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Vibrational Spectra of Orthodiamide Derivatives: The N-H Stretching Band of Some Benzimidazole Derivatives

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The aromatic diamides derived from *o*-phenylenediamines, when treated with P_2S_5, gave 2-arylbenzimidazole derivatives as crystalline products. The IR spectra of these compounds are, like benzimidazole itself, characterized by the very broad, structured and intensive band due to the N-H stretching vibrations. Lowering of the temperature has a remarkable effect on both the N-H stretching and N-H out-of-plane bending vibrations. On deuteration, the substructure of the N-H stretch is completely changed. The low-temperature and deuteration studies strongly suggest that the whole sbustructure is a result of Evans-type Fermi resonance interactions.

INTRODUCTION

In the last ten years, various amides, thioamides and their derivatives have been extensively studied in the laboratories of our two institutions. Attention has been paid both to the synthesis and structural (as well as spectroscopic) properties of these materials. Thus, a number of new amides have been synthesized and their reactions, structures and vibrational spectra have been studied in detail.[1–6]

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Among the problems deserving attention was the problem of the origin of the breadth and substructure of the N-H stretching bands in hydrogen bonded systems. A number of different explanations have been offered so far, covering the double-minimum potentials for the proton motion,[7–9] Fermi-resonance interactions of the X-H stretching with second order transitions,[10–13] strong coupling between the X-H stretching and low-frequency motions[14–18] *etc.* According to the theory of Witkowski and Maréchal,[14] both the breadth and the structure of the X-H stretching bands are caused by the anharmonic coupling between the ν(X-H) and σ(X...Y) vibrations (the latter is the hydrogen bond vibration). Some experimental evidence (the IR spectrum of imidazole)[14] seemed to be in agreement with the proposed theory. On the other hand, the theory of Bratos[19] predicted that the substructure of the X-H stretching bands may result from Fermi resonance interactions of the ν(X-H) band with overtones of the X-H...Y bending vibrations. Numerous studies seemed to confirm the predictions of this theory, as well.[20–22]

Soon it became clear that both mechanisms (the strong coupling and the Fermi resonance interactions) are valid and acceptable from the physical point of view, the real question being which one is operative in a particular spectrum. In the last few years, a method has been developed by Maréchal[23] for obtaining 'peeled-off spectra' (that is, spectra which are free of complications arising from the Fermi resonance interactions). After a spectrum has been 'peeled-off', one has the advantage of studying the spectrum as it would look if there were no Fermi resonance interactions. Unfortunately, the procedure for obtaining such spectra seems to be rather involved.[23]

In the present paper, we propose a simple method* for the detection of the Fermi resonance minima in the region of the N-H stretching vibrations of the 2-phenyl benzimidazole and 2-(*p*-methoxyphenyl) benzimidazole. These spectra are similar to the spectra of the chemically related parent compound – benzimidazole, and to the spectra of imidazole. The vibrational spectra of the last two compounds have been extensively studied by various techniques.[24–30]

The method proposed here could be applied in a number of hydrogen bonded compounds, which are chemically/structurally related.

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* The method is based on a parallel study of protiated and deuterated species of *chemically and structurally closely related compounds*, such as the two benzimidazole derivatives. Apart from the band position (centre of gravity) of the complex profile, only minor differences are expected in the NH stretching region of the IR spectra if Fermi resonance is at the origin of the band substructure.

EXPERIMENTAL

2-Phenyl benzimidazole and 2-(*p*-methoxyphenyl) benzimidazole (Figure 1) were prepared when the diamides of *o*-phenylenediamines were treated with P_2S_5 in a dry pyridine or dioxane medium. The structure was first assumed on the basis of the possible reaction mechanisms and close inspection of the IR spectra. This assumption was further confirmed by independent synthesis (of the 2-phenyl benzimidazole derivative) based on literature data.[31] The 2-(*p*-methoxyphenyl) benzimidazole was prepared in an analogous way.

