

The Crystal and Molecular Structure of Acetylhydrazonium Chloride at 110 K

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The structure of the title compound, $C_2H_7N_2O^+Cl^-$, has been determined using 1506 reflections collected at 110 K. The crystals are orthorhombic, space group $Pca2_1$ with cell dimensions: $a = 14.768(3)$ Å, $b = 4.767(1)$ Å, $c = 7.522(1)$ Å. The structure model was refined to an R of 0.029. In order to reduce the influence of valence electron asphericity low-angle data were excluded from the final refinements. The heavy atom parameters converged for a minimum $\sin \theta/\lambda$ cutoff of 0.65 Å $^{-1}$, leaving 863 reflections, the R is 0.037. The molecule, excluding the hydrogen atoms, is nearly planar with the hydrogen and $-NH_3^+$ group *synplanar*.

The structure determination of acetylhydrazonium chloride is part of a series of structure investigations of 3,6-pyridazinediones and related compounds, of which part of the purpose is to study the effect of hydrogen bonding on the $N-C=O$ fragment. The experimental results have been complemented by a series of theoretical studies (for a review see Refs. 1 and 2). The structure investigation of acetylhydrazonium chloride was carried out in order to study the effect on the $N-C=O$ fragment of introducing a hydrazonium group instead of an amine or hydrazine group.

EXPERIMENTAL

Oscillation and Weissenberg photographs revealed orthorhombic symmetry and the systematic absences characteristic of the space groups $Pca2_1$ and $Pcam$. The density indicated four molecules in the unit cell, and the later structure determination showed the space group to be $Pca2_1$.

A platy crystal of approximate dimensions $0.1 \times 0.4 \times 0.2$ mm was used in the experiments.

A computer-controlled Syntex P1 four-circle diffractometer with graphite-monochromatized $MoK\alpha$ radiation and equipped with a modified Enraf-Nonius liquid nitrogen cooling device was utilized in the determination of unit cell parameters and the recording of intensity data. Cell constants were determined by a least-squares treatment of the angular coordinates of fifteen reflections with 2θ -values between 43 and 55° . The temperature at crystal site was 110 K.

Three-dimensional intensity data were recorded using the $\omega-2\theta$ scanning mode with scan speed variable from 2.0 to $6.0^\circ \text{ min}^{-1}$, depending on the peak intensity of the reflection. Background counting time was equal to $0.7 \times$ (scan time) and the scan area was from $2\theta(\alpha_1) - 0.9^\circ$ to $2\theta(\alpha_2) + 0.9^\circ$. All reflections with 2θ -values less than 55° were recorded, whereas for the reflections above this limit only those were recorded which had intensities larger than 6 cps determined in a 2 s scan. The intensities of three standard reflections which were remeasured after every sixty reflections were essentially constant throughout the recording run.

The estimated standard deviations were taken as the square-root of the total counts with a 2% addition of the net intensities for experimental uncertainties. Of the 1546 reflections measured ($2\theta_{\text{max}} = 85^\circ$), the 1506 which had intensities larger than twice their standard deviations were used in the refinements. The intensities were corrected for Lorentz and polarization effects. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs which is described in Ref. 3.

The atomic scattering factors used were those calculated by Doyle and Turner⁴ for chloride, oxygen, nitrogen and carbon and of Stewart *et al.*⁵ for hydrogen.

CRYSTAL DATA

Acetylhydrazonium chloride, $C_2H_7N_2O^+Cl^-$, $M = 120.55$ amu. Space group $Pca2_1$, cell dimensions at 110 K: $a = 14.768(3)$ Å, $b = 4.767(1)$ Å, $c = 7.522(1)$ Å, $V = 529.5(1)$ Å³. D_{obs} (flotation, 19 °C) = 1.50 g cm⁻³, $Z = 4$, $D_{calc} = 1.512$ g cm⁻³, $F(000) = 232$.

