

Fig. 2. Stereoscopic view of the packing in the cell perpendicular to the *ac* plane.

separation of 4.94 Å. The torsion angles C(3)–C(2)–C(21)–Cl(21) and C(6)–C(1)–C(12)–Cl(12) are -74.1 (5) and $+161.6$ (6) $^\circ$ respectively. On the other hand, the Cl atoms in heptachlor, heptachlor epoxide, and isobenzan are fixed in semi-parallel orientations, with comparative Cl–Cl distances of 3.57 and 3.60 Å for the two independent molecules of isobenzan. Interatomic repulsion between these two Cl atoms would favour the conformation found in Alodan, giving also a favourable interactive Cl(12)–H(211) distance of 2.68 Å. Packing of the molecules in the unit cell (Fig. 2) results in a range of intermolecular Cl–Cl distances of 3.32–3.89 Å which is similar to that found for other members of this series of compounds and for the 1,2,3,4,5,6-hexachlorocyclohexane isomers (Smith, 1978) where van der Waals intermolecular forces operate.

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Refinement of 2-Nitroguanidine by Neutron Powder Diffraction

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Abstract. $C(NH_2)_2NNO_2$, $CH_4N_4O_2$, orthorhombic, *Fdd2*, $a = 17.6152$ (5), $b = 24.8502$ (7), $c = 3.5880$ (1) Å, $Z = 16$. The structure has been refined by profile analysis of powder neutron diffraction data at room temperature: $R_i = 0.057$ (for 324 integrated intensities) and $R_w = 0.020$. The molecules are linked together by a three-dimensional network of hydrogen bonds.

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Introduction. The crystal structure of 2-nitroguanidine was studied earlier by Bryden, Burkardt, Hughes & Donohue (1956) (referred to as BBHD hereafter), using visually estimated intensity data from rotation photographs. They reported the existence of hydrogen bonds, but did not report the H positions. This study was undertaken to determine the H positions by using the neutron powder diffraction method.

The sample powder was packed loosely in a cylindrical vanadium container, 20 mm in diameter and

50 mm long. A powder diffraction intensity profile was measured up to 118° in scattering angle by using the five-detector neutron diffractometer at the National Bureau of Standards reactor, with 1.542 \AA wavelength neutrons from a Cu (220) monochromator and collimation of $10'$, $20'$, $10'$ before and after the monochromator and before the detector respectively. Absorption was allowed for in the calculation of diffracted intensities by the method of the Debye-Waller-factor analogy (Hewat, 1979). The absorption effect calculated from the Rouse, Cooper, York & Chakera (1970) approximation method for the observed $\mu R = 0.33$ is the same as the effect of an overall temperature factor $B = -0.13 \text{ \AA}^2$. The refinement was carried out by means of a modification of the Rietveld (1969) method, which includes background intensity in the refinement (Trevino, Prince & Hubbard, 1980). Initial positions of H atoms were estimated from an idealized structure for the two amine groups. Isotropic temperature factors were assigned to each atom. Refinements of the structural parameters, including the scale factor, were carried out alternately with those of the profile parameters, such as the unit-cell dimensions, the half-width parameters, and the background intensities. The structural parameters, the unit-cell dimensions, and the residual indices obtained in the final cycle are given in Table 1 and the *Abstract*.* It should be noted in the table that the residual index, R_w , refers to the observed profile, which contains a high level of background caused by the H incoherent scattering, and hence is less

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36132 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final least-squares parameters of 2-nitroguanidine determined by neutron powder profile refinement*

| | x | y | z | B (\AA^2) |
|------|-------------|------------|-------------|----------------------|
| C | 0.1991 (4) | 0.1182 (3) | 0.1486 (27) | 1.7 (1) |
| N(1) | 0.2573 (3) | 0.0935 (2) | 0 | 2.2 (1) |
| N(2) | 0.1942 (3) | 0.1715 (2) | 0.1335 (25) | 2.8 (1) |
| N(3) | 0.1365 (3) | 0.0964 (2) | 0.3109 (20) | 1.8 (1) |
| N(4) | 0.1302 (3) | 0.0422 (2) | 0.3370 (22) | 2.1 (1) |
| O(1) | 0.1784 (4) | 0.0105 (3) | 0.1981 (29) | 3.1 (2) |
| O(2) | 0.0742 (5) | 0.2042 (4) | 0.4973 (32) | 3.8 (2) |
| H(1) | 0.2594 (10) | 0.0549 (6) | 0.007 (4) | 3.8 (3) |
| H(2) | 0.2974 (10) | 0.1171 (7) | -0.096 (5) | 4.8 (4) |
| H(3) | 0.2345 (8) | 0.1934 (6) | 0.008 (5) | 3.9 (4) |
| H(4) | 0.1521 (9) | 0.1899 (6) | 0.244 (4) | 3.5 (3) |