The IR spectra were recorded from KBr pellets, on a Perkin-Elmer 580 spectrometer. The deuteration was performed by dissolving the compounds in dioxane, followed by precipitation with D_2O. A VLT-2 low-temperature cell was used for low temperature studies. The cell was cooled with liquid nitrogen.

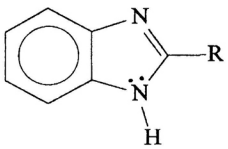

Figure 1. Structural formula of the studied benzimidazole derivatives: R = C_6H_5 (phenyl) or $CH_3OC_6H_4$ (*p*-metoxyphenyl).

RESULTS AND DISCUSSION

The discussion of the spectra would be much facilitated if the crystal structures of the compounds were known. Unfortunately, this is not the case. Nevertheless, one could make a reasonable assumption that hydrogen bonded chains exist in both compounds, similar to those found in the spectrum of the parent compound – benzimidazole.[31] The existence of hydrogen bonded (centrosymmetric) dimers was considered impossible on the basis of the particular structure of the (benz)imidazole ring.

The IR spectra of 2-phenyl benzimidazole recorded at RT and LNT are presented in Figure 2. Upon close inspection of the spectra, the following conclusions/observations could readily be made:

a) The RT and LNT spectra are very similar;
b) The complex band due to the ν(NH) vibrations (centered at about 2600 cm^{-1}) is shifted in the LNT spectrum by some 100 cm^{-1};
c) Despite this pronounced shift, the only difference in this part od the spectrum is reflected through slight changes in the relative intensities of the subbands;
d) The transmission minima have practically the same frequency in both the RT and LNT spectra;

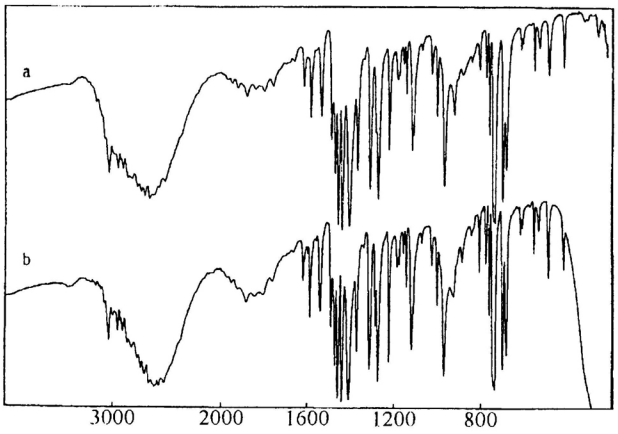

Figure 2. IR spectra of 2-phenyl benzimidazole at RT (a) and LNT (b).

e) The γ(NH) band is at $\approx$ 950 cm^{-1} (judged on the basis of the temperature/duteration behaviour of the bands in this region);

f) The intensity of the broad band at $\approx$ 1850 cm^{-1} increases on lowering the temperature.

The goal of the paper is to offer the most likely explanation for the substructure of the complex ν(NH) band. This is to be done on the basis of inspection and comparison of the IR spectra of the investigated materials. As mentioned in the introduction, at least two reasons could be at the origin of the substructure: coupling of the N-H stretching band with low-frequency motions (*e.g.* the N...N stretching vibration) and Fermi resonance interactions of the ν(NH) band with second order transitions of the internal modes. Conclusions b)–d) celarly show that both mechanisms are present; however, as long as the substructure of the band is in question, the spectra strongly suggest that the Fermi resonance mechanism is the important one. Let us explain this assertion in some more detail.

The red shift of the ν(NH) band centroid at LNT may be taken as an evidence that the N-H stretching is anharmonically coupled to some low frequency motions – most probably the hydrogen bond vibration σ(N...N). The latter mode is, namely, expected to fall in the 100 – 200 cm^{-1} region. The population of the corresponding energy levels will change dramatically from RT to LNT. Due to the anharmonicity present, it could be expected that the 'equilibrium' N-N distance will be shorter in the ground state of the σ(N...N) mode, as compared to the excited states of this mode. This may be viewed as a somewhat stronger hydrogen bond at LNT, thus resulting in a shift of the ν(NH) band to lower frequencies.

