Russian Chemical Bulletin, International Edition, Vol. 51, No. 1, pp. 99—104, January, 2002 99

Influence of the position of the nitro group on the structural and spectroscopic characteristics of *N´*-(nitrobenzylidene)isonicotinic hydrazides in the crystalline state

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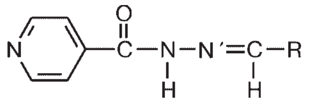
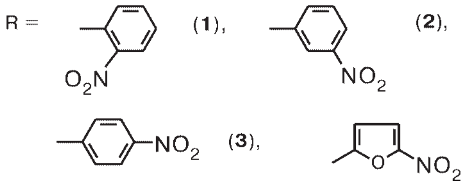
N´-Substituted isonicotinic hydrazides of the general formula Py—C(=O)—N(H)—N´=C(H)—R, where R is *o*- (**1**), *m*- (**2**), or *p*-nitrophenyl (**3**), were studied by IR spectroscopy and X-ray diffraction analysis. The position of the nitro group in these compounds has no effect on the type of the crystal structure. The crystal packings are based on stacks consisting of antiparallel planar molecules. The molecules from the adjacent stacks are linked to each other *via* the N—H...N_{Py} hydrogen bonds. Depending on the position of the nitro group, the N...N_{Py} distance increases in the series **3** > **1** > **2** and the energy of the hydrogen bonds decreases (according to the IR spectroscopic data) from 3.9 to 3.1 kcal mol^{-1}. Analysis of the IR spectra demonstrated that the intensity of absorption in the ν(C—H) stretching region of the pyridine ring increases substantially as the the N—H...N_{Py} hydrogen bond is strengthened. Some regularities of the changes, which are observed for the ν(NO_2) bands in the spectra of the nitrophenyl-containing conjugated molecules in solutions, persist in the crystalline state.

Key words: *N´*-(nitrobenzylidene)isonicotinic hydrazides, molecular and crystal structure, intermolecular hydrogen bonds, IR spectroscopic characteristics of hydrogen bonds and nitro groups.

N´-Substituted isonicotinic hydrazides (INH) of the general formula





attract interest because of their photoactivity[1] and biological activity.[2] Previously,[3] we have investigated the effects of the nature and the structure of the substituent R and the influence of the conditions of crystallization on the composition and structure of single crystals and on the character and geometry of the intermolecular hydrogen bonds. In the present study, we examined *o*-, *m*-, and *p*-nitrobenzylideneisonicotinic hydrazides (**1**, **2**, and **3**, respectively) by IR spectroscopy and X-ray diffraction analysis with the aim of revealing the dependence of the molecular and crystalline properties of the compounds of this series on the position of the nitro group in the substituent R. Isomer **2** differs from compounds **1** and **3** in that it crystallizes from aqueous alcohols as crystal hydrates. From this viewpoint, compound **2** resembles *N´*-(5-nitrofurfurylidene)isonicotinic hydrazide (**4**), which can form not only anhydrous crystals possessing the intermolecular NH...N_{Py} hydrogen bonds but also crystal hydrates of different compositions with other types of the intermolecular hydrogen bonds and a crystal solvate involving acetic acid and water.[3,4]

The geometric parameters of the *m*-nitrobenzylidene fragment in compound **2** are close to those of the nitrofuran fragment in **4**. Actually, we obtained a set of crystalline products for compound **2**, as in the case of compound **4** studied by us earlier, *viz*., anhydrous crystals, the crystal hydrates [**2** • H_2O] and [**2** • $1.5H_2O$], and the crystal solvate with acetic acid and water, *viz*., [**2** • H_2O • AcOH].*

In compound **3**, the substituent R has a more substantial effect (compared to compounds **1** and **2**) on the electron density redistribution within the conjugated mol-

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* The structural data for these compounds will be published in *Russian Chemical Bulletin*, *Int. Ed.* in 2002.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 96—100, January, 2002.