$R_I = \frac{\sum |I(\text{obs.}) - (1/c)I(\text{calc.})|}{\sum I(\text{obs.})} = 0.057$; $R_w = \frac{\{\sum w[y(\text{obs.}) - (1/c)y(\text{calc.})]^2 / \sum w[y(\text{obs.})]^2\}^{1/2}}{\sum w[y(\text{obs.})]^2} = 0.020$; $R_e = \frac{\{(N - P + C) / \sum w[y(\text{obs.})]^2\}^{1/2}}{\sum w[y(\text{obs.})]^2} = 0.016$; where I is the integrated intensity, y the profile intensity, N the number of independent observations, P the number of least-squares parameters, and C the number of constraint functions.

sensitive to the structure refinement than the index R_I , which represents integrated intensities.

Discussion. The crystal structure of 2-nitroguanidine was discussed quite extensively in the earlier study by BBHD (1956). The bond parameters obtained in this study agree with those of BBHD within two standard deviations, as is shown in Table 2. In Fig. 1, the three C-N bonds are quite different in length, 1.309 (7), 1.330 (8), and 1.359 (9) \AA for C-N(1), C-N(2), and C-N(3), respectively. The N(4)-O(1) bond is about 0.03 \AA longer than the N(4)-O(2) bond in the same

Table 2. *Bond lengths (\AA) and angles ($^\circ$)*

The parameters reported by Bryden, Burkardt, Hughes & Donohue (1956) are given for comparison.

| | This work | BBHD (original) |
|----------------|-----------|-----------------|
| C-N(1) | 1.309 (7) | 1.34 (2) |
| C-N(2) | 1.330 (8) | 1.34 (1) |
| C-N(3) | 1.359 (9) | 1.35 (2) |
| N(3)-N(4) | 1.354 (6) | 1.35 (2) |
| N(4)-O(1) | 1.261 (8) | 1.22 (2) |
| N(4)-O(2) | 1.227 (9) | 1.23 (2) |
| N(1)-H(1) | 0.96 (2) | - |
| N(1)-H(2) | 0.98 (2) | - |
| N(2)-H(3) | 1.00 (2) | - |
| N(2)-H(4) | 0.96 (2) | - |
| N(1)-C-N(2) | 120.1 (7) | 118 |
| N(1)-C-N(3) | 128.5 (6) | 129 |
| N(2)-C-N(3) | 111.3 (6) | 112 |
| C-N(3)-N(4) | 119.5 (6) | 118 |
| N(3)-N(4)-O(1) | 122.6 (6) | 124 |
| N(3)-N(4)-O(2) | 117.4 (7) | 115 |
| O(1)-N(4)-O(2) | 120.0 (7) | 121 |
| C-N(1)-H(1) | 119.0 (1) | - |
| C-N(1)-H(2) | 115.0 (1) | - |
| H(1)-N(1)-H(2) | 125.0 (1) | - |
| C-N(2)-H(3) | 121.0 (1) | - |
| C-N(2)-H(4) | 121.0 (1) | - |
| H(3)-N(2)-H(4) | 119.0 (1) | - |

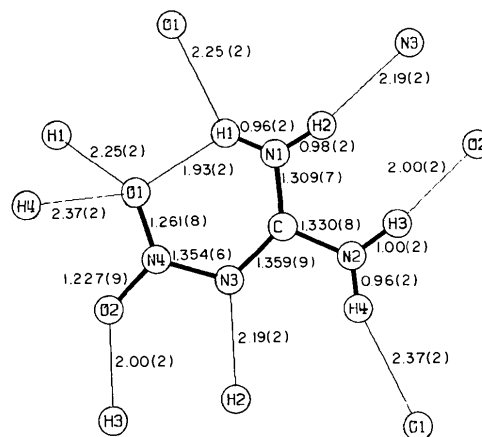


Fig. 1. The 2-nitroguanidine molecule and its hydrogen bonds. Distances are in \AA .

