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Characteristic features of intra- and intermolecular interactions in crystals of pyrrole-2-carbaldehyde isonicotinoylhydrazone and its hydrate

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Pyrrole-2-carbaldehyde isonicotinoylhydrazone (**1**) and its hydrate [$\mathbf{1} \cdot H_2O$] (**2**) were studied by single-crystal X-ray diffraction analysis. The introduction of the pyrrole substituent into *N´*-substituted isonicotinic hydrazide (INH) causes the intramolecular redistribution of the electron density compared to those in INHs studied earlier, which increases the basicity of the hydrazone nitrogen atom (N´) involved in intermolecular hydrogen bonding. This effect has not been observed in the structures of *N´*-substituted INHs and benzhydrazides studied previously. Intermolecular hydrogen bonds play a decisive role in the formation of the crystal structures of **1** and **2**.

Key words: pyrrole-2-carbaldehyde isonicotinoylhydrazone, pyrrole-2-carbaldehyde isonicotinoylhydrazone monohydrate, molecular structure, crystal structure, intermolecular hydrogen bonds, IR spectroscopy, X-ray diffraction analysis.

The design of materials possessing specific reactivities and exhbiting optical and conducting properties based on solid organic compounds gave impetus to the investigation and construction of the crystal structures of organic compounds (see, for example, the review[1]).

The functional groups are of great importance in the formation of supermolecular structures. These groups can be involved in intermolecular hydrogen bonding thus determining the orientation of molecules in the crystals and also making a contribution to intermolecular interactions.

In some cases, abundant experimental data for alone series (class) of compounds allows one to classify the hydrogen bonds and structural types, which can be used for the prediction of the structures of new representatives of this series.[1]

However, the prediction of the crystal structures of most classes of compounds is as yet impossible and calls for systematic structural studies.

N´-Aryl-substituted benzhydrazides (BHs) and isonicotinic hydrazides (INHs) of the general formula (Ph)Py—C(=O)—N(H)—N´=C(H)—R attract interest because some of these compounds exhibit photo-[2] and/or biological[3] activities both in the crystalline state and solutions. The activities of these compounds are to a large extent determined by hydrogen bonds. We are performing systematic studies on the effect of the substituent R and crystallization conditions on networks of intermolecular hydrogen bonds occurring in the crystals of BHs and INHs.

The molecules of a series of the previously studied *N´*-substituted INHs of the general formula Py—C(=O)—N(H)—N´=C(H)—R (R is 2-furyl,[4] 5-nitrofuryl,[5] 2-, 3-, or 4-nitrophenyl,[6] or 2-thienyl[7]) contain two strong proton-acceptor centers (nitrogen atom of the pyridine ring (N_{Py}) and the oxygen atom of the carbonyl group) and one proton-donor center (amide group NH). In the crystals of these compounds, both possible types of intermolecular hydrogen bonds are observed. Depending on the structure of the substituent R and the nature of the solvent, either NH...N_{Py} or NH...O=C[4,8] intermolecular hydrogen bonds occur, neither the O (or S) atoms of the substituent R nor the hydrazide nitrogen atom (N´) being involved in intermolecular hydrogen bonding. In addition, the results of X-ray diffraction analysis and IR spectroscopy for this series of compounds made it possible to assign the characteristic frequencies so that the character of intermolecular hydrogen bonds in the crystal can be predicted based on the IR spectra. In particular, if the NH stretching vibration frequency (ν(NH)) in the IR spectrum is higher than 3250 cm^{-1}, intermolecular hydrogen bonds of the amide type, *viz.*, NH_{amid}...O=C, occur in the crystal. If ν(NH) is lower than the above-mentioned value, the crystals contain intermolecular hydrogen bonds of the amide-pyridine type, *viz.*, NH_{amid}...N_{Py}.[4,5,7]

Pyrrole-2-carbaldehyde isonicotinoylhydrazone (PINH, **1**) or *N´*-(2-pyrrolylmethylene)isonicotinic hydrazide, belongs to a new type of INHs, which differs from INHs studied previously by the presence of two proton-

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donor centers, *viz.*, the amide NH group (NH_{amid}) and the NH group of the pyrrole ring (NH_{pyrr}). As a consequence, at least two different systems of intermolecular hydrogen bonds can occur in the crystals of **1**, *viz.*, NH_{amid}...O=C and NH_{pyrr}...N_{Py} in one case, and NH_{pyrr}...O=C and NH_{amid}...N_{Py} in another case.

