The influence of the nature of the solvent on the crystal structure and the character of formation of hydrogen bonds in *N'*-(5-nitrofurfurylidene)isonicotinehydrazide

S. M. Aldoshin, L. A. Nikonova, E. G. Atovmyan, A. N. Utenyshev, and D. B. Frolov*

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

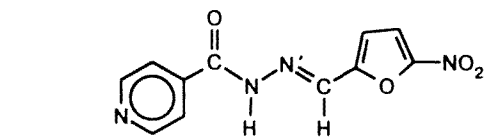
N'-(5-Nitrofurfurylidene)isonicotinehydrazide (**1**) was synthesized in the reaction of nicotinic acid hydrazide with 5-nitrofurfurol in anhydrous or aqueous ethanol. Crystals of different shape and color were obtained depending on the conditions of synthesis and the nature of the solvent. As was established by IR spectroscopy, compound **1** in the crystalline state forms solvates of various types. An X-ray study of two different crystals, one obtained by recrystallization from methanol (**1a**), and the other obtained from aqueous acetic acid (**1b**), was performed. In the crystal structure of **1a** intermolecular hydrogen bonds (IMHB) of the NH...N(Py) type occur; the crystals **1b** are built of solvates with one molecule of acetic acid in which the components are bonded by the IMHB (Ac)O—H...N(Py). The solvates are linked in an infinite chain by the amidohydrate IMHB C=O...W...H—N.

Key words: *N'*-substituted isonicotinehydrazide, molecular and crystal structure; intermolecular hydrogen bonds; X-ray analysis; crystal hydrates, crystal solvates; IR spectroscopy.

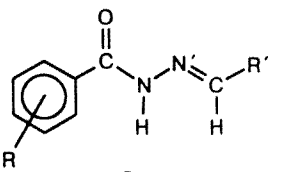
Previously, we established[1] that the crystal structure of *N'*-substituted benzhydrazides (BH) **2** and the character of the intermolecular hydrogen bond (IMHB) formed therein depend both on the nature of the substituents in the benzene ring and on those at the N' atom. With rare exception,[2] infinite chains of amide N—H...O=C or amidohydrate C=O...W...H—N (W is a water molecule) IMHB are formed in crystals, and these IMHB are apparently the proton transfer channels in the photochemical transformations of photoactive BH. Additionally, several *N'*-substituted BH are known to form solvates with a solvent molecule in crystals, for instance, with acetic acid or with acetonitrile.[3]

Our recent study[4] of two *N'*-substituted isonicotinehydrazides **3a,b** showed that the N atom of the pyridine ring successfully competes (as a stronger proton acceptor) with the oxygen atom of the carbonyl group to form IMHB with an N—H group. In the crystal, the N—H...N(Py) IMHB are formed while the carbonyl group remains "free" (in **3b**) or participates in some other specific intermolecular interaction (in **3a**). Thus, the presence of a stronger proton-acceptor center in the molecule of an *N'*-substituted hydrazide and the formation of an N—H...N(Py) IMHB creates a new channel for proton transfer during photochemical transformations.

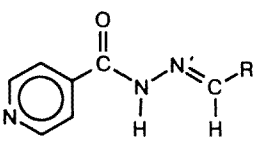
N'-(5-Nitrofurfurylidene)isonicotinehydrazide **1** is of interest, on the one hand, as one more representative of the series of *N'*-substituted isonicotinehydrazides, and,



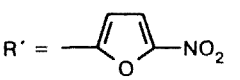
1

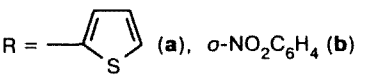


2a



3a,b





on the other hand, as an analog of *N'*-(5-nitrofurfurylidene)benzhydrazides **2a** whose numerous derivatives are photoactive in the solid phase. BH **2a** crystallizes from aqueous methanol as mono- or dihydrates; when heated *in vacuo*, the latter are readily turned into anhydrous products with a different crystal structure with chains of amide N—H...O=C IMHB (instead of the amidohydrate IMHB in the crystalline hydrate).[5] The hydrate water molecule in the crystals of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 2263—2268, September, 1996.

