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Low-Frequency Vibrational Spectra of Some Crystals Containing Intermolecular Hydrogen Bonds

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The study of low-frequency Raman and infrared spectra of molecular crystals was started in the "Rudjer Bošković" Institute about ten years ago. At that time mercury arcs were the only sources in Raman spectroscopy. Investigations in the region of the far infrared spectrum were scarce, because of experimental difficulties. Our interest was oriented mostly to lattices containing only the Van der Waals type of intermolecular forces, such as anthracene. The main difficulties arising in low-frequency Raman spectra are weak intensity, a relatively great number of bands, and the proximity of the exciting line, the wings of which are extended far in the region of Raman bands. We were, therefore, obliged to use large and very clear samples in order to eliminate the background to which weak bands were superimposed. Under such circumstances it was not possible to study lattices containing hydrogen bonds, since in the case of organic crystals lattice and hydrogen bond vibrations were localised in the same frequency region. Lasers became the usual sources in Raman spectroscopy about 1965. At that time the first far infrared spectrometers became also available and large computers came into use as standard equipment of research institutes. This improved the possibilities of performing measurements as well as calculations of vibrational spectra of molecules and crystals. All these circumstances contributed to a spectacular renaissance of Raman and far infrared spectroscopy and consequently initiated renewed interest in this field of research. At that time we began investigating some crystals containing intermolecular hydrogen bonds. Such crystals should be simple models suitable for studying energies and mechanisms of the hydrogen bond itself, and this type of studies might be of interest for the understanding of the structure of biological and some artificial polymers. Although the hydrogen bond has been studied for many years, direct investigations of its vibrational spectrum were undertaken only a few years ago. In fact, all previous studies concerned with vibrational spectroscopy investigated perturbations in the intramolecular vibrational spectrum caused by the presence of the hydrogen bond. Single crystal samples enable us to make a more precise polarisation analysis

of Raman as well as of infrared spectra. In fact, measurements performed with high-resolution spectrometers indicate that these spectra consist of many closely lying bands, and the assignment of all the bands would practically be impossible. By polarising the observed spectra it is possible to separate even very close bands of different

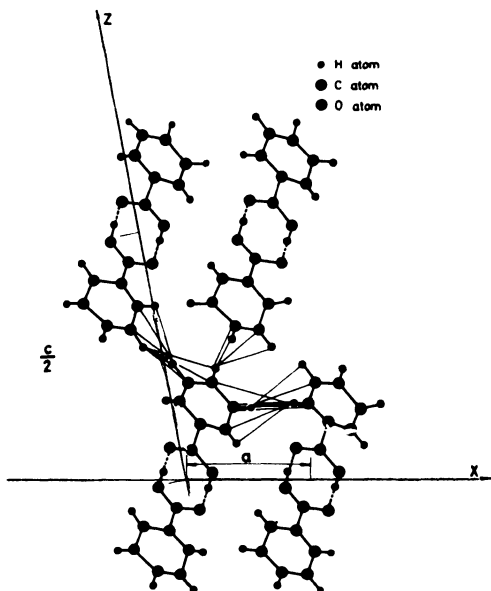


Fig. 1. Crystal structure of benzoic acid

The crystal structure of benzoic acid is given in Fig. 1. It crystallises in the monoclinic system, space group C_{2h}^5 ($P2_1/c$) [1] with four molecules in the unit cell. Molecules form dimers (Fig. 2) through the characteristic carboxylic ring. According to group-theory considerations, the vibrational spectrum of the lattice and the hydrogen bond can be assigned as follows:

$$\text{Lattice: } 3A_g + 3B_g + 2A_u + 1B_u = 9$$

$$\text{Hydrogen bond: } 3A_g + 3B_g + 3A_u + 3B_u = 12 .$$

The low-frequency Raman spectrum of a single crystal recorded in this experiment is given in fig. 3. These results, together with the far infrared measurements given by Wincke et al. [2], are used as basic frequencies for the assignment of the observed and calculated spectrum. All calculations were performed by the method of

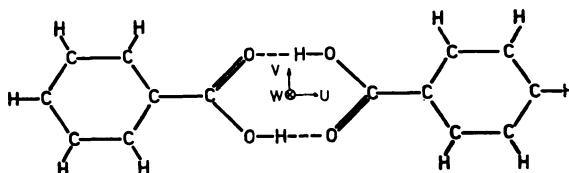


Fig. 2. Benzoic acid dimer

symmetry classes, since bands in single crystals are usually more intense and often narrower. Correlations between the molecular, site, and point group make it possible to separate by their symmetry classes, different normal modes, internal as well as external, in the crystal spectrum. This implies the knowledge of the crystal structure and relations between crystallographic and optical axes in the sample, since polarisation conditions require the latter to coincide with the incident and scattered beams.

