X-ray and IR spectroscopic studies of specific intermolecular interactions in *N'*-substituted isonicotinohydrazides

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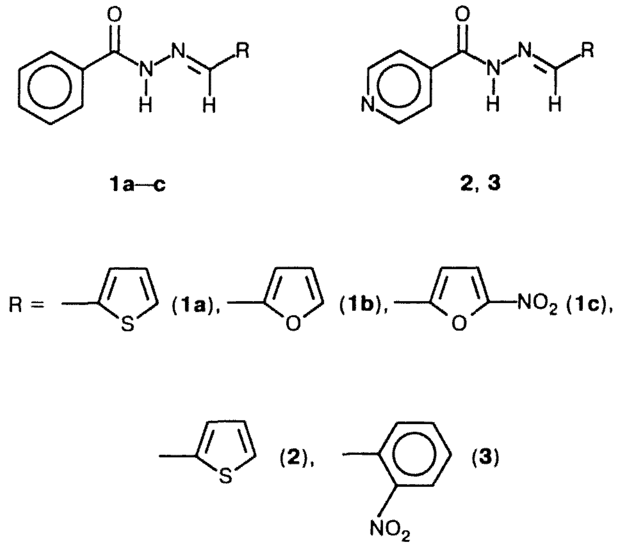
N'-Thenylidene- and *N'*-(*o*-nitrobenzylidene)hydrazides of isonicotinic acid have been studied by X-ray structural analysis and IR spectroscopy. In the crystalline state, these molecules are linked through intermolecular $N-H\cdots N_{Py}$ hydrogen bonds. Carbonyl groups are not involved in intermolecular hydrogen bonds. However, it was found that the C=O group participates in an attractive interaction with the sulfur atom of the thiophene group. The energy of this interaction is comparable with the energies of intermolecular $C=O\cdots H-N$ hydrogen bonds in amides.

Key words: molecular and crystal structure, IR spectroscopy, specific intermolecular interactions, intermolecular hydrogen bond, intermolecular attractive $S\cdots O$ interaction, *N'*-substituted isonicotinohydrazides.

Previously, based on X-ray structural studies of a wide range of benzohydrazides, including *N'*-arylidene derivatives (**1a—c**),[1—3] we have studied the characteristic features of molecular and crystal structure favorable for intermolecular proton phototransfer in crystals. Crystals of benzohydrazides are characterized[3] by the formation of chains of intermolecular hydrogen bonds of the amide type ($C=O\cdots H-N$). In crystals of **1c**, water molecules (W) are inserted into these chains ($C=O\cdots W\cdots H-N$). The topology of the chains of intermolecular hydrogen bonds appeared to be sensitive to the molecular structures of benzohydrazides. Thus, for example, the deviation of the molecule from planarity leads to the formation of centrosymmetric dimeric associates rather than of chains of intermolecular hydrogen bonds in crystals.[4]



With the aim of elucidating further the effect of the molecular structures of substituted hydrazides on their crystal structures and the character of specific intermolecular interactions, we performed an X-ray structural and IR spectroscopic study of *N'*-thenylidene- and *N'*-(*o*-nitrobenzylidene)isonicotinohydrazides (**2**, **3**), whose molecules contain, in addition to the carbonyl oxygen atom, one more strong proton-acceptor center, *viz.*, the nitrogen atom of the pyridine ring.

Experimental

Compounds **2** and **3** crystallize as yellow needle-like crystals in monoclinic space groups. The principal crystallographic parameters for **2** are as follows: $a = 10.040(3)$, $b = 13.607(4)$, $c = 8.589(5)$ Å, $\beta = 111.49(3)°$, $Z = 4$, $d = 1.301(2)$ g cm^{-3}, space group *Cc*. The principal crystallographic parameters for **3** are as follows: $a = 7.460(4)$, $b = 10.920(4)$, $c = 15.420(5)$ Å, g = 85.1(4)°, $Z = 4$, $d_{\text{calc}} = 1.403(3)$ g cm^{-3}, space group $P2_1/b$. The crystals of **2** with dimensions of 0.5×0.03×0.04 mm^3 were studied on an automated four-circle KM-4 diffractometer (Mo-Kα radiation); the crystals of **3** with dimensions of 0.4×0.04×0.05 mm^3 were studied on a three-circle DAR-UM diffractometer (Cu-Kα radiation). The numbers of independent nonzero reflections with $I > 2\sigma(I)$ were 769 and 959 for compounds **2** and **3**, respectively.