1066-5285/96/4509-2148 $15.00

2a usually occupies the cavity formed by *syn*-O atoms of nitrofuran, the N′ atom, and the O atom of the carbonyl group.

The presence of two proton-acceptor centers in the molecule of **1** and the capability of *N′*-(5-nitrofurfurylidene)hydrazides to form solvates, crystalline hydrates, and/or anhydrous products allows one to suggest that it should possible to obtain crystal structures of different composition, structure, and topology of IMHB by changing the solvent. In this connection we studied the effect of the conditions of synthesis and crystallization on the crystal structure of compound **1**.

Results and Discussion

Compound **1** was obtained by interaction between isonicotinic acid hydrazide and 5-nitrofurfurol in anhydrous or aqueous ethanol. The effect of the solvent composition on the character of the reaction products can be obtained even at the synthesis stage. The color of the product changes from red-brown to cream or light-yellow with increasing water content; sometimes it looks like a mechanical mixture of differently colored crystals. Thus, a mixture of red-brown and red crystals precipitates from the reaction solution in ethanol (10% H_2O); recrystallization from methanol or MeOH—H_2O (9 : 1) results in isolation of red crystals of **1a**, while transparent light-yellow crystals of **1b** are isolated from an aqueous solution of acetic acid. The latter grow turbid if kept in air and are turned into crystals of **1c**.

If the water content in the reaction medium reaches 50%, cream or yellow colored products are formed. One succeeds in obtaining crystals of two more types by recrystallization from aqueous acetic acid or aqueous ethanol: large goldish crystals, **1d**, and minute needles of pure yellow color, **1e**.

As was shown by IR spectroscopy, all crystals are built of molecules **1**; the variety of crystalline forms is due to the formation of crystalline solvates of different composition and, hence, of different crystal structure. Thus, all frequencies characteristic of molecule **1** are observed in the spectrum of compound **1a** and in the spectra of **1c—e**; in this case the high vibration frequency ν(C=O) (1682 cm^{-1}) and the intense band at 3120 cm^{-1} (Fig. 1, curve *1*) are evidence for the fact that the C=O group is "free" (like that in compound **3b**), while the NH group forms a strong IMHB, probably with the N atom of the pyridine cycle. The spectra of **1c** and **1d** are identical and show that compound **1** exists as a monohydrate in the crystal (see Fig. 1, curve *2*, the fundamental band of the hydrate water is at 3399 cm^{-1}) while its carbonyl group participates in specific intermolecular interactions (ν(C=O) 1672 cm^{-1}). Four bands are observed in the spectrum of compound **1e** in the region of the stretching vibration frequencies of the hydrate water (3700—3300 cm^{-1}): the first one is very narrow with a sharp peak at 3619 cm^{-1}, the second one is narrow but with a rounded peak at 3609 cm^{-1}, and

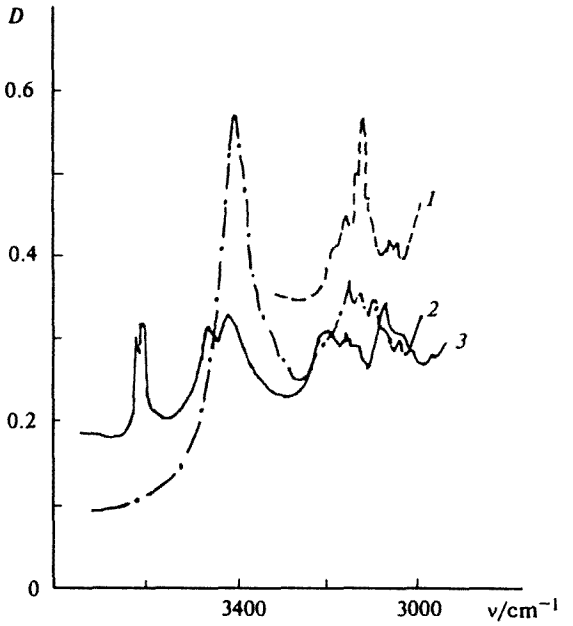


Fig. 1. IR spectra of compounds **1a** (*1*), **1c** and **1d** (*2*), and **1e** (*3*).

