Crystal and molecular structure of *N*-phenyl-4-nitrobenzamidoxime

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N-Phenyl-4-nitrobenzamidoxime has been studied by X-ray structural analysis. In two crystallographically independent molecules **1A** and **1B**, amidoxime groups adopt a planar *Z* configuration, and these fragments are in an *s-trans* conformation with respect to the =N—O and C—N(H) bonds; an intramolecular NH...O bond occurs. The nitrophenyl and phenyl groups are rotated with respect to the amidoxime plane [ONCN] by −57 and −32° in **1A** and −38 and −22° in **1B**, respectively. The rotation of the fragments about the C(1)—N(2) bond is −28 (**1A**) and −35° (**1B**). In crystals, molecules **1A** and **1B** are linked in oxime dimers through two intermolecular =N...(HO)′ hydrogen bonds; dimers form double chains through two NH...$(O_2N)''$ hydrogen bonds.

Key words: amidoxime, *N*-phenyl-4-nitrobenzamidoxime, structure, X-ray structural analysis, hydrogen bond.

Amidoximes [oximes of amides $R^1C(=NOH)NR^2R^3$] are of interest as synthons in organic chemistry, biologically active compounds, and subjects for studying intramolecular electronic and steric effects.[1,2] Considerable attention is given to the study of spatial structures of amidoximes,[2,3] the X-ray diffraction method being the most successfully employed (see Refs. 2, 4—11 and references cited therein). As part of continuing studies, we have performed X-ray diffraction study of *N*-phenyl-4-nitrobenzamidoxime (**1**), which exhibits the highest melting point among amidoximes reported in the literature.[1—11]

Experimental

Triclinic crystals of amidoxime **1**, $C_{13}H_{11}N_3O_3$, m.p. 184—186 °C, were obtained from isopropyl alcohol. At 20 °C, a = 9.636(5), b = 9.789(6), c = 15.816(9) Å, α = 72.93(5)°, β = 83.44(4)°, γ = 64.66(4), d_{calc} = 1.326 g cm^{-3}, Z = 4 (two independent molecules **1A** and **1B**), space group $P\bar{1}$. The unit-cell parameters and intensities of 1685 independent reflections with $F^2 \geq 3\sigma$ were measured on an automated four-circle Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, θ ≤ 25°). The structure was solved by the direct method using the MULTAN program and refined by the least-squares method. Hydrogen atoms (except for OH) were revealed from the difference Fourier series and were included in the final full-matrix refinement. The values of R factors are as follows: R = 0.063 and R_w = 0.078.

The geometry of the molecules and the atomic numbering scheme are shown in Fig. 1. Atomic coordinates are given in Tables 1 and 2; selected bond distances and bond angles are given in Tables 3 and 4.

Results and Discussion

X-ray structural study of amidoxime **1** demonstrated that two crystallographically independent molecules **1A** and **1B** are present in crystals. In both molecules, the amidoxime group adopts a *Z* configuration, the fragments have an *s-trans* conformation with respect to the ordinary N(1)—O(1) and C(1)—N(2) bonds (see Fig. 1), and a strong intramolecular N—H...O hydrogen bond (IaHB) formed through the amide NH group and the oxygen oxime atom occurs (Table 5).

Apparently, this intramolecular hydrogen bond contributes substantially to stabilization of a *Z* configuration typical of *N*-unsubstituted and *N*-monosubstituted amidoximes.[1,8] Thus, an increase in steric hindrances when passing from *N*-methyl-4-nitrobenzamidoxime[7] (**2**) to *N*-phenyl analog **1**, which we have studied, causes no

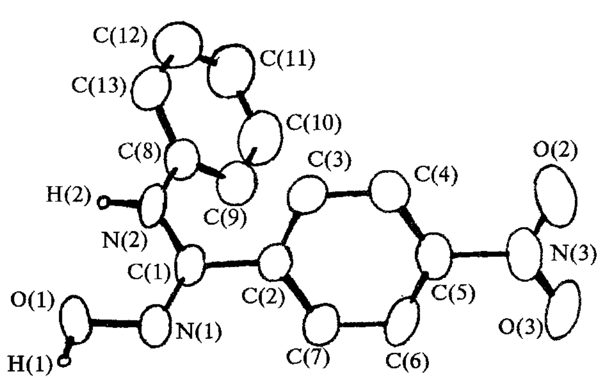

Fig. 1. Overall view of the molecule of amidoxime **1**.