The structures were solved by the direct method using the SHELL-86 program package[5] and were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were located from difference Fourier syntheses and only their positional parameters were refined. The final values of the *R* factors are $R = 0.025$ (**2**) and 0.055 (**3**); the atomic coordi-

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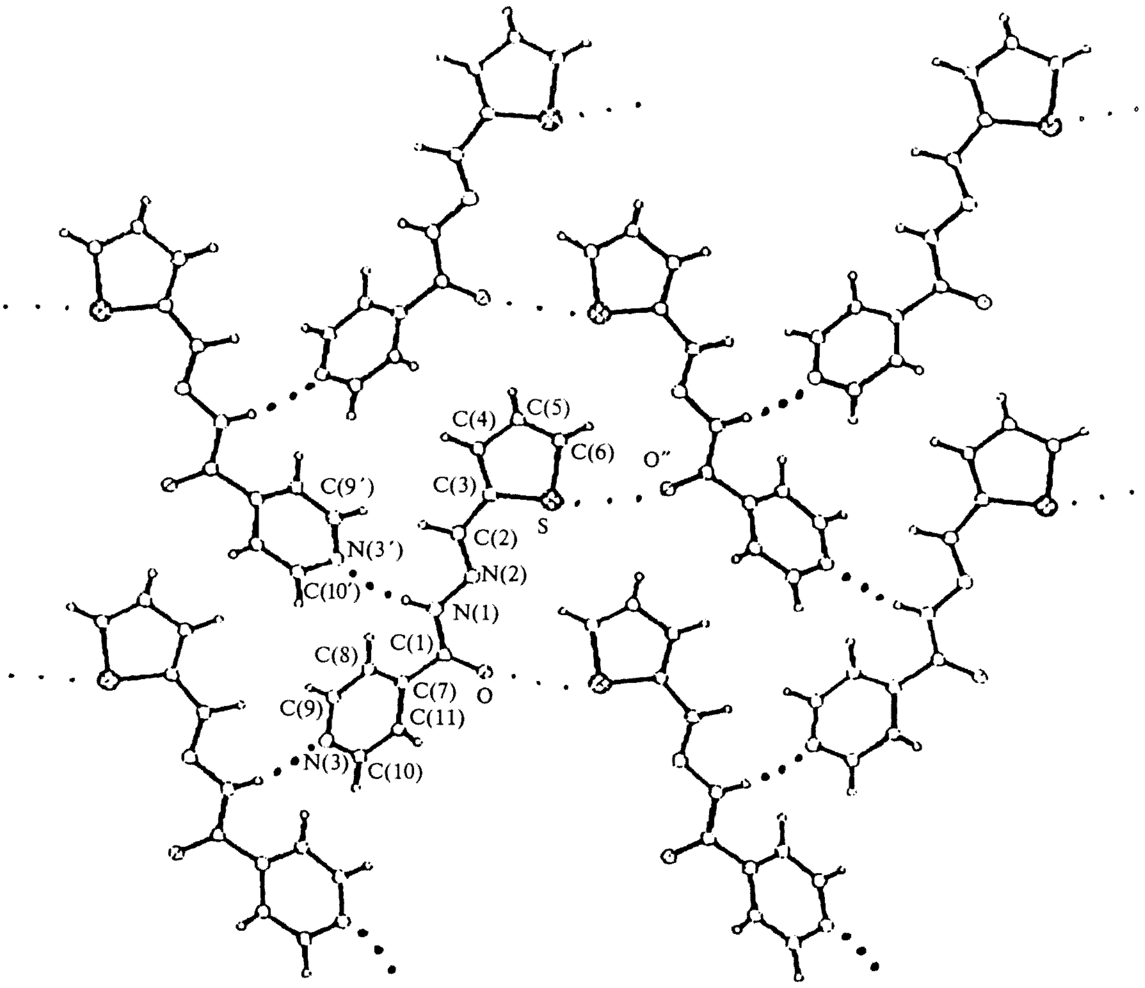

Fig. 1. Character of intermolecular hydrogen bond formation in crystals of **2**.

nates corresponding to these *R* factors are given in Tables 1 and 2.