A comparison of the 3800—400 cm^{-1} region of the IR spectrum of compound **1** with the results of IR spectroscopic and X-ray diffraction studies of other INHs led us to the conclusion that the intermolecular NH_{amid}...N_{Py} hydrogen bonds occur in the structure of **1** contains ($\nu(NH_{amid})$ = 3215 cm^{-1}). However, X-ray diffraction analysis of PINH (see below) demonstrated that the IR spectra do not necessarily allow one to unambiguously determine the character of intermolecular hydrogen bonding in the crystals of compounds containing the competing proton-donor and proton-acceptor groups.

In the present study, we report the results of X-ray diffraction study of PINH (**1**) and its crystal hydrate (**2**). Our aim was to examine the effect of the pyrrole substituent on the conformation and molecular packing in the crystal of **1** as well as on the network of intermolecular hydrogen bonds, to study the changes in the structure of **1** upon cocrystallization of PINH with water, and to perform a comparative analysis of the structures of **1** and **2** and the structures of a series of other known INHs.

Experimental

Synthesis. The reaction of isonicotinic hydrazide with pyrrole-2-carbaldehyde in aqueous EtOH afforded the crystal hydrate of *P*yrrole-2-carbaldehyde isonicotinoylhydrazone of composition 1 : 1 (**2**). Bright-yellow well-faceted crystals of **1** were obtained by recyrystallization of **2** from EtOH, m.p. of compound **1** is 230—232 °C. Pale-yellow crystals of **2** whose habitus is similar to that of anhydrous crystals of **1** were isolated by recrystallization from a concentrated solution of **2** in 50% aqueous EtOH. For crystal hydrate **2**, found (%): C, 56.88; H, 5.29; N, 24.38. $C_{11}H_{12}N_4O_2$. Calculated (%): C, 56.89; H, 5.21; N, 24.38. IR, ν/cm^{-1}: **1**, 3215, 3175 ($\nu(NH_{amid})$, $\nu(NH_{pyrr})$); **2**, 3400 ($\nu(O_wH)$), 3210 (br, ν(NH)).

IR spectra in the region of 3800—400 cm^{-1} were recorded on a Specord M-82 spectrometer (in KBr pellets and dilute solutions in THF, which was freshly distilled over CaH_2; in the region of C=O stretching vibrations, the spectra were measured in 0.1-cm cells).

Table 1. Principal crystallographic parameters of compounds **1** and **2**

Parameter	1	2
Molecular formula	$C_{11}H_{10}N_4O$	$C_{11}H_{10}N_4O\cdot H_2O$
M_w	214	232
Space group	$I4_1/a$	$P2_12_12_1$
a/Å	16.472(3)	6.437(3)
b/Å	16.472(3)	7.538(2)
c/Å	15.677(3)	23.736(5)
V/Å^3	4252.6(2)	1124.6(7)
Z	16	4
d/g cm^{-3}	1.335	1.370
Total number of reflections	2418	1186
R	0.046	0.035
R_w	0.055	0.060
GOOF	1.319	1.046

X-ray diffraction analysis. The X-ray diffraction data for the crystal of **1** were collected on a four-circle automated KUMA diffractometer (Cu-Kα radiation) in the angle range of 3.89—80.3°. The X-ray data for the crystal of **2** were collected on an automated CAD-4 diffractometer (Mo-Kα radiation) in the angle range of 1.71—25.03°. The structures of **1** and **2** were solved by direct methods based on 2230 and 1183 reflections with $I \geq 2\sigma(I)$ for **1** and **2**, respectively. The structures were refined with the use of the SHELXL-97 program package[9] based on F to R = 4.6 and 3.5% for **1** and **2**, respectively. The H atoms were located from difference syntheses. The nonhydrogen atoms were refined anisotropically. For the H atoms, only the positional parameters were refined. The principal crystallographic parameters of compound **1** and its hydrate **2** are given in Table 1. The atomic coordinates were deposited with the Cambridge Structural Database.