Conclusions c) and d), however, indicate that the whole substructure is a result of the Fermi resonance interactions. Namely, the frequency of most

of the other bands in the IR spectra is invariant to temperature changes, much in the same way as the frequencies of the transmission minima of the ν(NH) band. These minima are, therefore, explained as Evans holes,[33] caused by interactions of the broad ν(NH) fundamental with sharp second order transitions (quite possibly vibrations resulting from the 'mixing' of the δ(NH) mode with other modes of the same symmetry and similar energy).

The finding that the broad band at $\approx$ 1850 cm^{-1} grows in intensity as the temperature is lowered may again be explained as a result of the Fermi resonance interaction between the first overtone of the γ(NH) vibration and the ν(NH) vibration. The γ(NH) band appears at about 950 cm^{-1} (*cf.* Figure 2) and its overtone may be in a weak Fremi resonance interaction with the N-H stretching. Due to the red shift of ν(NH) at LNT,* the two levels become closer resulting in a somewhat stronger interaction which explains the intensity increase. This explanation is in line with the one that Claydon and Sheppard[34] have offered as the most likely explanation for the origin of the *'A, B, C'* trio in strongly hydrogen bonded systems. However, more quantitative work (*e.g.* study of the polarization properties of the complex band) is desirable in order to discuss this problem in detail.

All these conclusions may be further supported by inspection of the IR spectrum of 2-(*p*-metoxyphenyl) benzimidazole (Figure 3) and by comparison of the spectra of both derivatives (Figure 4).

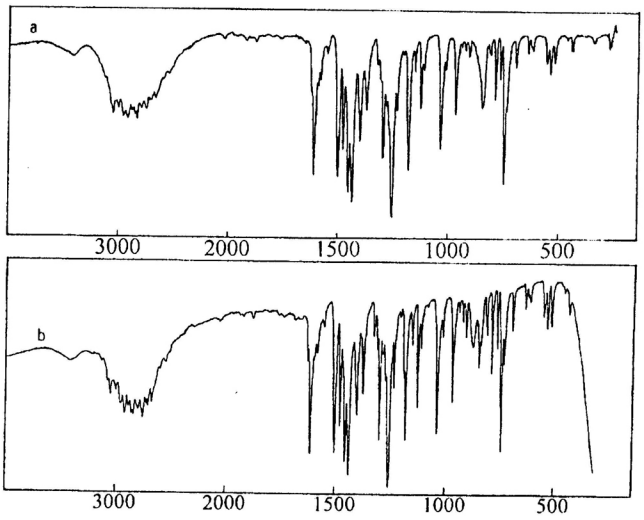

Figure 3. IR spectra of 2-(*p*-metoxyphenyl) benzimidazole at RT (a) and LNT (b).

* On the other hand, a *blue shift* is expected for the γ(NH) mode, when the temperature is lowered, which was also confirmed.