Calculations of energies were carried out in the atom-atom approximation using the 6-exp parameters.[6] The Coulomb energy component was calculated based on the charges determined by the PM3 method[7] (MOPAC 6.0)[8]. The energy of hydrogen bonds was taken into account using the potential proposed by E. M. Popov.[6]

The IR spectra were recorded on a Specord M-82 spectrometer in THF and in KBr pellets.

Results and Discussion

The central fragment of molecule **2** (Fig. 1) is approximately planar and has a *syn* orientation of the O, N(2), and S heteroatoms. The torsion angles of the turn about the N(1)—N(2) and C(2)—C(3) bonds are 3.4° and 3.2°, respectively. The deviation of the molecule from planarity is determined by a turn of the pyridine fragment about the C(1)—C(7) bond by 29.8°. The bond-length distribution in the acylhydrazone fragment of **2** (C(1)—O 1.229(3); C(1)—N(1) 1.350(3); N(1)—N(2) 1.386(2); C(1)—C(7) 1.502(3) Å) coincides with the analogous bond lengths in benzohydrazide **1a**[2] within the experimental error. Only the shortening of the C(2)—C(3) bond in **2** (1.431(3) Å) compared to that in **1a** (1.453 Å) can be noted.

Molecule **3** (Fig. 2) on the whole is more planar than **2**: although the angles of rotation about the N(1)—N(2) and C(2)—C(8) bonds are 4.0° and 5.0°, respectively, the angle of rotation of the pyridine fragment about the C(1)—C(3) bond in **3** (13.8°) is substantially smaller than that in **2**. The deviation from planarity is determined only by the rotation of the *o*-NO_2 group with respect to the phenyl ring by 37.9° due to steric hindrance induced by the H(2) atom. The substantial increase in the bond angle at the N(2) atom to 116.0° compared to the analogous values in molecules **2** (114.1°) and **1a** (113.5°)[2] that contain the thiophene fragment is noteworthy. For benzohydrazides with the furan substituent (**1b,c**), the values of this angle are within the range of 115.5°—117.2°.[1—3]

Unlike the structure of **1**, the crystal structures of **2** and **3** are characterized by the formation of intermolecu-