Table 1. Crystallographic data for compounds **1—3**

Parameter	**1**	**2**	**3**
Space group	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$
a/Å	7.510(2)	8.446(2)	7.970(2)
b/Å	10.910(2)	10.800(1)	10.672(2)
c/Å	15.476(3)	14.181(2)	14.905(2)
β/deg	94.87(2)	106.38(2)	100.6(3)
V/Å^3	1263.4(5)	1241.0(5)	1246.2(5)
d_{calc}/g cm^{-3}	1.421(2)	1.446(2)	1.440(2)
Z	4	4	4
$I > 4\sigma(I)$	1598	1562	1194
R	0.041	0.036	0.037
wR	0.122	0.099	0.097

Note. The molecular formula of compounds **1—3** is $C_{13}H_{10}N_4O_3$, M_w = 210.25.

ecule resulting in specific physicochemical properties of **3** and high reactivities of its other active centers.[5]

In the presents study, we examine the data from X-ray diffraction analysis and IR spectroscopy for anhydrous crystals of the isomeric series of *N´*-(nitrobenzylidene)isonicotinic hydrazides **1—3** and *N´*-(5-nitrofurfurylidene)isonicotinic hydrazide **4**.[4] Although the last-mentioned compound does not belong to the isomeric series, it (as mentioned above) is similar to compound **2** in a number of properties.

Experimental

The IR spectra were recorded on a Specord M-82 spectrometer in KBr pellets and the spectroscopic data were processed on a computer. To determine the stretching vibration frequencies of the C=O group, which are not perturbed by intermolecular interactions in the crystal, we prepared dilute solutions in THF, which was distilled over CaH_2 immediately before use (samples are insoluble in CCl_4).

Compound **1**, the hydrate of **2** (which has been described as anhydrous **2** in a number of papers cited in the study[6]), and compound **3** were prepared by the reactions of isonicotinic hydrazide with *o*-, *m*-, and *p*-nitrobenzaldehydes, respectively, in aqueous ethanol (all reagents were purchased from Aldrich). Hydrazides **1** (m.p. 235—236 °C) and **3** (m.p. 290—291 °C) were crystallized from aqueous ethanol. Anhydrous **2** (m.p. 231—232 °C) was obtained when either the reaction or crystallization were carried out in anhydrous MeOH, which has been preliminarily distilled over magnesium metal.

The X-ray diffraction data sets for crystals of **1—3** were collected on a four-circle KM-4 Kuma Diffraction diffractometer (Mo-Kα radiation, ω/2θ scanning technique, 3.05° < θ < 40.05°). We repeated the X-ray study of the crystal structure of **1** because the previous X-ray data have been obtained[7] from crystals of poor quality. Absorption was ignored. The structures were solved by direct methods using the SHELX-86 program package[8] and refined by the full-matrix least-squares method using the SHELXL-93 program package.[9] The positions of all H atoms were revealed from difference Fourier syntheses and refined isotropically. The crystallographic data for compounds **1—3** are given in Tables 1—3.

Table 2. Dihedral angles (α) between the planes of the pyridine ring (I), the central fragment of the molecule (II), the phenyl ring (III), and the nitro group (IV) in compounds **1—4**

Compound	α/deg		
	I—II	II—III	III—IV
1	16.9	8.7	38.9
2	8.0	0.3	12.5
3	8.0	0.3	12.3
4	12.9	—	7.2

Table 3. Bond lengths (d) in the central Py—C(=O)—N(H)—N=C(H)—R—NO_2 fragments of *N´*-substituted isonicotinic hydrazides **1—4**

Compound	d*/Å						
	Py—C	C—N	N—N	N=C	C—R	R—N	C=O
1	1.505	1.356	1.375	1.270	1.469	1.462	1.217
2	1.504	1.358	1.377	1.270	1.463	1.464	1.214
3	1.501	1.359	1.381	1.269	1.466	1.474	1.214
4	1.500	1.357	1.375	1.274	1.439	1.422	1.221

* The accuracy of the determination of the bond lengths is 0.002 Å.

Results and Discussion

The overall view of molecule **2** is shown in Fig. 1. Molecules **1**, **3**, and **4** have analogous structures. The central C(2)—C(1)—N(1)—N(2)—C(7)—C(8) fragment of molecules **1—3** is virtually planar (the torsion angles in these fragments are at most 5°). Molecules **2** and **3** adopt virtually identical conformations as evidenced by the dihedral angles between the planes of the pyridine ring (I), the central fragment (II), the phenyl ring (III), and the nitro group (IV), and these molecules are more planar than molecule **1** (see Table 2). Molecule **4** is also virtually planar. However, the conformations of molecules **1**, **2**, and **4** differ substantially. In molecule **4** containing the nitrofuran fragment as the substituent R, the electronegative O(1) and N(2) atoms, the O atom of the furan ring, and one of the O atoms of the nitro group are in the *syn* orientations. To the contrary, the O(1) and N(2) atoms and the O atoms of the nitro group in molecules **1** and **2** are in the *syn-anti* positions (see Fig. 1).

