Intra- and intermolecular interactions in crystals of *N'*-furfurylideneisonicotinic hydrazide and related compounds. IR spectroscopic and X-ray diffraction studies

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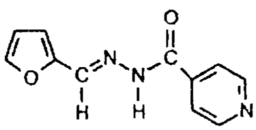
The reaction of isonicotinic hydrazide with furfural yielded *N'*-furfurylideneisonicotinic hydrazide. IR spectroscopic studies demonstrated that crystallization from different solvents afforded products with an intermolecular NH...O=C hydrogen bond. Conditions of crystallization were chosen under which single crystals with the NH...N_{Py} intermolecular hydrogen bond (**1**) were grown. X-ray diffraction analysis demonstrated that the molecular and crystal structure of **1** is identical to that of *N'*-thienylideneisonicotinic hydrazide (**2**). The crystal structure consists of layers. The molecules in the layers are linked in zigzag chains through NH...N_{Py} intermolecular hydrogen bonds. The molecules of the adjacent chains (in the layer) are linked through C=O...H—C intermolecular hydrogen bonds between the O atom of the carbonyl group and the α-H atom of the furan ring. (In the structure of **2**, the chains are linked through specific intermolecular interactions of different nature but with approximately identical energy.) The replacement of the thiophene fragment (**2**) by the furan ring (**1**) is accompanied by a change in the intramolecular electronic effects, which is reflected both in the geometric and spectral characteristics of the molecules in the crystal.

Key words: *N'*-substituted isonicotinic hydrazides, *N'*-substituted benzhydrazides, intermolecular hydrogen bond, IR spectra, X-ray diffraction analysis.

The molecular packing in crystals of organic compounds is determined mainly by dispersion interactions, which cause a decrease in the potential energy of the crystal lattice. Specific intermolecular interactions, such as intermolecular hydrogen bonds, make a rather insignificant contribution to the total energy of intermolecular interactions. However, the question of whether the molecular packing is determined by intermolecular hydrogen bonds or these interactions are determined by the packing remains open, and there is no unambiguous answer to this question.[1] Other types of specific intermolecular hydrogen bonds can also contribute to the formation of the crystal structure. For example, the analysis of the molecular and crystal structure of *N'*-thienylideneisonicotinic hydrazide (**2**)[2] demonstrated that an unusual contact between the O atom of the carbonyl group and the S atom of the thiophene fragment occurs in the crystal along with the expected N—H...N_{Py} intermolecular hydrogen bond between the N—H amide group and the N atom of the pyridine ring.[3] We confirmed the suggested O...S attractive interaction[3] by IR spectroscopy and demonstrated that the energy of this intermolecular interaction is comparable with the energy of an intermolecular hydrogen bond of medium strength.[2]

In this work, we report the results of IR spectroscopic and X-ray diffraction studies of *N'*-furfurylideneisonicotinic hydrazide (**1**), the furan analog of **2**. The aim of this work was to study the effect of the substituent at the *N'* atom on the molecular and crystal structure of *N'*-substituted isonicotinic hydrazide and to analyze specific intermolecular interactions in crystals of **1**.



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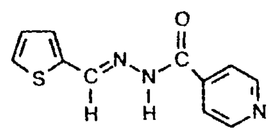

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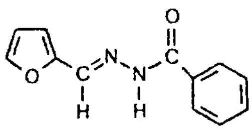

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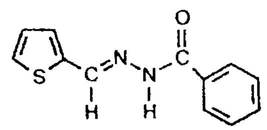

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Experimental

Pale-yellow crystals of compound **1** belong to the monoclinic system. The principal crystallographic data are as follows: $C_{11}H_9N_3O_2$, M = 215.21, *a* = 10.161(2) Å, *b* =

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14.080(3) Å, c = 8.065(2) Å, Z = 4, d_{calc} = 1.360(2) g cm^{-3}, V = 1051.1(3) Å^3, space group Cc.

