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Structural and spectroscopic evidence of hydrogen bonding in 3-bromo-5-hydroxy-2,6-dimethylpyridine and 3-chloro-5-hydroxy-2,6-dimethylpyridine

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Abstract

The crystal structures of 3-chloro-5-hydroxy-2,6-dimethylpyridine (ClHDMP) and 3-bromo-5-hydroxy-2,6-dimethylpyridine (BrHDMP) were determined at room temperature. Although ClHDMP is monoclinic, space group $P2_1/c$, and BrHDMP is orthorhombic, space group $Pna2_1$, the molecular conformation is essentially the same in both compounds. The structure consists of two parallel infinite chains of formula units linked through hydrogen bonds of the type O–H···N. There is no interconnection between the chains.

Fourier transform IR and Raman spectra of ClHDMP and BrHDMP were measured in the 50–3500 cm^{-1} frequency range at room temperature. The vibrational assignment of the observed bands is proposed. The appearance of the characteristic vibrational features in the spectra of these compounds is discussed in terms of strong asymmetric hydrogen bonding. The bands observed at approximately 2800–2850, 2500–2550 and 1800–1850 cm^{-1} are assigned to the O–H stretching modes and those at 1400–1410 and 900–950 cm^{-1} to δ(O–H) and γ(O–H) modes, respectively. The ν(O–H) vibrations of the hydrogen bonds appear at 130–140 cm^{-1}. The calculation of γ(O–H) frequencies and other parameters describing the strong hydrogen bonding, such as the Fermi coupling constant $|W|$, the separation of the unperturbed vibrational levels (Δ_0), etc., has been performed. The positions of γ(O–H) bands have been found to agree with those predicted from the perturbed ν(O–H) patterns. Comparison of the structural and vibrational characteristics of hydrogen bonds in ClHDMP and BrHDMP has indicated that a stronger hydrogen bonding exists in the bromo-derivative. © 1997 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen bonding; X-ray crystallography; 3-halo-5-hydroxy-2,6-dimethylpyridine; Vibrational spectroscopy

1. Introduction

The vibrational spectra of 2,6-dimethylpyridine have been studied previously by several authors [1–4]. The complete assignment of all vibrational modes based on Raman and IR spectra has been made by Green et al. [5] and Draeger [6]. No vibrational studies concerning 2,6-dimethylpyridine hydroxy- and halo-derivatives have been reported to our knowledge. However, a few investigations have been made concerning the vibrational spectra of halo- and hydroxy-substituted pyridines [7–9].

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Some vibrational modes were shown to be substituent-sensitive, whereas others were observed in a narrow frequency range for all pyridine derivatives.

A considerable effort has been made to study the shape of IR hydrogen stretching bands of hydrogen bonded systems. As the strength of hydrogen bonding increases in an X–H···Y system, the ν_{OH} infrared band moves towards lower frequencies, becomes greatly enhanced (in integrated intensity), and broadens. A very strong symmetrical hydrogen bonding can lead to broad and strong bands centred approximately in the region 1000–800 cm^{-1} [10,11]. When a strong asymmetric hydrogen bond is created, an IR spectrum

Table 1
Crystal data, details of data collection and structure refinement

Crystal data:		
Chemical formula	C_7H_8 NOBr	C_7H_8NOCl
Molecular weight	202.1	157.6
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$
a/Å	11.090(2)	4.914(2)
b/Å	14.852(3)	13.086(3)
c/Å	4.787(1)	11.411(1)
β/°		93.23(2)
V/Å^3	788.5(6)	732.6(6)
Z	4	4
Radiation wavelength (Å)	Mo Kα, 0.71073	Cu Kα, 1.5418
No. of reflections for cell parameters	32	23
θ range for cell parameters/°	10, 15	15, 35
μ/mm^{-1}	5.093	4.085
Temperature/K	296	294
Crystal color and form	Colourless, plate	
Crystal size/mm	0.12 × 0.2 × 0.4	0.15 × 0.2 × 0.35
D_c/Mgm^{-1}	1.702(1)	1.429(1)
Data collection:		
Diffractometer	Kuma KM-4	
Absorption correction	Empirical on ψ-scan	
No. of measured reflections	3467	2027
No. of independent reflections	1629	1014
No. of observed reflections	777	652
Observation criterion	$F > 4\sigma(F_o)$	
R_{int}/%	2.8	2.5
θ_{max}/°	68	60
Index range	h: 0,20	h: -5,0
	k: −22,0	k: −15,15
	l: −8,6	l: −13,13
Standard reflections	2, measured every 50 reflections	
Intensity variation/%	1.7	1.35
Refinement:		
Refinement on	F	
Quantity minimized	$\sum w(F_o-F_c)^2$	
Final R and wR factors	0.044 and 0.044	0.068 and 0.088
Weighting	$w = 1/[\sigma^2(F_o) + 0.0017F^2]$	
Goodness-of fit	1.29	1.83
No. of refined parameters	96	100
H-atoms	From geometry, U_{iso} refined	
$(\Delta/\sigma)_{max}$	0.011	0.524, 0.031 for U of H-atoms
$\Delta\rho_{min}$, $\Delta\rho_{max}$	−0.75, 0.85	−0.00, 0.69

has multiple, broad maxima associated with the ν_{OH} region (A-, B- and C-type bands), usually between 2700 and 1600 cm^{-1} [10–13]. Claydon et al. postulated that the A-, B-, C-type spectra are the result of strong Fermi resonance of ν_{OH} with $2\delta_{OH}$ and $2\gamma_{OH}$ [14]. Later studies suggested that the origin of this feature comes from the strong anharmonic coupling between the high-frequency ν(XH) mode and the low-frequency mode of the hydrogen bond (ν(X–H$\cdots$Y)) [15–17]. In recent theoretical work on profiles of hydrogen stretching infrared bands, an attempt was made to explain the phenomena on the basis of the strong anharmonic coupling between the high-frequency ν_{XH} and low-frequency lattice phonons [18].