nitro group. This elongation of the N—O bond is related to the strong hydrogen bonds involving the O(1) atom. A similar case of N—O bond elongation related to the hydrogen bonding has been found in the structure of ammonium nitrate phase IV (Choi, Mapes & Prince, 1972) and in the structure of 1,2,3-trinitroguanidinium nitrate (Choi & Prince, 1979). The molecular skeleton consisting of the central C atom and the four N atoms is approximately coplanar, with the largest deviation from the mean plane being 0.024 (9) Å (for the C atom). The four atoms in the nitro group are essentially coplanar ($\chi^2 = 1.07$), and the mean plane is twisted out of the plane of the molecular skeleton by 3.2 (5)° [the torsional angle about the N(3)—N(4) axis (right-hand screw system)]. The N(2) nitramine group shows no significant distortion, with almost perfect planarity ($\chi = 0.02$) and twofold symmetry about the N(2)—C axis, but the N(1) nitramine group is clearly non-planar and asymmetric. Both nitramine groups are essentially on the plane of the molecular skeleton, with torsional angles less than 3 standard deviations. The hydrogen-bonding scheme reported by BBHD was confirmed in this study. The bond parameters are given in Table 3. The intramolecular hydrogen bond N(1)—H(1)···O(1) has a very short H···O distance [1.93 (2) Å], which is caused by the molecular conformation. A part of the conformational strain is relieved by an increase of the N(1)—C—N(3) angle

Table 3. *Parameters of the hydrogen bonds*

| | N—H (Å) | H···O (Å) | N···O (Å) | \angle N—H···O (°) |
|-------------------------------|------------|--------------|--------------|-------------------------|
| N(1)—H(1)···O(1) | 0.96 (2) | 1.93 (2) | 2.59 (1) | 124 (1) |
| N(1)—H(1)···O(1) ^a | 0.96 (2) | 2.25 (2) | 3.022 (9) | 137 (1) |
| N(1)—H(2)···N(3) ^a | 0.98 (2) | 2.19 (2) | 3.146 (7) | 164 (1) |
| N(2)—H(3)···O(2) ^a | 1.00 (2) | 2.00 (2) | 3.00 (1) | 171 (1) |
| N(2)—H(4)···O(1) ^a | 0.96 (2) | 2.37 (2) | 3.290 (9) | 161 (1) |

[128.5 (6)°] and by a distortion of the N(4) nitro group. Among the four intermolecular hydrogen bonds, N(2)—H(3)···O(2) is particularly strong with an O(2)···H(3) distance of 2.00 (2) Å, and N(2)—H(4)···O(1) is very weak, judging from the O···H distance of 2.37 (2) Å.

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Structure of Ammonium D-Gluconate

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Abstract. C₆H₁₁O₇·NH₄⁺, orthorhombic, *P*2₁2₁2₁, *a* = 6.810 (4), *b* = 7.630 (4), *c* = 17.796 (9) Å, *M_r* = 213.2, *V* = 924.7 Å³, *Z* = 4, *D_m* = 1.53, *D_x* = 1.53 Mg m⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ \AA}) = 0.15 \text{ mm}^{-1}$, final *R* = 0.061 and *R_w* = 0.055 for 1104 non-zero reflexions. Unlike other α -hydroxycarboxyl moieties the —C(OH)COO⁻ group is not planar [the O—C—O torsion angles are 51.5 (6) and —130.4 (6)°]. All the hydroxy and ammonium H atoms are involved in intermolecular hydrogen bonds.

Introduction. Ammonium D-gluconate was prepared by combining an equimolar ratio of δ -D-gluconolactone (Fluka AG) and ammonium carbonate (POCh) in

water. After slow evaporation of water orthorhombic platy crystals of ammonium D-gluconate appeared. Analysis: calculated for C₆H₁₃NO₇: C 33.8, H 7.1, N 6.6%; found: C 34.7, H 6.8, N 6.7%. A specimen 0.55 × 0.45 × 0.35 mm was cut from a large crystal and sealed in a capillary.

Weissenberg photographs showed the space group to be *P*2₁2₁2₁. Data were collected on a Syntex *P*2₁ diffractometer with monochromatized Mo *K* α radiation. The intensities were measured by the 2 θ – ω scan technique. After each group of 100 reflexions two standards were measured; no significant change in intensity was observed. Of 1480 reflexions accessible below 2 θ = 60°, 1104 with *I* > 1.96 σ (*I*) were used for