The X-ray data were collected from a crystal of **1** of dimensions 0.4×0.1×0.08 mm on an automated four-circle KM-4 diffractometer using Cu$K\alpha$ radiation. The number of reflections with $I > 2\sigma(I)$ was 1165. The structure was solved by the direct method using the SHELX-86 program package[4] and refined anisotropically by the full-matrix least-squares method (SHELXL-93).[5] The hydrogen atoms were located from the difference Fourier synthesis, and only their positional parameters were refined. The final value of the R factor was 0.0341. The atomic coordinates are given in Table 1.

The IR spectra were recorded on a Specord M82 spectrometer as KBr pellets.

Results and Discussion

Compound **1** was synthesized from isonicotinic hydrazide and furfural according to a known procedure.[6] In the crystals of compound **1** obtained from different solvents (alcohols, water, aqueous THF, acetone, acetonitrile, and ethyl acetate), the amide N—H...O=C intermolecular hydrogen bond (**1a**) exists instead of the expected N—H...N$_{Py}$ hydrogen bond in spite of the facts that the N$_{Py}$ atom is a stronger proton acceptor than the C=O group and the solvents used were aprotic or weakly protic and could not block the N$_{Py}$ atom. On the contrary, we failed to obtain single crystals of **2** with the amide intermolecular hydrogen bond. Apparently, the replacement of the thiophene fragment in compound **2** by the furan group in **1** and the rearrangement of the electronic structure of the molecule are unfavorable for the formation of N—H...N$_{Py}$ intermolecular hydrogen bonds in crystals. The IR spectra of compound **2** (Fig. 1, curve *1*) are indicative of the possibility of formation of the amide intermolecular hydrogen bond in crystals of **2**.

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

Atom	x	y	z
O(1)	9666(2)	1829(2)	2200(2)
N(2)	11701(2)	432(2)	4296(2)
C(3)	13803(1)	−231(3)	6590(2)
O(4)	14241(2)	521(2)	7388(1)
C(5)	14675(2)	−1826(2)	6025(1)
N(6)	12558(1)	−336(3)	5095(1)
C(7)	14642(1)	−1135(3)	7230(1)
C(8)	9524(1)	895(3)	1764(2)
N(9)	16234(2)	−2799(2)	8488(2)
C(10)	10589(2)	221(2)	2859(2)
C(11)	15455(1)	−1275(3)	9067(1)
C(12)	7611(1)	1644(3)	−254(2)
C(13)	8471(1)	2269(3)	921(2)
C(14)	15489(1)	−2643(3)	6725(1)
C(15)	8283(1)	745(2)	272(2)
C(16)	16213(2)	−2111(2)	9626(2)
H(1)	843(1)	296(1)	109(1)
H(2)	1556(1)	−312(2)	584(2)
H(3)	1226(1)	−86(2)	468(1)
H(4)	1543(1)	−72(2)	990(2)
H(5)	1682(1)	−223(1)	1095(1)
H(6)	670(2)	178(1)	−126(2)
H(7)	1412(2)	−178(1)	458(2)
H(8)	1045(2)	−43(2)	235(1)
H(9)	787(1)	12(1)	−29(2)

In the IR spectrum of **1a** (Fig. 2, curve *1*), N—H stretching vibrations are characterized by a sharp strong band at 3269 cm^{-1}, which is typical of crystalline amides with the *trans*-amide group and the linear chain of N—H...O=C intermolecular hydrogen bonds as, for

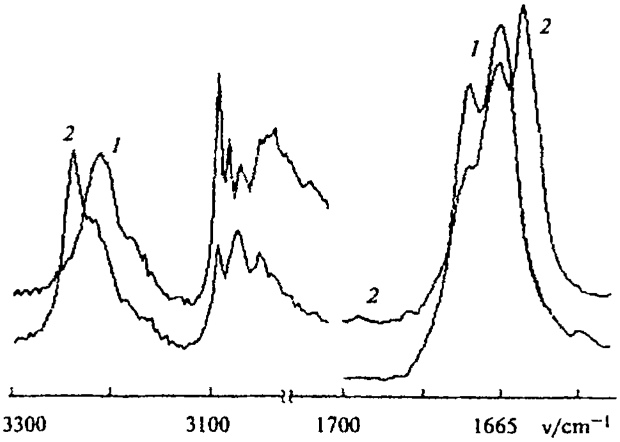

Fig. 1. IR spectra of N'-thienylideneisonicotinic hydrazide: *1*, crystals with the NH...N$_{Py}$ intermolecular hydrogen bond; *2*, a mixture of crystals with the NH...N$_{Py}$ and NH...O=C intermolecular hydrogen bonds.

