Russian Journal of Organic Chemistry, Vol. 37, No. 6, 2001, pp. 866–868. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 6, 2001, pp. 912–914.

X-ray Diffraction Analysis of the Structure of 3-Nicotinehydroxamic Acid and Pyrazinecarbohydroxamic Acid Monohydrate

N. K. Makhmudova, Z. Ch. Kadyrova, E. A. Del'yaridi, and Kh. T. Sharipov

Institute of General and Inorganic Chemistry, Academy of Sciences of Uzbekistan, Tashkent, 700170 Uzbekistan

Received November 10, 1999

Abstract—X-ray diffraction analysis of the crystal structure of 3-nicotine- and pyrazinecarbohydroxamic acids revealed that the molecules were present in keto tautomeric form and possessed Z-configuration. The system of the intermolecular hydrogen bonds is the most affected by the character of the aromatic substituent and the presence of crystallization water molecules in the structure.

Hydroxamic acids are used extensively as organic reagents in analytical chemistry, in the synthesis of drugs, herbicides etc [1, 2]. The presence in the molecule of hydroxamic acids of several functional groups NH, OH, C=O, various tautomeric forms and configurations of the hydroxamic moiety, and also a trend to formation of strong nonvalent interactions require the application to the structural studies of this class compounds of the modern physical methods. In extension of the studies on the structure of hydroxamic acids [3, 4] we solved the crystalline structures of 3-nicotinehydroxamic acid (**I**) and pyrazinecarbohydroxamic acid monohydrate $C_4H_3N_2CONHOH \cdot H_2O$ (**II**).

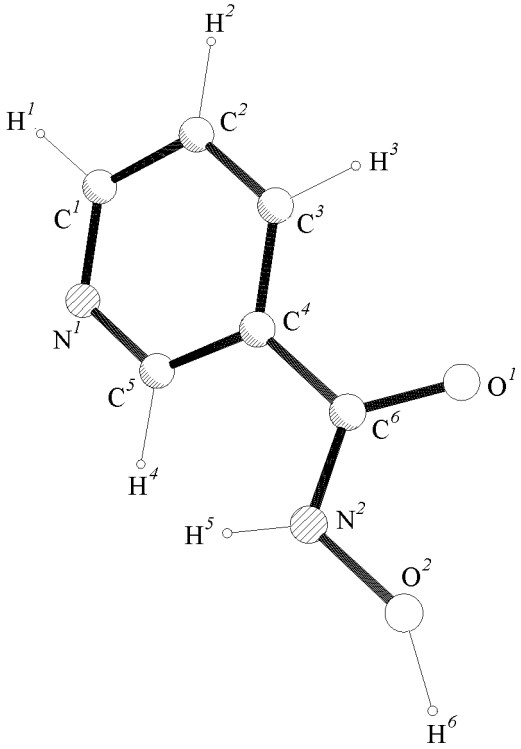

Fig. 1. Molecular structure of 3-nicotinehydroxamic acid (**I**).

A discrete structural unit of molecule **I** is present in the most common ketone form RCONHOH and possesses *Z*-configuration: C^6–O^1 1.284(14), C^6–N^2 1.343(14), N^2–H 0.92(4) Å, $C^6N^2O^2$ 117.0(1)° (Fig. 1). The comparison of geometrical characteristics of this structure with those of benzohydroxamic and salicylhydroxamic acids [5, 6] shows that in molecules **I** the C=O bond is weakened, the bond angle $C^6N^2O^2$ is increased by 3°. The angle $N^2C^6C^4$ equal to 118.0(9)° is decreased in approximately the same way. Therewith the bond C^4–C^6 between the hydroxamic moiety and the aromatic substituent is reduced to 1.451(14) Å.