The corresponding bond lengths in molecules **1—4** are identical to within the experimental error (see Table 3), except for the C—R and R—N bond lengths in compound **4**. This is, apparently, associated with the difference in the electronic structure of the furan and benzene rings.

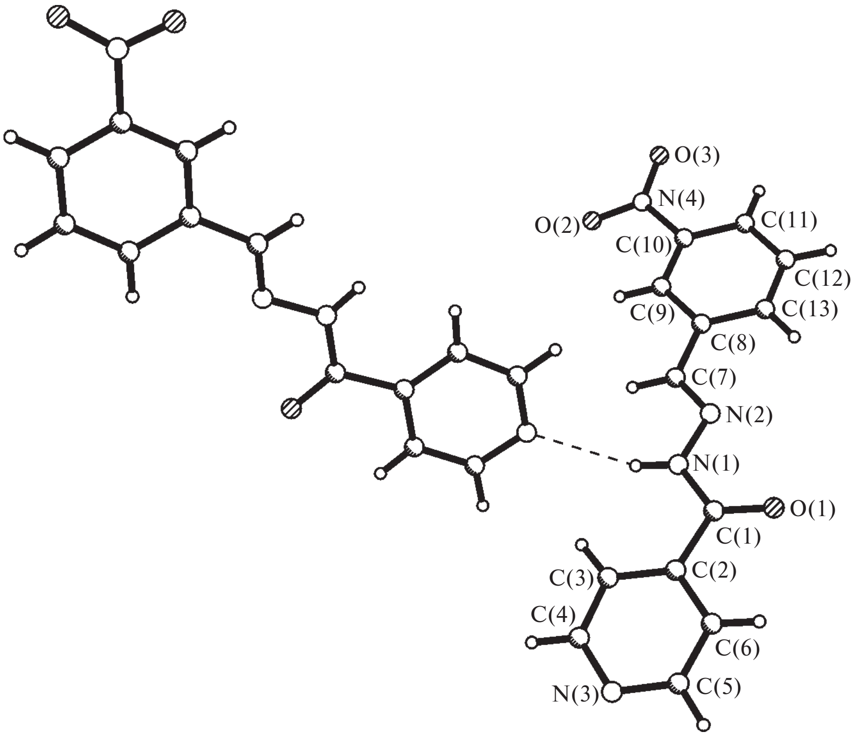

Fig. 1. Overall view of the molecule and the system of intermolecular NH...N_{Py} hydrogen bonds in isonicotinic hydrazide **2**.

In the crystals of **1**—**3**, the planar molecules are packed in stacks. This type of packing is very often observed in the crystals of *N*′-substituted benzo- and isonicotinic hydrazides[3,10] as well as in the crystals of many other organic compounds. In these stacks, the molecules are oriented antiparallel with respect to each other and are related by inversion centers along the short crystallographic axis (Fig. 2). This packing mode is, undoubtedly, determined by the high energy of interactions between the planar molecules packed in stacks (this suggestion is confirmed by the high melting points of the compounds under study).

In the crystals, the molecules from the adjacent stacks are linked to each other through the intermolecular N—H......N_{Py} hydrogen bonds (Table 4) typical of *N*′-substituted isonicotinic hydrazides. The fragment of the molecular packing in the crystal of **2** is shown in Fig. 1 (molecules **1**, **3**, and **4** are packed analogously). The longest N...N_{Py} distance is observed in the structure of **2**. Apparently, steric hindrances to the formation of closely spaced stacks are larger in the case of the *meta*-nitro group compared to the *ortho*- or *para*-nitro groups. Actually, in the structure of **2**, the short O(2)...N(4) contact (3.09 Å) between the nitro groups, which are related by the inversion center with the coordinates (½ ½ 0) and which belong to the molecules from the adjacent translationally equivalent (along the *b* axis) stacks, does not allow the molecules to come closer together. The shortest N...N_{Py} distance is observed in the structure of compound **3** whose molecule contains the *para*-nitro group and, correspondingly, is the longest one. In the crystal of **1**, the N...N_{Py} distance is shorter than that in the crystal of **2** because the nitro group is twisted out of the plane of the molecule by a larger angle.