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Table 1. Atomic coordinates of molecule **A** of amidoxime **1**

Atom	x	y	z	$B_{iso}^{eq}/Å^2$
O(1)	−0.3972(4)	0.2476(4)	−0.3790(3)	4.2(1)
O(2)	0.4316(5)	−0.5383(5)	−0.2495(3)	6.4(1)
O(3)	0.3159(6)	−0.6141(6)	−0.1351(4)	9.1(2)
N(1)	−0.2630(4)	0.1050(4)	−0.3661(3)	3.3(1)
N(2)	−0.2571(4)	0.1641(5)	−0.2337(3)	3.9(1)
N(3)	0.3218(6)	−0.5163(5)	−0.2007(4)	5.2(1)
C(1)	−0.1976(5)	0.0737(5)	−0.2911(4)	3.2(1)
C(2)	−0.0599(5)	−0.0782(5)	−0.2665(3)	2.8(1)
C(3)	0.0645(6)	−0.1088(6)	−0.3242(4)	3.8(1)
C(4)	0.1903(6)	−0.2542(6)	−0.3012(4)	4.0(1)
C(5)	0.1876(6)	−0.3631(6)	−0.2233(4)	3.8(1)
C(6)	0.0660(7)	−0.3344(7)	−0.1664(4)	4.5(2)
C(7)	−0.0584(6)	−1.1884(6)	−0.1888(4)	4.1(2)
C(8)	−0.1747(6)	0.1743(6)	−0.1694(4)	3.9(1)
C(9)	−0.2532(7)	0.2182(7)	−0.0960(4)	5.3(2)
C(10)	−0.1722(8)	0.2342(8)	−0.0322(5)	6.8(2)
C(11)	−0.0222(8)	0.2102(8)	−0.0436(5)	7.5(2)
C(12)	0.0532(7)	0.1693(7)	−0.1175(5)	6.3(2)
C(13)	−0.0214(6)	0.1515(6)	−0.1809(4)	4.6(2)
H(1)	−0.407(7)	0.269(6)	−0.428(4)	7(2)
H(2)	−0.352(5)	0.234(4)	−0.243(3)	0.3(8)

Table 2. Atomic coordinates of molecule **B** of amidoxime **1**

Atom	x	y	z	$B_{iso}^{eq}/Å^2$
O(1)	−0.2982(4)	0.0449(4)	−0.5195(3)	4.1(1)
O(2)	−1.2314(4)	0.6321(5)	−0.6415(4)	7.2(1)
O(3)	−1.1552(4)	0.7876(4)	−0.6116(3)	5.6(1)
N(1)	−0.4452(4)	0.1731(5)	−0.5272(3)	3.4(1)
N(2)	−0.4645(5)	0.0950(5)	−0.6498(3)	3.7(1)
N(3)	−1.1300(5)	0.6636(5)	−0.6243(3)	4.5(1)
C(1)	−0.5202(5)	0.1913(5)	−0.5965(4)	3.2(1)
C(2)	−0.6770(5)	0.3184(5)	−0.6066(3)	2.9(1)
C(3)	−0.7956(6)	0.2902(5)	−0.6316(4)	3.6(1)
C(4)	−0.9444(6)	0.4063(6)	−0.6361(4)	3.9(2)
C(5)	−0.9728(5)	0.5427(5)	−0.6173(4)	3.4(1)
C(6)	−0.8551(6)	0.5727(5)	−0.5937(4)	3.7(2)
C(7)	−0.7080(6)	0.4581(5)	−0.5886(4)	3.4(1)
C(8)	−0.5009(6)	0.1298(6)	−0.7405(4)	3.3(1)
C(9)	−0.4733(6)	0.0063(6)	−0.7751(4)	4.3(2)
C(10)	−0.5037(7)	0.0353(7)	−0.8640(4)	4.9(2)
C(11)	−0.5638(7)	0.1853(8)	−0.9167(4)	5.6(2)
C(12)	−0.5925(8)	0.3098(7)	−0.8836(5)	5.8(2)
C(13)	−0.5602(7)	0.2826(6)	−0.7947(4)	4.8(2)
H(1)	−0.270(7)	0.105(7)	−0.528(5)	13(2)
H(2)	−0.404(5)	0.009(3)	−0.634(2)	3(1)