The nitrogen atom from the heteroaromatic ring of acid **I** does not participate in the intermolecular hydrogen bonds. A single intermolecular hydrogen bond was found in the structure of compound **I**: N^2–H—O=C ($N^2 \cdots O$ 2.81, H···O 1.99 Å, N^2HO 146°) that links the molecules of compound **I** into chains (Fig. 2). As a result the bond C^4–C^6 is shortened virtually without hampering the planar structure of the CONHOH group (the torsion angle $O^2N^2C^6O^1$ 2.6°). Therewith the angle between the hydroxamic moiety and the aromatic ring is 9° increased as compared to the benzohydroxamic acid [6].

Pyrazinecarbohydroxamic acid monohydrate (**II**) in the crystal state exists in the keto-form RCONHOH [C^5=O^1 1.249(4), C^5–N^3 1.307(4), N^3–H^4 0.69(3) Å, $O^1C^5N^3$ 120.5(3)°] (Fig. 3). The hydroxamic group is virtually planar (torsion angle $O^2N^3C^5O^1$ 1.1°) and has *Z*-configuration as in

1070-4280/01/3706-0866$25.00

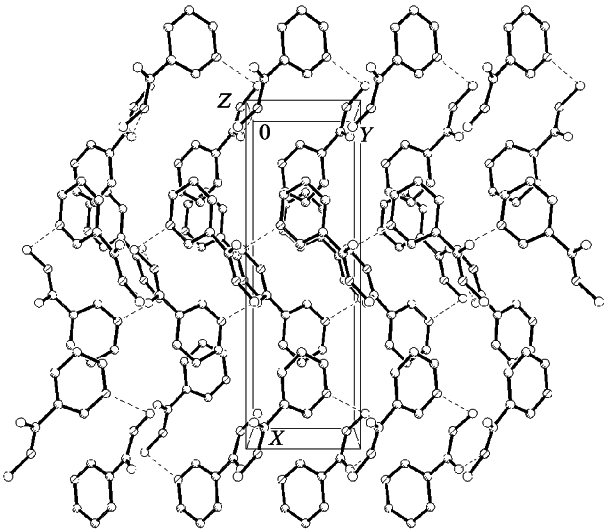

Fig. 2. Crystal structure of 3-nicotinehydroxamic acid (**I**).

the structure of acid **I** (angle $O^2N^2C^6O^1$ 2.6°). The orientation of the hydroxamic moiety with respect to the aromatic ring is directly dependent on the character of the intermolecular interactions. The water molecules bind the compound **II** molecules into dimers C=O···H–O*H, N–O–H···O*H_2 located along the cell diagonal (O^1···H^6–O^{*3} 2.08, O^1···O^{*3} 2.87 Å, $O^1H^6O^{*3}$ 170°; O^1···H^7O^{*3} 2.09, O^1···O^*44^3 2.82 Å, $O^1H^7O^{*3}$ 169°; N–O^2–H^5···O^{*3} 1.87, O^2···O^{*3} 2.69 Å, $O^2H^5O^{*3}$ 174°). An intermolecular hydrogen bond NH···N* joins the dimers in two-dimensional nets (N^3–H^4···N^{*2} 2.24, N^3N^{*2} 2.90 Å, $N^3H^4N^{*2}$ 160°) (Fig. 4).

Unlike acid **II** in whose molecule the intermolecular hydrogen bond arises between NH group

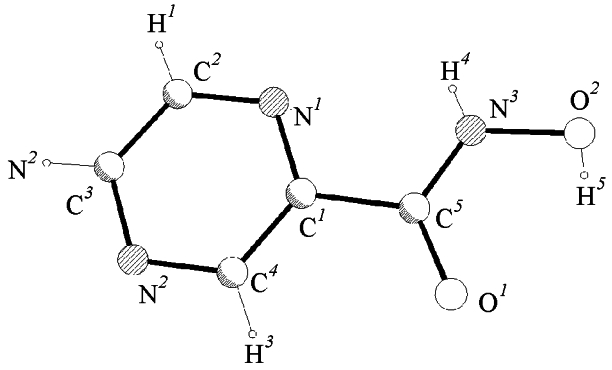

Fig. 3. Molecular structure of pyrazinecarbohydroxamic acid (**II**).

and a nitrogen of heterocycle, in the structure of acid **I** the amino group proton acceptor in formation of the only hydrogen bond is the C=O group. In the latter case the hydrogen bond is stronger. However the more branched system of hydrogen bonds in acid **II** causes its higher melting point as compared with acid **I**.