In our investigations the interest was concentrated mostly on aromatic molecular crystals. Hydrogen bonds of the type $O \dots H-O$, $N \dots H-N$ and $O \dots H-N$ were considered in the lattice of benzoic acid, imidazole, 1-M-thymine and N-M-uracil crystals.

“rigid molecule” given by Shimanouchi et al. [3]. In the first approximation the dimer was considered to be a single unit of the crystal lattice, and therefore the hydrogen bond was supposed to be sufficiently strong to act as a covalent bond rather than as an intermolecular force. On the other hand, vibrations of the hydrogen bond itself were studied in a model used earlier [4] to investigate vibrations of the carboxylic ring in formic and acetic acids. In all these cases hydrogen bonds are strictly isolated from the rest of the lattice and represent a distinct vibrational system. The rest of the molecule was considered to be concentrated in the centre of gravity of each monomer and the carboxylic ring was treated as an isolated vibrational system with heavy masses at its ends. Such a system has two stretching, two in-plane bendings, and two out-of-plane bendings in its vibrational spectrum, which are characteristic of the O...H—N bond. Buckingham’s atom-atom potential function $V = -Ar^{-6} + B \exp(-\alpha r)$ was used for Van der Waals intermolecular interactions. The values for A , B and α constants were those given by Kitaigorodski et al. [5], who obtained them from thermodynamical and crystallographic measurements on organic crystal lattices. These functions are, therefore, more appropriate for such calculations than force constants parametrically determined from vibrational measurements [6]. The results of these calculations are listed in the first column of Table 1, while the observed spectrum is given in the third column. It is clear from the comparison of these values that our approximation was too simplified and that monomers are real repeat units in the crystal lattice. Consequently, the hydrogen bond should be treated as an intermolecular bond. However, the potential function describing the hydrogen bond had to be of the form described for the carboxylic ring.

The programme for these calculations was made by one of us (K.F.) and the calculations were performed on the computer CAE 90-40 using the FORTRAN II language. The results of these calculations are given in the second column of Table 1.

