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The X-Ray Structure of 2-Aminocyclohexanone Oxime Hydrochloride

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Synopsis. The crystal structure of the title compound was determined by the X-ray method. The space group is $P\bar{1}$, with a=8.537(1), b=5.223(3), c=9.505(1) Å, α=91.04(2), β=80.58(1), γ=99.16(3)°, and Z=2. The hydroxyl group of the oxime takes the *anti* conformation to the amino group in the solid state. The molecules, linked together by NH···Cl and OH···Cl hydrogen bridges, form columns in the crystal.

2-Aminocyclohexanone oxime is easily converted into α-amino-ε-caprolactam by means of the Beckmann rearrangement reaction, which is well-known to be highly stereospecific in that the group *anti* to the hydroxyl group migrates in an acid-catalyst solution. In the solid state, however, it is anticipated that, because of the steric hindrance, the hydroxyl group of the oxime can not take the *syn* conformation to the amino group. In order to elucidate the stable conformation in the crystalline state, an X-ray structural analysis of two salts, hydrochloride and sulfate, was undertaken; the results show that hydroxyl groups take the *anti* conformation in both molecules, as might be expected.

The crystal data for both molecules are summarized in Table 1. The sulfate recrystallized from aqueous and ethanol solutions showed a disordered structure, with the sulfate ion disordered statistically about the two-fold crystallographic axis of the space group C2 and with several improbable bond dimensions being observed. Therefore, in this paper we will report only on the crystal structure of hydrochloride.

Experimental

The title compound was recrystallized from an aqueous solution as colorless plates elongated in the b direction. The unit-cell parameters were refined by the least-squares fit of 14 reflections as measured on a Hilger & Watts automatic four-circle diffractometer. The density was measured by flotation in a carbon tetrachloride-hexane mixture. A crystal with dimensions of 0.25×0.35×0.5 mm³ was used for the data collection. The intensities of 1074 reflections with $2\theta \leq 114°$ were measured by the $2\theta-\omega$ step-scan technique with Ni-filtered Cu $K\alpha$ radiation. No significant changes were observed in the intensities of the standard reflections measured periodically throughout the data collection. The measured intensities were corrected for Lorentz-polarization factors, but no absorption correction was applied. 895 reflections with $F \geq 2\sigma(F)$ were used in the refinement of the structure.

TABLE 1. CRYSTAL DATA

	$C_6H_9(=NOH)$-$NH_3^+Cl^-$	$2C_6H_9(=NOH)$-$NH_3^+ \cdot SO_4^{2-}$
Chemical formula	$C_6H_{13}N_2OCl$	$C_{12}H_{26}N_4O_6S$
Formula weight	164.5	352.4
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C2
a/Å	8.537(1)	9.673(8)
b/Å	5.223(3)	7.053(2)
c/Å	9.505(1)	12.936(4)
α/°	91.04(2)	—
β/°	80.58(1)	103.16(4)
γ/°	99.16(3)	—
V/Å³	410.7	859.4
D_{obsd}/g cm⁻³	1.32	1.35
D_{calcd}/g cm⁻³	1.328	1.362
Z	2	4

Structure Determination and Refinement

The structure was solved by the usual Patterson and Fourier methods and refined by the block-diagonal least-squares procedure, using the HBLS VI program[1] with anisotropic temperature factors for all the non-hydrogen atoms and isotropic ones for the hydrogen atoms. In the refinement, the function minimized was $\Sigma w(|F_o|-|F_c|)^2$, with the weighting scheme of $w=[\sigma^2(F_o)+a|F_o|+b|F_o|^2]^{-1}$, where $\sigma(F_o)$ is the standard deviation based on the counting statistics. The final refinement (a=0.0652, b=−0.0006) led to the R value of 0.070. All the scattering factors were taken from the International Tables for X-Ray Crystallography.[2] The final atomic parameters are shown in Table 2.[3]

Results and Discussion

The bond lengths and angles of the atoms, excluding the hydrogen atoms, are shown in Fig. 1, together with the atomic numbering system. The estimated standard deviations of the bond lengths are 0.005—0.010 Å, while those of the bond angles are 0.4—0.5°. X-Ray structural analysis shows that the hydroxyl group of the oxime takes the *anti* conformation to the amino group in the crystalline state. The cyclohexane ring takes a chair form, and the ring C–C bond lengths and angles are in essential agreement with the values obtained in 3,3,5,5-tetramethylcyclohexanone oxime,[4] 3,3,5-trimethyl-5-phenylcyclohexanone oxime,[5] and 1,4-cyclohexane-dihydroxyimine.[6] The distance of the C(1)–N(1) bond (1.294 Å) suggests its double-bond character; the coplanarity of the C(1), C(2), C(6), N(1), and O atoms is due to this double-bond character(Table 3). The N(1)–O bond distance (1.404 Å) is also within the expected range of values.[7]

