# Rearrangement of the crystal structure during solid-phase elimination of solvate acetic acid from *N'*-(5-nitrofurfurylidene)isonicotinic hydrazide monohydrate

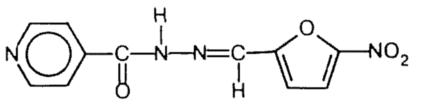
**S. M. Aldoshin,* E. G. Atovmyan, L. A. Nikonova, A. N. Utenyshev, and I. I. Chuev**

*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
*142432 Chernogolovka, Moscow Region, Russian Federation.*
*Fax: 007 (096) 515 3588*

A new crystal modification of *N'*-(5-nitrofurfurylidene)isonicotinic hydrazide (**1**) was studied by IR spectroscopy and X-ray structural analysis. The compound studied is the product of solid-phase desolvation of solvate hydrate **1** of the composition [MeCOOH · **1** · $H_2O$]. Spontaneous elimination of solvate acetic acid results in complex overall rearrangement of the crystal structure and formation of a new system of intermolecular hydrogen bonds. The crystal hydrate of 1 : 1 composition (**1c**) was formed from compound **1**. In the crystal structure of **1c**, molecules **1** are linked in infinite chains through intermolecular C=O...W...H—N hydrogen bonds. The second hydrogen atom of the molecule of the crystallization water is involved in formation of an intermolecular O—H...N(Py) hydrogen bond with the nitrogen atom of the pyridine ring of the molecule of the adjacent chain.

**Key words:** *N'*-substituted isonicotinic hydrazide; molecular and crystal structure; IR spectroscopy; intermolecular hydrogen bond.

Previously,[1] we demonstrated that crystal structures with various networks of intermolecular hydrogen bonds form depending on the conditions of synthesis and/or crystallization of *N'*-(5-nitrofurfurylidene)isonicotinic hydrazide (**1**). In some cases (crystallization from methanol), intermolecular N—H...N(Py) hydrogen bonds arise, and the molecules are packed in stacks (in crystals of **1a**). Otherwise (in a concentrated aqueous solution of acetic acid), solvates with acetic acid form (**1b**) through intermolecular O—H...N(Py) hydrogen bonds, and C=O...W...H—N bonds exist, which are typical of derivatives of benzhydrazides.[2] In the latter case, solvated molecules **1** are also packed in stacks. On storage in air, crystals **1b** gradually decompose because of solid-phase elimination of solvate acetic acid to form a compound, which is (according to the data of IR spectroscopy) crystal hydrate **1c**. In this work, the desolvation process was studied by IR spectroscopy, and the structure of the product of this reaction was studied by X-ray structural analysis with the aim of studying the characteristic features of this solid-phase reaction.



**1**

## Experimental

The IR spectra were recorded on a Specord M-82 spectrometer using KBr pellets or Nujol mulls. Golden yellow crystals **1c** have a orthorhombic syngony. The principal crystallographic data are as follows: $C_{11}H_8N_4O_4 \cdot H_2O$, $M_r$ = 278.22, $a$ = 12.693(2) Å, $b$ = 12.963(4) Å, $c$ = 15.434(3) Å, $Z$ = 8, $d_{calc}$ = 1.455(2) g cm$^{-3}$, $V$ = 2539.5(4) Å$^3$, space group *P*cab.

Experimental data were collected from a crystal of **1** with dimensions of 0.4×0.3×0.7 mm on an automated four-circle KM-4 diffractometer (Cu-Kα radiation). A total of 2979 reflections with $I > 2\sigma(I)$ were obtained. The structure was solved by the direct method using the SHELX-86 program package[3] and refined anisotropically by the full-matrix least-squares method. The positions of H atoms were located from the difference Fourier synthesis. Only their positional parameters were refined. The final value of the $R$ factor was 0.050. The atomic coordinates are given in Table 1.

The energy of intermolecular interactions was calculated using the 6-exp potential with the corresponding parameters.[4]

## Results and Discussion

The IR spectroscopic study of the desolvation process demonstrated that **1b** is a very unstable compound. Its crystals are preserved under either acetic acid vapor or a protective hydrocarbon coating. When samples were prepared as KBr pellets for IR spectroscopic study,

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2501—2505, October, 1996.

