

## Structure of Nitroacetamide

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**Abstract.**  $C_2H_4N_2O_3$ , monoclinic,  $P2_1/c$ ,  $a = 8.385$  (2),  $b = 5.126$  (1),  $c = 10.812$  (2) Å,  $\beta = 110.90$  (1)°,  $Z = 4$ ,  $D_m = 1.59$ ,  $D_x = 1.59$  Mg m<sup>-3</sup>. The crystal structure is closely related to that of chloroacetamide. The effect of the nitro group as a substituent is discussed in a general context. Among the 1255 unique reflections, 663 were considered observed. The final  $R$  value is 0.053.

**Introduction.** This structure determination is part of a study of aliphatic nitro compounds, nitronate salts and tautomeric forms of these compounds. The present structure determination was carried out primarily to investigate the  $O_2N-CH_2$  configuration and to compare the structure of nitroacetamide with that of nitromalonamide in which the nitro group is bonded to an  $sp^2$ -hybridized C atom (Simonsen & Thorup, 1979).

The ammonium salt of nitroacetamide was prepared as described by Steinkopf (1904). 10 g ammonium salt was ion-exchanged on a column giving 7.8 g nitroacetamide. Suitable single crystals were obtained from a benzene–ethanol solution (10% ethanol) by evaporation at room temperature.

Crystal symmetry, space group, and preliminary unit-cell dimensions were deduced from precession photographs. Refined cell constants were obtained from a Guinier powder photograph taken with Cu  $K\alpha$  radiation ( $\lambda = 1.54050$  Å) and calibrated with silicon as an internal standard.

A single crystal with dimensions  $0.1 \times 0.3 \times 0.3$  mm was chosen for data collection on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). All reflections  $+h, \pm k, \pm l$  in the range  $2^\circ < \theta < 30^\circ$  were measured with the  $\omega$ -scan technique ( $\Delta\omega = 1.00^\circ + 0.35^\circ \tan \theta$ ). The intensities were corrected for Lorentz and polarization effects, but no corrections were made for absorption or extinction [ $\mu(\text{Mo } K\alpha) = 0.141$  mm<sup>-1</sup>]. Symmetry-equivalent reflections were averaged giving a unique set of 1255 observations. The internal consistency index  $R_{ic}(F^2) = \sum ||F|^2 - \langle |F|^2 \rangle| / \sum |F|^2$

was 0.025. Among the unique reflections, 663 with  $|F|^2 > 2.5\sigma(|F|^2)$  were considered observed and used in the structure refinement. During data collection a minor decrease (approximately 5%) in the intensities of the control reflections was observed. An attempt to correct for this effect produced slightly poorer agreement with respect to internal consistency as well as to structure refinement; therefore no correction was applied for decay.

The structure was solved by direct methods using *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Refinement and analysis of the structure was performed with the program systems *SHELX* (Sheldrick, 1976) and *XRAY* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Complex scattering factors for the neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). In the full-matrix minimization of  $\sum w(|F_o| - |F_c|)^2$  the weighting function was  $w = 1.0/[\sigma^2(|F_o|) + 0.001|F_o|^2]$ , where  $\sigma(|F_o|^2)$  is derived from counting statistics. Isotropic thermal parameters were used for H atoms and anisotropic thermal parameters for all other atoms. At the end of refinement (maximum shift  $0.01\sigma$ ) the residuals were:  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.053$  and  $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.057$ . That these values are somewhat higher than expected from the internal consistency can probably be ascribed to the quality of the crystal, which was not completely satisfactory. Final atomic parameters are given in Table 1.\*

**Discussion.** The bond angles around the C(2) atom are close to  $109^\circ$  (Fig. 1) and the bond distances C(1)–C(2) 1.524 and C(2)–N(2) 1.481 Å are within the normal range of C–C and C–NO<sub>2</sub> single bonds.

\* Lists of structure factors, anisotropic thermal parameters and distances of atoms from least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35975 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2$ )

$B_{eq}$  is equivalent to the anisotropic parameters actually refined for non-H atoms (Hamilton, 1959).