Results and Discussion

In the anhydrous crystal of **1** (Fig. 1), the PINH molecule as a whole is planar. The torsion angles about the N(1)—N(2) and C(2)—C(3) bonds are 2.1 and 1.6°, respectively. The molecular structure is distorted from pla-

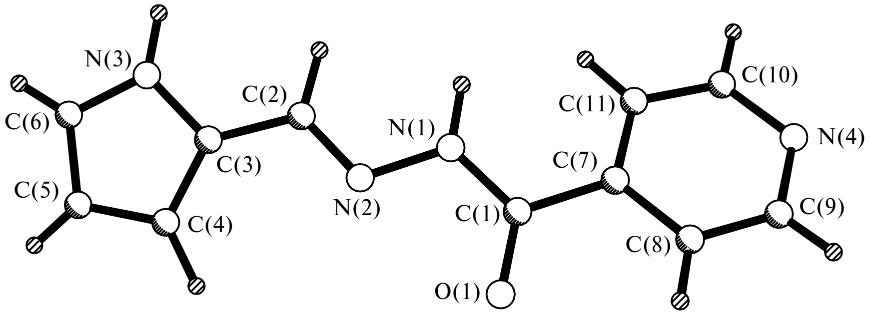

Fig. 1. Molecular structure of pyrrole-2-carbaldehyde isonicotinoylhydrazone (**1**).

Table 2. Bond lengths (*d*) in the central fragment of the PINH molecule in the structure of **1** and its hydrate **2** and the range of these bonds in INHs studied previously

Bond	*d*/Å		
	1	**2**	Other INHs
C(1)—O(1)	1.226(2)	1.231(4)	1.214—1.222
C(1)—N(1)	1.344(2)	1.345(4)	1.348—1.358
N(1)—N(2)	1.386(2)	1.386(5)	1.372—1.380
N(2)—C(2)	1.282(2)	1.271(4)	1.269—1.276
C(2)—C(3)	1.438(2)	1.441(2)	—
C(1)—C(7)	1.507(2)	1.501(4)	1.500—1.504

narity due to rotation of the pyridine ring with respect to the central C(3)—C(2)—N(2)—N(1)—C(1)—C(7) fragment about the C(1)—C(7) bond by 15.6°, which is in the range of changes in this angle in INHs studied previously (8—34°). The bond lengths in the central fragment are close to the corresponding values in other INHs (Table 2).

In the crystal of **1** (Fig. 2), the molecules are related by a fourfold screw axis. In the crystal structure, there are many shortened intermolecular contacts between the H atoms and the heteroatoms of the PINH molecule (Table 3). The intermolecular NH_{amid}...O=C and NH_{pyrr}...N_{Py} hydrogen bonds play a decisive role in the crystal structure. Most of shortened contacts, including the intermolecular NH_{amid}...O=C hydrogen bonds, occur between the molecules related by a screw fourfold axis. This gives rise to helical chains of intermolecular hydrogen bonds, *viz.*, ...O=C—N—H...O=C—N—H..., between the amide groups (see Figs. 2 and 3, *a*), which link the central fragments of molecules **1**. The intermolecular N—H_{amid}...O=C hydrogen bond is nearly linear (the N—H—O angle is 170°). The N...O and H...O distances (3.04 and 2.21 Å, respectively) are rather long,[10,11] but the energy of the interaction can be high because the vector of the N—H bond is directed toward the lone electron pair of the O atom (C=O...H angle is 124°).[12]

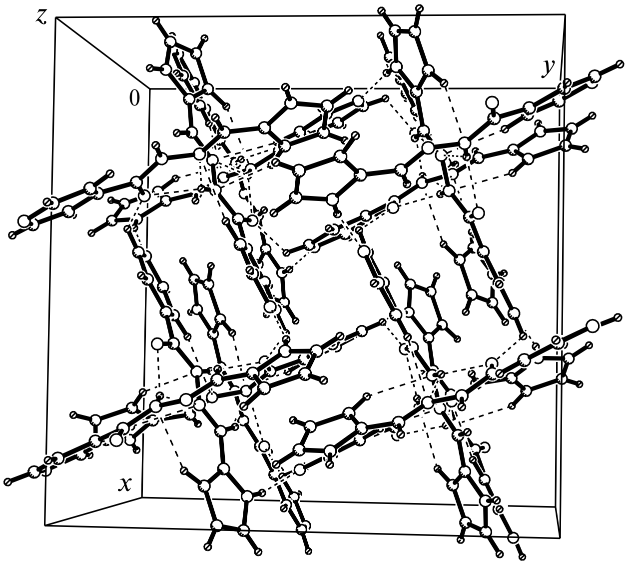

Fig. 2. Crystal structure of pyrrole-2-carbaldehyde isonicotinoylhydrazone (**1**).