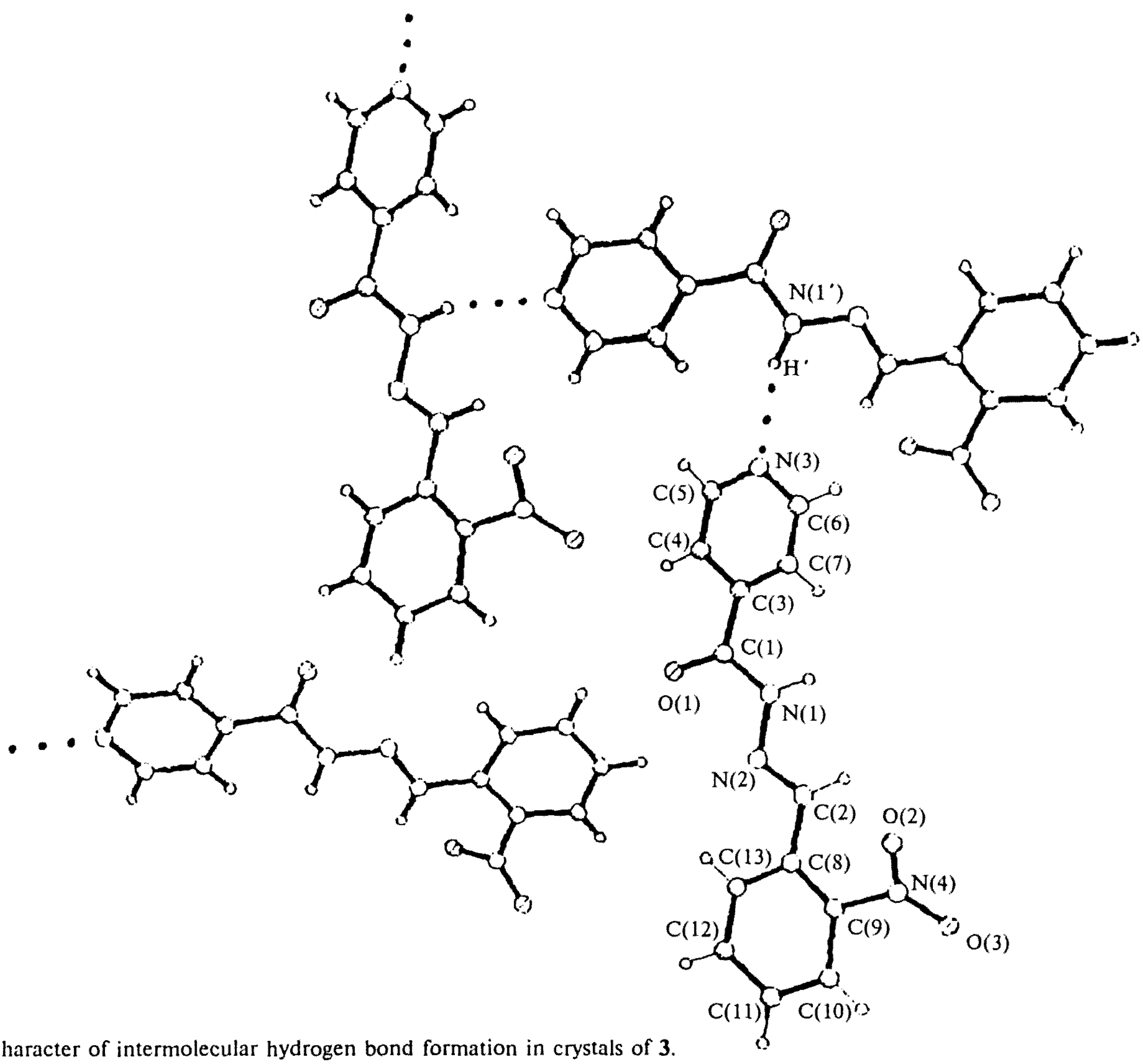

Fig. 2. Character of intermolecular hydrogen bond formation in crystals of **3**.

lar NH···N_{Py} hydrogen bonds rather than of hydrogen bonds of the amide type (C=O···H—N). The geometric parameters of these intermolecular hydrogen bonds in **2** [N(1)—N(3′) 3.094(3), H(N(1))···N(3′) 2.25(1) Å, N(1)—H(N(1))—N(3′) angle 167(1)°] and in **3** [N(1′)—N(3) 3.071(4), H(N(1′))···N(3) 2.23(2) Å, N(1′)—H(N(1′))—N(3) angle 168(1)°] allow the classification of these bonds as weak linear intermolecular

Table 1. Atomic coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **2**

Atom	*x*	*y*	*z*
S	3464(3)	2022(3)	967(3)
O	7773(3)	651(3)	6081(3)
N(1)	6390(3)	−346(3)	3971(3)
N(2)	5486(3)	404(3)	3109(3)
N(3)	10279(3)	−2626(3)	7401(3)
C(1)	7520(3)	−154(3)	5386(3)
C(2)	4501(3)	128(3)	1744(3)
C(3)	3459(3)	779(3)	646(3)
C(4)	2406(3)	521(3)	−802(4)
C(5)	1589(4)	1336(3)	−1635(3)
C(6)	2026(3)	2177(3)	−868(3)
C(7)	8465(3)	−1031(4)	6052(4)
C(8)	8663(3)	−1764(3)	5048(3)
C(9)	9559(3)	−2538(3)	5800(3)
C(10)	10137(3)	−1901(4)	8367(3)
C(11)	9262(3)	−1088(3)	7748(4)
H(1)	621(2)	−95(2)	367(2)
H(2)	435(1)	−60(2)	144(2)
H(4)	220(2)	−15(1)	−124(2)
H(5)	102(2)	121(1)	−254(2)
H(6)	163(2)	277(2)	−126(2)
H(8)	805(2)	−179(2)	385(2)
H(9)	978(1)	−307(2)	505(2)
H(10)	1064(2)	−196(1)	953(2)
H(11)	922(2)	−69(1)	844(2)