2. Experimental

2.1. Preparation

In order to obtain 3-chloro- and 3-bromo-5-hydroxy-2,6-dimethylpyridines, a mixture of 10 g of 3-chloro- or 3-bromo-2,6-dimethylpyridine with 50 cm^3 of acetic anhydride was refluxed in a round-bottomed flask on a hot-plate at 120°C for 3 h. The reaction products were distilled under reduced pressure and the fractions 100–130°C/10 mmHg in the case of the chloro-derivative, and 126–140°C/7 mmHg for the bromoderivative, were collected. Each of the obtained fractions was dissolved in 3% hydrochloric acid and the reaction mixtures were kept at 60°C for 4 h, and then for 24 h at room temperature. Then they were carefully neutralized with a 10% NaOH solution to pH 6.5–7 (prior to neutralization, a few drops of chloroform were added). The reaction mixtures contained two products: 3-chloro- or 3-bromo-2-methyl-6-pyridylmethanol and 3-chloro- or 3-bromo-5-hydroxy-2,6-dimethylpyridine. The pyridylmethanols were extracted from the mixtures with chloroform and to the remaining solutions more 10% NaOH solution was added, until the products precipitated in the form of colorless crystals. The products were then filtered off and recrystallized from a mixture of water and ethanol.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å^2 $\times 10^3$) for 3-bromo-5-hydroxy-2,6-dimethylpyridine

	x	*y*	*z*	*U*(eq)^a
Br	1123	475	0	54(1)
C(1)	1733(9)	1304(7)	-2661(19)	34(3)
C(2)	947(8)	1912(8)	-3783(20)	38(3)
C(3)	1364(7)	2524(8)	-5697(17)	35(4)
C(4)	2582(8)	2488(7)	-6428(19)	32(3)
C(5)	2937(8)	1286(7)	-3458(21)	37(4)
C(6)	3830(9)	652(8)	-2291(27)	59(4)
C(7)	3048(9)	3149(8)	-8539(21)	44(4)
N	3297(6)	1901(5)	-5396(24)	32(3)
O	659(6)	3160(5)	-6957(15)	51(3)

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å^2 $\times 10^3$) for 3-chloro-5-hydroxy-2,6-dimethylpyridine

	x	*y*	*z*	*U*(eq)^a
Cl	2809(4)	4602(2)	6087(2)	57(1)
C(1)	5354(13)	3759(5)	6574(6)	37(2)
C(2)	6523(14)	3126(5)	5771(6)	38(2)
C(3)	8505(15)	2446(6)	6178(6)	42(2)
C(4)	9248(15)	2417(6)	7358(6)	38(2)
C(5)	6154(15)	3716(6)	7742(6)	40(3)
C(6)	5018(19)	4376(7)	8691(8)	63(3)
C(7)	11345(16)	1690(6)	7834(7)	54(3)
N	8064(13)	3030(5)	8119(5)	41(2)
O	9850(11)	1823(4)	5442(4)	55(2)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.2. X-ray diffraction

Weissenberg photographs indicated the orthorhombic space group Pna2$_1$ for BrHDMP. The systematic extinctions were: 0kl, k + l = 2*n* + 1 and h0l, h = 2*n* + 1. Crystal data and experimental details are given in Table 1. The empirical absorption correction was applied (for lamina) using the SHELXTL PC package [19]. The Br-atom coordinates were found from the Patterson map, and the remaining atoms were located in the successive structure factor-Fourier calculations. The structure was refined using the full-matrix, least-squares method (on F_0). The H-atoms were placed at the idealized positions. The hydrogen positional parameters were not refined but were adjusted in the last cycles of the refinement. The atomic scattering factors for neutral atoms and the corrections for anomalous dispersion were used as in the SHELXTL PC program system [19], which was also used for all the structure calculations and the structure drawings (on an IBM PC computer).

Investigations of several samples of 3-chloro-5-hydroxy-2,6-dimethylpyridine indicated that the crystal exhibits pseudo-orthorhombic symmetry owing to the growth twinning. The pseudo-symmetry results from a superposition of two monoclinic cells (space group P2$_1$/c). The two twin individuals are related by the transformation matrix [-1 0 0 0 -1 0 0 0 1]. The diffraction intensities were collected using two separate crystal orientation matrices, which allowed the reflections from the given individual to be measured. Nonetheless, about 20% of the intensity data consisted of superimposed reflections. Overlapping has been observed for the reflections with h = 4*n* and 0kl. The total intensity from these reflections is $I_T = I_A + kI_B$, where A and B denote the twin components and *k* is a scaling factor related to the twin volume fractions; $V_A/V_B \approx 0.65/0.35$. The *k* factor has been calculated from the intensity ratio I_A/I_B of the overlapping-free reflections. The data set of the intensities from the stronger individual was corrected, and then taken to the structural refinement. The H-atoms were positioned on geometric grounds; they were included in the structure factor calculations with only U_{iso} varied. Conventional full-matrix, least-square refinement of the atomic positional and thermal parameters along with isotropic extinction and absorption factors gave R = 6.86% and wR = 8.79%. Somewhat higher values of the discrepancy factors, as compared to those obtained in the case of BrHDMP, are probably caused by an incomplete compensation of the twinning effect. This problem will be the subject of further considerations.