STRUCTURE DETERMINATION AND REFINEMENTS

The phase problem was solved by the MULTAN program assembly⁶ (modified assembly). The heavy atom structure model was refined with anisotropic temperature factors to a conventional R of 0.035. The hydrogen atoms were found as the seven largest peaks in a difference Fourier synthesis calculated using this structure model. These were included in the refinement with isotropic thermal parameters. Full-matrix least-squares refinement of all positional and thermal parameters converged to an R of 0.029 and an R_w of 0.040. The "goodness of fit" ($\{[\sum w(F_o - |F_c|)^2]/(m - s)\}^{1/2}$) (G) is 2.22.

In order to remove the influence of the valence electron asphericity on the heavy atom parameters, the minimum $\sin \theta/\lambda$ cutoff value for data used in the refinements was increased systematically. The heavy atom parameters converged to their final values for a cutoff of 0.65 Å⁻¹. The variations in the parameters between this refinement and the refinement with a minimum $\sin \theta/\lambda$ cutoff of 0.75 Å⁻¹ were all less than twice their e.s.d.'s. The number of reflections in the refinement, final R , R_w and G

factors are as follows: cutoff 0.65 Å⁻¹: 863, 0.037, 0.051, 2.02; cutoff 0.75 Å⁻¹: 562, 0.040, 0.053, 1.83. The heavy atom parameters from the refinement with a minimum $\sin \theta/\lambda$ cutoff of 0.65 Å⁻¹ are listed in Table 1, together with the hydrogen parameters obtained in the refinement using all data. A list of observed and calculated structure factors is available from the author upon request.

DISCUSSION

Bond lengths and bond angles are listed in Fig. 1 where also the numbering of the atoms is indicated. There is one intermolecular hydrogen bond involving the N-C=O fragment: N3-H3 \cdots O (in position: $x, 1+y, z$), N \cdots O distance $2.821(3)$ Å, \angle N3-H3 \cdots O: 160° . This hydrogen bond is similar to the one found for related molecules.¹ Compared to 1,2-diformylhydrazine the C=O bond is probably significantly shortened while the C-N bond is significantly lengthened; in 1,2-diformylhydrazine these bonds are $1.2380(2)$ and $1.3316(2)$ Å, respectively, and in the present structure $1.230(3)$ and $1.362(3)$ Å. Taking into consideration the lengthening of the C-N and C=O bonds induced by the introduction of a methyl group at the carbon atom (C=O: 0.008 Å, C-N: 0.012 Å, see Ref. 2 for a discussion of this), the substitution of an ammonia group leads to a significant decrease in the conjugation over the N-C=O fragment. The N-N bond [$1.415(3)$ Å] is of the same length as those found in carbohydrazide⁸ [$1.4103(3)$ and $1.4156(3)$ Å], where the hybridizations of the nitrogen atoms are similar

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by: $\exp \{-2\pi^2[U_{11}(a^*h)^2 + \dots + 2U_{23}(b^*c^*kl)]\}$. The parameters given for nonhydrogen atoms are those obtained in the refinement using only data with $\sin \theta/\lambda \geq 0.65$ Å⁻¹.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	.89031(4)	.71534(11)	.84253(0)	.0203(3)	.0118(2)	.0135(2)	-.0002(1)	.0005(2)	.0010(2)
O1	.90306(17)	-.14609(41)	.31975(26)	.0225(9)	.0089(5)	.0185(10)	.0018(4)	.0007(5)	.0002(4)
C2	.86931(15)	.08875(40)	.33358(42)	.0154(7)	.0105(5)	.0123(6)	.0001(4)	-.0007(8)	-.0000(7)
N3	.88610(17)	.29066(46)	.20970(26)	.0187(8)	.0089(5)	.0160(6)	.0010(6)	.0009(6)	.0008(5)
N4	.95079(17)	.22887(47)	.07654(28)	.0205(9)	.0112(6)	.0133(6)	.0006(6)	.0004(5)	.0013(5)
C5	.80732(23)	.17847(58)	.48058(42)	.0220(11)	.0176(10)	.0196(9)	.0032(7)	.0044(7)	-.0007(7)

