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Key indicators

Single-crystal X-ray study
 $T = 101$ K
Mean $\sigma(\text{C}-\text{C}) = 0.001$ Å
 R factor = 0.050
 wR factor = 0.095
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

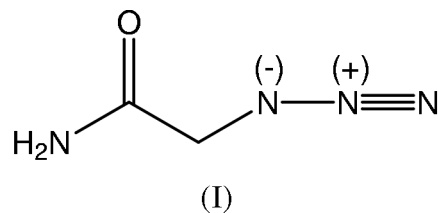
Azidoacetamide, a neutral small organic azide

The structure of the title compound, $\text{C}_2\text{H}_4\text{N}_4\text{O}$, was determined and found to be almost planar, excluding H atoms. The N—N bond lengths of 1.130 (2) and 1.231 (2) Å in the azide group exhibited a resonance effect and the characteristic organic azide structure.

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Comment

Azide compounds constitute a category of energetic materials. Since their properties are of great interest, much effort has been devoted to clarify their decomposition processes, conformation and molecular structures with molecular orbital calculations. However, there have been few experimental studies of the molecular structures in crystals, since azide compounds are potentially explosive and it is difficult to safely treat crystals. In this study, the structure determination of the title compound, azidoacetamide, (I), was carried out to obtain more knowledge about azide compounds.



Azidoacetamide is the smallest compound of the neutral organic azides whose crystal structures have been determined. In this study, it was revealed that non-H atoms were close to planar as the maximum deviation from the least-squares plane was less than 0.184 Å.

Azidoacetamide easily releases the N6—N7 part as a nitrogen molecule. However, the N6—N7 bond length of 1.130 (2) Å is longer than the N≡N bond length of 1.0977 Å (Sasada, 1984). The N5—N6 bond length of 1.231 (2) Å is slightly shorter than the N=N bond length of 1.247 Å in azomethane ($\text{CH}_3\text{N}=\text{NCH}_3$) (Sasada, 1984). Therefore, the bond lengths are influenced by the resonance effect.

Table 4 summarizes the bond lengths and angles of the azide groups in organic azide compounds whose structures have already been determined. In $\text{C}_3\text{N}_3(\text{N}_3)_3$ (Knaggs, 1935) and $[(\text{H}_2\text{N})_2\text{CN}_3]\text{Cl}$ (Henke & Bärnighausen, 1972), the conjugated systems were extended over the molecules. CH_3N_3 (Livingston & Rao, 1960) is the archetypical alkyl azide. Since the table indicates that the bond lengths in azide groups are almost the same, it could be said that these parameters would be characteristic of organic azide compounds.

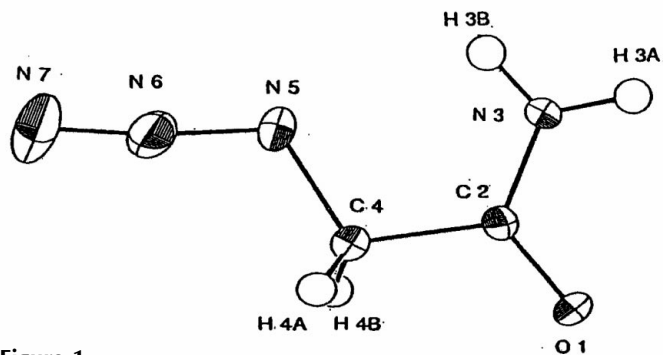


Figure 1
ORTEP drawing of azidoacetamide showing the atom labelling and with displacement ellipsoids at the 50% probability level. H atoms are drawn circles of arbitrary radius.

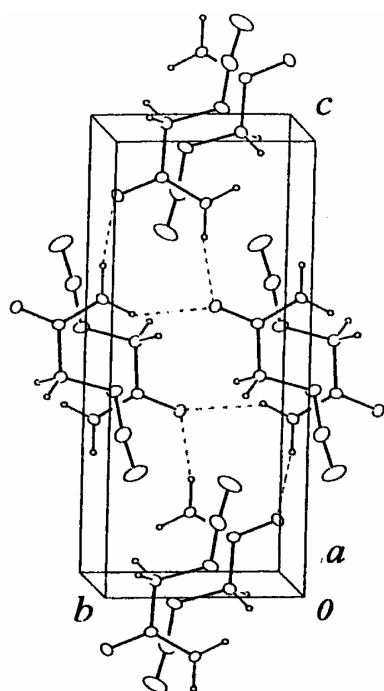


Figure 2
Packing diagram of azidoacetamide. Hydrogen bonds are indicated by dotted lines.

The molecular arrangement indicates that two acetamide groups are favourably located so that the H atoms form hydrogen bonds in the *bc* plane. The O...HN distances are typical hydrogen-bond distances. The same interactions can be found in the intramolecular N5...H3B—N3 arrangement. However, H3B is not in an effective position to form a hydrogen bond. Therefore, H3B—N3 is shorter than H3A—N3.

Experimental

Chloroacetamide and sodium azide were mixed in water and stirred until the water evaporated. The residue was dissolved in acetone and the solution filtered and allowed to evaporate. Azidoacetamide was obtained as colourless crystals. Single crystals were prepared by recrystallization from benzene.