**Table 1.** Coordinates of nonhydrogen atoms (×$10^4$) and hydrogen atoms (×$10^3$) of molecule **1c**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| O(1) | 451(1) | 10949(1) | 7428(3) |
| O(2) | 1605(1) | 11136(1) | 4484(2) |
| O(3) | 1899(1) | 13083(1) | 4132(1) |
| O(4) | 2093(1) | 12742(1) | 2758(1) |
| OW | 580(1) | 12430(1) | 8694(2) |
| N(1) | 795(1) | 9504(1) | 6655(2) |
| N(2) | 1078(1) | 10076(1) | 5942(2) |
| N(3) | −387(1) | 8198(1) | 9583(2) |
| N(4) | 1962(1) | 12489(1) | 3514(1) |
| C(1) | 491(1) | 10007(1) | 7376(1) |
| C(2) | 188(1) | 9338(1) | 8129(1) |
| C(3) | 613(1) | 8371(1) | 8276(1) |
| C(4) | 306(1) | 7835(1) | 9012(1) |
| C(5) | −801(1) | 9127(1) | 9425(1) |
| C(6) | −537(1) | 9721(1) | 8718(1) |
| C(7) | 1290(1) | 9560(1) | 5261(2) |
| C(8) | 1587(1) | 10082(1) | 4477(2) |
| C(9) | 1856(1) | 9722(1) | 3678(1) |
| C(10) | 2051(1) | 10593(1) | 3154(1) |
| C(11) | 1885(1) | 11406(1) | 3672(1) |
| H(1) | 48(1) | 1197(1) | 837(1) |
| H(2) | 50(1) | 1222(1) | 921(1) |
| H | 74(1) | 878(1) | 659(1) |
| H(3) | 116(1) | 814(1) | 788(1) |
| H(4) | 60(1) | 714(1) | 913(1) |
| H(5) | −133(1) | 934(1) | 984(1) |
| H(6) | −90(1) | 1038(1) | 862(1) |
| H(7) | 126(1) | 882(1) | 524(1) |
| H(9) | 188(1) | 903(1) | 352(1) |
| H(10) | 228(1) | 1062(1) | 253(1) |

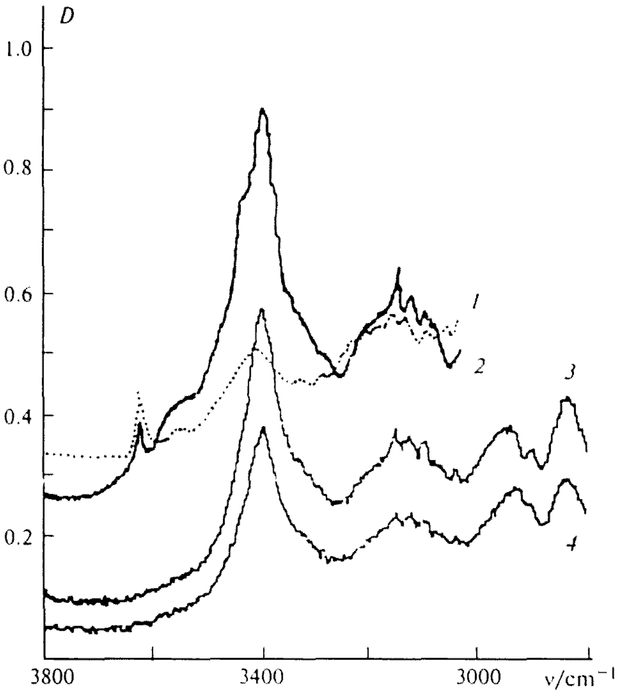


**Fig. 1.** IR spectra of **1b** in Nujol mulls (*1*) and in KBr pellets (*2*) and of **1c** (*3*, *4*).

almost complete elimination of acetic acid and rearrangement of the crystal structure occured due to the mechanical action exerted on the freshly prepared crystals **1b**. It was possible to reveal the characteristic bands corresponding to ν(OH) of hydration water molecules and to ν(C=O) of solvate acetic acid (1773 cm$^{-1}$)[5] only in the spectrum of **1b**, taken as highly-diluted Nujol mulls.