Table 3. Bond lengths (d/Å) in molecules **1A** and **1B**

Bond	**1A**	**1B**
O(1)—N(1)	1.418(4)	1.422(4)
O(1)—H(1)	0.75(6)	0.72(6)
O(2)—N(3)	1.216(6)	1.221(5)
O(3)—N(3)	1.202(5)	1.204(4)
N(1)—C(1)	1.301(5)	1.308(5)
N(2)—C(1)	1.361(5)	1.348(5)
N(2)—C(8)	1.410(5)	1.422(6)
N(2)—H(2)	0.87(4)	0.78(6)
N(3)—C(5)	1.477(6)	1.461(5)
C(1)—C(2)	1.488(5)	1.479(5)

Table 4. Bond angles (φ/deg) in molecules **1A** and **1B**

Angle	**1A**	**1B**
N(1)—O(1)—H(1)	100(5)	84(5)
O(1)—N(1)—C(1)	109.8(3)	110.8(3)
C(1)—N(2)—C(8)	126.4(4)	127.9(4)
C(1)—N(2)—H(2)	117(3)	123(3)
C(8)—N(2)—H(2)	115(3)	110(3)
N(1)—C(1)—N(2)	123.3(4)	123.0(4)
N(1)—C(1)—C(2)	115.5(4)	113.9(4)
N(2)—C(1)—C(2)	120.9(4)	122.9(4)
C(1)—C(2)—C(3)	119.6(4)	117.9(4)
C(1)—C(2)—C(7)	119.5(4)	121.4(4)
C(3)—C(2)—C(7)	120.9(4)	120.6(4)
C(4)—C(5)—C(6)	122.7(4)	121.9(4)
N(2)—C(8)—C(9)	118.0(4)	118.3(4)
N(2)—C(8)—C(13)	121.8(4)	122.0(4)
C(9)—C(8)—C(13)	120.1(5)	119.7(5)

change in the configuration of the amidoxime group, bond lengths (Table 6), and bond angles.

The difference in the spatial structure of molecules **1A** and **1B** is small and is observed in the angles between the planar fragments. Thus, the rotation of the nitrophenyl group around the C(1)—C(2) bond is larger in molecule **1A** (−57°) than in **1B** (−38°). These values are substantially smaller than the angles of rotation of the *C*-aryl cycle in other *N*-monosubstituted benzamidoximes,$^{5-7}$ for which this nonplanarity is typical. It should be emphasized that in (*Z*)-benzamidoximes studied previously, the bending angle of the *C*-phenyl ring with respect to the plane of the amidoxime group depends only slightly on the nature, number, and positions of substituents in the benzene ring (see Table 6). Thus, in (*Z*)-*N*-benzylbenzamidoxime^{6} (**3**) and (*Z*)-*N*-phenyl-2,6-dichlorobenzamidoxime^{5} (**4**), these angles are nearly equal. In the above-mentioned amidoxime **2**, the rotation of the 4-nitrophenyl group is even larger than that in the molecules of amidoxime **1** and in the more sterically overcrowded molecules of *N*,*N*-disubstituted arylamidoximes **5**—**8** (see Table 6).

Based on these facts, we can say forcefully that a weak interaction of the electron systems of the *C*-aryl and amidoxime group exists in arylamidoximes **1**—**8** and their analogs.