2.3. Raman and IR measurements

Infrared spectra in the 450–3500 cm^{-1} frequency range were recorded from a KBr pellet with a Perkin Elmer 2000 FT-IR spectrometer. Far-infrared spectra in the range 50–600 cm^{-1} were measured in nujol

Table 3
Selected bond distances (Å) with estimated standard deviations in parentheses for 3-bromo- and 3-chloro-5-hydroxy-2,6-dimethylpyridine (BrHDMP and ClHDMP)

	BrHDMP	ClHDMP		BrHDMP	ClHDMP
C(1)Br or Cl	1.897(10)	1.735(7)	O–H(1)	0.740(6)	0.869(5)
C(1)–C(2)	1.365(14)	1.384(10)	C(2)–H(2)	0.987(9)	0.971(8)
C(1)–C(5)	1.389(13)	1.369(10)	C(6)–H(61)	1.005(11)	0.981(9)
C(2)–C(3)	1.372(15)	1.380(10)	C(6)–H(62)	1.175(13)	0.959(9)
C(3)–C(4)	1.397(12)	1.376(09)	C(6)–H(63)	0.979(11)	0.946(9)
C(3)–O	1.367(13)	1.367(09)	C(7)–H(71)	0.980(10)	0.967(8)
C(4)–C(7)	1.500(14)	1.482(11)	C(7)–H(72)	0.993(10)	0.959(8)
C(4)–N	1.278(13)	1.340(09)	C(7)–H(73)	0.975(11)	0.978(8)
C(5)–C(6)	1.477(15)	1.516(12)			
C(5)–N	1.361(14)	1.351(09)			

Hydrogen bond contacts for BrHDMP: O–H(1)$\cdots$N$_{\mathrm{I}}$, 2.726(9) Å; N$_{\mathrm{I}}$$\cdots$H(1), 1.978(7) Å; O–H(1)$\cdots$N$_{\mathrm{I}}$ bond angle, 175.1(6)°; C(4)$\cdots$H(1)$_{\mathrm{II}}$, 2.855(9) Å; C(5)$\cdots$H(1)$_{\mathrm{II}}$, 2.874(10) Å; O$\cdots$H(1)$_{\mathrm{I}}$, 2.665(7) Å. Symmetry code: i, *x* – 1/2, 1/2 – *y*, *z*; ii, 1/2 + *x*, 1/2 – *y*, *z*.

Hydrogen bond contacts for ClHDMP: O–H$\cdots$N$_i$, 2.752(7) Å; N$\cdots$H(1), 1.890(6) Å; O–H(1)$\cdots$N bond angle, 171.4(4)°; C(6)–H(61)$\cdots$O$_i$ 3.404(10) Å; O$_i$$\cdots$H(61) 2.555(5) Å; C(61)–H(61)$\cdots$O$_i$ angle, 144.4(6). Symmetry code: i, *x*, 1/2 – *y*, 1/2 + *z*.

suspensions. Raman spectra were recorded in a backscattering configuration with a Perkin Elmer 2000 FT-IR spectrometer equipped with a Raman module. As an excitation source, the 1064 nm line of a YAG:Nd^{3+} laser was used. The output power was 100 mW and spectral resolution was 4 cm^{-1}. An InGaAs detector operated at liquid nitrogen temperature was used.

3. Crystal structure determination

The final atomic coordinates for the non-hydrogen atoms and the equivalent isotropic thermal parameters are listed in Table 2 for BrHDMP and ClHDMP. Some selected interatomic distances and angles are given in Table 3 and Table 4. The conformation of the BrHDMP molecule is shown in Fig. 1 and that of the ClHDMP molecule in Fig. 2. The dimensions of the pyridine ring and the C–O bond lengths found here correspond well to data available from the Cambridge Structural Database. The equations of the least-squares plane through the molecule and the distances from this plane are given in Table 5 and Table 6, respectively. The two methyl groups carbons C(6) and C(7) are almost coplanar with the ring-forming atoms.

Table 4
Bond angles (°) with estimated standard deviations in parentheses for 3-bromo- and 3-chloro-5-hydroxy-2,6-dimethylpyridine

	BrHDMP	ClHDMP
C(2)–C(1)–Br or Cl	117.8(7)	119.1(5)
C(2)–C(1)–C(5)	121.2(9)	120.9(6)
C(5)–C(1)–Br or Cl	121.0(8)	120.0(8)
C(1)–C(2)–C(3)	119.1(8)	118.3(6)
C(2)–C(3)–O	124.1(7)	122.3(6)
C(2)–C(3)–C(4)	117.9(9)	119.4(7)
C(4)–C(3)–O	118.0(9)	118.3(7)
C(3)–C(4)–N	122.0(9)	121.1(6)
C(3)–C(4)–C(7)	118.4(9)	121.1(7)
C(7)–C(4)–N	119.6(8)	117.7(6)
C(1)–C(5)–N	117.1(9)	119.6(6)
C(1)–C(5)–C(6)	123.6(9)	125.1(7)
C(6)–C(5)–N	119.3(8)	115.3(6)
C(4)–N(1)–C(5)	122.6(8)	120.8(6)
C(1)–C(2)–H(2)	120.0(10)	120.2(7)
C(3)–C(2)–H(2)	120.9(10)	121.5(7)
H(61)–C(6)–H(62)	107.7(10)	107.8(9)
H(61)–C(6)–H(63)	108.2(11)	108.9(9)
H(62)–C(6)–H(63)	103.2(10)	110.7(9)
H(61)–C(6)–C(5)	109.3(10)	109.0(8)
H(62)–C(6)–C(5)	117.6(9)	109.4(8)
H(63)–C(6)–C(5)	110.5(10)	110.9(8)
H(71)–C(7)–H(72)	108.9(9)	108.9(8)
H(71)–C(7)–H(73)	108.0(10)	107.2(8)
H(72)–C(7)–H(73)	105.6(10)	107.9(8)
H(71)–C(7)–C(4)	110.5(9)	111.0(7)
H(72)–C(7)–C(4)	111.2(9)	111.4(7)
H(73)–C(7)–C(4)	112.3(9)	110.2(7)