two broader bands are at 3461 and 3418 cm^{-1} (see Fig. 1, curve *3*). According to the data of our previous investigations of *N′*-(5-nitrofurfurylidene)benzhydrazides,[1] one can assume that molecules **1** form a dihydrate in crystal structure **1e**, and one of the water molecules is in the cavity formed by the electronegative atoms.

The structure of crystals **1a** and **1b** was studied by X-ray analysis. The results of the studies of the other crystalline modifications will be published elsewhere.

The character of the formation of IMHB in structures **1a** and **1b** is presented in Figs. 2 and 3, respectively. The distribution of the bond lengths and bond angles in molecules **1a** and **1b** coincides, within experimental error, with analogous values found in the derivatives of compounds of this class studied previously.[4] The central fragments of both molecules are nearly planar: they are rotated about the N(1)—N(2) and N(2)—C(7) bonds by 3.8° and 1.1° (**1a**) and 9.0° and 1.6° (**1b**), respectively. The nitro group is rotated 7.2° with respect to the furan ring plane in **1a** and 1.9° in **1b**. The departure from planarity is due to rotation of the pyridine ring about the C(1)—C bond by 12.9° and 20.1° in molecules **1a** and **1b**, respectively.

N—H...N(Py) IMHB are formed in crystal structure **1a** (see Fig. 2). The geometric parameters of this IMHB [(N(1)...N(3), 3.003(3) Å; N(3)...H(N(1)), 2.24(2) Å; N(3)—H(N(1))—N(1) angle, 168.9°] allow one to classify it as a weak linear bond[6] (see Fig. 2). However, the low vibration frequency of the N—H bond (3120 cm^{-1}) is evidence for a fairly high energy of the N—H...N(Py) interaction; it is higher than that in **3a,b** (3210 and 3196 cm^{-1}, respectively), which is in agreement with the longer N—H...N(Py) distance (3.094 and 3.071 Å in