Thus the analysis of the crystal structures of acids **I** and **II** and comparison of their geometrical characteristics show that the hydroxamic acids are present in the ketone tautomeric form and *Z*-configuration. The increased number of heteroatoms in the aromatic ring results in the elongation of the C–C bond connecting the heterocycle with the –C(O)NHOH group to 1.503 Å, and in the shortening of bonds C=O, C–N, N–O, N–H in the hydroxamic fragment. The character of the intermolecular hydrogen bonds and packing of the hydroxamic acid molecules gets also changed. Another aromatic moiety and the presence of crystal-

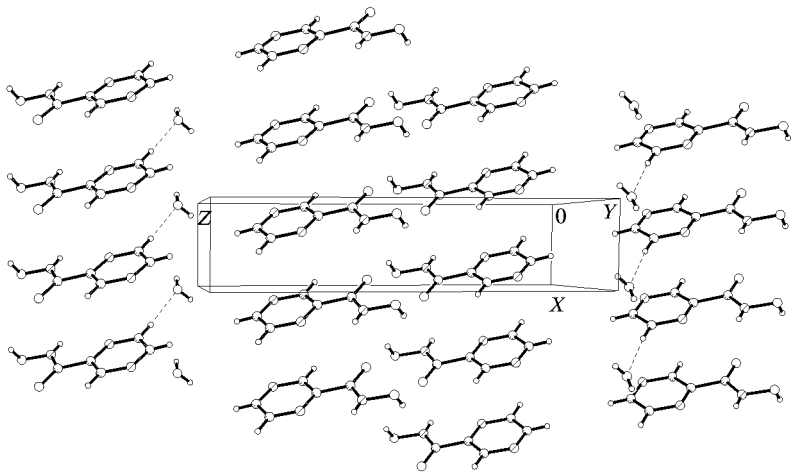

Fig. 4. Crystal structure of pyrazinecarbohydroxamic acid monohydrate (**II**).

Table 1. Atomic coordinates ($\times 10^4$, Å) and their equivalent thermal factors B_{eq}($\times 10^3$, Å^2) in the structure of 3-nicotinehydroxamic acid (**I**)[a]

Atom	*x*	*y*	*z*	B_{eq}
C^1	7630(8)	6800(18)	–2650(16)	213(24)
C^2	7264(8)	4809(19)	–1600(16)	332(24)
C^3	7838(8)	3071(18)	–822(15)	318(24)
C^4	8764(8)	3291(18)	–1030(15)	287(24)
C^5	9080(8)	5305(19)	–2073(15)	323(24)
C^6	9377(8)	1560(18)	–142(15)	299(24)
N^1	8526(7)	7082(17)	–2852(14)	330(23)
N^2	10177(7)	955(16)	–799(14)	318(23)
O^1	9157(6)	771(16)	1255(13)	379(22)
O^2	10767(6)	–715(16)	96(13)	374(23)
H^1	718(3)	8083(26)	–3315(26)	–
H^2	655(3)	4660(26)	–1419(26)	–
H^3	757(3)	1553(26)	–30(26)	–
H^4	980(3)	5421(26)	–2282(26)	–
H^5	1022(3)	903(26)	–1889(26)	–
H^6	1140(3)	–1792(26)	212(26)	–

[a] Atom designation as on Fig. 1.