The character of the structural rearrangements during desolvation of **1b** according to the data of IR spectroscopy is presented in Fig. 1, in which the spectra of **1b** taken as Nujol mulls (*1*) and KBr pellets (*2*) as well as the spectrum of **1c** (the product of complete desolvation of **1b**) (*3*), are shown. Two bands at 3630 and 3420 cm$^{-1}$ in the ν(OH) region are clearly visible in spectrum *1*. The shape and positions of the bands are typical of ν(OH) of water molecules in the crystal hydrates of benzhydrazides studied previously,[2] in which one hydrogen atom of the water molecule is bound with the oxygen atom of the C=O group of the benzhydrazide through an intermolecular hydrogen bond (a broad low-frequency band), and the second hydrogen atom of the water molecule is directed toward the nitrofuran fragment of the same benzhydrazide molecule (a narrow high-frequency band). However, it should be noted that the band at 3420 cm$^{-1}$ is slightly asymmetrical, which could be indicative of the presence of an impurity of **1c** in the sample of **1b**.

The IR spectrum of **1b** taken as KBr pellets (see Fig. 1, curve *2*) shows that substantial rearrangement of the structure of **1b** occurs. As in the case of the product of complete transformation of **1b** to **1c**, the major band ν(OH) of water of hydration is observed at 3399 cm$^{-1}$ (spectrum *3*). However, the shoulder at 3420 cm$^{-1}$ and the narrow band at 3630 cm$^{-1}$ indicate that some water molecules occupy the same sites. The absence of the ν(C=O) band of solvate acetic acid at 1773 cm$^{-1}$ in the spectrum of **1c** indicates that **1b** in KBr pellets is an almost completely desolvated compound. The 3800—400 cm$^{-1}$ region of the IR spectrum of crystals of **1** suitable for X-ray structural analysis, which were obtained by recrystallization of compound **1** from a dilute aqueous solution of acetic acid (see Fig. 1, spectrum *4*), is identical to the spectrum of **1c**. This indicates that their molecular and crystal structures are identical. Therefore, we could study the process of structural rearrangements during solid-phase elimination of solvate acetic acid.

The network of intermolecular hydrogen bonds in crystals **1c** and an overall view of molecule **1** are shown in Fig. 2. The central fragment of the molecule is planar; the angles of rotation about the C(1)—N(1), N(1)—N(2), N(2)—C(7), and C(7)—C(8) bonds are 0.2, 4.5, 0.5, and 1.5°, respectively. The nitro group is twisted relative to the plane of the furan ring about the N(4)—C(11) bond by 8.7° (in **1b**, by 1.9°). The departure from