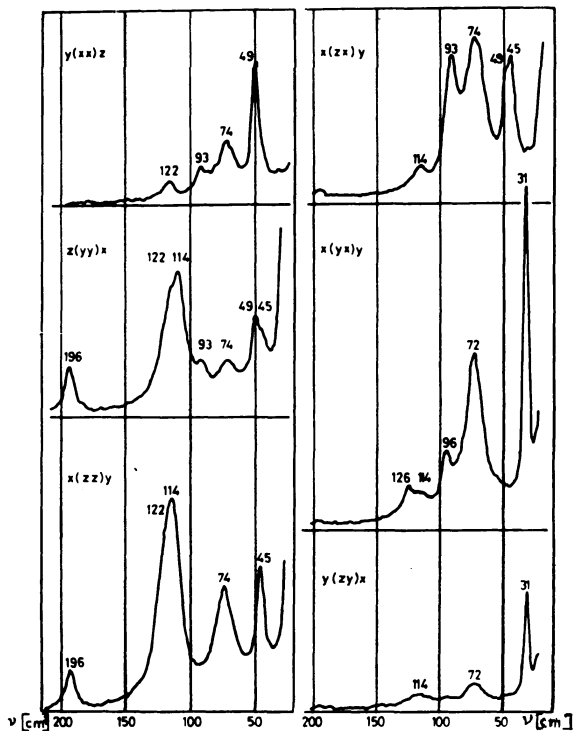
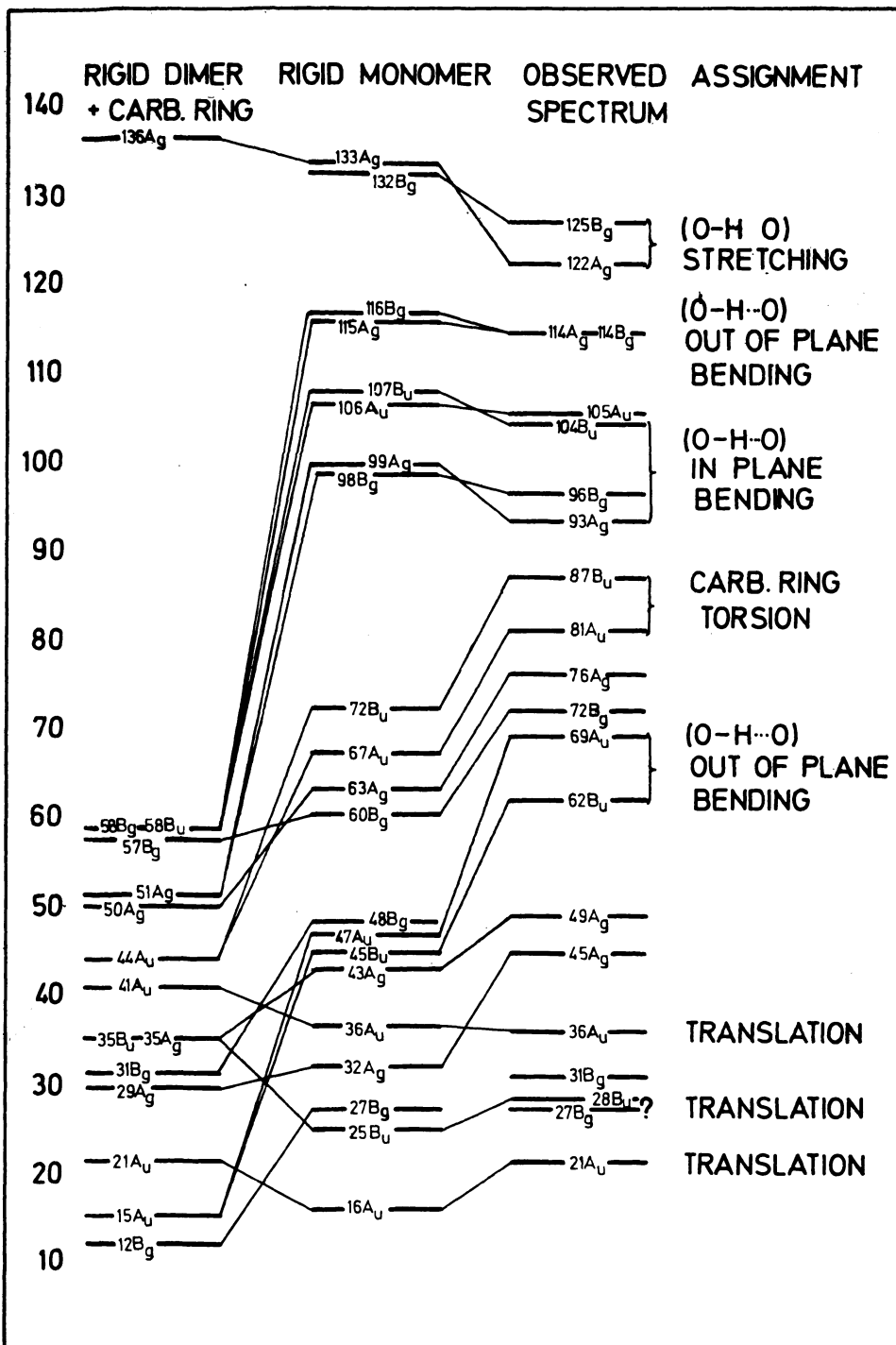


Fig. 3. Raman spectrum of benzoic acid single crystal

Table 1



The agreement between experimental and theoretical results is better in the upper than in the lower part of the spectrum. It should be emphasized that the translational modes, together with the stretching mode of the hydrogen bond are in good agreement even in the most simplified model. In fact, in pure translational modes, dimers move as a whole, while in the case of the stretching mode both monomers perform