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/B$
O(1)	1051 (2)	3813 (3)	4004 (1)	3.18 (5)
O(2)	2925 (3)	2603 (4)	7111 (2)	4.94 (7)
O(3)	4561 (3)	2393 (4)	5995 (2)	5.00 (7)
N(1)	1237 (3)	8156 (4)	3800 (2)	3.55 (6)
N(2)	3536 (2)	3525 (4)	6354 (2)	3.01 (5)
C(1)	1661 (3)	5932 (4)	4439 (2)	2.29 (5)
C(2)	3001 (3)	6178 (4)	5825 (2)	2.87 (6)
H(1)	1707 (31)	9588 (60)	4142 (25)	3.83 (61)
H(2)	445 (37)	8148 (54)	2942 (30)	4.40 (60)
H(3)	2504 (30)	7001 (51)	6411 (27)	3.81 (57)
H(4)	4005 (37)	7104 (64)	5785 (30)	5.43 (72)

Hence the C(2) atom must be  $sp^3$  hybridized, thus differing from the corresponding C in nitromalonamide (Simonsen & Thorup, 1979). Each of the molecular fragments O(2), O(3), N(2), C(2) and O(1), N(1), C(1), C(2) has a planar configuration.\* The two planes make a dihedral angle of  $83.1(5)^\circ$  (Fig. 1).

It is well documented that hydrogen bonds have a pronounced influence on the bond lengths in carboxylic acids and amides (Derissen, 1971; Nahrngbauer, 1970; Ottersen, 1975*b*). To facilitate comparison the compounds in Table 2 have been divided into groups (I–IV) with similar hydrogen-bonding schemes. When a series of substituted acids ( $R\text{COOH}$ ;  $R = -\text{H}, -\text{CH}_3, -\text{CH}_2\text{Cl}, -\text{CHCl}_2, -\text{CH}_2\text{NO}_2$  etc.) is considered,

\* See previous footnote.

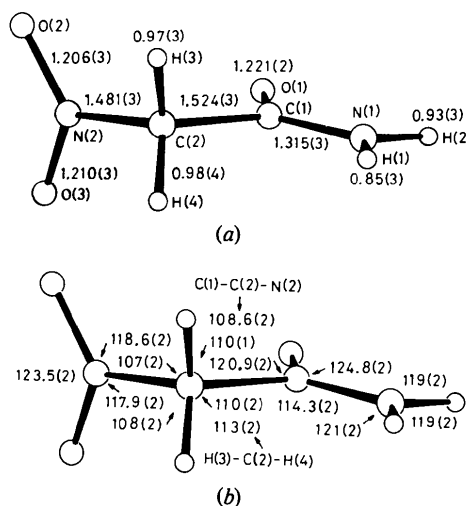


Fig. 1. Perspective drawing of the nitroacetamide molecule showing (a) bond distances ( $\text{\AA}$ ) and (b) angles ( $^\circ$ ), with the atom-numbering scheme. Estimated standard deviations are given in parentheses.

substituent electrical effects, which influence properties such as IR frequencies and acid strength, are observed (Ferguson, 1975). In Table 2, bond distances are quoted for some groups (I–IV) of compounds ( $R\text{COOH}$ ,  $R\text{CONH}_2$ ) which indicate a systematic influence on the bond lengths such that  $\text{C}=\text{O}$ ,  $\text{C}-\text{NH}_2$  and  $\text{C}-\text{OH}$  are shortened and  $R-\text{C}$  elongated as  $R$  becomes more electronegative. Although the observed differences are small, we are convinced that the effect is real. Ottersen (1975*a*) has observed a similar effect by a comparison of hexahydro-3,6-pyridazinedione and di-

Table 2. Bond lengths ( $\text{\AA}$ ) in nitroacetamide compared with corresponding bonds in related compounds