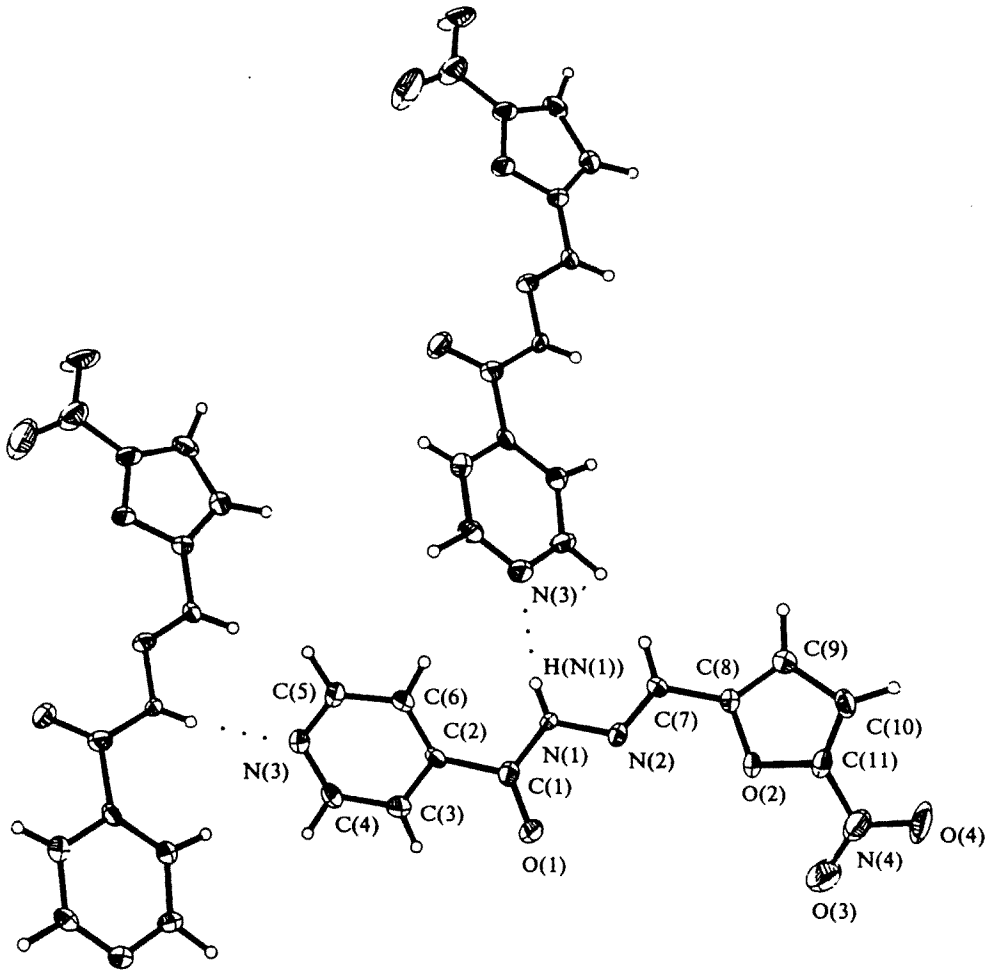


Fig. 2. The character of formation of IMHB in the structure of **1a**.

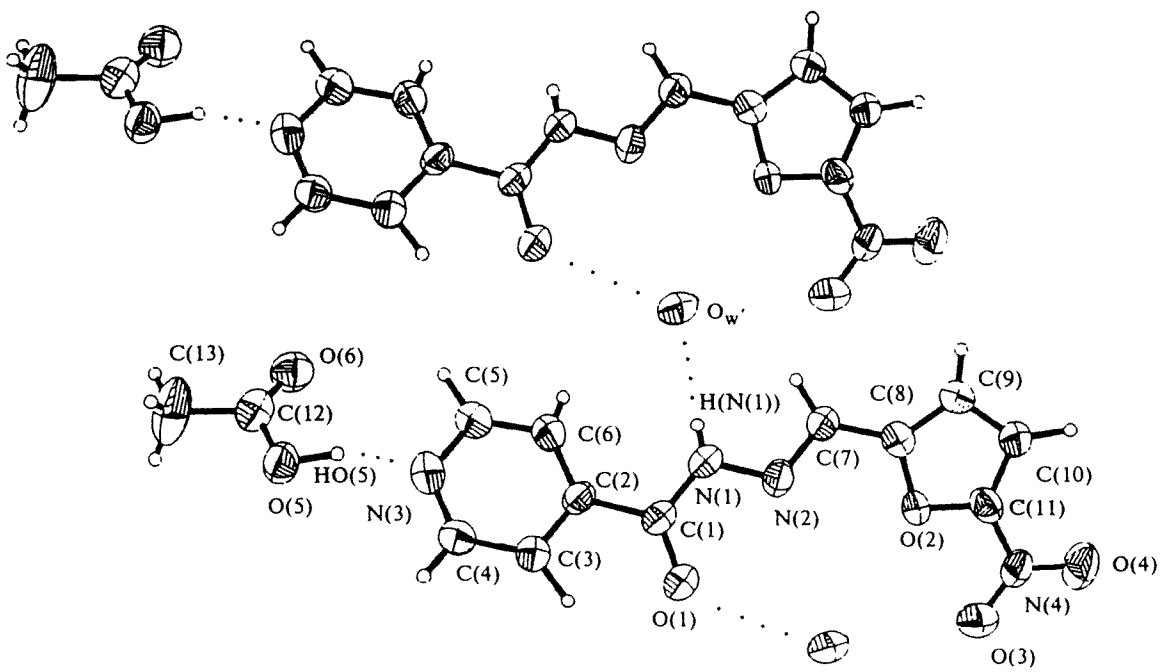


Fig. 3. The character of formation of IMHB in the structure of **1b**.