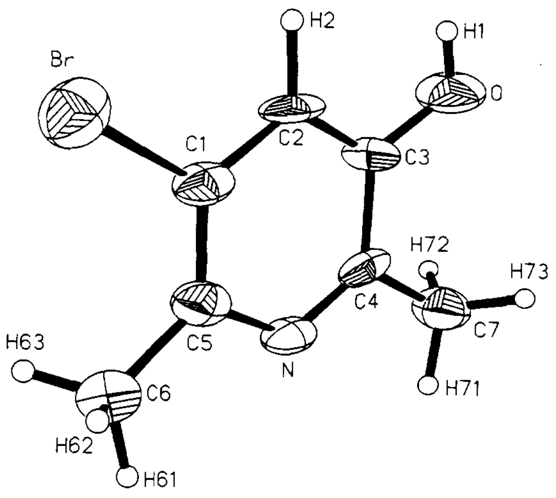

Fig. 1. Molecular structure of 3-bromo-5-hydroxy-2,6-dimethylpyridine showing the numbering of the atoms. Thermal ellipsoids are drawn at the 50% probablity level.

The crystal structure arrangements are shown in Fig. 3 and Fig. 4. The asymmetric unit consists of one formula unit. The strongest intermolecular hydrogen bonding contact $(O–H\cdots N_{1/2-x,\ 1/2+y,\ z})$ for

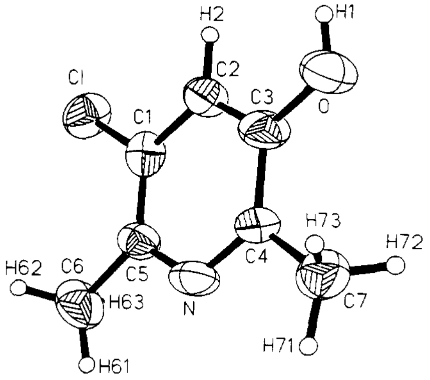

Fig. 2. Molecular structure of 3-chloro-5-hydroxy-2,6-dimethylpyridine showing the numbering of the atoms. Thermal ellipsoids are drawn at the 50% probablity level.

Table 5
Deviations of atoms from the least-squares plane through the pyridinium molecule for the BrHDMP crystal

Atom	Deviations/Å	Atom	Deviation/Å
Br	-0.0126	O	0.0240
C(1)	-0.0068	H(1)	-0.0008
C(2)	0.0026	H(2)	0.0089
C(3)	0.0169	H(61)	-0.0289
C(4)	0.0078	H(62)	-0.8635
C(5)	-0.0245	H(63)	-0.8145
C(6)	-0.0183	H(71)	0.0161
C(7)	0.0113	H(72)	-0.7827
N	-0.0291	H(73)	0.7849

The equation of the plane in crystal coordinates is: $2.318x + 9.621y - 3.509z = 0.729$.

Table 6
Deviations of atoms from the least-squares plane through the pyridinium molecule for the ClHDMP crystal

Atom	DeviationsÅ	Atom	Deviation/Å
Cl	-0.0406	O	0.0527
C(1)	-0.0057	H(1)	0.0527
C(2)	-0.0052	H(2)	-0.0291
C(3)	-0.0048	H(61)	0.0148
C(4)	-0.0072	H(62)	0.8090
C(5)	0.0020	H(63)	-0.7585
C(6)	0.0086	H(71)	-0.0009
C(7)	-0.0223	H(72)	-0.7982
N	-0.0219	H(73)	0.7694

The equation of the plane in crystal coordinates is: $3.503x + 9.005y - 2.003z = 3.9487$.

BrDMHP has a length of 2.726(9) Å, with the O–H···N angle equal to 175.1(6)°. It seems that the intermolecular contacts of C–H···N type are weak due to the thermal excitations of the methyl groups. The molecular conformation for the ClHDMP crystal is essentially the same as that found for BrHDMP. However, the crystal structure packing exhibits a monoclinic deformation. Apart from the intermolecular hydrogen bond of O–H···N type, persisting in both structures and which appears to be a little longer (2.752 Å) than in BrHDMP (2.726 Å), another weak hydrogen bonding contact, namely, C(6)–H(61)···O of length 3.40(4) Å can be observed. The O-atom thus may act simultaneously as a donor and acceptor. In this way the molecules form chains running along the z-axis (Table 7). Interchain distances shorter than Van der Waals contacts are not observed.