In the crystal structures of **1**—**3**, there are also other rather short intermolecular contacts, for example, the contact between the O atom of the C=O group and the α-H atom of the Py ring (see Fig. 2). The α-C_{Py}(H)...O=C distances are 3.42, 3.12, and 3.20 Å in the crystals of **1**—**3**, respectively. However, it should be noted that the

Table 4. Geometric, spectral, and energy (E_{HB}) characteristics of the intermolecular hydrogen bonds in compounds **1**—**4**

Parameter	1	2	3	4
d/Å				
N...N	3.10	3.28	3.03	3.00
H...N	2.25	2.42	2.12	2.24
C=O...α-C_{Py}	3.42	3.12	3.20	—
ω/deg				
N—H...N	165	161	166	169
ν(N—H)/cm^{-1}	3196	3243	3191	3180*
ν(C=O)/cm^{-1}	1680	1693	1686	—
δ(N—H)/cm^{-1}	1561	1548	1564	—
E_{HB}/kcal mol^{-1}	3.8	3.1	3.9	4.0

* The ν(NH) frequency (3120 cm^{-1}) reported in the study[4] is a misprint.

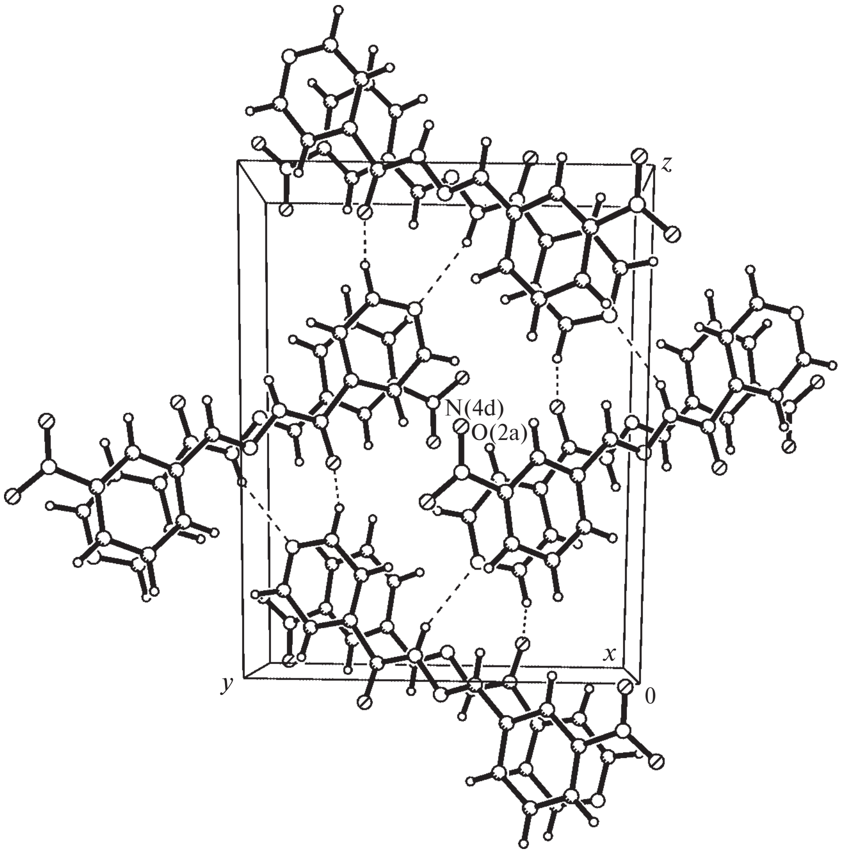

Fig. 2. Stacked packing in the crystal of **2**.

C—H—O angles are too small (130—140°) and the H...O distances are too long (2.87, 2.34, and 2.47 Å, respectively) to consider these contacts as intermolecular hydrogen bonds. Actually, as can be seen from Table 4, the ν(C=O) frequency decreases as the O...C_{Py} distance increases, whereas the inverse dependence would be observed for intermolecular hydrogen bonds. This inconsistency cannot be attributed to the difference in the position of the nitro group in the phenyl fragment because the ν(C=O) frequencies in dilute solutions of **1**, **2**, and **4** in THF are approximately equal (1703—1706 cm^{-1}). We failed to obtain the corresponding data for compound **3** because it is insoluble in appropriate solvents. The differences in ν(C=O) for compounds **1—3** are attributed both to intramolecular interactions and intermolecular interaction in the crystal to the intermolecular C—H...O=C hydrogen bond. It should be noted that in the structure of *N*′-(furfurylidene)isonicotinic hydrazide **5** studied by us previously,[11] the intermolecular C—H...O=C hydrogen bond (H is the α-hydrogen atom of the furan ring) was revealed by IR spectroscopy, the C...O distance in **5** (3.31 Å) being larger than those in compounds **2** and **3**. Note that the C—H...O angle (158°) in **5** is larger than the corresponding angles in compounds **2** and **3** (135 and 130°, respectively). In addition, the H atom in *N*′-(furfurylidene)isonicotinic hydrazide is directed toward one of the lone electron pairs of the O atom (the C=O...H angle is 124°). Probably, it is the above-mentioned factors that are responsible for the fact that this contact belongs to intermolecular hydrogen bonds.