Table 3. Geometric parameters of the intermolecular hydrogen bonds (IHB) in the structure of **1**

IHB X—H...Y	Distance/Å		Angle/deg	
	X...Y	H...Y	X—H—Y	H...O=C
N(1A)H...O(1B)	3.045	2.21	170	124
C(4B)H...N(1A)	3.587	2.60	153	—
C(11A)H...N(2B)	3.497	2.52	178	—
N(1A)H...N(2B)	3.302	2.50	170	—
N(3)H...N(4)	2.971	2.06	174	—
C(9)H...O(1)	3.145	2.55	165	101

A series of shortened intermolecular contacts between the molecules (see Fig. 3, *a*, Table 3) can be assigned to weak intermolecular hydrogen bonds. Thus, the amide N(1A) atom forms an intermolecular hydrogen bond with one of the H atoms of the pyrrole ring of the adjacent molecule B (N(1A)...HC(4B)); the N(1A)...H distance is 2.61 Å. The hydrazide N(2B) atom, in turn, forms a contact with the H_β atom of the pyridine ring of the molecule A (N(2B)...HC(11A)). The contact between the amide H atom, which is simultaneously involved in the intermolecular N(1A)—H...O(1B)=C hydrogen bond, and the hydrazide N atom (N(1A)H...N(2B)) is of most interest. The amide H atom lies in the N(1A)N(2B)O(1B) plane due to which this intermolecular hydrogen bond can be assigned to bifurcate bonds. The geometric parameters of the N(1A)H...N(2B) hydrogen bonds (N...N and H...N are 3.302 and 2.50 Å, respectively; the N—H—N angle is 170°) are close to those of the intermolecular NH_{amid}...N_{Py} hydrogen bonds in the crystals of *N*′-(3-nitrobenzylidene)isonicotinic hydrazide (**3**) (3.28 Å, 2.42 Å, and 161°, respectively).[6] Previously,[6] the IR spectroscopic study (ν(NH) = 3243 cm^{-1}) demonstrated that the intermolecular NH_{amid}...N_{Py} hydrogen bond is rather strong (3.1 kcal mol^{-1}) in spite of a rather long distance. It is believed that there is an attractive interaction between the amide H atom and hydrazide N(2) atom in compound **1**. That is why we assigned the ν(NH) band in the spectrum of **1** at 3215 cm^{-1} to the NH_{amid} vibration induced by the intermolecular hydrogen bond with N_{Py}. Apparently, this band in the spectrum of **1** is observed at a lower frequency compared to that in the spectrum of **3** (geometric parameters of the intermolecular hydrogen bonds being similar) due to the simultaneous involvement of the amide H atom in the intermolecular N—H_{amid}...O=C hydrogen bond.

Since the hydrazide N(2) atom is involved in intermolecular hydrogen bonding in none of the *N*′-substituted