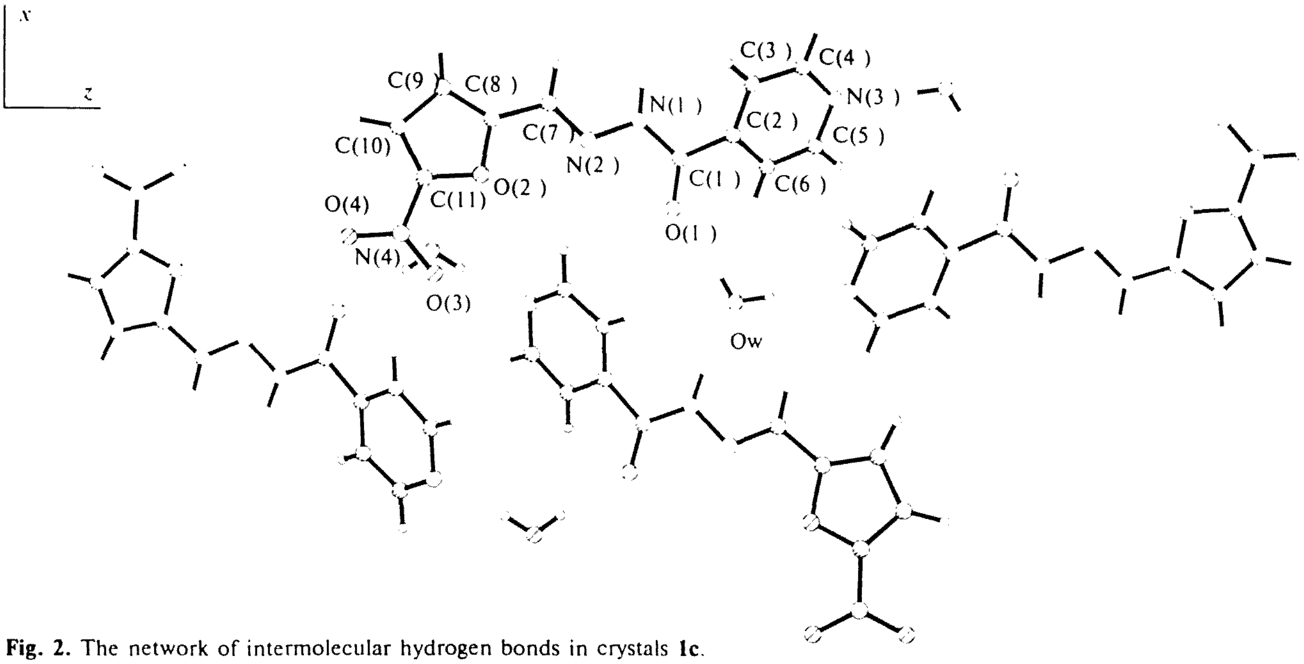


**Fig. 2.** The network of intermolecular hydrogen bonds in crystals **1c**.

planarity is caused by twisting of the pyridine substituent about the C(1)—C(2) bond by 28.7° (in **1b**, by 20.1°). The bond lengths and bond angles in **1c** agree with the corresponding angles for crystals **1b** studied previously to within the experimental error. Therefore, desolvation and rearrangement of the crystal structure cause only slight changes in the geometry of molecule **1**.

As mentioned above, acetic acid is readily eliminated from crystals of **1b**. This indicates that, first, molecules of acetic acid are weakly held in the crystal through intermolecular hydrogen bonds and intermolecular interactions, and, second, the crystal packing of molecules **1** should permit a rather free movement of these molecules in the crystal. Actually, as can be seen from the projection of the crystal structure of **1b** along the "*a*" direction perpendicular to the axis of stacks of molecules **1** (Fig. 3), there are channels, in which only molecules of acetic acid are located. The "walls" of these channels are formed by nitrofuran fragments of molecules **1** and nitrogen atoms of pyridine fragments. As was mentioned previously,[1] no short contacts and specific interactions between the atoms of acetic acid and the nitrofuran fragment were found. Therefore, the molecules of acetic acid are held in the channels primarily through intermolecular hydrogen bonds, whose energy is −4.7 kcal $mol^{-1}$, and through intermolecular interactions with nitrofuran fragments.

Based on the data of IR spectroscopy, it can be suggested that the processes of desolvation and rearrangement of the crystal structure **1b** → **1c** occur consecutively. In the course of desolvation, crystal domains **1b′** form, in which molecules of acetic acid are absent, whereas water molecules occupy the same sites. Calculations of the energy of crystal structure **1b′** confirmed the possibility of its formation. Taking into account the optimized position of molecule **1c** (**1**×$H_2O$) in the unit cell of **1b**, the crystal-lattice energy after elimination of acetic acid increases to −30.1 kcal $mol^{-1}$ compared to