The above-considered example demonstrates once again that the presence (or absence) of intermolecular hydrogen bonds in the crystals cannot be judged from the geometric parameters of the X—H...Y contact. This conclusion is also supported by the relationship between the ν(N—H) frequencies and the N...N_{Py} distances.

The ν(N—H) stretching vibration frequencies, the δ(N—H) bending frequencies, and the energies of the intermolecular hydrogen bonds (E_{HB}) for compounds **1—4** are given in Table 4. The energies E_{HB} were calculated according to empirical equations,[12] which relate the frequency of the ν(N—H) vibration perturbed by the intermolecular hydrogen bond to the frequency of the nonperturbed ν_0(N—H) vibration frequency. For one of the structurally similar compounds, the ν_0(N—H) frequency is 3371 cm^{-1} (according to the data of the present study). It can be seen in Table 4 that there are the inverse linear dependences between the N...N_{Py} distances and the energies E_{HB} as well as between ν(N—H) and δ(N—H).

Taking into account the structural characteristics of the intermolecular hydrogen bonds,[13,14] the N—H...N_{Py} contact in the structure of **2** cannot be assigned to the hydrogen bonds, *i.e.*, the attractive intermolecular interactions between NH and N_{Py} must be absent. However, as can be seen in Table 4, the dependences of ν(N—H) and E_{HB} for compound **2** on the N...N_{Py} distances are analogous to those observed for compounds **1**, **3**, and **4**. It should be noted that the value of E_{HB} (3.1 kcal mol^{-1}) indicates that even at such a long (from the structural standpoint) distance, the force field created by the N_{Py} atom has a substantial effect on vibrations of the N—H group (ν(N—H) is more than 100 cm^{-1} lower than ν_0(N—H); see Table 4).

Previously,[11] we noted that the existence of the of the intermolecular N—H...N_{Py} hydrogen bond can be, in particular, judged from a substantially higher absorption in the region of ν(C—H) vibrations of the Py ring (3100—2700 cm^{-1}) compared to absorption in the spectra of N'-substituted isonicotinic hydrazides in which the N_{Py} atom is not involved in specific interactions. The results of the present study demonstrate that the intensities of the bands in this frequency region increase as the intermolecular hydrogen bond is strengthened (Fig. 3; Table 4). We can only state this interesting experimental fact for which no unambiguous explanation presently exists.

The data from X-ray diffraction analysis and IR spectroscopy for N'-(nitrobenzylidene)isonicotinic hydrazides provide a unique possibility of analyzing the spectral characteristics of the nitro groups in aromatic compounds containing a system of conjugated bonds. In these compounds, the nitro groups are active π-acceptors causing electron density redistribution between the molecular fragments. As a result, the frequencies (ν) and intensities (A) of the bands of symmetric and antisymmetric stretching vibrations of the nitro group are changed compared to nonsubstituted nitrobenzene (NB).