hydrogen bonds. However, according to the IR spectroscopic data, intermolecular NH · · · N$_{Py}$ hydrogen bonds formed should be considered as strong because the N—H stretching frequency (ν(NH) is 3210 and 3196 cm^{-1} in **2** and **3**, respectively) is substantially lower than ν(NH) in **1a** (3257 cm^{-1}), in which a rather strong (according to both the spectral and geometric parameters) linear amide-type hydrogen bond N—H · · · O=C occurs. Therefore, despite the considerable distances between the atoms involved in the intermolecular hydrogen bonds in **2** and **3**, the force field of the nitrogen atom of the pyridine ring has a more substantiall effect on the N—H stretching vibration than the force field of the oxygen atom of the carbonyl group. Apparently, this is associated with the fact that in the structures **2** and **3**, the H atom of the amide group interacts with the lone electron pair of the nitrogen atom of the pyridine ring (in **2**, the H(N(1))—N(3′)—C(9′) and H(N(1))—N(3′)—C(10′) angles are 120.9° and 119.6°, respectively; the analogous angles in **3** are 129.1° and 117.6°, respectively), whereas in the structure of **1a**, the N—H bond is directed toward the region of the lowest electron density distributed about the oxygen atom of the carbonyl group (the COH′ angle in **1a** is 161.5°).[9]

In the crystal structure of **3**, the C=O bond of the carbonyl group is not involved in an intermolecular hydrogen bond, which occurs rather rarely in compounds containing the amide group. The C=O bond (1.203(3) Å) is not elongated compared to the analogous bond in **1a** (1.223(3) Å), in which an intermolecular C=O · · · H—N hydrogen bond occurs. In accordance with this fact, the C=O stretching band in compound **3** (ν(C=O) 1681 cm^{-1}, "free" carbonyl) is shifted compared to ν(C=O) in compound **1a** (1640 cm^{-1}) to the higher frequency region. This effect of an intermolecular hydrogen bond on the C=O bond length and on its stretching frequency has been noted previously.[10]

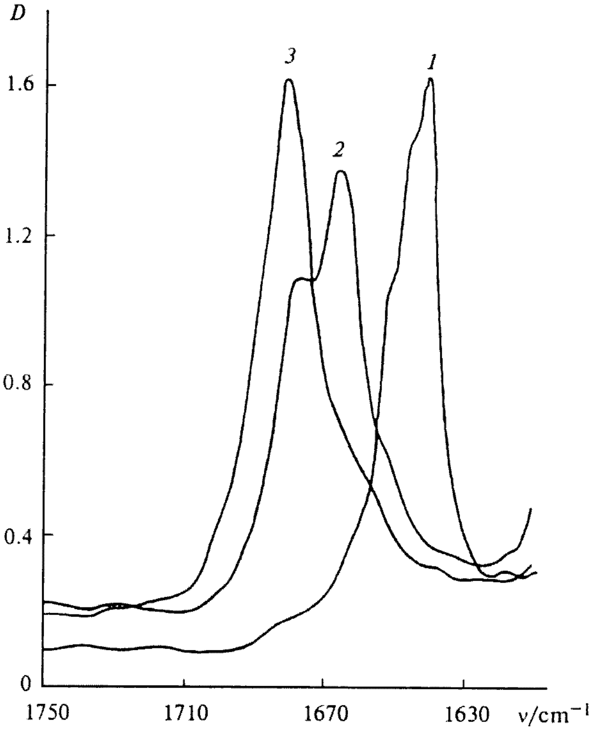

Fig. 3. IR spectra of compounds **1a** (*1*), **2** (*2*), and **3** (*3*) in the region of the ν(C=O) stretching vibrations.