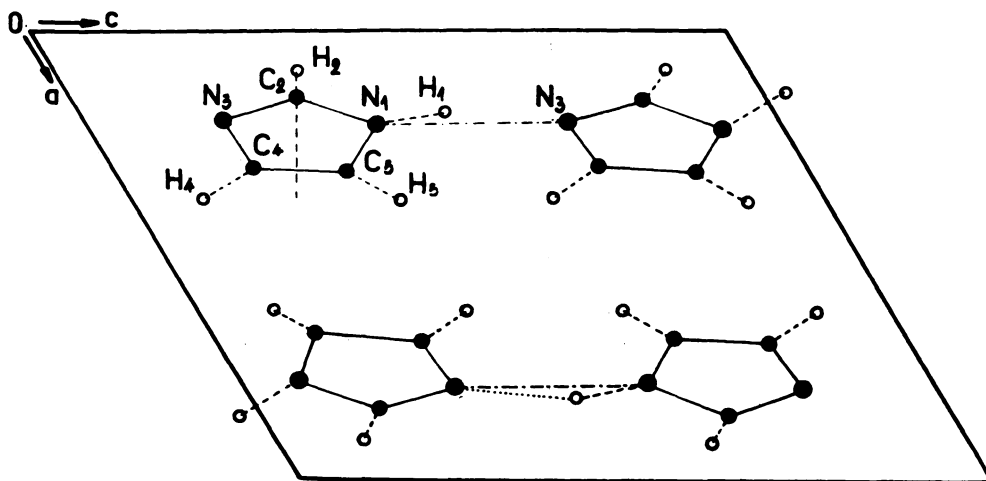


Fig. 4. Crystal structure of imidazole

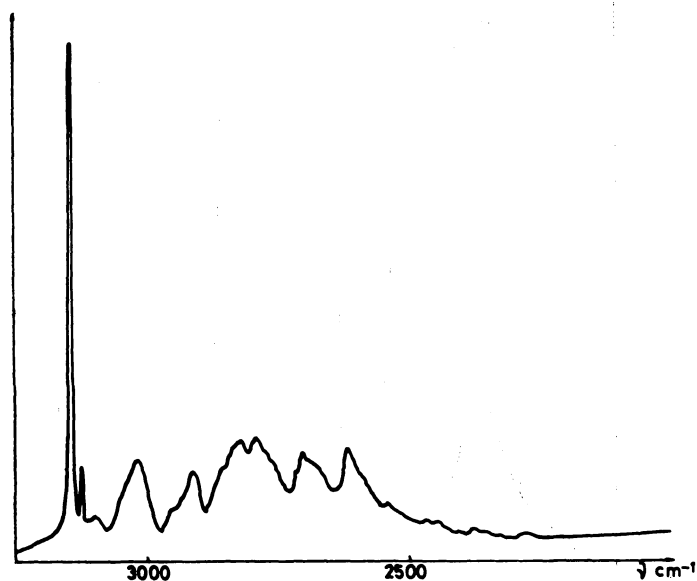
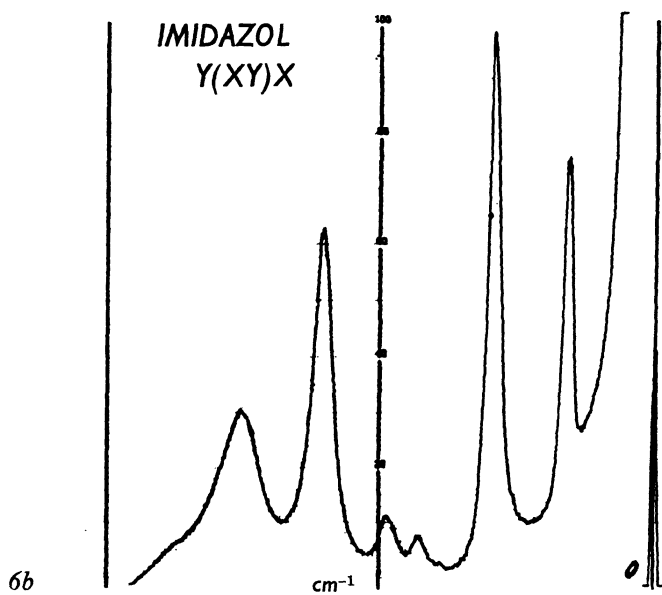
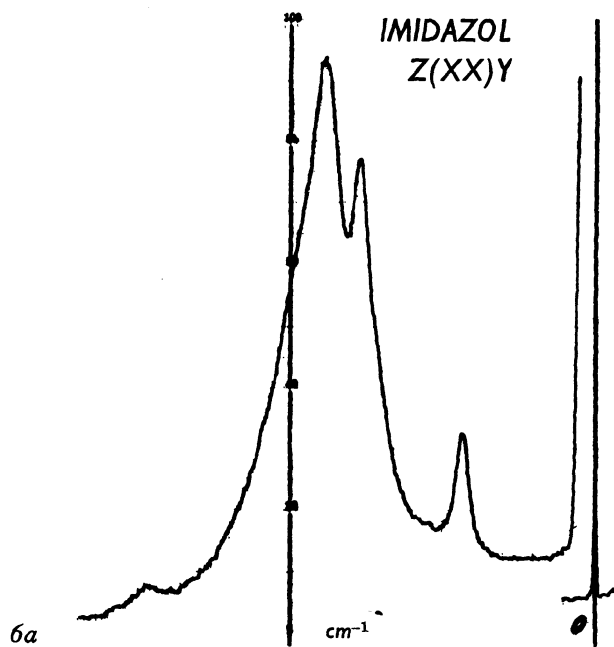