The *N*-phenyl C(8)—C(13) group in amidoxime **1** is also noncoplanar with the amidoxime group. The angle of rotation of this group around the N(2)—C(8) bond is −32 and −22° in molecules **1A** and **1B**, respectively. These values are substantially smaller in **1** than in amidoxime **4**, in which chlorine atoms in the *ortho* position of the *C*-phenyl group cause the rotation of the *N*-phenyl group by 52°.

Because of this conformation of the aryl fragments, very short nonbonded contacts between the phenyl and nitrophenyl atoms in molecules of amidoxime **1** (for example, the distance between the centers of the C(2)—C(3) and C(8)—C(13) bonds in molecule **1B** is shortened to 3.00 Å) is attributable to a greater contribu-

Table 5. Hydrogen bonds of molecules of amidoxime **1**

D—H...A	Type	d(D...A)	d(H...A)	d(H...D)	Angle DHA
			/Å		/deg
N_A(2)—H_A(2)...O_A(1)	IaHB*	2.537	2.203	0.873	102.30
N_B(2)—H_B(2)...O_B(1)	IaHB*	2.557	2.351	0.776	96.16
N_A(2)—H_A(2)...O_A(2)	InHB	3.132	2.293	0.873	161.53
N_B(2)—H_B(2)...O_B(2)	InHB	3.158	2.422	0.776	158.95
O_A(1)—H_A(1)...N_B(1)	InHB	2.789	2.185	0.749	138.34
O_B(1)—H_B(1)...N_A(1)	InHB	2.747	2.568	0.718	96.72

* The five-membered rings are planar within 0.11 Å.

Table 6. C=N and C—N bond lengths (*d*), angles of rotation of the fragments (φ), and degree of pyramidality[13] (C_p^N = 9 – 0.025Σ angles) of the amine nitrogen atom in benzamidoximes **1**—**8** of the general formula R—C(X)=NOH

Compound	R	X	Isomer	d(C=N)	d(C—N)	φ(C—Ar)[a]	φ(C—N)[a,b]	C_p^N	References
				/Å		/deg			
1A	4-$O_2NC_6H_4$	NHPh	*Z*	1.301(5)	1.361(4)	–57	–28	0.00	[c]
1B	4-$O_2NC_6H_4$	NHPh	*Z*	1.308(5)	1.348(4)	–38	–35	0.00	[c]
2	4-$O_2NC_6H_4$	NHMe	*Z*	1.299(3)	1.337(3)	–79	0	0.00	7
3	Ph	$NHCH_2Ph$	*Z*	1.272	1.367	76	–24	0.20	6
4	2,6-$Cl_2C_6H_3$	NHPh	*Z*	1.289(3)	1.360(3)	80	1	0.00	5
5A	4-$O_2NC_6H_4$	$N(CH_2CH_2)_2O$	*E*	1.278(4)	1.394(4)	–53	–25	0.43	8
5B	4-$O_2NC_6H_4$	$N(CH_2CH_2)_2O$	*E*	1.279(4)	1.387(4)	–58	–22	0.55	8
6	4-MeC_6H_4	NMe_2	*E*	1.287	1.383	58	–19	0.28	10
7	4-ClC_6H_4	NMe_2	*E*	1.281(5)	1.357(6)	90	–12	0.13	9
8	Ph	NEt_2	*Z*	1.277(8)	1.350(8)	–72	–18	0.00	11

[a] Calculated from Newman projections using data reported in the cited works.

[b] Deviations of the lone pair of the nitrogen atom from the normal orientation with respect to π(C=N).

[c] This work.

tion of the packing effect rather than to the effects of intramolecular interactions.