In the crystal structure of **2**, the carbonyl group also does not participate in an intermolecular hydrogen bond; however, the C=O bond length (1.229(3) Å) coincides with that in **1a** (1.223(3) Å) within experimental error; the maximum of the ν(C=O) band appears at 1665 cm^{-1}, *i.e.*, this maximum is shifted by 16 cm^{-1} to lower frequency relative to the ν(C=O) band of the "free" carbonyl in **3** (Fig. 3). The same and even smaller values of the shift are observed in the spectra of a wide range of analogous compounds that we have studied, in crystals of which the C=O groups are involved in intermolecular hydrogen bonds of different nature and with different geometry. The difference in the ν(C=O) values in **2** and **3** cannot result from the difference in the substituents R, because in dilute solutions of **2** and **3** in THF, the ν(C=O) frequencies are 1697 and 1700 cm^{-1}, respec-

Table 2. Atomic coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **3**

Atom	*x*	*y*	*z*
O(1)	5779(4)	2815(4)	5186(4)
N(1)	6358(4)	1292(4)	4243(4)
N(2)	7070(3)	545(3)	4863(3)
N(3)	9589(4)	−2841(4)	4146(4)
N(4)	4231(4)	4724(4)	2409(4)
C(1)	5805(4)	2432(4)	4450(4)
C(2)	7664(3)	−490(3)	4618(3)
C(3)	5258(4)	3169(4)	3719(4)
C(4)	4337(4)	4236(4)	3918(4)
C(5)	3835(3)	5002(3)	3255(3)
C(6)	5126(3)	3679(3)	2222(3)
C(7)	5671(4)	2918(4)	2847(4)
C(8)	8432(3)	−1261(3)	5255(3)
C(9)	9242(4)	−2366(4)	5058(4)
C(10)	9888(4)	−3230(4)	5671(4)
C(11)	9697(4)	−2840(4)	6536(4)
C(12)	8923(4)	−1678(4)	6765(4)
C(13)	8310(3)	−963(3)	6126(3)
O(2)	10052(4)	−2025(4)	3601(4)
O(3)	9422(3)	−3930(3)	3991(3)
H(1)	659(2)	112(2)	382(2)
H(2)	7949(2)	−64(2)	397(2)
H(4)	384(1)	347(1)	463(1)
H(5)	222(1)	570(1)	315(1)
H(6)	513(2)	338(2)	149(2)
H(7)	617(2)	238(2)	275(2)
H(11)	−5(2)	429(2)	296(2)
H(12)	902(1)	−111(1)	750(1)
H(13)	787(2)	−19(2)	625(2)

tively. The shift of the maximum of the ν(C=O) band by 16 cm^{-1} and the elongation of the carbonyl bond in **2** compared to **3** may be an indication of the participation of the oxygen atom of the C=O bond in compound **2** in specific intermolecular interactions comparable in energy with intermolecular hydrogen bonds.

Analysis of the molecular packing in crystals of **2** suggests that participation of the oxygen atom of the carbonyl group in an O···S′ specific interaction is possible. The S···O′′ distance (3.250 Å) is equal to the sum of the van der Waals radii. The vector of the S···O′′ contact lies in the plane of the thiophene cycle and is approximately parallel to the S—C(3) bond. The angle between the S···O′′ and S—C(3) vectors is 168.1°. The formation of this contact is explained[11] by the possibility of a specific orbital n—σ* interaction between the lone electron pair of the carbonyl oxygen atom and the antibonding orbital of the S—C(3) bond. We attempted to estimate the energy of this interaction by the semiempirical quantum-chemical PM3 method[7] using the MOPAC 6.10 program package.[8] The value of the energy of the S···O interaction (−0.32 kcal mol^{-1}) obtained confirms its attractive character. In future, we plan to study these interactions by *ab initio* methods.

Thus, the study performed demonstrates that in crystals of *N*′-arylidenehydrazides of isonicotinic acid containing two proton-acceptor centers (C=O and N_{Py}) different in strength, an NH···N_{Py} intermolecular hydrogen bond occurs. It was shown that the "free" oxygen atom of the carbonyl group may participate in intermolecular attractive O···S interactions with the sulfur atom of the thiophene ring.

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