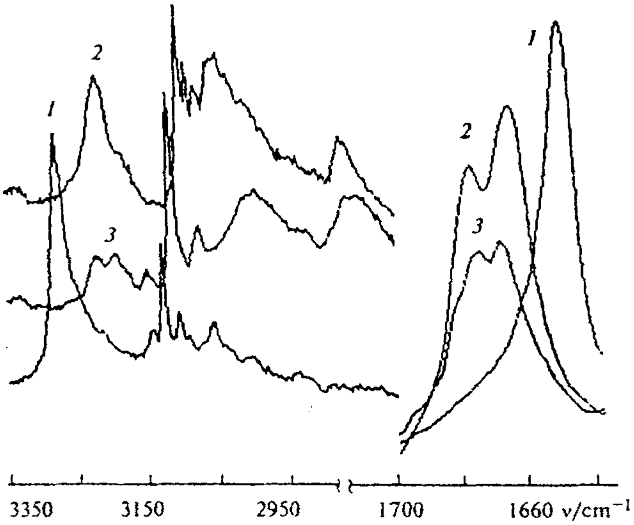

Fig. 2. IR spectra of crystalline samples of N'-furfurylideneisonicotinic hydrazide with the NH...O=C (*1*) and NH...Npy (*3*) intermolecular hydrogen bonds and samples of N'-thienylideneisonicotinic hydrazide with the NH...N$_{Py}$ intermolecular hydrogen bond (*2*).

example, in the case of *N'*-furfurylidene- (**3**)[7] and *N'*-thienylidenebenzhydrazides (**4**)[8] studied previously (see also Fig. 1, curve *2*). The sharp, rather strong band at 3119 cm^{-1} and the weaker band at 3098 cm^{-1} are determined by stretching vibrations of the nonequivalent C—H bonds of the furan ring. Except for the band at 3047 cm^{-1}, the ν(C—H) bands of the pyridine ring are weak and similar in position and intensity to the ν(C—H) bands of the benzene ring in the spectrum of compound **3**. On the contrary, in the spectrum of **2**, in which the NH...N$_{Py}$ intermolecular hydrogen bond occurs (see Fig. 2, curve *2*), a relatively strong absorption is observed in the 3050—2750 cm^{-1} region, and a broad band appears at 2860 cm^{-1}, which is also typical of other crystalline compounds with intermolecular hydrogen bonds described above. The ν(N—H) band is weaker and is substantially shifted to the low-frequency region (3210 cm^{-1}; a shoulder at 3180 cm^{-1}), which is typical of the N—H...N$_{Py}$ intermolecular hydrogen bond.[2] Two sharp bands at 3092 and 3080 cm^{-1} can be assigned to ν(C—H) stretching vibrations of the thiophene ring. Comparing these bands in curves *1* and *2* (see Fig. 1), it can be concluded that the band at 3092 cm^{-1} is attributable to the ν(C—H) stretching vibration at the α position of the thiophene ring. Apparently, its relatively high intensity in the spectrum of **2** is due to a specific S...O intermolecular interaction. When the amide intermolecular hydrogen bond is present in crystals of **2** (see Fig. 1, curve *2*), the S...O interaction is absent, and the intensity of the band at 3092 cm^{-1} is substantially weaker although its position in the spectrum remains unchanged.