molecules **3a** and **3b**, respectively). The formation of the N—H...N(Py) IMHB in crystal **1a** is the reason that the carbonyl group remains "free" and does not participate in specific intermolecular interactions, which affects the ν(C=O) frequency. The crystalline structure is built of stacks formed by molecules **1** following the "head-to-tail" principle (*i.e.*, related by an inversion center); the stacks are extended in the direction of the *z* axis (the stacking energy is −11.7 kcal mol^{-1}). The energy of intermolecular interactions between the adjacent stackings is equal to −5.3 kcal mol^{-1}. The total energy of the crystal packing is −26.5 kcal mol^{-1} (including the IMHB energy).

A quite different character of the IMHB is observed in the structure of crystals **1b** obtained from an aqueous solution of acetic acid (see Fig. 3). Molecules **1** crystallize as solvatohydrates [MeCOOH · **1** · H_2O]. The acetic acid molecule forms an (Ac)O—H...N(Py) IMHB with geometric parameters O(5)...N(3), 2.642(8) Å; H(O(5))...N(3), 1.69(9) Å; O(5)—H(O(5))—N(3) angle, 167.6(5)°. The carbonyl group of the MeCOOH molecule remains "free" (the O(6)...H(5) distance is equal to 2.89 Å), with a stretching vibration band at 1773 cm^{-1}. The water molecule occupies the site typical of BH **2a**, binding the adjacent molecules of **1** by an amido-hydrate IMHB with geometric parameters O(1)...O_w, 2.906(7) Å; N(1)...O_w, 2.899(8) Å; H(N(1))...O_w, 2.05(9) Å; N(1)—H(N(1))—O_w angle, 163.7(7)° (see Fig. 3). The O_w...O(2), O_w...O(3), and O_w...N(2) distances are equal to 3.164(7), 3.382(7), and 3.182(7) Å, respectively. Though the H atoms of the water molecule are not located in the Fourier synthesis, their typical orientation has been confirmed by IR spectral data, according to which two bands correspond to the vibrations of these atoms in the IR spectra. The broad band with a gently sloping peak at 3420 cm^{-1} is assigned to vibrations of the hydrogen atom participating in the O(1)...H—O_w IMHB; the narrow band with a sharp peak at 3630 cm^{-1} is characteristic of vibrations of the H atom directed to the nitrofuran fragment. The shape of the band and its high frequency are evidence for the absence of an IMHB between this H atom and the O(2) and O(3) atoms.

Crystal structure **1b** is characterized by stacking of the [**1** · MeCOOH] solvates according to the "head-to-tail" principle with the energy of intermolecular interaction equal to −14.9 kcal mol^{-1} (the solvates are related by the rotational axis 2_1 along *y*) (Fig. 4). Molecules **1** in stackings are shifted with respect to each other. As a result of this shift, an acetic acid molecule occupies a position between the nitro groups of the associates that lie above and below it (Figs. 4 and 5) without forming a separate channel. No shortened contacts between the C(12), C(13), O(5), and O(6) atoms of the acetic acid molecule and the O(2a,b), O(3a,b), O(4a,b), and N(4a,b) atoms of nitrofuran fragments arise with this mutual orientation (see Fig. 5). The crystallization water molecules are localized in the channels formed by the stacking molecular associates along the *y* direction. The

