EFFECT OF HYDROGEN BONDING ON THE FREQUENCY OF THE OUT-OF-PLANE DEFORMATION VIBRATIONS OF THE NH BONDS IN PYRAZOLE AND IMIDAZOLE MOLECULES

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The assignment of the frequency of the out-of-plane deformation vibration of pyrazole on the basis of an investigation of the temperature dependence of the IR spectrum is reexamined.

In an investigation of the vibrational spectra of pyrazole in various aggregate states, we proposed [1] an assignment of the observed bands of pyrazole to the various types of normal vibrations that were fundamentally in agreement with the assignment adopted by Zecchina and co-workers [2]. The differences in the assignment involved a number of frequencies, particularly the NH out-of-plane deformation vibrations (γ_{NH}). The band at 515 cm^{-1} in the IR spectrum of the gas was assigned to the γ_{NH} vibration of pyrazole [1], while the band at 612 cm^{-1} in the IR spectrum of a crystalline sample was assigned to this vibration. For the similarly constructed imidazole molecule, the band at 512 cm^{-1} was assigned to the γ_{NH} vibration in the spectrum of the gas, while the band at 930 cm^{-1} was assigned to this vibration in the spectrum of the crystalline compound (see [3, 4]). Thus the assignments of the γ_{NH} vibrations for pyrazole and imidazole proved to be different for the crystalline states. Such a large shift in the γ_{NH} vibration of imidazole (515-930 cm^{-1}) as the aggregate stage changes seems unusual and is explained by the presence of a strong intermolecular hydrogen bond that increases the frequency of the deformation vibrations. The affiliation of the 930 cm^{-1} band with the γ_{NH} vibration is confirmed by the dependence of its position and intensity on the temperature [3, 4].

The following arguments constitute evidence in favor of the assignment of the 612 cm^{-1} frequency to the γ_{NH} vibration in the IR spectrum of crystalline pyrazole [1]. The band at 612 cm^{-1} in the spectra of solutions gradually vanished upon successive dilution, during which a band at 530 cm^{-1} appeared in the spectrum of the gas. A band at 593 cm^{-1} was observed in place of the band at 515 cm^{-1} (gas) in the spectrum of a complex of pyrazole with $CdCl_2$. It would seem that the character of the shift of the γ_{NH} band (515 for the gas, 530 for the solution, and 593 cm^{-1} for the crystal) should have led to a γ_{NH} frequency of ~600 cm^{-1} in the crystalline state. On the other hand, in analogy with imidazole, the band at 890 cm^{-1}, which, like the 612 cm^{-1} band, decreases partially on dilution, might have been assigned to the γ_{NH} vibration in crystalline pyrazole. However, we were unable to follow the behavior of the latter at low concentrations because of absorption of the solvent (CS_2 and CCl_4) in thick layers. Thus, both the band at 612 cm^{-1} and the band at 890 cm^{-1} can be assigned to the γ_{NH} vibration in the pyrazole crystal.

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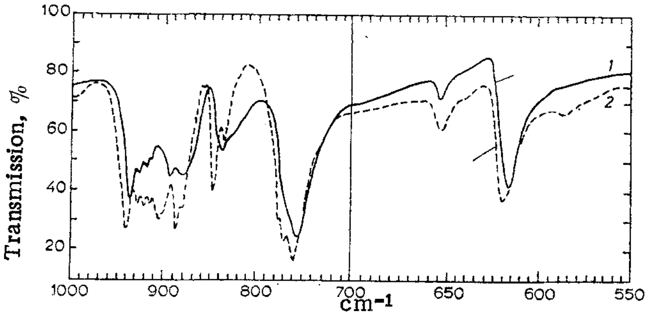

Fig. 1. IR spectra of pyrazole in KBr pellets: 1) spectrum at 25°C; 2) spectrum at −180°.

To resolve this alternative, in the present research we studied the behavior of these two bands as the temperature changes. The IR spectrum of crystalline pyrazole in a KBr pellet was obtained with a UR-10 spectrometer at −180°C. It was found that only the band at 890 cm^{-1} increases in intensity as the temperature is lowered and is shifted to 910 cm^{-1}, while the position of the band at 612 cm^{-1} does not change (see Fig. 1). Similar behavior was observed for the band at 930 cm^{-1} in the IR spectrum of imidazole [3], in which a decrease in temperature from ±20 to −180° led to an increase in the intensity and frequency of this vibration of 20 cm^{-1}. It has been reported [4] that the γ_{ND} band of crystalline 1-D_1-imidazole increases from 672 cm^{-1} by ~20 cm^{-1} during a similar change in temperature.

Thus the band at 890 cm^{-1} in the spectrum of crystalline pyrazole is more correctly assigned to the γ_{NH} vibration, while the band at 612 cm^{-1} is more correctly compared with the band at 672 cm^{-1} in the spectrum of the gas. The latter band is related to the out-of-plane deformation vibration of the pyrazole ring (γ ring) [1]. The behavior of this band on passing from the gas to the crystal (672-612 cm^{-1}) corresponds qualitatively to the change in frequency upon "heavy atoming" of the molecule.*

Thus, the assignment of the bands of pyrazole in the IR spectrum of a crystalline sample presented in [1] should be altered. The considerable shifts of the frequency of the γ_{NH} vibration in pyrazole and in imidazole on passing from the gaseous state to the crystalline state, which are due to the formation of strong intermolecular hydrogen bonds, should be emphasized. This phenomenon, together with the sensitivity of the γ_{NH} band to the temperature, can be considered to be a characteristic peculiarity of the vibrational spectra of heterocycles that are similar to imidazole and pyrazole.

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*The vibrations of the γ ring have frequencies of 672 cm^{-1} in $^{14}N_2$-pyrazole, 662 cm^{-1} in $^{15}N_2$-pyrazole, and 659 cm^{-1} in 1-D_1-pyrazole.

†The N...N distance is 2.83 Å in imidazole [5, 6] and 2.86-2.93 Å in pyrazole [7].