Atom	x	y	z	B	Atom	x	y	z	B
H3	.878(1)	.466(5)	.234(4)	2.1(5)	H41	1.010(2)	.225(4)	.126(4)	2.4(5)
H42	.938(1)	.042(5)	.027(3)	2.0(5)	H43	.950(1)	.370(5)	-.005(3)	1.5(4)
H51	.761(2)	.042(5)	.498(4)	4.7(7)	H52	.835(3)	.176(7)	.570(6)	5.8(9)
H53	.781(2)	.357(5)	.457(5)	3.7(6)					

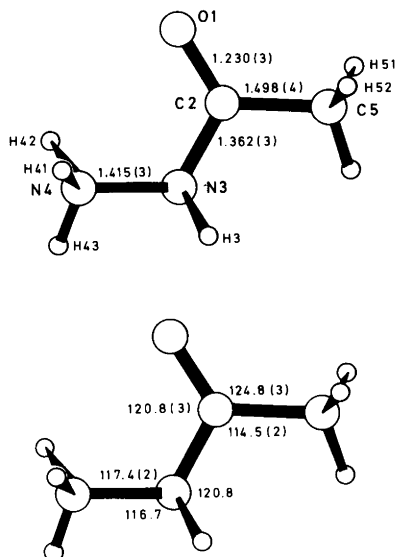


Fig. 1. Bond lengths (Å) and bond angles (°).

to those in the present structure. The N3 lone pair is probably involved in the N–N bonding which decreases its possibility of participating in the conjugation over the N–C=O fragment.¹

The molecule is less planar than 1,2-diformylhydrazine;⁷ deviations from a least-squares plane through O1, C2 and N3 are: C5, –0.015 Å; N4, 0.142 Å and H3, 0.250 Å. The planarity around N3 is similar to that found for the corresponding atoms in carbohydrazide.⁸ The dihedral angle O1–C2–N3–N4 is –6.5° (4).

Both the O1–C2–N3 and the C2–N3–N4 angles have decreased significantly compared with those found for 1,2-diformylhydrazine [123.56(1) and 119.38(1)°, respectively] and for carbohydrazide⁸ (*synplanar* O–C–N–N arrangement: 122.37(2) and 120.74(2)°, respectively). These decreases and the *synplanar* O1–C2–N3–N4 arrangement may indicate a weak charge-transfer bonding between the oxygen and –NH₃⁺ group.

Some details of the hydrogen bonding are shown in Fig. 2. In addition to the N3–H3···O1 hydrogen bond mentioned above there are three hydrogen bonds from the ammonia group to chloride atoms. The hydrogen bond data are as follows: N4–H41···Cl (in position: 2–x, 1–y, –0.5+z), N4···Cl: 3.095(2) Å, ∠N4–H41···Cl: 154°; N4–H2···Cl (x, –1+y, –1+z), N4···Cl: 3.145(2) Å, ∠N4–H42···Cl: 160°; N4–H43···Cl (x, y, –1+z),

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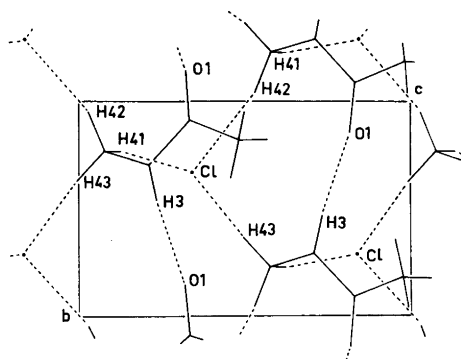


Fig. 2. Projection of the crystal structure as viewed along the *a*-axis. Atoms located between $-0.25 \leq X \leq 0.25$ are shown. Hydrogen bonds are shown by broken lines.

N4···Cl: 3.045(2) Å, ∠N4–H43···Cl: 156°. These four bonds give hydrogen-bonded layers in (100) plane. The layers are kept together by van der Waals' contacts.

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