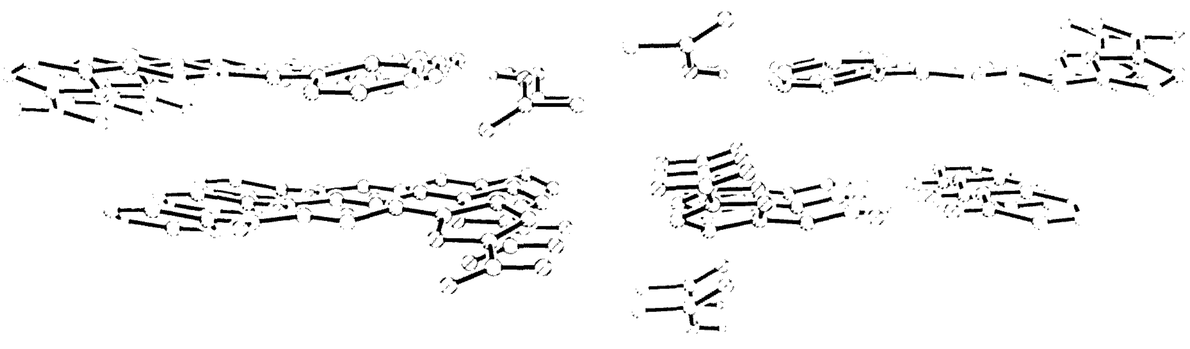


**Fig. 3.** Projection of crystal structure **1c** onto the *oyz* plane.

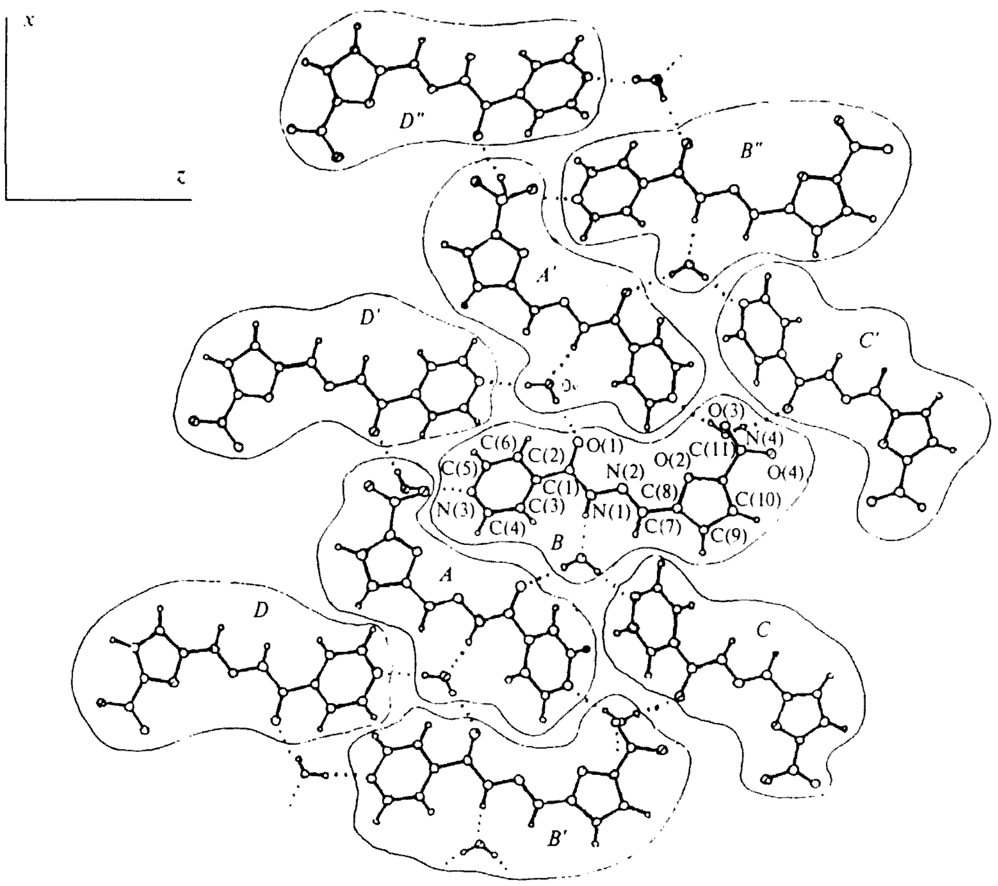


**Fig. 4.** Projection of crystal structure **1b** onto the *oyz* plane.

$-31.5$ kcal mol$^{-1}$ for **1b**. However, the density of these crystals decreases to 1.178 g cm$^{-3}$, compared to 1.433(2) g cm$^{-3}$ for **1b**. From Fig. 3 it follows that elimination of molecules of acetic acid should result in a decrease in parameter $c$ ($c$ = 15.434 Å in **1c**, whereas in **1b**, $c$ = 33.240 Å). The artificial contraction of this parameter in **1b**′ demonstrated that such compression of the crystal along the $c$ axis is barrierless up to $c$ = 27.240 Å. In this case, the lattice energy decreases to $-44.1$ kcal mol$^{-1}$, whereas the density of the crystal increases to 1.523 g cm$^{-3}$. Parameter $c$ was decreased from 33.240 Å to 27.240 Å with a step of 0.5 Å (with fixed values of all other parameters of the unit cell of **1b**′), and the lattice energy was calculated at each point. A further decrease in parameter $c$ in **1b**′ to 15.240 Å caused the lattice energy to increase to $-41.8$ kcal mol$^{-1}$. In this case, stack structure **1b**" with intermolecular C=O...W...H—N hydrogen bonds forms, which is typical of *N*′-(5-nitrofurfurylidene) benzhydrazides.[2] However, in this structure the nitrogen atom of the pyridine ring does not participate in intermolecular hydrogen bonding. As was demonstrated previously,[1,6] the nitrogen atom of the pyridine ring has an even greater tendency to form intermolecular hydrogen bonds than the carbonyl group C=O. Apparently, this tendency accounts for the fact that rearrangement of the crystal structure after elimination of molecules of acetic acid does not end in formation of structure **1b**", but proceeds further with the destruction of chains of intermolecular C=O...W...H—N hydrogen bonds. It follows from the analysis of the initial structure **1b** and the final structure **1c** (see Fig. 2) that mutual penetration of adjacent chains occurs, which results in cleavage of intermolecular