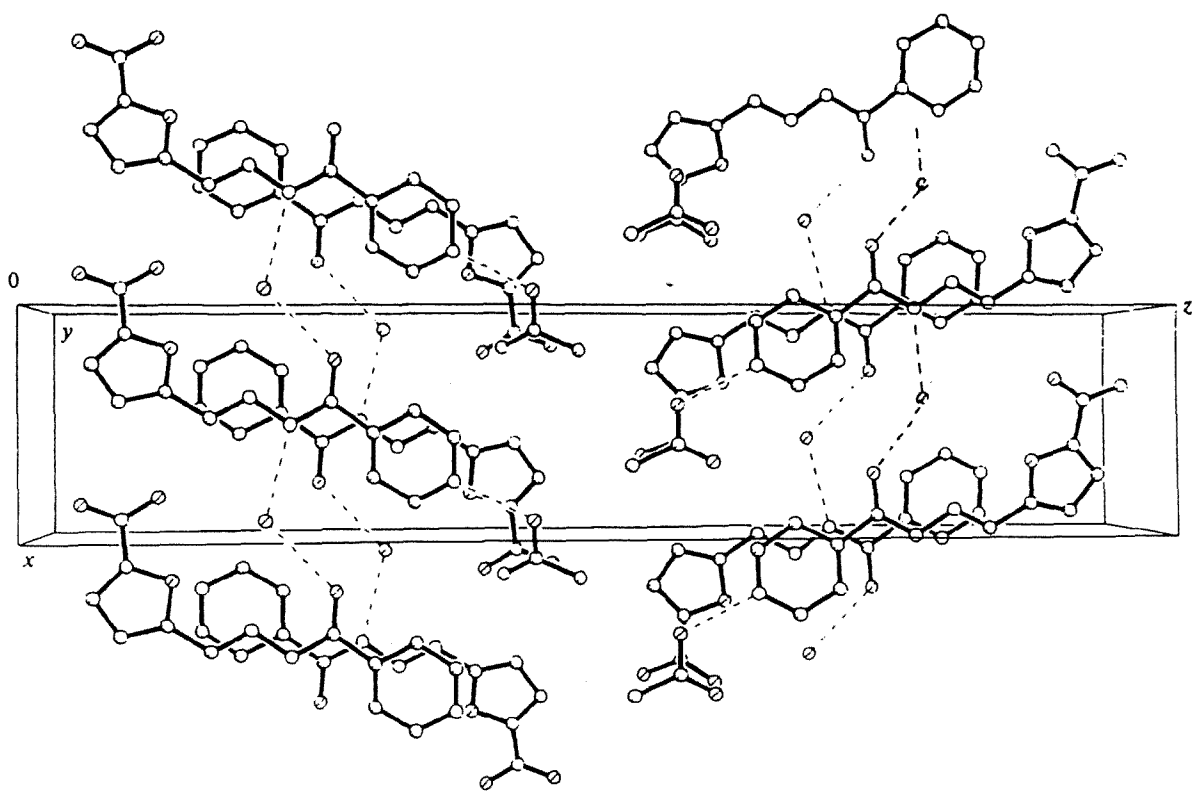


Fig. 4. The crystal structure of **1b**.

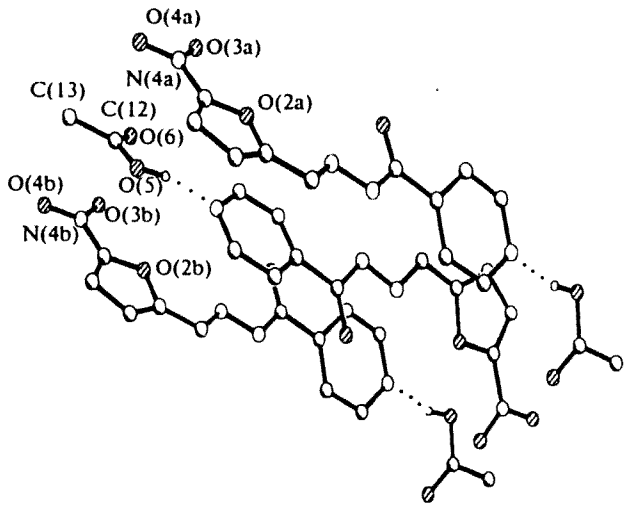


Fig. 5. The character of the arrangement of the solvate molecules in the crystal **1b**.

distance between the O atoms of the water molecules in the channel is 5.016 Å. The channel size is determined by the distance between the O(3), N(4), C(3), and C(4) atoms belonging to the molecules in adjacent stackings: O(3)...C(3)′, 3.346 Å; O(3)...C(4)′, 3.430 Å; N(4)...C(3)′, 4.635 Å; N(4)...C(4)′, 4.499Å. The total energy of crystal **1b** is equal to −31.5 kcal mol^{-1} (with allowance for the IMHB).