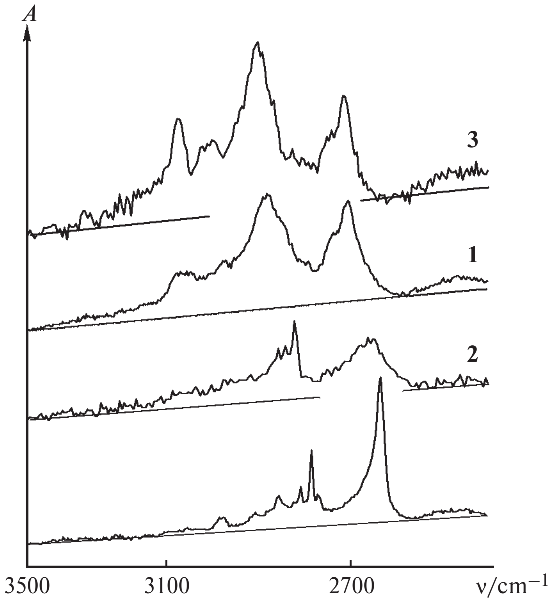

Fig. 3. IR spectra of compounds **1**—**3** in the region of the ν(N—H) and ν(C—H) vibrations of the Py ring. The curves are numbered according to the identifying numbers of the compounds. The lowest curve represents the spectrum of N'-(furfurylidene)isonicotinic hydrazide possessing the intermolecular NH......O=C hydrogen bond.

The effects of substituents in the NB molecules on the spectral characteristics of the vibration bands of the nitro group have been studied in detail only for *para*-substituted NB[5] due, apparently, to the fact that the *para*-substituents exert a more unambiguous effect on ν and A compared to the substituents in other positions. It should be noted that the spectral studies of the mutual influence of the groups in molecules with conjugated bonds were carried out in solutions and, hence, these results cannot be correctly compared with our data on the vibration frequencies of the nitro groups in the crystalline state. However, based on the results of the study[5] and other investigations of the authors cited therein, we can point out a series of regularities analogous to those observed in solutions.

The intensities of all symmetric vibrations A_s in the spectra of *para*-substituted NB are higher than the intensities of antisymmetric vibrations A_{as}, as distinguished from nitrobenzene. For all compounds studied by us (**1**—**3**, where **3** can be considered as *para*-substituted NB), this intensity ratio persists.

The presence of potential π-donor substituents in the *para* position of the NB molecule leads to a decrease in both the ν_{as} and ν_s frequencies (analogous situation is also observed in the case of compound **3**). Interestingly, the ν_{as} and ν_s frequencies in the spectrum of **3** are virtually identical with the corresponding values found in the spectrum of p-nitroaniline in CCl_4. Compared to NB, the ν_{as} frequencies in the spectra of **1** and **2** are lower, whereas the ν_s frequencies have higher values (Table 5).

In solutions of *para*-substituted NB, the ν_{as} and ν_s bands (primarily, ν_s) are split.[15] In the spectra of the crystalline samples of the compounds under study, splitting of the ν_s band was observed only for compound **1**. Apparently, this splitting results from the same factors as in solutions (rather than is associated with the crystalline state) because this effect was not observed for compounds **2** and **3**.

The above-considered data suggest that some spectral characteristics of the NO_2 groups are determined only by intramolecular electronic effects and are independent of the aggregation state of the compound and interactions with the environment, be it is formed by the solvent molecules in solutions or the adjacent molecules of the compound in the crystal.

Table 5. Frequencies of the symmetric stretching (ν_s) and antisymmetric stretching (ν_{as}) vibrations of the nitro group in the crystalline samples of **1**—**4** and in solution of nirobenzene (NB) and *p*-nitroaniline (NA) in CCl_4

Compound	ν_s	ν_{as}
	cm^{-1}	
1	1366, 1352	1519
2	1355	1526
3	1336	1511
4	1349	1521
NB	1349	1532
NA	1338	1511

Hence, the crystals of isonicotinic hydrazides under consideration are characterized by the stacked packing formed by antiparallel elongated planar molecules regardless of the position of the nitro group. This packing is typical of many *N´*-substituted benzo- and isonicotinic hydrazides. The molecules located in the adjacent stacks are linked to each other through the N—H...N_{Py} hydrogen bonds, the N...N_{Py} distance being determined by the position of the nitro group and increasing in the series of the *para*-, *ortho*-, and *meta*-substituted derivatives. The intermolecular N—H...N_{Py} hydrogen bonds are characterized by the N...N_{Py} distances, which are larger than the crystallographic criteria for intermolecular N...N hydrogen bonds. As the intermolecular N—H...N_{Py} hydrogen bond is strengthened, the intensity of IR absorption in the region of ν(C—H) vibrations of the Py ring increases substantially compared to the spectra of isonicotinic hydrazides in which the N_{Py} atom is not involved in intermolecular hydrogen bonding. Some regularities of the changes in the ν(NO_2) frequencies in the IR spectra of compounds with conjugates systems and the nitrophenyl fragments, which were observed in solutions, persist in the crystalline samples.

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Received March 28, 2001