C=O...W...H—N hydrogen bonds and an increase in parameter $a$ to 12.693 Å in **1c** compared to $a$ = 6.733 Å in **1b**. In Fig. 4, *A* and *A*′ and *B*, *B*′, and *B*" are the molecules that form different chains in structure **1b** but belong to one layer perpendicular to the $y$ axis (see Fig. 3). Linking of these chains is accompanied by cleavage of intermolecular C=O...W hydrogen bonds in the chain of **1b** (*A*...*A*′; and *B*...*B*′) and by formation of new intermolecular C=O...W...H—N hydrogen bonds (*B*"...*A*′...*B*...*A*...*B*′) between molecules of linked adjacent chains. The molecules in these chains are noncoplanar (the angle between their planes is 39.8°). The disruption of the coplanar arrangement of the molecules in the chains provides for mutual penetration of pairs of adjacent molecular layers perpendicular to the $y$ axis. As a result, the nitrogen atoms of the pyridine rings of the molecules located in a single layer form intermolecular (Py)N...W hydrogen bonds with the hydrogen atoms of water molecules that form chains of intermolecular hydrogen bonds C=O...W...H—N in the adjacent layer *C...B*, *C'...B"*, *D...A*, *D'...A* (see Fig. 2). Therefore, two adjacent layers are linked, which is accompanied by an increase in parameter *b* of **1c** to 12.963 Å compared to *b* = 7.005 Å in **1b** due to disruption of the coplanar arrangement of the molecules in layers (see Fig. 4).

Although this rearrangement of the crystal structure produces energetically more favorable and denser structure **1c** with energy of −32.5 kcal mol$^{-1}$ (compared to −31.5 kcal mol$^{-1}$ of **1b**) and density of 1.455 g cm$^{-3}$ (compared to 1.433 g cm$^{-3}$ of **1b**), this process requires additional activation energy for breaking intermolecular hydrogen bonds. We failed to model this stage of the process adequately with the use of the 6-exp potential. Rearrangement of structure **1b** to **1c** is accompanied by an increase in the unit-cell volume of **1c** (2539.5 Å$^3$) compared to that of **1b** (1567.8 Å$^3$); the number of molecules increases from 4 in **1b** to 8 in **1c**.