Compound	Ref.	Method	Group	C–C	C–NH <sub>2</sub>	C=O	C–OH	C–NO <sub>2</sub>	N–O
O <sub>2</sub> NCH <sub>2</sub> CONH <sub>2</sub>		X-ray	I	1.524 (3)	1.315 (3)	1.221 (2)		1.481 (3)	1.206 (3) 1.210 (3)
HCONH <sub>2</sub>	(1)	X-ray	I		1.319 (2)	1.243 (2)			
CH <sub>3</sub> CONH <sub>2</sub>	(2)	X-ray	I	1.510 (3)	1.336 (4)	1.243 (4)			
CH <sub>3</sub> CONH <sub>2</sub>	(3)	X-ray	I	1.513 (5)	1.324 (6)	1.241 (6)			
HCONH <sub>2</sub>	(4)	m.w.	II		1.367	1.212			
HCONH <sub>2</sub>	(5)	e.d.	II		1.368 (3)	1.212 (3)			
CH <sub>3</sub> CONH <sub>2</sub>	(6)	e.d.	II	1.519 (6)	1.380 (4)	1.220 (3)			
ClCH <sub>2</sub> CONH <sub>2</sub>	(7)	e.d.	II	1.53	1.36	1.21			
HCOOH	(8)	e.d. monomer	III			1.217 (3)	1.361 (3)		
CH <sub>3</sub> COOH	(9)	e.d. monomer	III	1.520 (5)		1.214 (3)	1.364 (3)		
FCH <sub>2</sub> COOH	(10)	m.w. and e.d.	III	1.534 (8)		1.202 (4)	1.344 (10)		
CH <sub>3</sub> COOH	(11)	X-ray	IV	1.482 (8)		1.220 (6)	1.318 (7)		
O <sub>2</sub> NCH <sub>2</sub> COOH	(12)	X-ray	IV	1.510 (2)		1.204 (1)	1.297 (2)	1.478 (2)	1.209 (2) 1.215 (2)
F <sub>3</sub> CCOOH	(13)	X-ray	IV	1.526 (5)		1.213 (5)	1.303 (5)		

e.d. = electron diffraction (gas phase); m.w. = microwave spectroscopy (gas phase). (1) Ottersen (1975*b*). (2) Ottersen (1975*b*). (3) Denne & Small (1971). (4) Stubgaard (1978). (5) Kitano & Kuchitsu (1974). (6) Kitano & Kuchitsu (1973). (7) Kimura, Aoki & Kurita (1954). (8) Almenningen, Bastiansen & Motzfeld (1969). (9) Derissen (1971). (10) van Eijck, van der Plaats & van Roon (1972). (11) Nahrngbauer (1970). (12) von Deuten & Klar (1980). (13) Nahrngbauer, Lundgren & Andersen (1979).

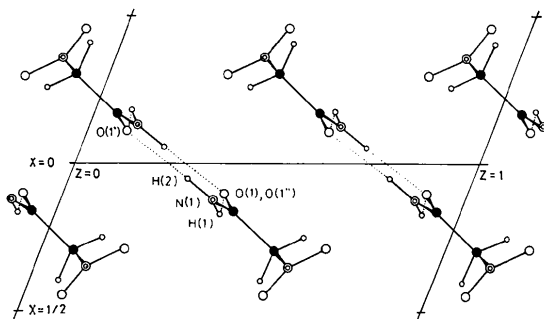


Fig. 2. Projection of the crystal structure along  $b$ . The dotted lines represent the hydrogen bonds. The dimensions of the two different hydrogen bonds are:  $H(2)\cdots O(1^a)$  2.06 (3),  $N(1)\cdots O(1^a)$  2.972 (2) Å,  $N(1)-H(2)\cdots O(1^a)$  168 (2)° and  $H(1)\cdots O(1^b)$  2.23 (3),  $N(1)\cdots O(1^b)$  2.917 (3) Å,  $N(1)-H(1)\cdots O(1^b)$  138 (2)°.  $O(1^a)(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ ;  $O(1^b)(x, 1 + y, z)$ .

formohydrazide. The nitroacetamide bond distances fit well into this pattern.

Only intermolecular hydrogen bonds occur in nitroacetamide. They are centered around the  $2_1$  axes and connect molecules to form bands nearly coincident with the planes  $(\bar{2}02)$ . The nitro groups are not involved in hydrogen bonds (Fig. 2).

The crystal structure of nitroacetamide is closely related to that of chloroacetamide (unstable form) (Katayama, 1956). Chloroacetamide crystallizes in the space group  $P2_1/a$  with  $a = 7.45$ ,  $b = 5.15$ ,  $c = 10.27$  Å,  $\beta = 102.5^\circ$  and  $Z = 4$ . The two reflections  $202$  and  $\bar{2}02$  which are the strongest for nitroacetamide are also the strongest reflections for chloroacetamide.

A powder diagram of nitroacetamide crystallized from boiling benzene exhibited about twice as many lines as a diagram obtained from a crushed single crystal grown in a benzene-ethanol solution at room temperature. The former diagram indicates the existence of another crystal modification. Chloroacetamide (Katayama, 1956) and acetamide (Denne & Small, 1971) have also been found to crystallize in two modifications.

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