Thus, by varying the crystallization conditions of compound **1** one can control its crystal structure and the character of its intermolecular hydrogen bonds. Recrystallization of isonicotinehydrazide **1** from a methanol solution leads to the formation of a N—H...N(Py) IMHB and of a new (compared with crystals **2a**) channel for possible phototransfer of the amide proton. Acetic acid, too weak to protonate the pyridine nitrogen atom, nevertheless blocks the N—H...N(Py) channel that forms a solvate due to the formation of an IMHB between the H atom of the hydroxyl group and the N atom of the pyridine cycle.

Table 1. Coordinates of nonhydrogen atoms (×10^4) and hydrogen atoms (×10^3) in the structure of **1a**

Atom	*x*	*y*	*z*
O(1)	448(5)	2191(3)	9538(2)
O(2)	1319(4)	5774(2)	7877(2)
O(3)	−341(7)	5264(3)	6125(3)
O(4)	229(5)	7215(3)	5645(2)
N(1)	1954(5)	3750(3)	10371(2)
N(2)	1807(5)	4443(3)	9528(2)
N(3)	1727(5)	265(3)	12851(2)
N(4)	347(6)	6383(4)	6257(3)
C(1)	1219(6)	2607(4)	10306(3)
C(2)	1422(5)	1854(3)	11229(3)
C(3)	384(6)	784(4)	11221(3)
C(4)	589(6)	40(4)	12041(3)
C(5)	2717(7)	1300(4)	12849(3)
C(6)	2583(6)	2103(4)	12064(3)
C(7)	2569(6)	5493(3)	9564(3)
C(8)	2396(6)	6234(3)	8689(3)
C(9)	3067(6)	7345(4)	8469(3)
C(10)	2410(7)	7617(4)	7480(3)
C(11)	1380(6)	6649(4)	7175(3)
H(3)	−37(6)	54(4)	1067(3)
H(4)	−3(6)	−76(4)	1199(3)
H(5)	351(7)	146(4)	1350(4)
H(6)	323(6)	284(4)	1218(3)
H(7)	321(5)	587(3)	1009(3)
H(9)	386(6)	790(4)	892(3)
H(10)	264(6)	837(4)	714(3)
H(11)	235(5)	407(3)	1086(3)

Table 2. Coordinates of nonhydrogen atoms (×10^4) and those of hydrogen atoms (×10^3) in the structure of **1b**

Atom	*x*	*y*	*z*
O(1)	2303(9)	2598(9)	2592(2)
O(2)	1728(9)	2951(9)	1189(2)
O(3)	−1835(9)	4236(9)	1050(2)
O(4)	−1525(9)	3663(9)	402(2)
O(5)	9270(9)	2663(9)	4355(2)
O(6)	11693(9)	4450(9)	4092(2)
O_w	−802(9)	2579(9)	1985(2)
N(1)	5053(9)	2335(9)	2204(2)
N(2)	3872(9)	2483(9)	1862(2)
N(3)	7550(9)	2575(9)	3741(2)
N(4)	−864(9)	3699(9)	752(2)
C(1)	4121(9)	2498(9)	2563(2)
C(2)	5437(9)	2469(9)	2925(2)
C(3)	4512(9)	2036(9)	3297(3)
C(4)	5664(9)	2110(9)	3640(3)
C(5)	8435(9)	2948(9)	3286(3)
C(6)	7362(9)	2952(9)	2926(3)
C(7)	4770(9)	2061(9)	1528(2)
C(8)	3592(9)	2251(9)	1162(2)
C(9)	4053(9)	1840(9)	777(3)
C(10)	2429(9)	2319(9)	540(2)
C(11)	1039(9)	2962(9)	801(2)
C(12)	10991(9)	3583(9)	4376(3)
C(13)	11864(9)	3567(9)	4785(5)
H(3)	342(10)	205(10)	323(10)
H(4)	565(10)	139(10)	389(10)
H(5)	1015(10)	373(10)	330(10)
H(6)	795(10)	323(10)	274(10)
H(7)	579(10)	209(10)	148(10)
H(9)	512(10)	157(10)	69(10)
H(10)	196(10)	169(10)	27(10)
HN(1)	633(10)	241(10)	219(10)
HO(5)	848(10)	255(10)	411(10)
H(13A)	1337(10)	442(10)	482(10)
H(13B)	1084(10)	415(10)	495(10)