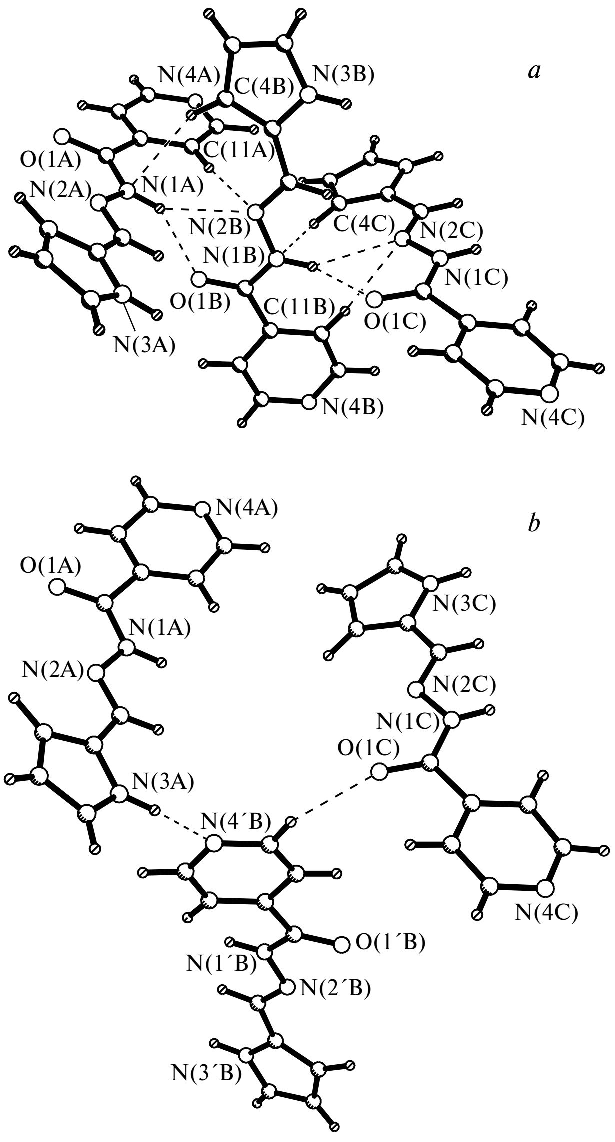

Fig. 3. Network of hydrogen bonds between the PINH molecules located along the same screw axis 4_1 (*a*) and along the adjacent axes (*b*).

BHs and INHs studied earlier, it can be assumed that the pyrrole substituent acting as a strong π-donor in a system of conjugated bonds enhances the basicity of the N(2) atom through the shift of the π-electron density from R to N(2) and then to the O(1) atom of the carbonyl group. The shift of the electron density in the molecules of *N*´-substituted INHs NC_5H_4—C(=O)—N(H)—N´=C(H)—R under the influence of R is supported by the following changes in the stretching frequencies ν(C=O) (cm^{-1}) in the IR spectra of dilute solutions of INHs in THF.

R	ν(C=O)	R	ν(C=O)
5-Nitrofuryl	1707	Phenyl	1696
3-Nitrophenyl	1706	2-Thiophenyl	1696
2-Nitrophenyl	1704	4-Dimethylaminophenyl	1690
2-Furyl	1698	2-Pyrryl	1689

It can be seen that the replacement of electron-withdrawing substituents by electron-donating substituents lowers the ν(C=O) frequency. This indicates that the C=O bond is weakened due to the shift of the π electrons of this bond toward the O atom with the resulting increase in the negative charge on the O atom. It can be assumed that in the case of the N(2)=C(2) double bond, the displacement of the π-electron density to the N atom leads to an increase in its basicity in compound **1** compared to other INHs due to which the N atom can be involved in intermolecular hydrogen bonding.

The NH group of the pyrrole ring and the N$_{\text{Py}}$ atom form a strong virtually linear (N—H—N angle is 174°) intermolecular N—H...N$_{\text{Py}}$ hydrogen bond between the ends of the molecules located along different axes 4_1 (see Figs. 2 and 3, *b*). The N...N$_{\text{Py}}$ and H...N$_{\text{Py}}$ distances (2.971 and 2.06 Å, respectively) are shorter than the intermolecular hydrogen bonds between the NH$_{\text{amid}}$ and N$_{\text{Py}}$ atoms in other INHs. For example, the shortest intermolecular N—H$_{\text{amid}}$...N$_{\text{Py}}$ hydrogen bond (N...N$_{\text{Py}}$, 2.991 Å; H...N$_{\text{Py}}$, 2.18 Å; N—H—N, 174°) was found in the crystals of *N*´-furfurylideneisonicotinic hydrazide.[4] It can be seen from Fig. 3, *b* that the H$_\alpha$ atom of the Py ring (H—C(9)) forms an intermolecular hydrogen bond with the O(1) atom of the carbonyl group, which (as was demonstrated above) is also involved in the intermolecular NH$_{\text{amid}}$...O=C hydrogen bond.

Therefore, a complex network of rather strong and weak intermolecular hydrogen bonds, including bifurcate bonds, is present in the crystals of **1**. In the crystal chemistry, the role of intermolecular hydrogen bonds in the formation of crystal structures of organic compounds has long been debated because the energy of intermolecular hydrogen bonds is generally much lower than the energy of dispersion interactions between large organic molecules.[13] Previously, we have noted[5,6,14] that the high melting temperatures of *N*´-substituted INHs (230—290 °C) arise from the stacked packing of long planar molecules linked *via* strong intermolecular hydrogen bonds, the geometry, and, consequently, the energy of intermolecular hydrogen bonds being determined by the packing. In the crystal structure of **1**, stacks are absent and the melting point is 231 °C. Hence, it can be stated that a branched network of intermolecular hydrogen bonds plays an essential role in the formation of the crystal structure of **1**.

