

Structure of 2-Nitriminoimidazolidine*

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Abstract. $C_3H_6N_4O_2$, $M_r = 130.107$, monoclinic, $P2_1/n$, $a = 5.2089$ (5), $b = 17.0775$ (11), $c = 6.8283$ (4) Å, $\beta = 111.411$ (6)°, $V = 565.49$ Å³, $Z = 4$, $d_{\text{calc}} = 1.528$, d_{obs} (flotation) = 1.50 Mg m⁻³. Full-matrix least-squares refinement using 1881 observed reflexions with $2\theta < 100^\circ$ terminated at $R = 0.050$ and $R_w = 0.049$. The e.s.d.'s in bonding are 0.0015 Å and 0.09° (average values, not involving H atoms). The molecule has a planar guanidine moiety, where the C–N 'double' bond is slightly longer than the other two. The imidazolidine ring is somewhat twisted. Libration correction gave an average lengthening of 0.011 Å for distances involving C, N and O atoms. The corrected N–O distances differ by 0.01 Å, in contrast to the non-corrected values that were equal. The difference may be real as the hydrogen bonding involves only one of the O atoms. The hydrogen-bonding system comprises one bifurcated N–H \cdots O and one linear N–H \cdots N interaction.

Introduction. The title compound was prepared from nitroguanidine and ethylenediamine dihydrochloride (Fluka) by the method of McKay & Wright (1947). Recrystallization from methanolic solution by evaporation gave nicely formed, colourless platelets. Attempts to cool the crystals to approximately 115 K, in order to collect data at this temperature, invariably failed due to breakage of the crystals. The space group was uniquely determined as $P2_1/n$ from the systematic extinctions. The cell parameters were determined from a least-squares fit to 39 reflexions with $25^\circ < 2\theta < 60^\circ$, measured on an automatic Syntex PI diffractometer at approximately 292 K (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å). Except for the temperature the conditions for data collection were as described by Nordenson & Hvoslef (1981). The total number of reflexions considered was 2253; 1881 of these had $I > 3\sigma(I)$, and were treated as observed. The data were converted to relative structure amplitudes in the usual way by programs locally adapted to a CDC 6600 computer by Groth (1973). This reference covers all computer programs used, unless otherwise stated.

The structure was solved by direct methods (Germain, Main & Woolfson, 1971), and refined by full-matrix least-squares techniques. The H atoms were located from a difference Fourier synthesis and refined with isotropic thermal parameters, whereas the non-hydrogen atoms were refined with anisotropic thermal parameters. Final atomic coordinates are given in Table 1.† The e.s.d. of an observation of unit weight was 3.1, and a final difference Fourier synthesis had no regions of electron density larger than 0.25 e Å⁻³, except for the positions of C(1) and N(5), where the densities were –0.4 e Å⁻³. The atomic scattering factors used were those of Doyle & Turner (1968) for C, N and O, and those of Stewart, Davidson & Simpson (1965) for H.

Absorption and extinction corrections were not applied.

† Lists of structure factors and anisotropic thermal parameters, data concerning some subset refinements and rigid-body motion, and torsion angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36065 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and isotropic B values

The e.s.d.'s in the last figure are given in parentheses. For non-hydrogen atoms $B_{\text{eq}} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$; $\sigma(B_{\text{eq}}) = 0.04\text{--}0.06$ Å².

	x	y	z	B_{eq}/B (Å ²)
C(1)	0.2021 (2)	0.45309 (6)	0.7987 (2)	2.75
C(2)	0.3079 (3)	0.33101 (7)	0.7075 (2)	4.02
C(3)	0.1413 (3)	0.32238 (7)	0.8485 (3)	4.11
N(1)	0.1113 (2)	0.40261 (6)	0.9056 (2)	3.74
N(2)	0.1724 (2)	0.53013 (5)	0.8319 (1)	3.14
N(3)	0.3100 (2)	0.41571 (6)	0.6767 (2)	3.54
N(5)	0.2639 (2)	0.58205 (6)	0.7255 (1)	3.37
O(2)	0.2311 (2)	0.65153 (5)	0.7621 (2)	4.79
O(3)	0.3711 (2)	0.56319 (6)	0.5977 (2)	4.96
H(N1)	0.028 (3)	0.417 (1)	0.981 (2)	4.5 (3)
H(N3)	0.396 (3)	0.439 (1)	0.603 (2)	5.7 (4)
H(C2)1	0.500 (4)	0.312 (1)	0.778 (3)	6.4 (4)
H(C2)2	0.229 (3)	0.305 (1)	0.569 (3)	5.6 (4)
H(C3)1	–0.038 (4)	0.299 (1)	0.772 (3)	7.1 (5)
H(C3)2	0.228 (4)	0.289 (1)	0.972 (3)	7.1 (4)

* On Nitroguanidines. III.

