

THE N-H STRETCHING REGION OF SOME IMIDES AND THIOIMIDES

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ABSTRACT

The multiplet structure of $\nu\text{N-H}$ and $\nu\text{N-D}$ bands of solid phthalimide, monothioptthalimide, dithioptthalimide, isatin, saccharin and of their deuterated analogues has been explained as being a result of Fermi resonance of the fundamentals of $\nu\text{N-H}$ and $\nu\text{N-D}$ with combinations and/or overtones. The submaxima of 3080 and 2970 cm^{-1} of saccharin as well as pronounced doublet at 2465 and 2345 cm^{-1} of d-phthalimide move to lower frequency in the low temperature ir spectra, while the "windows" remain fixed at 3045 and 2380 cm^{-1} , respectively. These examples could be a striking demonstration of Evans type Fermi resonance.

INTRODUCTION

The investigation of the ir spectra of some cyclic compounds, such as phthalimide (I), monothioptthalimide (II), dithioptthalimide (III), isatin (IV), saccharin (V) and thiosaccharin (VI) is a part of broader ir studies currently undertaken in our laboratory on compounds containing C(=O)-N-H or C(=S)-N-H groups¹.

From the available results of x-ray studies, it follows that the molecular crystals of phthalimide², isatin³ and saccharin⁴ consist of centrosymmetric dimer molecules formed via $\text{N-H}\dots\text{O}$ hydrogen bonds. No structural information have been reported for II, III and VI. Since the x-ray analysis shows only one type of hydrogen bond for I, IV and V and, on the other hand, the ir spectra show multiple bands in the N-H stretching region for all of the above mentioned compounds, except for VI, we decided to study the ir spectra more closely, paying special attention to the N-H stretching region.

EXPERIMENTAL

The samples of imides were commercial products, which were purified by repeated crystallization. Thioimides were prepared by treating of imides with P_2S_5 . Deuterated analogues were obtained by treatment with D_2O and successive evaporation of the liquid.

The ir spectra were recorded on a Perkin Elmer 580 spectrophoto-

meter using KBr discs. For recording the ir spectra at liquid nitrogen temperature (LNT) the variable VLT cell (RIIC) was used.

RESULTS AND DISCUSSION

In the ir spectra of solid I, II, III and IV, broad bands occur at around 3200 cm^{-1} with many subbands at low frequency side (Table I). In the spectrum of solid V, however, three strong bands occur (at 3090, 2970 and 2700 cm^{-1} , the one at 2970 cm^{-1} being the strongest among them), while in the spectrum of thiosaccharin only one strong and quite sharp band at about 3360 cm^{-1} appears.

On deuteration all these bands move to lower frequency and some of them have profoundly altered their structure.

Table I. The ir $\nu\text{N-H}$ bands, the maxima and minima on them, and overtones and combinations (in cm^{-1})

	IR BAND		OVERTONES OR COMBINATIONS	APPROXIMATE ASSIGNMENT		IR BAND		OVERTONES OR COMBINATIONS	APPROXIMATE ASSIGNMENT	
	MAXIMA	MINIMA				MAXIMA	MINIMA			
PHthalimIDE	3200 vs. b			$\nu\text{N-H}$	ISATIN	3190 vs. b			$\nu\text{N-H}$	
		3100	1740+1370*	$\nu\text{C=O}+\delta\text{N-H}$			3125	1730+1405	$\nu\text{C=O}+\nu\text{N-H}$	
	3060 m			$\nu\text{N-H}$			3105 s		$\nu\text{N-H}$	
	2920 w		2x1470	$\nu\text{C-C}$			3055 w		$\nu\text{C-H}$	
	2850 w		1470+1370	$\nu\text{C-C}+\delta\text{N-H}$			3030 w		$\nu\text{C-H}$	
	2720 m		2x1370	$\delta\text{N-H}$		2920 w		2x1460	$\nu\text{C-C}$	
						2880 w		1460+1405	$\nu\text{C-C}+\nu\text{N-H}$	
						2810 w		2x1405	$\delta\text{N-H}$	
PHthalimIDE-D	2465 vs			$\nu\text{N-D}$	SACCHARIN	3090 vs. b			$\nu\text{N-H}$	
		2380	2x1205	$\delta\text{N-D}$			3045	1720+1350*	$\nu\text{C=O}+\delta\text{N-H}^*$	
	2345 vs			$\nu\text{N-D}$		2970 vs. b		$\nu\text{N-H}$		
DIthio-PHthalimIDE	3215 vs. b			$\nu\text{N-H}$	SACCHARIN-D	2700 s		2x1350	$\delta\text{N-H}$	
		3140	1750+1415	$\nu\text{C=O}+\delta\text{N-H}$			2300 vs			$\nu\text{N-D}$
	3113 s			$\nu\text{N-H}$				2375**		
	2880 w		1470+1415	$\nu\text{C-C}+\delta\text{N-H}$			2260 s		2240**	$\nu\text{N-D}$
	2830 w		2x1415	$\delta\text{N-H}$		2200 vs		2170**	$\nu\text{N-D}$	
DIthio-PHthalimIDE	3190 vs. b			$\nu\text{N-H}$	SACCHARIN-D				$\nu\text{N-D}$	
			1460+1430	$\nu\text{C-C}+\delta\text{N-H}$			2155 m			$\nu\text{N-D}$
	2885 w		2x1430	$\delta\text{N-H}$						
	2850 w			$\delta\text{N-H}$	THIO-SACCHARIN	3350 vs			$\nu\text{N-H}$	

vs, s, b, m, w = very strong, strong, broad, medium, weak

* This band can be seen in LNT spectrum, on deuteration disappears

** There are many new bands in the spectrum of saccharin. These which are involved in overtones and combinations are hidden under the very strong and complex band of $\nu\text{S}=\text{O}_2$, between 1100 and 1200 cm^{-1}