4. Vibrational characteristics

BrHDMP crystallizes in the $Pna2_1$ structure with

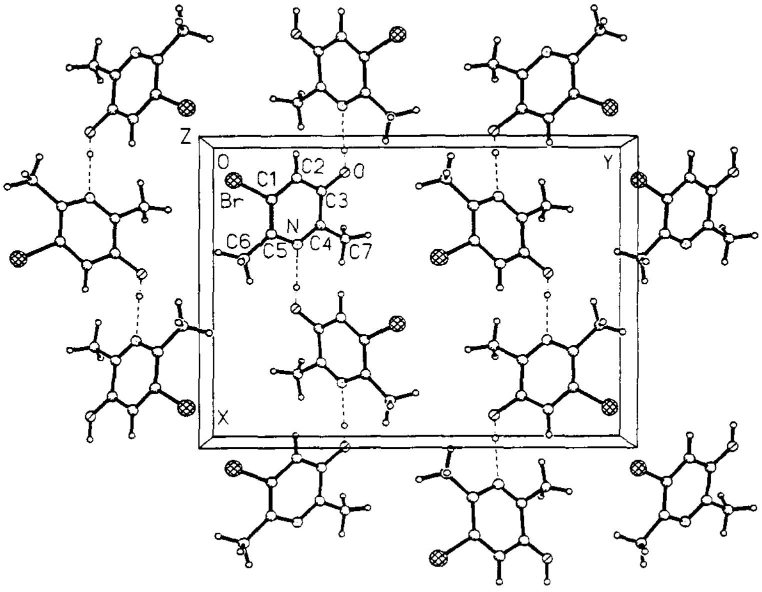

Fig. 3. Perspective view of the BrHDMP crystal structure.

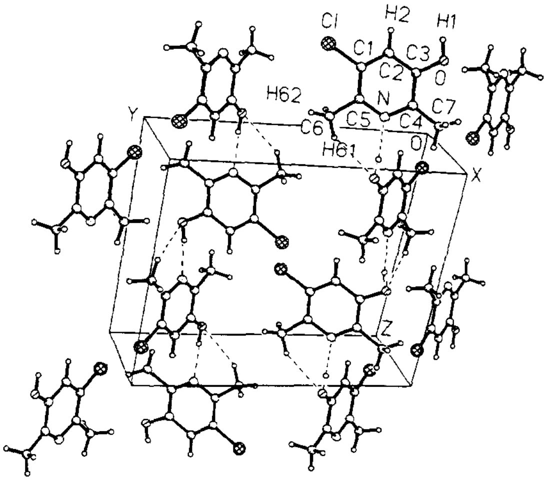

Fig. 4. Perspective view of the ClHDMP crystal structure.

four molecules in the unit cell, and ClHDMP in the $P2_1/c$ monoclinic structure with four molecules in the unit cell. The results of a Factor Group Analysis (FGA) are presented in Table 8 and Table 9, for BrHDMP and ClHDMP, respectively. The recorded Raman and IR spectra are presented in Fig. 5 and Fig. 6.

The powder IR and Raman spectra consist of fewer bands than expected because no Factor Group splitting is observed. Therefore, it is convenient to take into consideration all the vibrations of a single molecule. There are 48 internal modes for a free molecule, consisting of 18 atoms. All the observed bands and the assignment proposed (in Wilson notation [20]) are listed in Table 10. The assignment of the majority of the ring stretching and bending vibrational modes is straightforward and therefore will not be discussed here. These modes were observed in a narrow frequency range for all pyridine derivatives. In this paper we will focus on the vibrational modes which are strongly substituent-dependent and therefore can be observed in a wide frequency range. It is difficult to distinguish the ν(C–O), in-plane ring bending ν_{12} and the H–O–C bending. The ν_{12} vibration was observed at 1271 cm^{-1} for 2,6-dimethylpyridine [5], 1133 cm^{-1} for 2,6-dichloropyridine [8] and at 1025 cm^{-1} for pyridine N-oxide [21]. The above examples show that this vibration is sensitive to the electronegative substituent, with the highest value for 2,6-dimethylpyridine. Therefore, we expect this vibration to be observed for ClHDMP and BrHDMP below 1270 cm^{-1}. Bearing in mind that Person et al. observed the H–O–C bending vibration for 3-hydroxypyridine at 1195 cm^{-1} [9], we assign the strong and medium intensity IR bands at 1295 cm^{-1} to ν(C–O) and the remaining two strong infrared bands at 1244–1246 and 1217–1214 cm^{-1} to ν_{12} and the H–O–C bending modes, respectively. In the 800–900 cm^{-1} frequency range, one strong infra-red singlet, one strong infra-red doublet, and only one weak Raman band with a shoulder are observed. Former studies on 3-methyl-4-nitropyridine N-oxide [22] and 2,6-dimethylpyridine crystals [4,5] have shown that in this region strong IR bands due to the out-of-plane C–H deformational and pyridine-ring–methyl-group stretching modes were observed. However, the γ(C–H) modes were observed as very

Table 7
H-atom coordinates (× 10^4) and isotropic displacement coefficients (Å^2 × 10^3) for 3-chloro-5-hydroxy-2,6-dimethylpyridine

	x	*y*	*z*	*U*
H(1)	9164	1915	4732	63(13)
H(2)	5914	3153	4947	37(12)
H(61)	5931	4197	9449	116(14)
H(62)	5405	5080	8537	132(15)
H(63)	3121	4271	8732	89(14)
H(71)	11665	1776	8672	85(14)
H(72)	10824	996	7673	67(13)
H(73)	13078	1816	7478	108(14)

Table 8
Factor group analysis for the 3-bromo-5-hydroxy-2,6-dimethylpyridine crystal

C_{2v}	*n(N)*	*n(T)*	*n(T′)*	*n(L)*	*n*(int)	IR	Raman
A_1	54	1	2	3	48	*z*	*xx,yy,zz*
A_2	54	0	3	3	48	–	*xy*
B_1	54	1	2	3	48	*x*	*xz*
B_2	54	1	2	3	48	*y*	*yz*

Table 9
Factor group analysis for the 3-chloro-5-hydroxy-2,6-dimethylpyridine crystal