Table 2. Comparison of the bonding distances (Å) in the nitroguanidine moieties of some related molecules

The bonding distances are from high-angle refinements and are corrected for libration.

Compound	C(1)—N(1)	C(1)—N(2)	C(1)—N(3)	N(2)—N(5)	N(5)—O(2)	N(5)—O(3)
This work	1.347	1.353	1.344	1.348	1.242	1.258
MNG ^(a)	1.334	1.378	1.328	1.327	1.248	1.269
MNNG ^(b)	1.403	1.339	1.316	1.364	1.236	1.241
CNG ^(c)	1.335	1.343	1.344	—	—	—

Notes: (a) *N*-methyl-*N'*-nitroguanidine (Nordenson, 1981); (b) *N*-methyl-*N*-nitroso-*N'*-nitroguanidine (Nordenson & Hvoslef, 1981). The values given are the average values for three independent molecules. (c) *N*-Cyanoguanidine (Hirshfeld & Hope, 1980). The refinement conditions are not the same. These results are from a deformation refinement; they are, however, corrected for libration.

Discussion. The previous papers in this series dealt with the structures of *N*-methyl-*N*-nitroso-*N'*-nitroguanidine, MNNG (Nordenson & Hvoslef, 1981) and its denitrosated analogue, *N*-methyl-*N'*-nitroguanidine, MNG (Nordenson, 1981). The apparent influence of the nitroso substituent on the bonding distances was rather large, particularly for the adjacent C—N bond which was 0.07 Å longer in MNNG than in MNG, and for the C=N of the nitrimino group which was 0.04 Å shorter. Although these differences are in qualitative agreement with expectations, they seem somewhat large, and may be affected by environmental differences. The present work deals with a compound closely related to MNG, but with some important differences: (1) the cyclization involving the two amino groups imposes serious constraints on the valence angles of the guanidine moiety; (2) as a result of these constraints the intramolecular hydrogen bond may be expected to be somewhat weaker than in MNNG and MNG; and (3) both amino N atoms have an alkyl substituent.

Since the title compound could not be analysed at 115 K, as were the others, a direct comparison is not strictly relevant. It turns out, however, that all compounds could be well approximated by rigid-body models (Schomaker & Trueblood, 1968), and the bonding distances derived from refinements using only reflexions with $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$, corrected for libration, are compared in Table 2.

Fig. 1 shows the molecule with thermal ellipsoids, bonding distances and angles. The torsion angles are given in Table 3. The nitroguanidine moiety is exactly planar, whereas the imidazolidine ring is slightly twisted. The twist is probably the result of repulsive interactions between the alkyl H atoms.

The two C—N bonds common to the imidazolidine ring and the guanidine moiety are close to those found in other guanidine compounds (Nordenson, 1981, and references therein), whereas the formal double bond C(1)=N(2) is somewhat longer. The two N—O bonds of the nitro group are equivalent, as derived directly from the refinement, but become different (0.01 Å) when libration correction is applied. This difference may be the result of hydrogen bonding, as the O atom

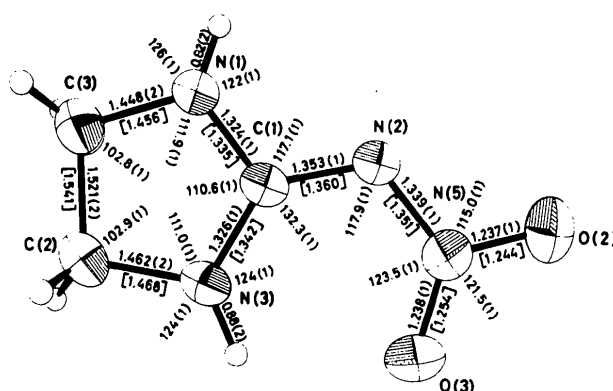


Fig. 1. 2-Nitriminoimidazolidine with thermal ellipsoids scaled to 50% probability (Johnson, 1976). The atomic notation, bonding distances (Å) and angles (°) with the e.s.d. of the last figure given in parentheses, and bonding distances corrected for libration (Schomaker & Trueblood, 1968), given in square brackets, are included in the figure. The C—H distances have a mean value of 0.984 Å, and the angles involving these H atoms range from 106 to 116°, with an average value of 111°.