The multiplet structure of the bands in the N-H and N-D stretching region we have tried to explain as being a result of Fermi resonance of the fundamentals of $\nu\text{N-H}$ or $\nu\text{N-D}$ with vibrations involving H or D atoms. Since on lowering the temperature, the dimensions of the

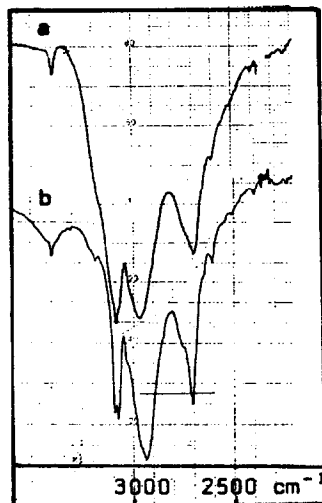


Fig. 1. ν N-H bands of saccharin a) at room temperature b) at LNT

unit cell decrease and in hydrogen bonded systems the X-H...Y distances contract consequently, it should be expected that the ν X-H bands should move to lower frequency. We have, therefore, used the low temperature technique for an explanation of the structure of the ν N-H and ν N-D bands.

On the presumption that the greatest intensity region within the band system as a whole represents approximately the main frequency of ν N-H, we found that the striking demonstration of the low temperature affect can be seen on the ν N-H band of saccharin (Fig. 1). In the three bands system, the centroid of the subbands at 2970 cm^{-1} at the LNT moves to lower frequency for about 35 cm^{-1} and its intensity increases, while the intensity of the subband at 3090 cm^{-1} markedly lowers and its maximum shifts to

3070 cm^{-1} . It is remarkable, however, that the minimum at 3045 cm^{-1} becomes deeper and remains unchanged in frequency. (The sharp ν C-H band which was hidden under the intense 3090 cm^{-1} subband, appears at 3100 cm^{-1}). This behaviour is characteristic of an Evans type Fermi resonance^{5,6}. Namely, the broad ν N-H band overlaps the combination of ν C=O and δ N-H ($1720+1350\text{ cm}^{-1}$) and Fermi resonance modifies the band shape which manifests itself by the appearance of transmission hole that is the minimum of absorption at 3045 cm^{-1} . The third subband at 2700 cm^{-1} at LNT becomes sharper and more intense, but it does not move to lower frequency. It is due to the overtone of δ N-H ($2 \times 1350\text{ cm}^{-1}$). This overtone falls on the wing of the broad ν N-H band and it is intensified by strong Fermi resonance.

An other striking demonstration of Evans type Fermi resonance can be seen in the spectrum of deuterated phthalimide (Fig. 2). In this spectrum, the ν N-D band shows a pronounced double structure with maxima at 2445 and 2345 cm^{-1} and minimum at 2380 cm^{-1} . At room temperature, the both bands of the doublet have nearly the same intensity, whereas at LNT the continuum moves to lower frequency, but the minimum remains fixed. The frequency of the minimum corresponds to the overtone of the δ N-D, which appears at 1205 cm^{-1} .

The appearance of the minima at around 3100 cm^{-1} on the ν N-H bands of phthalimide, monothiophthalimide and isatin may be explained

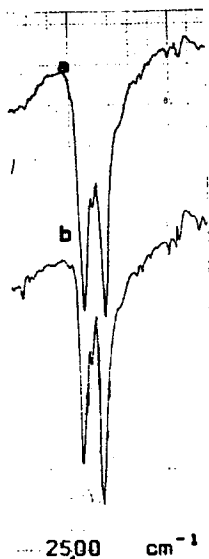


Fig. 2. $\nu\text{N-D}$ band of phthalimide-d
a) at room temperature b) at LNT

as a result of Evans type Fermi resonance, too. (Table I). Namely, the combinations of $\nu\text{C=O}$ and $\nu\text{N-H}$ fall at the minima on the $\nu\text{N-H}$ bands of each mentioned compounds. In the case of dithiophtalimide, however, there is no possibility for such type of combinations and on its $\nu\text{N-H}$ band there is no minimum. The subbands of low intensity, which appear below 3000 cm^{-1} in the spectra of this series of compounds are ascribed to overtones and/or combinations (Table I). These overtones and combinations fall near the $\nu\text{N-H}$ band where they are intensified by weak or moderate Fermi interaction.

The structure of the $\nu\text{N-D}$ band of deuterated saccharin can also be explained as a result of Evans type Fermi resonance.

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REFERENCES

- ¹O. Grupce and I. Petrov, *J. Mol. Structure*, 115(1984) 119, 115 (1984) 481.
- ²V. E. Matzat, *Acta Cryst.* B28 (1972) 415.
- ³G. H. Goldschmidt and F. J. Lewellyn, *Acta Cryst.* 3 (1950) 294.
- ⁴J. C. J. Bart, *J. Chem. Soc., B* (1968) 376.
- ⁵J. C. Evans, *Spectrochim. Acta* 16 (1960) 994.
- ⁶M. F. Claydon and N. Sheppard, *Chem. Comm.* (1969) 1431.
- ⁷S. Bratos, *J Chem. Phys.* 63 (1975) 3499.