C_{2h}	*n(N)*	*n(T)*	*n(T′)*	*n(L)*	*n*(int)	IR	Raman
A_g	54	0	3	3	48	–	*xx,yy,zz,xz*
B_g	54	0	3	3	48	–	*xy,yz*
A_u	54	1	2	3	48	*y*	–
B_u	54	2	1	3	48	*x,y*	–

weak Raman bands, whereas $\nu(C-CH_3)$ were observed as weak to medium intensity ones. Therefore, we assign the strong IR bands at 880–877 cm^{-1} to the $\gamma(C-H)$ mode and those at 817–805 to the ring–CH_3 stretch. The ring–halogen stretching and bending modes were located in the 200–400 cm^{-1} frequency range. In the earlier vibrational studies of 2,6-dichloro-, 2,6-dibromo-, 3,5-dichloro-, and 3,5-dibromopyridines [8], 4-chloropyridine N-oxide [23] and 3-bromo-, 3-chloropyridines [7], the ring–halogen stretching modes were observed as strong Raman and weak to medium IR bands at 428–384 and 319–275 cm^{-1} range for chlorine and bromine, respectively. The bending modes were located at 280–294 cm^{-1} for chloro- and 200–250 cm^{-1} for bromo-derivatives. In recent studies, a band at 398 cm^{-1} is assigned to $\nu(C-Cl)$, 272 cm^{-1} to $\delta(C-Cl)$ and 267–261 cm^{-1} to $\nu(C-Br)$. The latter band is split into two components. However, in the crystal structure of BrHDMP all bromine atoms are crystallographically equivalent and only one $\nu(C-Br)$ band is expected. The observed splitting may be due to the O–H torsional mode, observed as a very strong IR band at 267 cm^{-1} for 3-hydroxypyridine [9]. The bands below 200 cm^{-1} originate from the translational and librational modes [22].

Strong intermolecular hydrogen bonding exists in the ClHDMP and BrHDMP crystals (see Table 3). A coupling of the $\nu(O-H)$ modes in the O–H···N hydrogen bonds with other fundamental vibrations,

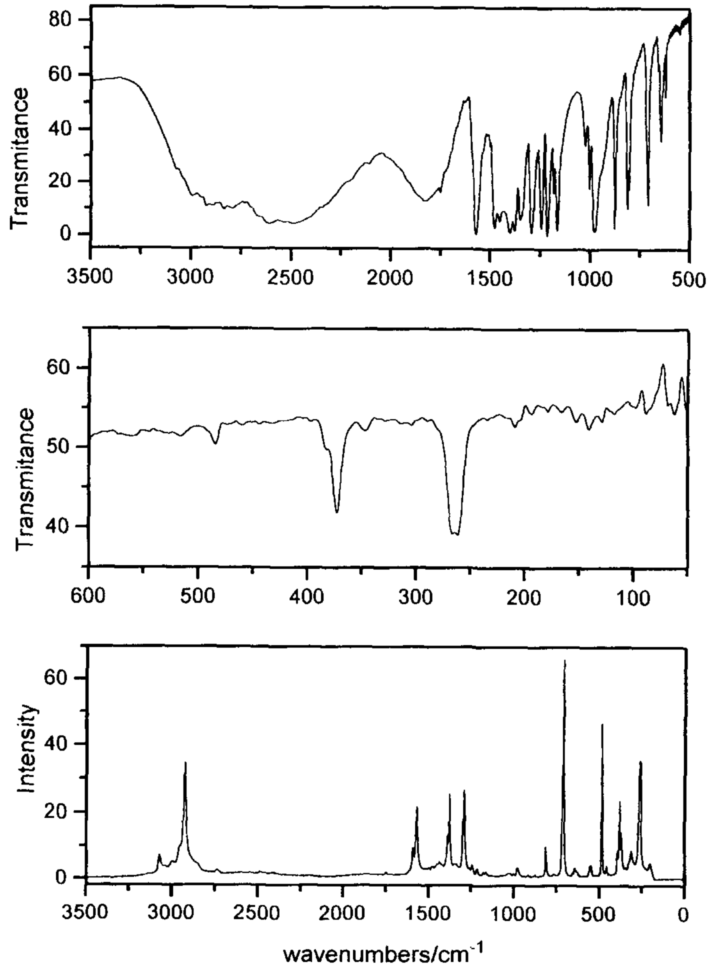

Fig. 5. IR and Raman spectra of polycrystalline BrHDMP.

overtones and combination vibrations is a basic problem of the vibrational theory of H-bonded systems. According to the theory of Bratos and Hadzi [24], the potential function defining the ν(O–H···N) vibrations is strongly anharmonic. The additional structure of the broad ν(O–H···N) absorption bands can be interpreted in terms of coupling with overtones and combination vibrations corresponding to other fragments of the molecule. The strong coupling with the low frequency bridge modes can destroy the fine structure of this band. They are the main factor governing the broadening mechanism. The coupling of the ν(O–H···N) transitions with the overtones of δ(O–H···N) and γ(O–H···N) modes creates the broad maxima or minima on the envelope of the ν(O–H···N) continuum, giving Hadzi's ABC trio [10,14,25].