We used the major characteristics of the spectrum of **2** in the ν(X—H) region (see Fig. 2, curve *2*) for identifying the character of intermolecular hydrogen bonds in the products of crystallization of **1**. We succeeded in growing crystals of **1** suitable for X-ray diffraction study by choosing conditions of crystallization from dry THF. The IR spectrum of these crystals (see Fig. 2, curve *3*) has ν(N—H) bands in the same region as in the case of compound **2**. The high-frequency ν(C—H) band of the furan ring is substantially stronger than that in the spectrum of **1a** and is shifted to the low-frequency region (3108 cm^{-1}). In the 3050—2750 cm^{-1} region, two broad strong bands at 3000 and 2850 cm^{-1} appear. The ν(C=O) bands in the 1750—1650 cm^{-1} region in the spectra of compounds **1** and **2** are virtually identical (see Fig. 2, curves *2* and *3*). The spectrum of **1a** (Fig. 2, curve *1*) has a narrow strong ν(C=O) band with a maximum at 1650 cm^{-1} (see also Fig. 1, curve *2*), while the averaged maximum of the ν(C=O) band in the spectra of **1** and **2** is observed at 1670 cm^{-1}. The similarity of the spectra of **1** and **2** in the ν(N—H) and ν(C=O) regions indicates that we obtained crystals with the desired NH...N$_{Py}$ intermolecular hydrogen bond and also that the C=O group, as in the case of **2**, is involved

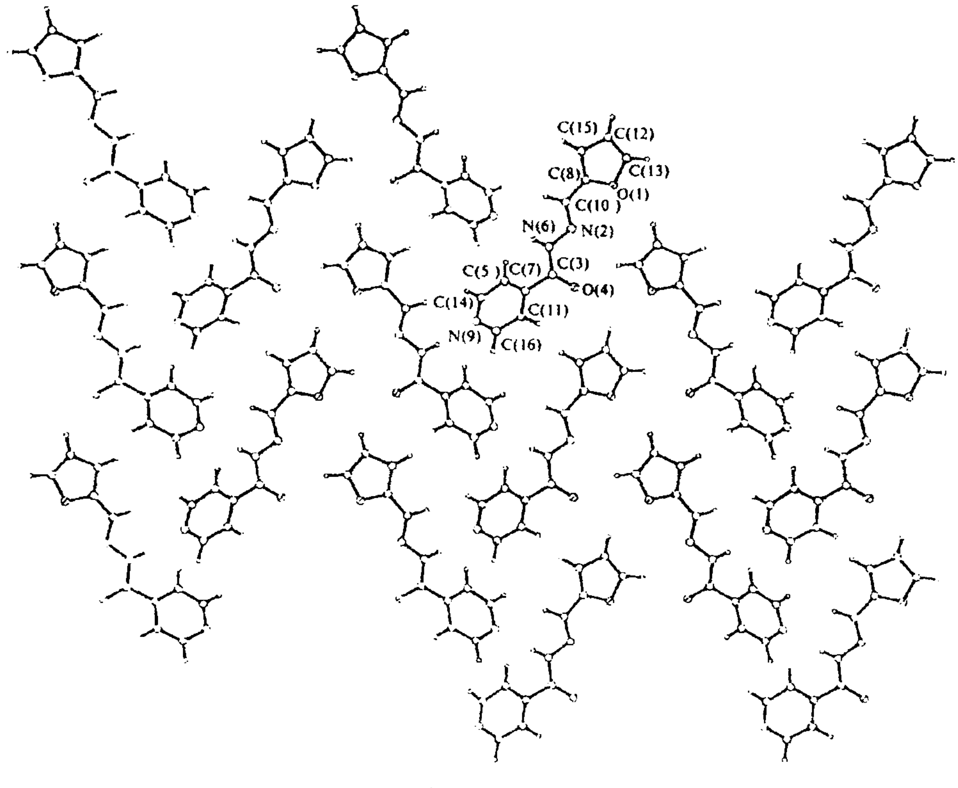

Fig. 3. Molecular and crystal structure of *N'*-furfurylideneisonicotinic hydrazide.

in specific intermolecular interactions of moderate strength.