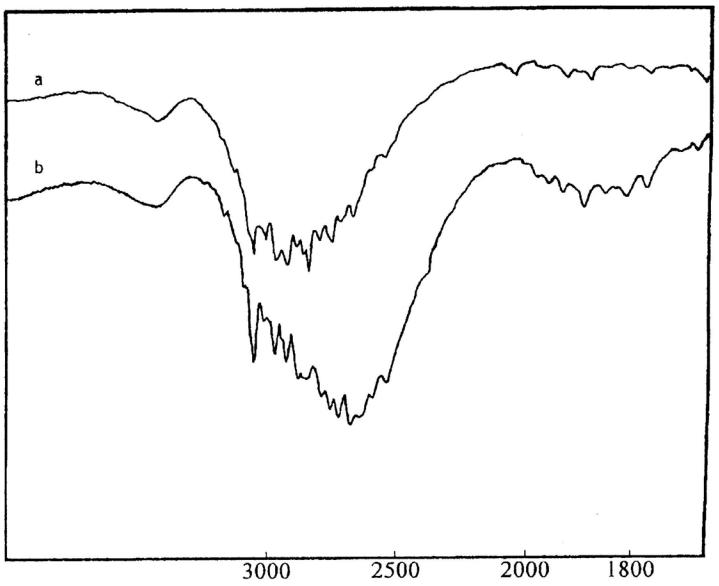

Figure 4. The N-H stretching region in the RT IR spectra of 2-(*p*-metoxyphenyl) benzimidazole (a) and 2-phenyl benzimidazole (b).

Some additional observations may now be made:

g) The spectra of both benzimidazole derivatives are similar;

h) The complex ν(NH) band of 2-(*p*-metoxyphenyl) benzimidazole lies about 250 cm^{-1} higher than the corresponding band in 2-phenyl benzimidazole;

i) The transmission minima in both derivatives appear at the same frequencies;

j) The out-of-plane bending band of the 2-(*p*-metoxyphenyl) benzimidazole is at $\approx$ 880 cm^{-1}, (judged, again, by inspection of the RT/LNT and protiated/deuterated samples);

k) No band in 1900–1800 cm^{-1} region could be found (this is an important difference between the two derivatives).

Due to the chemical similarity of both compounds, it is not surprising that their IR spectra are also very similar. Some difference in the hydrogen bond strength (explaining the shifts of the ν(NH) and γ(NH) vibrations) is self-evident. However, this would imply a rather diferent pattern of the ν(NH) band in the two benzimidazole derivatives if the strong coupling of the ν-σ type was the cause of the substructure. Identical frequencies of the transmission minima in 2-phenyl bezimidazole and 2-(*p*-metoxyphenyl) benzimidazole once again point to Fermi resonance as the main reason for the appearance of the subbands.

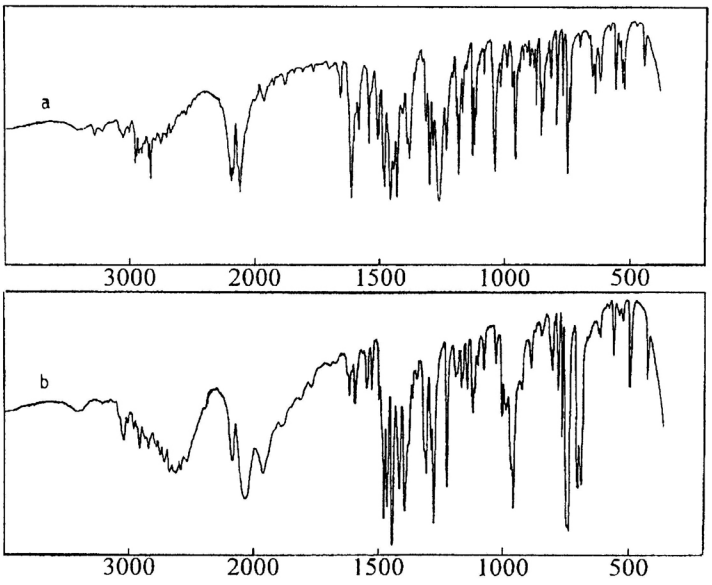

Figure 5. LNT IR spectra of partly deuterated 2-(*p*-metoxyphenyl) benzimidazole (a) and 2-phenyl benzimidazole (b).

Observation k) is compatible with the larger frequency difference ($\approx$ 1050 cm^{-1}) between ν(NH) and 2γ (NH) bands in 2-(*p*-metoxyphenyl) benzimidazole; under these conditions, the resonance interaction between the corresponding levels simply vanishes. For comparison, the frequency difference in 2-phenyl banzimidazole is $\approx$ 650 cm^{-1}.