Fig. 5. Fine structure of the (N-H) band in the Raman spectrum of imidazole crystal



Figs. 6a, b. Some of the recorded low-frequency Raman spectra of imidazole single crystals

vibrations along their common axis. In all these vibrations monomers behave as rigid bodies. It is interesting to note that good agreement is also obtained for in-plane and out-of-plane bendings of the hydrogen bridge. One may conclude that also in these cases monomers perform vibrations as a whole. In contrast to this, in the case of torsional and asymmetric out-of-plane bending modes, coupling should occur between hydrogen bond vibrations and some internal modes of the molecule. This results in an increase in frequency of the transition. We may, therefore, conclude that in-plane and symmetric out-of-plane vibrations of the hydrogen bridge do not couple too strongly with internal molecular modes. This result was useful in spectroscopic investigations of similar compounds.

Imidazole also crystallises in the monoclinic system, point group C_{2h}^5 ($P2_1/C$), with four molecules in the unit cell [7]. Fig. 4 represents the structure of this crystal. Molecules are linked by hydrogen bonds of the type $N...H-N$ ($R = 2.86 \text{ \AA}$) forming infinite chains through the crystal. In the case of imidazole, hydrogen bridges are not isolated systems (as they are in the case of benzoic acids) and one should expect a stronger coupling of their vibrations to external as well as to internal vibrational modes of the crystal. The observed "fine structure" of the band $\nu(N-H)$ (Fig. 5) indicates such a coupling. Starting from the chain as a repeat unit, which is characteristic of this crystal structure, normal modes analysis gives the following vibrational spectrum:

$$\text{Lattice modes: } 3A_g + 3B_g + 2A_u + 1B_u$$

$$\text{Hydrogen bond vibrations: } 3A_g + 3B_g + 3A_u + 3B_u.$$

Some of the recorded low-frequency Raman spectra are given in figs. 6. Experimental data reproduce almost the whole spectrum that is predicted theoretically (one band is missing) with excellent polarisation ratios for all the bands. Because of the presumably strong coupling of hydrogen bond vibrations to other modes, the "rigid molecule" approximation could not be used in the case of imidazole. We, therefore, had to use a new programme which gives the possibility of indicating the degree of coupling for every mode. Such a programme was made in Dortmund (P.B.), where the calculations were performed. In this programme vibrational energies were calculated as a result of all atom-atom pair interactions in the unit cell and its nearest neighbours. The crystal is approximated by a system of molecules, a quasi macromolecules, in which all intra- and intermolecular forces are considered. It is evident that the number of bonds to be considered grows rapidly with the cut-off of the potential function and that rather large computers are needed. The same type of the potential function as in the case of benzoic acid, was used for Van der Waals interactions, while for hydrogen bond vibrations special constants were used only for stretching modes. All bending modes were described by internal coordinates of single molecules. Reasonably good agreement was obtained between the observed and calculated internal as well as external spectra. The potential energy distribution (PED) of normal modes ($\partial V/\partial q_i$) indicates couplings between external and internal