Table 2. Positional ($\times 10^4$, for H $\times 10^3$) and thermal parameters (B_{eq} for non-H $\times 10$, B_{iso} for H $\times 10$), with their estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}(or B_{iso})/Å^2 [a]
Cl	2488(2)	11190(3)	6166(1)	35(0.7)
O	5640(5)	1259(8)	1810(4)	39(2)
N(1)	4914(5)	3101(9)	2669(5)	32(3)
N(2)	3557(6)	6546(9)	4322(5)	36(3)
C(1)	3797(6)	3945(11)	2124(6)	31(3)
C(2)	2964(7)	5940(11)	2907(6)	31(3)
C(3)	1141(7)	5150(12)	3187(7)	40(4)
C(4)	578(7)	4413(12)	1753(7)	44(4)
C(5)	1386(8)	2287(12)	1050(7)	44(4)
C(6)	3213(7)	3057(12)	739(7)	41(4)
H(O)	617(7)	60(11)	230(7)	39(17)
H1(N2)	472(7)	708(10)	407(6)	27(15)
H2(N2)	307(8)	488(11)	494(7)	45(18)
H3(N2)	303(8)	842(11)	498(7)	44(18)
H(C2)	326(6)	819(10)	230(6)	25(14)
H1(C3)	48(8)	654(11)	386(7)	47(18)
H2(C3)	96(6)	345(9)	383(5)	11(12)
H1(C4)	67(8)	608(12)	126(7)	47(18)
H2(C4)	−61(8)	341(12)	206(7)	50(19)
H1(C5)	97(8)	183(11)	18(7)	53(20)
H2(C5)	105(7)	25(10)	172(6)	29(15)
H1(C6)	360(6)	484(11)	6(7)	34(17)
H2(C6)	359(9)	100(14)	23(9)	81(25)

a) The equivalent isotropic temperature factor defined by W. C. Hamilton (*Acta Crystallogr.*, **12**, 609 (1959)).

Table 3. Deviations of the atoms(l/Å) from the least-squares plane

C(1)	−0.001(14)	C(2)	−0.011(14)	C(6)	0.007(15)
N(1)	0.015(14)	O	−0.009(14)	N(2)[a]	0.080(14)

a) Atom not included in the calculation of the plane.

Table 4. Hydrogen-bond system

Donor D-H	Acceptor A	Distance l/Å D-H	H···A	D···A	Angle ϕ/° D-H···A
N(2)-H1(N2)	Cl(i)	0.98(6)	2.39(6)	3.354(5)	170(5)
N(2)-H2(N2)	Cl(ii)	1.05(7)	2.22(7)	3.252(5)	170(5)
N(2)-H3(N2)	Cl(iii)	1.25(7)	1.89(7)	3.133(5)	170(5)
O-H(O)	Cl(iv)	0.81(6)	2.29(6)	3.104(4)	175(6)

Symmetry code: (i) $1-x$, $2-y$, $1-z$
(ii) x, $y-1$, z
(iii) x, y, z
(iv) $1-x$, $1-y$, $1-z$.

The C–N bond length, 1.524(8) Å, to the positively charged quaternary nitrogen atom N(2) is very near the values of 1.509 and 1.510 Å found in 1,2-cyclohexanediamine hydrobromide.[8]

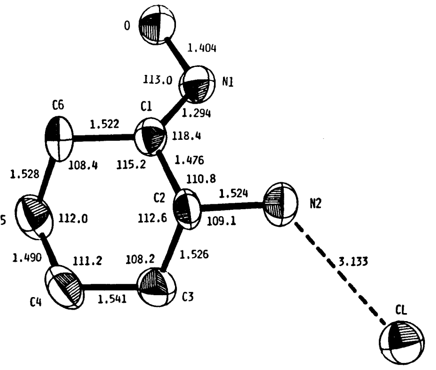

Fig. 1. ORTEP drawing of the molecule with atomic numbering, bond distances(l/Å) and bond angles(ϕ/°). The ellipsoids are drawn to enclose 50% probability.

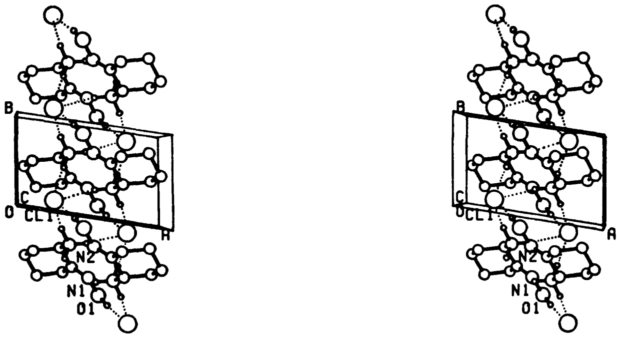

Fig. 2. A stereoview of the packing of the molecule in the unit cell. The hydrogen bonds are shown by dotted lines. For H-atoms only the atoms contributed to the hydrogen bonds are drawn for clarity.

The packing of the molecules in the crystal is shown in Fig. 2. The molecules, linked together by NH···Cl and OH···Cl hydrogen bridges, form columns parallel to the b axis. This column structure reasonably explains the pronounced cleavage parallel to (010). The dimensions of the hydrogen bonds are given in Table 4.

References

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