Crystal data

$C_2H_4N_4O$
 $M_r = 100.08$
 Monoclinic, $P2_1/n$
 $a = 6.648$ (4) Å
 $b = 5.1190$ (9) Å
 $c = 13.124$ (5) Å
 $\beta = 99.36$ (2)°
 $V = 440.7$ (5) Å³
 $Z = 4$

$D_x = 1.509$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 192 reflections
 $\theta = 1.0$ – 26.4 °
 $\mu = 0.13$ mm⁻¹
 $T = 100$ K
 Prism, colourless
 $0.2 \times 0.2 \times 0.2$ mm

Data collection

DIP Image Plate diffractometer
 φ scans
 1544 measured reflections
 848 independent reflections
 848 reflections with $I > 0$

$R_{int} = 0.029$
 $\theta_{max} = 26.4$ °
 $h = 0 \rightarrow 8$
 $k = -6 \rightarrow 6$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R(F) = 0.050$
 $wR(F^2) = 0.095$
 $S = 1.14$
 848 reflections
 80 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + 0.03F_o^2]$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.22$ e Å⁻³
 $\Delta\rho_{min} = -0.29$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C2	1.242 (1)	N5—C4	1.478 (1)
N3—C2	1.326 (1)	N6—N7	1.130 (2)
N5—N6	1.231 (2)	C2—C4	1.503 (2)
N6—N5—C4	115.2 (1)	O1—C2—C4	118.4 (1)
N5—N6—N7	173.5 (1)	N3—C2—C4	118.4 (1)
O1—C2—N3	123.2 (1)	N5—C4—C2	110.3 (1)
N6—N5—C4—C2	-163.6 (1)	N3—C2—C4—N5	-2.9 (1)
O1—C2—C4—N5	176.9 (1)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>
N3 ⁱⁱ —H3A ⁱⁱ ...O1	0.96 (2)	2.01 (1)	2.960 (1)
N3 ⁱ —H3B ⁱ ...O1	0.89 (2)	2.15 (1)	2.899 (1)
N3—H3B...N5	0.89 (2)	2.23 (1)	2.656 (1)

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x, y - 1, z$

Table 3

Contact distances (Å).

O1...N3 ⁱ	2.899 (1)	N7...H4B ^v	2.946 (9)
O1...N3 ⁱⁱ	2.960 (1)	C2...H3A ⁱⁱ	2.906 (9)
O1...H3A ⁱⁱ	2.01 (1)	H3A...H3A ⁱⁱ	2.72 (1)
O1...H3B ⁱ	2.15 (1)	H3A...H3A ^{vii}	2.72 (1)
O1...H4A ⁱⁱⁱ	2.626 (9)	H3A...H3B ⁱⁱ	2.90 (1)
N6...N7 ^{iv}	2.991 (1)	H3B...H4A ^{vi}	2.70 (1)
N7...N7 ^{iv}	2.943 (1)	H3B...H4B ^{viii}	2.90 (1)
N7...N7 ^v	2.943 (1)	H4B...H4B ^{ix}	2.76 (1)
N7...H3A ^{vi}	2.94 (1)		

Symmetry codes: (i) $x, y - 1, z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, -y, -z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (vi) $1 - x, 1 - y, -z$; (vii) $\frac{3}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z$; (viii) $2 - x, 1 - y, -z$; (ix) $2 - x, -y, -z$.

Table 4

Summary of bond lengths and angles (\AA , $^\circ$) of azide group in organic azide compounds.

	C—N	N—N	N—N	C—N—N	N—N—N
CH_3N_3	1.47 (2)	1.24 (1)	1.12 (1)	120 (2)	180
$\text{C}_3\text{N}_3(\text{N}_3)_3$	1.38	1.26	1.11	114	180
$[(\text{H}_2\text{N})_2\text{CN}_3]\text{Cl}$	1.393 (4)	1.265 (4)	1.110 (4)	114.2 (3)	170.8 (3)
This work	1.478 (1)	1.231 (2)	1.130 (2)	115.2 (1)	173.5 (1)

The H atoms were refined and the C—H and N—H distances are in the range 0.89 (2)–1.01 (1) \AA . The H-atom U_{iso} values are less than 0.038 \AA^2 .

Data collection: *DIP Image Plate Control Software* (MacScience, 1992); cell refinement: *MAC-DENZO* (Otwinowski & Minor, 1996); data reduction: *maXus* (Mackay *et al.*, 1997); program(s) used to solve

structure: *maXus*; program(s) used to refine structure: *maXus*; molecular graphics: *maXus*; software used to prepare material for publication: *maXus*.

References

- Henke, V. H. & Bärnighausen, H. (1972). *Acta Cryst.* **B28**, 1100–1107.
 Knaggs, I. E. (1935). *Proc. R. Soc. Ser. A*, **150**, 576–602.
 Livingston, R. L. & Rao, C. N. R. (1960). *J. Phys. Chem.* **64**, 756–759.
 Mackay, S., Edwards, C., Henderson, A., Gilmore, C., Stewart, N., Shankland, K. & Donald, A. (1997). *maXus*. The University, Glasgow, Scotland.
 MacScience (1992). *DIP Image Plate Control Software*. MacScience Co. Ltd, Yokohama, Japan.
 Otwinowski, Z. & Minor, W. (1996). *Methods Enzymol.* **276**, 307–326.
 Sasada, Y. (1984). *Kagaku Binran Kisohe* 2, 3rd ed., pp. 649–683. Tokyo: Maruzen.