Table 3. Torsion angles (°) for 2-nitriminoimidazolidine

The e.s.d.'s are 0.10 to 0.19°.

N(2)—C(1)—N(1)—C(3)	177.0	C(1)—N(1)—C(3)—C(2)	8.0
N(3)—C(1)—N(1)—C(3)	-3.5	C(1)—N(3)—C(2)—C(3)	7.7
N(1)—C(1)—N(2)—N(5)	179.8	N(1)—C(3)—C(2)—N(3)	-8.9
N(3)—C(1)—N(2)—N(5)	0.4	C(1)—N(2)—N(5)—O(2)	180.0
N(1)—C(1)—N(3)—C(2)	-3.1	C(1)—N(2)—N(5)—O(3)	0.7
N(2)—C(1)—N(3)—C(2)	176.4		

of the longer bond is the acceptor for two hydrogen bonds, whereas O(2) does not participate in the hydrogen bonding. The same effect is observed in both MNG and MNNG. A peculiar feature of the imidazolidine ring is the highly significant difference in the two N—C_{sp³} bonds. The difference in environment between N(1)—C(3) and N(3)—C(2) can hardly explain this difference in bonding.

The comparison in Table 2 shows that (1) the zwitterionic character of the title compound is not so pronounced as in MNG, (2) the guanidine moiety is intermediate between MNG and MNNG, except for

Table 4. *Details of the hydrogen-bonding system*

The e.s.d.'s are about 0.02 Å for distances involving H atoms, 0.001 Å for the other distances, and 1° for the angles.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$\angle D-H\cdots A$	$\angle H\cdots A-R$	Symmetry code for A
N(1)—H \cdots N(2)	0.82 Å	2.13 Å	2.942 Å	172°	129/113°	$-x, 1-y, 2-z$
N(3)—H \cdots O(3)	0.88	2.12	2.619	115	107	x, y, z
N(3)—H \cdots O(3)	0.88	2.14	2.945	152	165	$1-x, 1-y, 1-z$

The $O\cdots H\cdots O$ angle of the bifurcated interaction is 93° and the $H\cdots O\cdots H$ angle is 87°. The two angles given for the $H\cdots A-R$ for the first bond are $H\cdots N(2)-C(1)$ and $H\cdots N(2)-N(5)$ respectively.

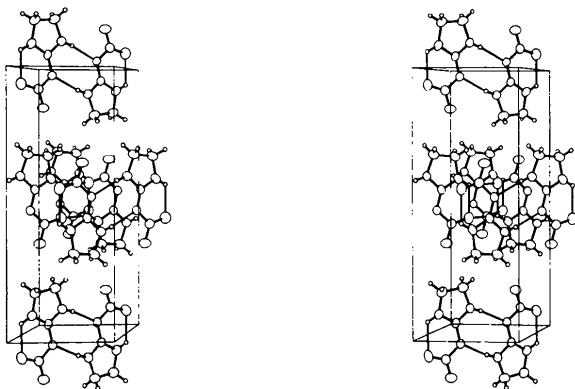


Fig. 2. Stereodrawing (Johnson, 1976) showing the unit-cell contents and the hydrogen-bonding system. The view is towards the c axis at an angle of $\sim 20^\circ$, with the a axis pointing to the right and the b axis pointing up.

$C(1)-N(3)$ which is longer, and (3) the average $C-N$ bond of the guanidine moiety is significantly longer than in the closely related cyanoguanidine.

Fig. 2 shows the crystal structure, and the details of the hydrogen-bonding system are given in Table 4. The crystal consists of hydrogen-bonded bands along $[\bar{1}01]$. The bands thus formed interact by van der Waals forces between the alkyl part and $O(2)$ along $[010]$ to form almost exactly planar sheets in the (101) plane. The separation of the sheets is approximately 3.3 Å, and the $N(2)-N(5)-O(2)$ fragment is approximately above the $C(1)-N(1)-C(3)$ fragment in the closest

contact. The $N-H\cdots N$ interaction is also found in MNG, and similar interactions are present both in nitroguanidine (Bryden, Burkardt, Hughes & Donohue, 1956) and in one of the modifications of MNNG.

$H(N3)$ is engaged in a bifurcated hydrogen bond, in which $O(3)$ acts as a double acceptor. As shown by Newton, Jeffrey & Takagi (1979) such bifurcation may stabilize the system by as much as 17 kJ mol $^{-1}$.

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