X-ray diffraction analysis of compound 1 demonstrated that the molecular and crystal structures of **1** and **2** are very similar (Figs. 3 and 4). The bond lengths in the ketohydrazone fragments of **1** and **2** are identical within the experimental error (C(7)—C(3), 1.501(3) [1.498(2)] Å; C(3)—N(6), 1.348(3) [1.352(2)] Å; N(6)—N(2), 1.372(3) [1.384(2)] Å; N(2)—C(10), 1.276(3) [1.282(2)] Å; C(10)—C(8), 1.436(3) [1.431(2)] Å; and C(3)—O(4), 1.224(2) [1.228(2)] Å). The planarity of molecule **1** is distorted due to the rotation of the pyridine ring by 34.0°, which is slightly larger than that in the structure of **2** (29.8°). In the crystal of **1**, the NH...N_{Py} intermolecular hydrogen bond (N_{Py}...N, 2.991(3) Å; and N_{Py}...H, 2.18(1) Å) is shorter than that in the structure of **2** (3.094(3) and 2.25(1) Å, respectively) and is more linear (the N_{Py}—H—N angle is 174(1)° and 166(1)° in **1** and **2**, respectively). The angle between the N_{Py}...N line and the plane of the pyridine ring, in which the lone electron pair of the N_{Py} atom is located, is substantially smaller in **1** (9.3°) than in **2** (18.2°).

The geometric parameters obtained indicate that the NH...N_{Py} intermolecular hydrogen bond in the crystals of **1** is stronger than that in **2**. However, the differences in the geometry of the NH...N_{Py} intermolecular hydrogen bond in the crystals of **1** and **2** could not be discriminated in the ν(N—H) region of the spectrum (see Fig. 2) except for a doublet in the low-frequency region (3216 and 3189 cm^{-1}) of the spectrum of **1**, which can be assigned to ν(N—H) vibrations.

Some differences are observed in the geometry of the pyridine ring of molecules **1** and **2**, namely, the bond angle at the C(7) atom is larger in **1** (C(11)—C(7)—C(5) 118.4(2)°) than in **2** (117.3(3))°, and the bonds at the pyridine N(9) atom (C(16)—N(9), 1.340(3) [1.330(3)] Å; and C(14)—N(9), 1.325(3) [1.304(3)] Å) are elongated.

The above-mentioned geometric differences indicate that in molecule **1** the interaction between the π-electron systems of the ketohydrazone and pyridine fragments is stronger. Some spectral features of compounds **1**—**4** are also attributable to the difference in the degree of delocalization of the π-electron density. Thus, the spectra of compounds **1** and **3** (the furan substituent) have a strong ν(C=N) band at 1625 and 1622 cm^{-1}, respectively, while in the spectra of **2** and **4**, the analogous band is hardly noticeable at 1634 and 1619 cm^{-1}, respectively.

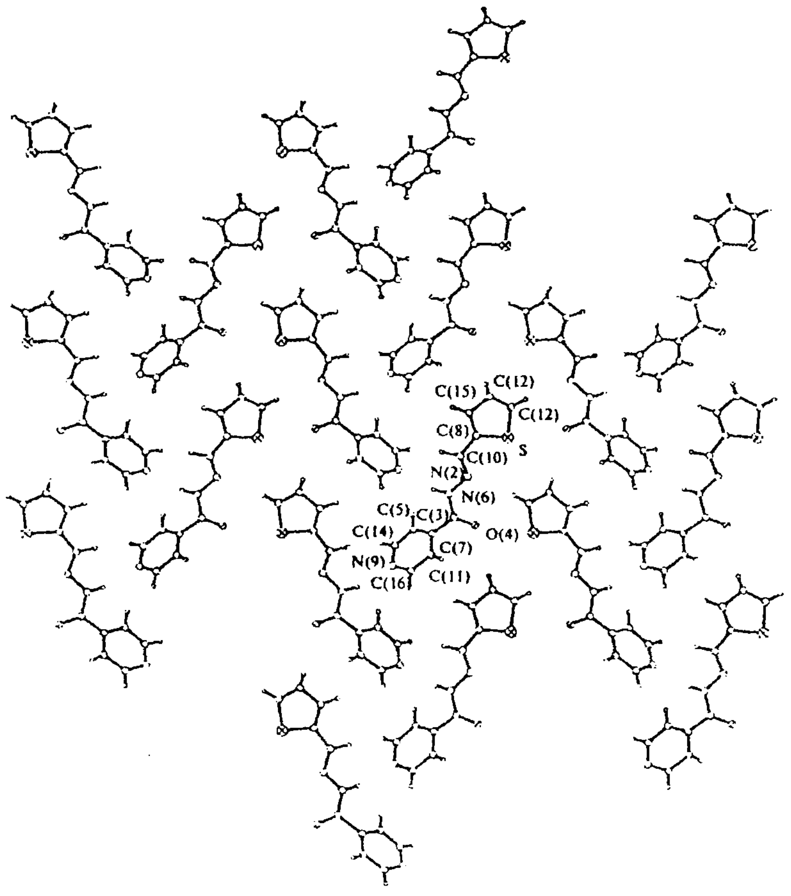

Fig. 4. Molecular and crystal structure of *N'*-thienylideneisonicotinic hydrazide.