The overall view of the PINH molecules and the network of intermolecular hydrogen bonds in crystal hydrate **2** are shown in Fig. 4. The central C(3)—C(2)—N(2)—N(1)—C(1)—C(7) fragment of the molecule, like that in **1**, is virtually planar (the torsion angles about the N(1)—N(2) and C(2)—C(3) bonds are 2.1 and 0.8°, respectively). The molecule is distorted from planarity due to rotation of the pyridine fragment about the C(1)—C(7) bond with respect to the plane of the central fragment by 31.7°. The bond lengths in the central

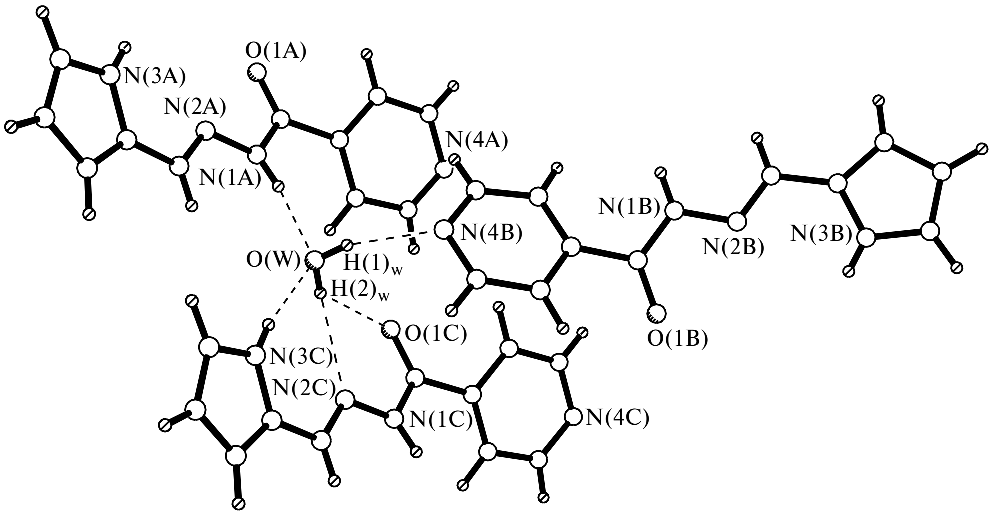

Fig. 4. Network of intermolecular hydrogen bonds in the structure of hydrate **2**.

fragment in crystal hydrate **2** are identical (to within the experimental error) with the corresponding bond lengths in **1**, except for the shortened N(2)—C(2) bond (see Table 2). Apparently, this shortening is attributable to the fact that the conformation of the PINH molecule in **2** differs from that in the structure of **1**. In molecule **1**, the O(1), N(2), and N(3) atoms are in the *syn-anti* positions, whereas these atoms in **2** are in the *syn-syn* positions, *i.e.*, the pyrrole ring in the hydrate is rotated about the C(2)—C(3) bond by 180°. Apparently, this is associated with the formation of the crystal hydrate. As can be seen from Fig. 4, one water molecule in the crystal of **2** is linked to three PINH molecules *via* five intermolecular hydrogen bonds, whereas no short contacts are observed between the PINH molecules. The geometric parameters of these intermolecular hydrogen bonds are given in Table 4.

It can also be seen from Fig. 4 that the intermolecular O(1A)...H(1)O_w and N(3A)H...O_w hydrogen bonds fix the water molecule within the cavity of the PINH molecule formed by the *syn*-arranged O(1), N(2), and H(N(3)) atoms. This is favorable for the formation of the intermolecular O_wH(1)...N(2A) hydrogen bond. As can be seen from Table 2, the conformational transformation is accompanied by a shortening of the N(2)—C(2) bond and an increase in the N(1)—N(2)—C(2) angle (115.3 and 117.5° in **1** and **2**, respectively) and a small decrease in the N(2)—C(2)—C(3) angle (120.5 and 119.4° in **1** and **2**, respectively). These changes may be indicative of a decrease in the π conjugation between the C=N bond and the pyrrole ring in the structure of **2**. Losses in the conjugation energy are compensated by the formation of the above-considered three intermolecular hydrogen bonds between PINH and the water molecule. It can be assumed that it is this conformation of the PINH molecule that is preferred in aqueous solutions.