modes, especially in the region of out-of-plane bendings. The same feature is observed in most of the vibrations involving the hydrogen bond. However, for some of these, e.g. stretching modes are practically pure internal or external vibrations. Two examples of such vibrations are given in Fig. 7 as obtained from a plotter at the output of the computer. The first represents the stretching mode $\nu(N-H)$ at 2820 cm^{-1}

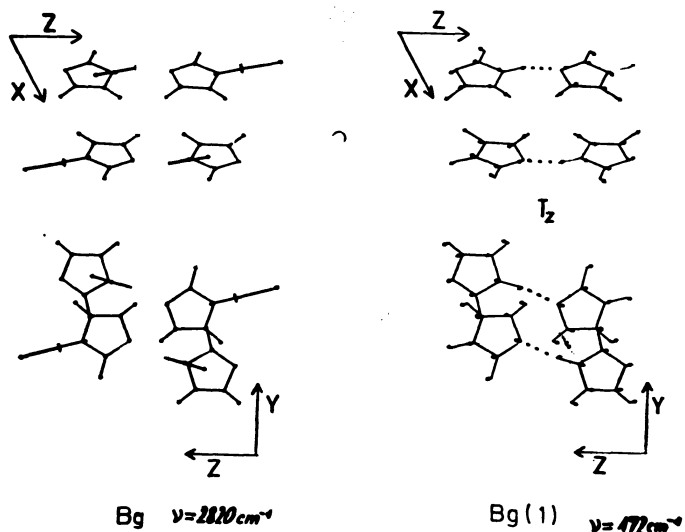
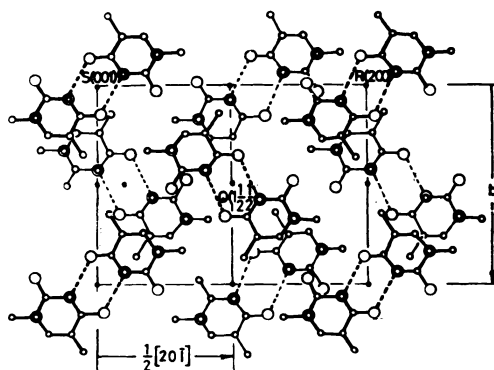


Fig. 7. Cartesian displacements for molecular $\nu(N-H)$ and hydrogen bond $\nu(N-H\dots N)$ stretching modes in imidazole



- Carbon
- Oxygen
- Nitrogen

Fig. 8. Crystal structure of *M*-thymine

and the second is a lattice vibration corresponding to pure hydrogen bond stretching in which molecules vibrate as rigid bodies along the hydrogen bridges.

The spectrum given in table II was obtained by taking into account only such normal modes which exhibit their PED mostly (more than 50%) in hydrogen bond vibrations. The assignment given in the last column comes from eigenvector components. The last two frequencies represent librational and torsional modes of the molecules around their inertial axis passing through the C₂—H₂ bonds, and strongly coupled to hydrogen bond vibrations.

Table 2.

$\nu(\text{cm}^{-1})$		Symmetry	Assignment
Observ.	Calc.		
179	240	A _u	$\nu(\text{N}\dots\text{H}-\text{N})$
172	247	B _g	
142	133	A _u	
114	124	B _g	i. p. bend.
88	107	A _g	o. p. bend.
—	189	B _u	
—	193	A _g	lib. (V)
114	107	B _u	torsion (V)