The compounds studied in the present work exhibit coupling of the ν(O–H···N) modes with the δ(O–H···N) and γ(O–H···N) overtones. These compounds are very good materials from this point of view because (i) the fundamental ν(O–H···N) band of relatively high intensity is located in a region convenient for analysis and (ii) good quality single crystals can be obtained. Their structural properties (obtained from X-ray studies) can be compared to the spectroscopic results. Some interesting information can be obtained by comparison of our results with

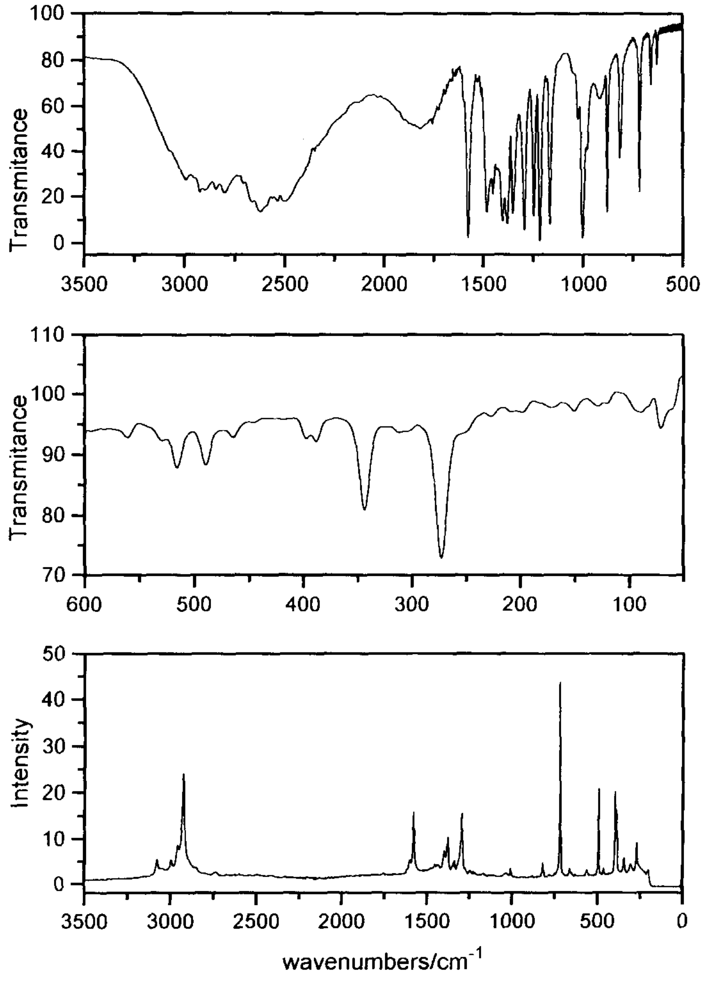

Fig. 6. IR and Raman spectra of polycrystalline ClHDMP.

those obtained by Grech et al. [26]. The studies of several imidazole derivatives showed that when a stronger hydrogen bond is created, a marked approaching of the ν(NH···N) and 2γ(NH···N) bands and a strong intensity increase of the latter take place [26]. Similar behaviour has been observed in the present studies. Because of the appearance of the strong hydrogen bonding in the compounds studied, the maxima of the ν(O–H···N) and 2γ(O–H···N) bands shift towards each other and a strong intensification of the latter was observed. It is known for weaker hydrogen bonds, when the distance between the positions of 2γ(O–H···N) and ν(O–H···N) is large enough, that the anharmonicity of the γ(OH···N) vibrations (expressed by the value of $2\nu_{01} - \nu_{02}$) increases with the increase of the hydrogen bond strength [26]. For stronger hydrogen bonds appearing in the compounds studied, the position of the overtone peak approaches the maximum of the ν(O–H···N) band. The overtone 2γ and the γ(O–H···N) bands show fine structure arising from the coupling of the γ and ν modes with the internal vibrations of the pyridine ring. Table 11 compiles all the data concerning structural and vibrational characteristics of the hydrogen bonds in ClHDMP and BrHDMP. The parameters Δ, Δ_o, R and $|W|$ (defined by Odinokov and Iogansen [27]) are the observed splitting (Δ), the intensity ratio (R), the separation of the unperturbed vibrational levels (Δ_o) and the Fermi coupling constant $|W|$. These parameters have

Table 10
Vibrational frequencies for 3-chloro-5-hydroxy-2,6-dimethylpyridine (ClHDMP) and 3-bromo-5-hydroxy-2,6-dimethylpyridine (BrHDMP)

ClHDMP		BrHDMP			
Raman	IR	Raman	IR		Assignment
3077w	3076sh	3073vw	3972vw		ν(C–H)
3045vw		3045vw			
2996w	2995w	2999w	2996w		ν_{as} (CH$_3$)
2957w		2948sh	2953vw		
2927s	2926w	2927s	2927w		ν_s (CH$_3$)
	2901w		2894w		δ_{as} (CH$_3$) overtone
	2850s,b		2840s,b		A
	2550s,b		2500s,b		B ν(OH)
	1819s,b		1833s,b		C
1600w		1593w	1592sh	ν_{8a}	ring stretch
1578m	1577s	1572m	1572s	ν_{8b}	ring stretch
	1530vw		1538vw		
	1512vw		1501vw		
	1482s	1478m	ν_{19b}		ring stretch
1453vw	1451w	1453w			δ_{as} (CH$_3$)
1433vw	1432vw				
	1400s,b		1410s,b		δ(O–H)
1398w	1404s	1390w	1401m	ν_{19a}	ring stretch
1377m	1380s	1378m	1378m		δ(CH$_3$)
1344w	1351s	1351vw	1349s	ν_{14}	in-plane ring bend
1336w		1339vw	1341sh		
1295m	1294s	1294m	1294s		ν(C–O)
1246vw	1246s	1245vw	1244s	ν_{12}	in–plane ring bend
		1222vw			
	1217s	1214vw	1214s		H–O–C bend
		1183vw	1182w		
	1167s	1165vw	1165s		δ(C–H)
1031vw	1026w	1028vw	1025w		CH$_3$ rock
1007w	1004s	979w	981s	ν_1	ring stretch
	979w	1004vw	1004m		CH$_3$ rock
	921m,b		948sh		γ(O–H)
	880s		877s		γ(C–H)

been calculated in two steps: at first only the $\nu \rightarrow 2\delta$ interaction and then only the $((\nu, 2\delta \rightarrow 2\delta)$ interaction was considered. This simplification is justified because both unperturbed levels ν_0 and $2\delta_0$, while being close to each other, stand apart from a far-lying $2\gamma_0$ level [27].