Table 4. Geometric parameters of the intermolecular hydrogen bonds (IHB) in the structure of **2**

IHB X—H...Y	Distance/Å		X—H—Y angle /deg
	X...Y	H...Y	
O_wH(2)...N(4C)	2.837	1.92	162
N(1B)H...O_w	2.852	1.92	169
O_wH(1)...O(1A)	2.936	2.22	144
N(3A)H...O_w	2.972	2.10	173
O_wH(1)...N(2A)	3.011	2.06	131

The intermolecular hydrogen bonds between the water molecule and two other PINH molecules, *viz.*, O_w—H(2)...N(4C) and O_w...H—N(1B), are nearly linear (geometric parameters are given in Table 4). These bonds are rather strong because the distance between the H atom of the water molecule and the N(4C) atom and the distance between the amide H atom and O_w are 1.92 Å, which is much smaller than the sum of the van der Waals radii of these atoms (2.66 and 2.45 Å, respectively).[10,11]

Analysis of the network of intermolecular hydrogen bonds in crystal hydrate **2** showed that the O atom of the water molecule is involved in two (rather than in one) intermolecular hydrogen bonds (see Fig. 4) in contrast to the crystal hydrates of *N*′-substituted BHs[15] and INHs[5,8,14] studied by us earlier. Taking into account the (N(1B))H...O_w...H(N(3A)) angle (128°) and the dihedral angle between the plane of the water molecule and the plane passing through the N(1B)—H...O_w...H—N(3A) atoms (75°), the network of intermolecular hydrogen bonds about the molecule can be considered as "classical" (four intermolecular hydrogen bonds are located in two mutually perpendicular planes). However, the formation of the intermolecular O_w—H(1)...N(2A) hydrogen bond (which is facilitated by the favorable arrangement of the N(2) atom and water molecule) confirms that the proton-acceptor ability of the N(2) atom in PINH is rather high.

Hence, the amide-type intermolecular $NH_{amid}...O=C$ hydrogen bonds (in **1**) or the amide-hydrate-type intermolecular $NH_{amid}...O_w—H...O=C$ hydrogen bonds (in **2**) occur in the crystal structures under consideration, like in BHs[15] and some INHs.[4] At the same time, two other active centers (N_{Py} and NH_{pyrr}) are involved in either direct intermolecular $NH_{pyrr}...N_{Py}$ hydrogen bonds (in **1**) or hydrogen bonds *via* the water molecule, *viz.*, $NH_{pyrr}...O_w—H\cdots N_{Py}$ (in **2**). It should be noted that the N_{Py} atom is a stronger proton-acceptor than the O atom of the C=O group, and NH_{pyrr} is a stronger proton-donor group than NH_{amid}. The formation of intermolecular hydrogen bonds between the N_{Py} and NH_{pyrr} atoms in both structures provides support for the general rule known for solutions. According to this rule, a stronger base interacts with a stronger acid rather than with a weaker acid thus providing the largest gain in energy of the intermolecular interaction.

The results of the present study allowed us to make the following conclusions:

— conformation of the PINH molecule is virtually identical with that of INHs studied earlier; the molecule as a whole is planar and its planarity is distorted only due to rotation of the pyridine ring with respect to the remaining portion of the molecule;

— simultaneous presence of the proton-donor and π-donor pyrrole substituents in the PINH molecule facilitates the formation of branched networks of intermolecular hydrogen bonds in the crystals of **1** and **2**; these networks involve the hydrazide N atom whose basicity is higher than that in other INHs;

— occurrence of two proton-donor groups in the PINH molecule (which distinguishes hydrazide **1** from INHs studied earlier) allow the O atom of the water molecule in crystal hydrate **2** to be involved in two intermolecular hydrogen bonds rather than in one hydrogen bond, as was observed in hydrates of BHs and INHs;

— cocrystallization of PINH with the water molecule is accompanied by changes in the confirmations and some geometric parameters of the PINH molecule;

— three-dimensional networks of intermolecular hydrogen bonds play an essential role in the formation of the crystal structures of **1** and **2**.

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