Experimental

The intermolecular interaction energy was calculated using the "6-exp" potential with pertinent parameters.[7] IR spectra

were recorded on a Specord M82 spectrometer (solid specimens in KBr pellets).

X-Ray study of crystals 1a and 1b. Crystals **1a** are red monoclinic; main crystallographic parameters: $C_{11}P_8N_4O_4$, a = 13.735(2) Å, b = 7.518(1) Å, c = 10.864(3) Å, β = 97.5(2)°, V = 1112.1(2) Å^3, Z = 4, d_{calc} = 1.552(2) g cm^{-3}, space group $P2_1/n$. Crystals **1b** are light-yellow rhombic; main crystallographic parameters: $C_{11}P_8N_4O_4 \cdot H_2O \cdot CH_3COOH$, a = 6.733(3) Å, b = 7.005(1) Å, c = 33.270(3) Å, V = 1567.8(3) Å^3, Z = 4, d_{calc} = 1.431(2) g cm^{-3}, space group $P2_12_12_1$.

The experimental data from a crystal of **1a** of the size 0.6×0.1×0.2 mm^3 was obtained on a three-circle DAR-UM diffractometer (Cu-Kα radiation), that from a crystal of **1b** of the size 0.7×0.5×0.3 mm^3 was obtained on an automatic four-circle KM-4 diffractometer (Cu-Kα-radiation). The number of independent reflections with $I > 2\sigma(I)$ was 918 (**1a**) and 1068 (**1b**).

The structures were solved by direct methods using the SHELX-86[8] program package and refined anisotropically by the full-matrix least squares method. The hydrogen atoms were located in the difference Fourier synthesis; only their positional parameters were refined. The atomic coordinates listed in Tables 1 and 2, respectively, correspond to the final values of the reliability factors R = 0.058 (**1a**) and 0.070 (**1b**).

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 93-03-04355).

References

1. E. G. Atovmyan, S. M. Aldoshin, and L. O. Atovmyan, *Mol. Cryst. Liq. Cryst.*, 1990, **178**, 231.
2. I. I. Chuev, S. M. Aldoshin, and M. Yu. Antipin, *Zh. Strukt. Khim.*, 1996, in press [*J. Struct. Chem.*, 1996 (Engl. Transl.)].
3. I. Goldberg and Z. Stein, *Acta Crystallogr.*, 1984, **C40**, 666.
4. 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.)].
5. S. M. Aldoshin, A. N. Chekhlov, E. G. Atovmyan, O. A. Kozina, V. S. Nedzvetskii, V. G. Andreev, A. S. Kulikov, L. O. Atovmyan, and L. M. Yagupol'skii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1312 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1153 (Engl. Transl.)].
6. L. M. Babkov, G. A. Puchkovskaya, S. P. Makarenko, and T. A. Gavrilko, *Spektroskopiya molekulyarnykh kristallov s vodorodnymi svyazyami* [*Spectroscopy of Molecular Crystals with Hydrogen Bonds*], Naukova Dumka, Kiev, 1989 (in Russian).
7. G. V. Timofeeva, N. I. Chernikova, and P. M. Zorkii, *Usp. Khim.*, 1980, **69**, 966 [*Russ. Chem. Rev.*, 1980, **69** (Engl. Transl.)].
8. G. M. Sheldrick, *SHELX-86; Program for Crystal Structure Determination*, University of Cambridge, Cambridge (England), 1986.

Received November 17, 1995