The parameters obtained by us listed in Table 11 are in good agreement with those reported by Odinokov and Jogansen for other strongly H-bonded complexes [27]. The calculated γ(O–H···N) frequencies agree very well with the experimental results. The Fermi coupling constant ($|W|$), the R value and the γ(O–H···N) frequency are higher for BrHDMP compared with the chloro-derivative due to stronger hydrogen bonding in the former crystal. This statement is in agreement with the results of the X-ray analysis (Table 3) since the r(OH···N) distance is shorter for BrHDMP crystal than for ClHDMP.

5. Conclusions

The IR and Raman spectra of the compounds studied are consistent with the crystal structures determined in the present work. The IR contours in the 1500–3000 cm^{-1} frequency range are typical for a strong asymmetric hydrogen bond, clearly showing the A, B and C structure in the ν_{OH} stretching mode region. The δ(OH) and γ(OH) modes are observed in the IR spectra at 1400–1410 and 921–928 cm^{-1}, while

Table 10 Continued

ClHDMP		BrHDMP			
Raman	IR	Raman	IR		Assignment
820w	817s	814w	814s		ring–CH$_3$ stretch
811sh	810s	806sh	805s		
		718sh	719sh		ring–CH$_3$ stretch and
719s	718s	711vs	711s	ν_4	out-of-plane ring deformation
		658vw	659vw		
662w	661w	647w	646m	ν_{6b}	in-plane ring deformation
	630w	620vw	620w		
563w	560w	549w		ν_{16a}	out-of-plane ring deformation
	530w	545w			
	516w				γ(C–O)
495m	489w	489sh		ν_{6a}	in-plane ring deformation
		486s	484w		
465w	464w	460w			δ(C–CH$_3$)
398m	398w				ν(C–Cl)
		396w			
389m	388w	384m	382sh	ν_{16b}	out-of-plane ring deformation and δ(C–O)
		373m	373m		
344w	343s	347vw	347w		
	312w	314w			δ(C–CH$_3$)
305w	303w				
271w	272s				δ(C–Cl) and OH torsion
		267s	266s		ν(C–Br) and OH torsion
		262s	261s		
			208w		γ(C–CH$_3$)
			135w,b		ν(O–H···N)
	150w				translational and librational modes
	89w				
	71w				

Table 11
Structural and vibrational characteristics of hydrogen bonds in 3-chloro- and 3-bromo-5-hydroxy-2,6-dimethylpyridine

	ClHDMP	BrHDMP
$r(\mathrm{O{-}H\cdots N})/\text{Å}$	2.752(7)	2.726(9)
	2850	2840
$\nu(\mathrm{O{-}H\cdots N})$	2550	2500
$2\gamma(\mathrm{O{-}H\cdots N}) = \nu(\mathrm{C})$	1819	1833
$\delta(\mathrm{O{-}H\cdots N})$	1400	1410
$\gamma(\mathrm{O{-}H\cdots N}) = \gamma_0$	921	948
$\nu(\mathrm{AB})$	2681	2604
ν_0	2674	2538
$\mathrm{A,B}_{\text{band area}}$	75457	76503
$\mathrm{C}_{\text{band area}}$	4130	8461
$\Delta = \nu(\mathrm{AB}) - \nu(\mathrm{C})$	862	771
$\Delta_0 = \nu_0 - 2\gamma_0$	832	642
$R = \dfrac{\mathrm{C}_{\text{bandarea}}}{\mathrm{A,B}_{\text{bandarea}}}$	0.0547	0.111
$\nu_o(\mathrm{OH}) = \bar{\nu}(\mathrm{ABC}) = \dfrac{\bar{\nu}(\mathrm{AB}) + R\nu(\mathrm{C})}{R+1}$	2636	2527
$\gamma(\mathrm{OH\cdots N}) \approx \frac{1}{2}(2\gamma_o) = \frac{1}{2}(\nu_o - \Delta_o) = \frac{1}{2}\dfrac{\bar{R}\nu(AB)(\mathrm{AB} + \nu(\mathrm{C})}{R+1}$	931	955
$\lvert W\rvert = \Delta_{\surd}R/(R+1)$	191	231

Calculations were carried out on a PC using MicroCal Origin software.

the $\nu(\mathrm{O{-}H\cdots N})$ vibration occurs at about 135 cm^{-1}. The γ(OH) frequencies, determined from the A,B, and C bands, have been found to agree with those measured by IR spectroscopy. These calculations have been performed in a way described by Odinokov et al. [27]: at first only the $\nu \rightarrow 2\delta$ and then only the $(\nu,2\delta) \rightarrow 2\gamma$ interaction was considered. The determined O–H···N distance in the BrHDMP crystal (2.726 Å) is shorter than in the ClHDMP crystal (2.752 Å). Due to stronger hydrogen bonding in the bromo-derivative compared with the chloro-derivative, a frequency increase of the $\gamma(\mathrm{O{-}H\cdots N})$ band and an intensity increase of the C band has been observed.

The bands above 200 cm^{-1} originate from the internal vibrations and those below this limit from the external vibrations. The vibrational spectra of ClHDMP are very similar to those of BrHDMP. The substitution of the Cl atom by the heavier Br atom results in lowering of most of the vibrational frequencies by a few reciprocal centimeters. The most characteristic change occurs in the low frequency region where the 398 cm^{-1} ν(C–Cl) band is replaced by the 261–267 cm^{-1} ν(C–Br) mode.

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