In crystals **1c**, water molecules link molecules **1** in three-dimensional blocks perpendicular to the *b* axis through the intermolecular hydrogen bonds. The parameters of the intermolecular hydrogen bonds are as follows: O(1)...OW = 2.745 Å (2.906 Å in **1b**), H(2)(OW)...O(1) = 1.97 Å, OWH(2)—(OW)—O(1) = 169.1°, the energy is −3.1 kcal mol$^{-1}$; N(1)'...OW = 2.754 Å (2.889 Å in **1b**), H(N(1)'...OW = 1.84 Å (2.05 Å in **1b**), N(1)'—H(N(1)'—OW = 172.8° (164.0 Å in **1b**), the energy of intermolecular hydrogen bonds is −4.8 kcal mol$^{-1}$; H(1)—(OW)...N(Py)' = 1.95 Å, OW...N(Py)' = 2.791 Å, OWH(1)—(OW)—N(Py)' = 175.4°, the energy of this intermolecular hydrogen bond is −3.3 kcal mol$^{-1}$. Therefore, one water molecule in **1c** forms three intermolecular hydrogen bonds, unlike two bonds in **1b**. In crystals **1c**, all three centers of hydrogen bonds in molecule **1** are involved in intermolecular hydrogen bonding with three water molecules. In crystals **1b**, two centers are involved in hydrogen bonding with water molecules, whereas the third N(Py) center forms an intermolecular hydrogen bond with a molecule of acetic acid: N(Py)...H—O = 1.69 Å, N(Py)...O(Ac) = 2.642 Å, N(Py)—H(Ac)—O(Ac) = 168°, and the energy is −4.7 kcal mol$^{-1}$. In crystals **1a**, only two centers of hydrogen bonds of molecule **1** are involved in intermolecular hydrogen bonding: N...N(Py)' = 3.003 Å, N—H...N(Py)' = 2.24 Å. The carbonyl C=O group does not participate in intermolecular hydrogen bonding.

In crystals **1a—c**, molecules **1** form stacks in head-to-tail fashion; the interaction energies are −11.7, −14.9, and −9.8 kcal mol$^{-1}$, respectively. Crystal structure **1b** provides energetically more favorable packing of molecules **1** in stacks, whereas the network of intermolecular hydrogen bonds, which forms a rigid two-dimensional layer framework, is stronger in structure **1c**.

Solid-phase transformation of **1b** to **1c** affords an energetically more stable crystal structure and is possible because of specific structure **1b**, in which two types of open channels occur, namely, channels along the axis of stacks of molecules and channels perpendicular to these stacks. In the first type of channels, water molecules are located, which link stacks through intermolecular C=OW...H—N hydrogen bonds. It is known[2] that water molecules are rather strongly held in these channels. Molecules of acetic acid are located in channels of the second type, and these molecules are readily eliminated. Desolvation of **1b** is accompanied by transformation to structure **1c** with complete rearrangement of the system of intermolecular hydrogen bonds.

## References

1. S. M. Aldoshin, L. A. Nikonova, E. G. Atovmyan, A. N. Utenyshev, and D. B. Frolov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2263 [*Russ. Chem. Bull.*, 1996, **45**, 2148 (Engl. Transl.)].
2. E. G. Atovmyan, S. M. Aldoshin, and L. O. Atovmyan, *Mol. Cryst. Liq. Cryst.*, 1990, 178, 231.
3. G. M. Sheldrick, *SHELX-86; Program for Crystal Structure Determination*, University of Cambridge (England), 1986.
4. G. V. Timofeeva, N. I. Chernikova, and P. M. Zorkii, *Usp. Khim.*, 1980, **69**, 966 [*Russ. Chem. Rev.*, 1980, **69** (Engl. Transl.)].
5. E. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Methuen & Co. LTD, London, John Willy and Sons, Inc., New York, 1957.
6. I. I. Chuev, S. M. Aldoshin, E. G. Atovmyan, D. B. Frolov, and A. N. Utenyshev, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 896 [*Russ. Chem. Bull.*, 1996, **45**, 851 (Engl. Transl.)].

*Received March 18, 1996;*
*in revised form June 13, 1996*