Recently we started studies on 1-M-thymine and N-M-uracil crystals and molecules as typical compounds of biological interest.*) The crystal structures of these compounds are given in Figs. 8 and 9, respectively. 1-M-thymine crystallises in the monoclinic system, point group C_{2h}⁵ (P2₁/c) [8] with four molecules in the unit cell. Crystals of N-M-uracil are orthorhombic with space group D_{2h}^{2g} (Ibam) [9] and eight molecules in the unit cell. As can be seen from Figs. 10 and 11, the structures of both molecules are similar. In addition, both compounds form dimers with hydrogen bonds of the type O...H—N, with R(N...O) = 2.83 Å. Single crystals were grown from solution and did not exceed dimensions of 1–3 mm. They could not, therefore, be oriented by optical methods, which are usually applied in other cases. Raman spectra of single crystals were recorded only for those orientations in which the transmitted laser beam conserved its complete linear polarisation. The same was required for scattered light. This requirement was relatively simple to fulfil for N-M-uracil, which is orthorhombic, but it caused difficulties in the case of 1-M-thymine, which is monoclinic. From the form of the intensity matrices we were able to determine the direction of the binary axis in both crystals. Some of the recorded Raman spectra of N-M-uracil single crystals are given in Figs. 12 and 13. The

*) The authors are indebted to Dr. J. N. Herak, who kindly supplied us with single crystal samples.

not have too much influence on transitions which are predominantly associated to hydrogen bond vibrations. Since these transitions are of the same type and strength in both lattices, they should correspond to the same frequencies in the observed spectra. On the other hand, we made correlations between the symmetry group of the dimer, which is C_{2h} for both molecules, with the site and factor group of each lattice.

In this manner we defined the symmetry classes of different hydrogen-bond vibrations in both lattices separately. Finally, taking the frequency distribution of hydrogen-bond vibrations in the carboxylic ring as starting values, we were able to give a tentative assignment (Table III) to the bands which might be taken as frequencies appropriate to vibrations of the $(O \dots H - N)$ bonds.