Table 2. Atomic coordinates ($\times 10^4$, Å) and their equivalent thermal factors ($B \times 10^3$, Å^2) in the structure of pyrazinecarbohydroxamic acid (**II**)[a]

Atom	*x*	*y*	*z*	*B*
O^1	1043(7)	4290(2)	4166(1)	303(3)
O^2	–1591(7)	2066(2)	4680(1)	324(1)
O^3	316(7)	1470(2)	581(1)	315(4)
N^1	–3540(7)	3171(2)	2388(2)	247(1)
N^2	–1343(8)	5501(3)	1835(2)	283(5)
N^3	–2243(9)	2537(3)	3913(2)	269(2)
C^1	1733(9)	3999(3)	2862(2)	214(4)
C^2	–4249(11)	3549(4)	1634(2)	279(5)
C^3	–3092(11)	4664(3)	1358(2)	290(4)
C^4	–664(10)	5137(3)	2595(2)	252(5)
C^5	–861(8)	3610(3)	3708(2)	221(5)
H^1	–573(7)	311(3)	132(2)	341(1)
H^2	–369(7)	415(3)	86(2)	341(1)
H^3	67(7)	563(3)	291(2)	341(1)
H^4	343(7)	217(3)	368(2)	341(1)
H^5	–284(7)	250(3)	494(2)	341(1)
H^6	151(7)	125(3)	23(2)	341(1)
H^7	–96(8)	93(3)	60(2)	341(1)

[a] Atom designation as on Fig. 3.

lization water in acid **II** causes the formation of net structures instead of chains observed in the structure of acid **I**.

EXPERIMENTAL

3-Nicotinehydroxamic acid (**I**) and pyrazinecarbohydroxamic acid (**II**) were prepared by reaction of 3-nicotinamide or pyrazinecarboxamide respectively with hydroxylamine along procedure [1]. The fine crystalline powder of compound **I** melts at 135°C. Single crystals of compound **I** colorless: *a* 14.848(2), *b* 4.882(2), *c* 8.449(1) Å, space group $Pca2_1$, *Z* 4, *V* 612.5(2) Å^3. From the powder of acid **II** possessing diamagnetic properties and melting at 162°C by recrystallization from water–alcohol mixture were obtained well-formed single crystals of acid **II** monohydrate $C_2H_5N_3O_2 \cdot H_2O$: *a* 3.752(4), *b* 11.157(3), *c* 16.461(3) Å, γ 95.00(2)°, space group *P*2/*n*, *Z* 4, *V* 686.4(4) Å^3.

A complete set of experimental data for solving the structures of compounds **I, II** was obtained on automatic four-circle diffractometer Syntex $P2_1$ (CuK_α-radiation, graphite monochromator, $\theta/2\theta$-scanning).

Both structures were solved by direct method of determination of structural amplitude signs with the use of SHELX-86 software. The nonhydrogen atoms were refined by the least-squares procedure in the full-matrix anisotropic approximation, the hydrogen atoms were localized by difference synthesis and included into refinement isotropically U_H 0.05 Å^2. The number of independent reflexes with $I > 1.96\sigma(I)$ included into refinement was 460 for acid **I** and 727 for acid **II**. The final values of *R*-factor are 0.07 and 0.038 for compounds **I** and **II** respectively. The atomic coordinates and equivalent thermal factors B_{eq} given in the form $B_{eq} = 1/3(V_{11} + V_{22} + V_{33})$ are listed in Tables 1 and 2.

REFERENCES

1. Zhungietu, G.I. and Artemenko, A.I., *Gidroksamovye kisloty* (Hydroxamic Acids), Kishinev: Shtiintsa, 1986, 138 p.
2. Pilipenko, A.T. and Zul'figarov, O.S., *Gidroksamovye kisloty* (Hydroxamic Acids), Moscow: Nauka, 1989.
3. Kadyrova, Z.Ch., Makhmudova, N.K., Sharipov, Kh.T., and Parpiev, N.A., *Uzb. Khim. Zh.*, 1996, no. 5–6, p. 11.
4. Sharipov, Kh.T., Makhmudova, N.K., Khodashova, T.C., Parpiev, N.A., and Porai-Koshits, M.A., *Koord. Khimiya,* 1983, vol. 9, no. 2, pp. 266–271.
5. Larsen, I.K., *Acta Cryst. Ser B*, 1978, vol. 34, pp. 962–964.
6. Gottlicher, S. and Paulus, H., *Chem. Ber.,* 1982, vol. 115, no. 1, pp. 393–395.