The steric hindrances in molecules **1A** and **1B** are minimized also owing to rotation of the corresponding fragments around the C(1)—N(2) bond (see Table 6). In this case, a configuration of the bonds at the N(2) atom remains nearly planar, which points to conjugation in the PhNC=NOH phenylamidoxime fragment. An analogous situation is observed also in *N*-benzylamidoxime **3** with a slight pyramidality (C_p^N = 0.2) of the amine nitrogen atom.[6] In *N*-methyl- and *N*-phenylamidoximes **2** and **4**, this twist of the fragments and pyramidality of the bonds of the amide nitrogen atom are absent, whereas in *N,N*-disubstituted amidoximes **5** and **8**, these values depend strongly on the nature of substituents at the nitrogen atom and on the configuration of C=N bonds (see Table 6).

A substantial noncoplanarity of the nitro group and *C*-phenyl ring, mentioned in Ref. 7 for the molecule of amidoxime **2** (–12°), is absent in molecules **1A** and **1B** (≈4°), which may result from the differences in the crystal packing and the character of intermolecular hydrogen bonds (InHB).

The C=N bond lengths in molecules **1A** and **1B**, as in *N*-methyl analog **4**, is slightly larger compared to the standard value typical of oximes[12] (1.281 Å) and amidoximes **3**—**8**, which is attributable not only to the result of competition of electronic (n—π interactions) and steric effects but to the effect of intra- and intermolecular hydrogen bonds as well (see Table 5).

The C(1)—N(2) bond length is typical of $X{=}C_{sp^2}{-}N_{sp^2}$ bonds,[12] whereas the N(2)—C(8) bond is slightly longer [1.353(7) Å], which is characteristic of monosubstituted benzamidoximes, in which competition of steric and electronic effects is observed.

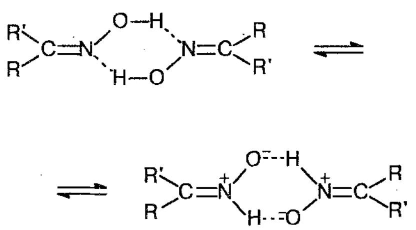
The stereochemical features of the structure of amidoxime **1** in crystals are determined, apparently, not only by the competition of the steric and electronic effects of the fragments of the molecule but by the system of hydrogen bonds as well. In addition to the participation in the above-mentioned N(2)H(2)...O(1) intramolecular hydrogen bond, both the amide and oxime groups form also intermolecular hydrogen bonds of two types, which determine to a larger extent the crystal structure of amidoxime **1** (see Table 5).

Molecules **1A** and **1B** are linked with each other through two short O—H...N′= hydrogen bonds with the participation of oxime groups to form oxime dimers, which is typical of many oximes and amidoximes.

Note that although hydrogen atoms of the aryl and amide groups were revealed unambiguously, we failed to locate protons of the oxime group from the difference

Fourier series, and these atoms were placed in positions calculated from stereochemical considerations. The final refinement of atomic coordinates revealed a substantial increase in the parameters of thermal vibrations of these protons ($B_{\text{iso}}^{\text{eq}}$ is 9(2) and 13(2) Å^3 for molecules **1A** and **1B**, respectively). It is possible that this fact is determined by migration of the proton according to Scheme 1 (*cf.* Ref. 10).

Scheme 1



A rather short contact between the oxime O(1) atom and the O(3) atom of the nitro group of the adjacent molecule of the same type (3.178 and 3.015 Å for chains ...**1A**...**1A**... and ...**1B**...**1B**..., respectively) points also to the possibility of the proton of the OH group and the O(3) atom participating in a weak bifurcated hydrogen bond.

The amide H(2) atom is involved in a stronger bifurcated bond. This atom forms the intramolecular N(2)H...O(1) hydrogen bond and the intermolecular NH...O hydrogen bond with the O(3) atom of the nitro group of the adjacent molecule of the same type (**1A**...**1A**... and **1B**...**1B**), as a result of which infinite double chains are formed. Therefore, each molecule of amidoxime **1** is linked to three molecules through hydrogen bonds, which is, apparently, provides a rather high melting point of amidoxime **1** (186 °C) compared to those in a great number of other amidoximes reported in the literature (see Refs. 1—11 and references cited therein).

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