The study of partly deuterated compounds (*cf.* Figure 5 and 6) confirms the correctness of the above assumptions. Evidently, the substructure of the ν(ND) bands in both compounds (see Figure 6) is much less pronounced. This may be explained as a result of the mixed character of the δ(NH) and δ(ND) vibrations (as briefly mentioned above). Due to the mixing of vibrational modes which have the same summetry and similar energy, it is quite probable that there are numerous bands with δ(NH) character in the 1500–1200 cm^{-1} region (*i.e.* in the region where most of the bands result from in-plane vibrations of the benzimidazole part of the molecules; all of them belong to the A' symmetry type, in the approximation of C_s symmetry). The double excitations (overtones and/or combinations) of these modes, all having some δ(NH) character, produce numerous transmission minima (Evans holes) on the broad ν(NH) bands. On deuteration, the in-plane bending is shifted in a region (around 1000 cm^{-1}) where coupling is severily restricted. The δ(ND) band is, therefore, expected, to be 'more pure' as compared to δ(ND). The new bands at around 1070 and 990 cm^{-1} in the spectra of both deuterated samples (*cf.* Figure 5), must originate from vibrations

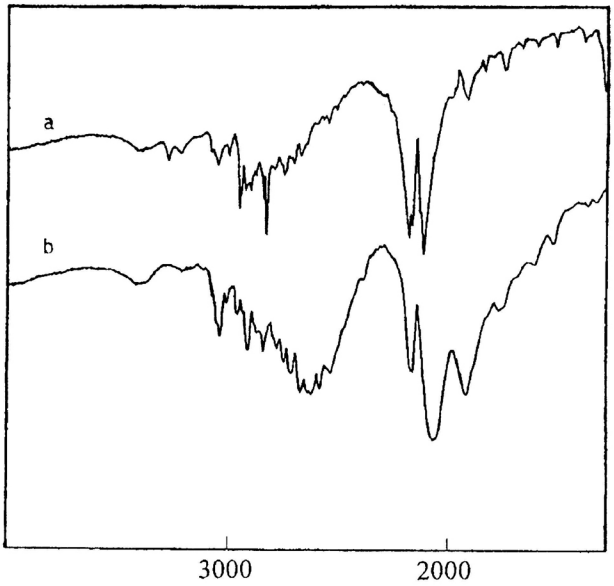

Figure 6. The N-H and N-D stretching regions in the LNT IR spectra of partly deuterated samples of 2-(*p*-metoxyphenyl) benzimidazole (a) and 2-phenyl benzimidazole (b).

which have a δ(ND) character. If this is correct, then the second order transitions of these fundamentals are expected to produce Fermi resonance minima on the ν(ND) band. Holes are indeed observed in the LNT IR spectra of both benzimidazole derivatives (*cf.* Figure 5), at frequenies close to 2145 and 1990 cm^{-1}. These values are in excellent agreement with the expected values of the first overtones of the bands with δ(ND) character, *i.e.* 2×1070 and 2×990 cm^{-1} Other transmission minima could not be positively identified in the IR spectra of the deuterated samples.

From the arguments presented above, it seems obvious that Fermi resonance interactions are at the origin of the substructure of the ν(NH) bands. Further work on other benzimidazole derivatives is in progress.

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SAŽETAK

Spektri vibracija derivata ortodiamida: Vrpce istezanja N-H veze za derivate benzimidazola

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Kristali derivata 2-arilbenzimidazole pripravljeni su iz *o*-fenilendiamina i P_2S_5. Infracrveni spektri benzimidazola i pripravljenih derivata posjeduju intenzivnu vrlo široku apsorpcijsku vrpcu s finom strukturom koja je rezultat vibracije istezanja veze N-H. U niskotemperaturnim spektrima opažene su znatne promjene vibracija istezanja i savijanja veze N-H. Fina struktura vrpce istezanja veze N-H potpuno se promijeni deuteriranjem benzimidazola i pripravljenih derivata. Dobiveni rezultati upućuju na zaključak da je struktura vrpce istezanja veze N-H rezultat interakcija Fermijevih rezonancija.