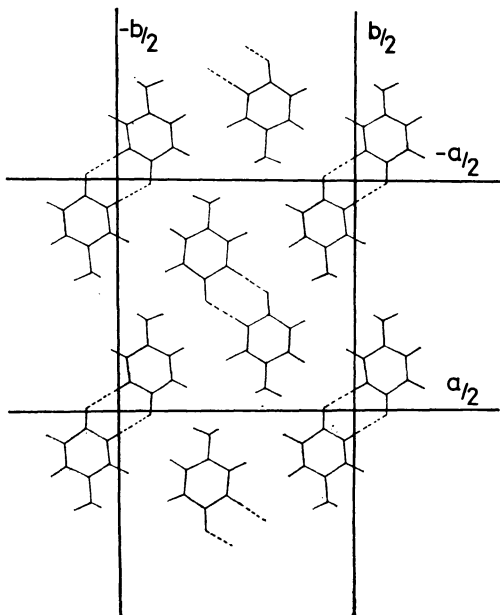


Fig. 9. Crystal structure of *N-M-uracil*

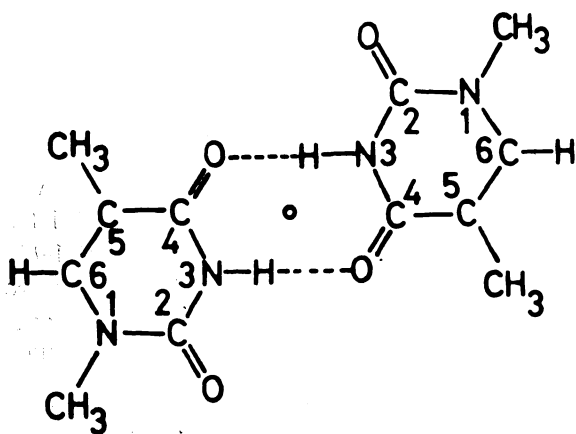


Fig. 10. Dimer of *M-thymine*

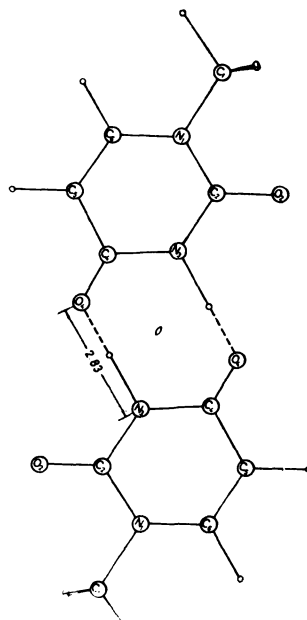


Fig. 11. Dimer of *N-M-uracil*

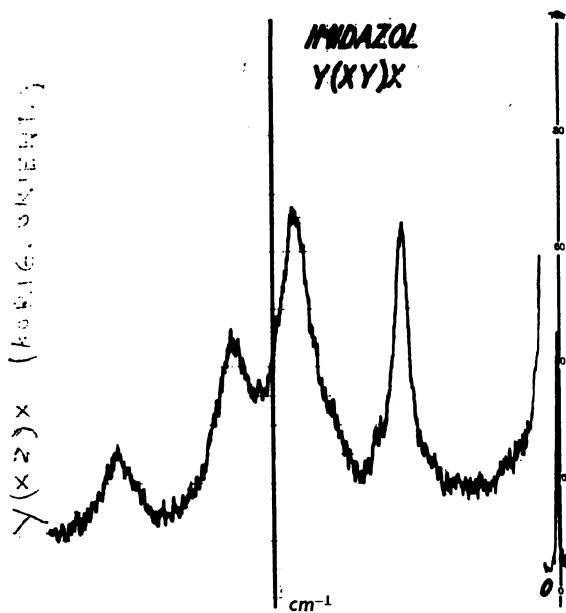


Fig. 12. Recorded Raman spectrum of *N-M-uracil* single crystals

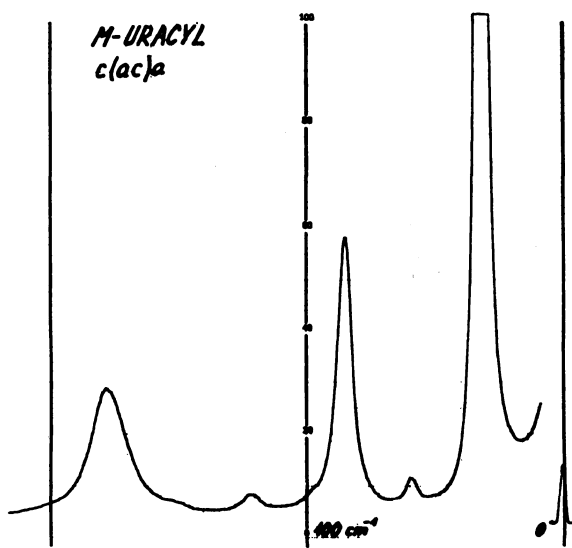


Fig. 13. Recorded Raman spectrum of *N-M-uracil* single crystals

Table 3

Carboxylic ring C_{2h}	M-Thymine (cryst.)		M-Uracil (cryst.)	
	C_{2h}	$\nu(\text{cm}^{-1})$	D_{2h}	$\nu(\text{cm}^{-1})$
$A_g = \nu_1$ str. (O...H-N)	$A_g + B_g$	138+140	$A_{1g} + B_{1g} + B_{2g} + B_{3g}$	150
$A_g = \nu_2$ } i.p. bend.	$A_g + B_g$	72+72	$A_{1g} + B_{1g} + B_{2g} + B_{3g}$	86
$B_u = \nu_3$ }	$A_u + B_u$	95	$A_{1u} + B_{1u} + B_{2u} + B_{3u}$	90
$A_u = \nu_4$ torsion	$A_u + B_u$	67	$A_{1u} + B_{1u} + B_{2u} + B_{3u}$	60
$A_u = \nu_5$ } o. p. bend.	$A_u + B_u$	80	$A_{1u} + B_{1u} + B_{2u} + B_{3u}$	80
$B_g = \nu_6$ }	$A_g + B_g$	104+107	$A_{1g} + B_{1g} + B_{2g} + B_{3g}$	121

interpretation of our spectra is based on the assumption that the crystal field does Calculations of these spectra are in progress in our laboratory, but it is already evident that this problem will present further difficulties due to the complexity of motions and the relatively large number of molecules in the unit cell, especially in the case of N-M-uracil.

In conclusion we should emphasise that the results obtained so far, even though very interesting and useful, indicate that intermolecular interactions in general, and especially in the case of the hydrogen bridge, should be studied theoretically and experimentally on a large number of lattices. It seems that only a comparative study would give a better understanding of intermolecular interactions, which is one of the fundamental questions in molecular physics.

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