However, the C=N bond lengths in molecules **1** and **3** (1.276(3) and 1.280(3) Å, respectively) and in molecules **2** and **4** (1.282(2) and 1.294(2) Å, respectively) are equal within the experimental error.

The crystal structures of **1** and **2** are identical (see Figs. 3 and 4). The molecules are packed in layers in which zigzag chains are formed through NH...N_{Py} intermolecular hydrogen bonds. There are short contacts between the molecules of the adjacent chains in the layer: C=O...S in **2**,[2] and C(13)—H(1)...O(4)—C(3) between the H atom of the furan ring and the O atom of the carbonyl group in **1** (C(13)...O(4), 3.306(3) Å; H(1)...O(4), 2.37(1) Å; C(13)—H(1)—O(4), 158(1)°; H(1)—O(4)—C(3), 124(1)°). Based on the geometric parameters, this contact can be assigned to a weak intermolecular hydrogen bond. This is confirmed by the spectral data. Thus, the ν(C=O) band is shifted to the low-frequency region (1670 cm^{-1}) relative to the "free" carbonyl (1682 cm^{-1}) in crystals of similar compounds,[2,9] and the changes in the ν(C—H) band of the furan ring at 3119 cm^{-1} are also typical of the perturbing effect of an intermolecular hydrogen bond (the low-frequency shift and an increase in the intensity; see Fig. 2, curves *1* and *3*).

The spectra of **3**, **4**, and **1a** with N—H...O=C intermolecular hydrogen bonds have a broad band at 638, 629, and 626 cm^{-1}, respectively, which is typical of crystalline amides. This band (known as Amide V) is determined by out-of-plane bending vibrations of the N—H group involved in intermolecular hydrogen bonding. In the 620—640 cm^{-1} region of the spectra of crystalline *N'*-substituted isonicotinic hydrazides (compounds **1** and **2**, *o*-nitrobenzylidene- (**5**),[2] and 5-nitrofurfurylidene- (**6**)[9]), in which N—H...N_{Py} intermolecular hydrogen bonds occur, analogous bands are not observed. Apparently, this band is shifted to the high-frequency region (at approximately 700 cm^{-1}) as a result of the strong interaction of the N—H group with the N_{Py} atom. However, C—H bending vibration bands of the pyridine (686 cm^{-1}) and benzene (695 cm^{-1}) rings of compound **5** are observed in this region. Therefore, we failed to reliably identify the Amide V band. It can be only noted that the spectrum of compound **1** has a moderately strong band at 702 cm^{-1}, molecule **2** shows a band at 686 cm^{-1} with a shoulder at 700 cm^{-1}, molecule **5** exhibits a superposition of a broad moderately strong band and two sharp bands at 695 cm^{-1} and 686 cm^{-1}, and in the spectrum of **6**, a broadened band at 686 cm^{-1} is observed.

The results outlined above demonstrate that if specific intermolecular interactions in crystals occur mainly through N—H...N_{Py} intermolecular hydrogen bonds, the replacement of the thiophene fragment in the molecule of *N'*-thienylideneisonicotinic hydrazide (**2**) by the furan ring (**1**) is not accompanied by a change in the crystal structure. However, this replacement leads to a substantial change in the intramolecular electronic effects, which is reflected both in the geometric and spectral characteristics of the molecules in crystals. Using *N'*-furfurylidene-isonicotinic hydrazide as an example, it was demonstrated that the desired crystal structure in which definite type of intermolecular hydrogen bonds (C=O...HN; N_{Py}...HN) occurs can be obtained by choosing the conditions of crystallization.

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