showed that the spectra were similar but not identical. The subbands on the N-H stretching band were found at 3325, 3220, 3180, 3120, 3035, 3008 and 2970 cm^{-1}. But in this case, it seems that the Fermi resonance can not be solaly responsible for the shape of the N-H stretching band. While the structure of the part of the νN-H band, below 3200 cm^{-1} could be explained by the Evans' type Fermi resonance, as in the case of α phase; in the frequency region higher than 3200 cm^{-1}, the possibility for Fermi resonance is reduced because overtones and combinations fall outside this region. At the other hand, taking into account changes that happened on partial deuterations, in the infrared spectra of β phase, subband at 3320 cm^{-1} could be assigned to other kind of hydrogen bond. That means that in β phase crystals, there exist at least two types of hydrogen bonds.

The γ phase could be obtained only at low temperature by recrystallization in the refrigerator. It is most unstable modification.

It may exist at temperature lower than 273K. It is also difficult to obtain it in pure condition. In it's infrared spectrum, N-H stretching vibration appears as a strong band at 3240 cm^{-1}. This band is always followed by some week bands, which are due to impurity, probably to the α and β phases , which could be present together with this phase.

The δ phase was obtained by fast crystallization from melted thiobenzanilide. This modification was also obtained by recrystallization from toluene and xylene, but the crystals so obtained, were not pure. On standing at room temperature, this phase converts fast, to α phase. On cooling to liquid nitrogen temperature, this phase, like all others, does not change. In the infrared spectrum of this modification, the N-H stretching band, related to other modifications, appears at the highest frequency, at 3324 cm^{-1} as a single and intensive band.

Comparing the N-H stretching region in the infrared spectra of thiobenzanilide polymorphs (see fig. 1), it could be noticed that bands belonging to the stretching N-H vibration are in the ascending order, going from α to δ phase. If the criterium for the strength of the hydrogen bond is lowering of the N-H stretching mode frequency, then the strongest hydrogen bond is formed in α phase, whiles the weekest one is in the δ phase.

It's seems that strongest hydrogen bond stabilizes α phase and makes this modification of the thiobenzanilide most stable.

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