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(*S*)-*N*-Nitrosoazetidine-2-carboxylic acid

Maria Gdaniec,[a]* Maria J. Milewska[b] and Tadeusz Połoński[b]

[a]Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland, and [b]Department of Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland

Correspondence e-mail: magdan@amu.edu.pl

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.100
Data-to-parameter ratio = 7.7

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

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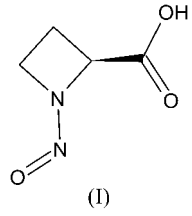
The crystal structure determination of the title compound, $C_4H_6N_2O_3$, reveals that the *N*-nitrosamine moiety adopts the *E* conformation. The azetidine N atom is slightly pyramidalized, as evidenced by its displacement from the plane containing the three attached atoms by 0.038 (2) Å.

Comment

N-Nitrosamines are of widespread interest due to their strong carcinogenic and mutagenic properties (Loeppky & Outram, 1982). Since the molecular geometry of these compounds critically influences their biological activity, the stereochemistry of *N*-nitrosamines has been studied using various experimental techniques (Połoński *et al.*, 1996, and references therein). Particularly, non-planarity and, connected with it, inherent chirality of the *N*-nitrosamine chromophore strongly influence the circular dichroism spectra (Shustov *et al.*, 1992). As a correct interpretation of these spectra is assisted by a detailed knowledge of the chromophore geometry, we performed an X-ray crystallographic study of (*S*)-*N*-nitrosoazetidine-2-carboxylic acid, (I). The N atom of the *N*-nitrosamino group in (I) is included in the strained four-membered ring that may lead to its pyramidal configuration and the intrinsic chirality of the chromophore (Shustov & Rauk, 1995). Additionally, due to a restricted rotation about the partially double N—N bond, the molecules of (I) can exist as either the *E* or *Z* stereoisomer. In aqueous solution, the equilibrium between these two forms is shifted towards the *E* conformer (Gaffield *et al.*, 1981).



(I)

Nitroso groups are known to exhibit orientational disorder in the solid state (Gdaniec *et al.*, 1995; Połoński *et al.*, 1996; Olszewska *et al.*, 2001), which often leads to situations in which both stereoisomers, *Z* and *E*, occupy the same site in the crystal. However, the crystal structure of (I) reveals that the *N*-nitrosamine moiety is ordered, and adopts the *E* conformation (Fig. 1). No residual electron-density peaks were found in the nearest vicinity of this group, indicating that the crystal indeed consists solely of the *E* stereoisomer. Bond lengths and angles of the azetidine-2-carboxylic acid fragment of (I)

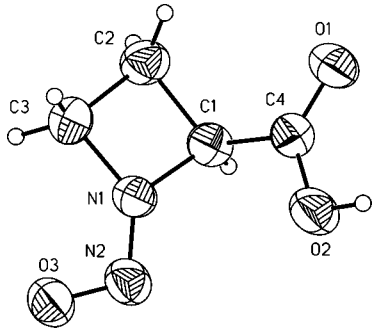


Figure 1
View of the molecule of (I), drawn with 50% probability displacement ellipsoids.

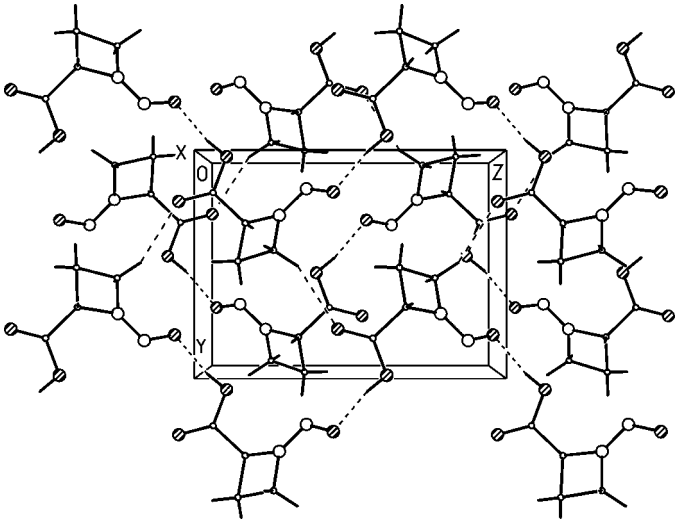


Figure 2
The crystal packing, viewed down the *a* axis.

(Table 1) agree well with the geometry of similar molecules bearing substituents inducing sp^2 hybridization at the azetidine N atom (Blessing & Smith, 1982; Cesari *et al.*, 1975; Nastopoulos *et al.*, 1992). An inspection of the torsion angles about the N—N bond [C3—N1—N2—O3 = −4.1 (3)° and C1—N1—N2—O3 = −177.14 (19)°] shows that the *N*-nitrosamine chromophore of (I) is slightly distorted from planarity. The azetidine ring atoms C1 and C3 deviate in the same direction from the plane defined by N1, N2 and O3 of the *N*-nitrosamino group [0.056 (4) and 0.077 (6) Å, respectively]. This leads to a slightly pyramidal configuration of the azetidine N atom, as evidenced by the displacement of 0.038 (2) Å of atom N1 from the plane containing the three neighbouring atoms N2, C1 and C3. The azetidine ring also deviates slightly from planarity, with a puckering parameter (Cremer & Pople, 1975) of 0.034 (2) Å and endocyclic torsion angles of −2.68 (17), 2.54 (16), −2.54 (16) and 2.69 (17)° (Table 1).

The molecules of (I) are connected by a hydrogen bond between the nitroso O atom and the carboxylic acid hydroxyl group into a polymeric chain extending in the [001] direction (Table 2 and Fig. 2). All C—H H atoms of (I) are involved in intermolecular contacts (shorter than 2.8 Å) with the O or N atoms of neighbouring molecules.

Experimental

The title compound, (I), was obtained from (*S*)-azetidine-2-carboxylic acid by *N*-nitrosation with HNO_2, according to the literature method of Lijinsky *et al.* (1970), and crystallized from benzene–hexane (m.p. 388–389 K).

Crystal data

$C_4H_6N_2O_3$
M_r = 130.11
Orthorhombic, $P2_12_12_1$
a = 6.6521 (11) Å
b = 7.948 (2) Å
c = 10.848 (2) Å
V = 573.5 (2) Å^3
Z = 4
D_x = 1.507 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13–30°
μ = 1.13 mm^{-1}
T = 293 (2) K
Prism, yellow
0.4 × 0.2 × 0.2 mm

Data collection

Kuma KM-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1160 measured reflections
630 independent reflections
586 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 67.8°
$h = -7 \rightarrow 0$
$k = -9 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections every 100 reflections
intensity decay: <1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.100
S = 1.07
630 reflections
82 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.0432P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.200 (2)	N1—C1	1.468 (3)
O2—C4	1.311 (3)	C1—C4	1.507 (3)
O3—N2	1.254 (2)	C1—C2	1.548 (3)
N1—N2	1.285 (2)	C2—C3	1.544 (3)
N1—C3	1.468 (3)		
N2—N1—C3	133.81 (18)	C4—C1—C2	116.42 (18)
N2—N1—C1	130.13 (18)	C3—C2—C1	89.60 (16)
C3—N1—C1	95.83 (16)	N1—C3—C2	87.31 (16)
O3—N2—N1	111.61 (18)	O1—C4—O2	125.0 (2)
N1—C1—C4	115.36 (17)	O1—C4—C1	122.0 (2)
N1—C1—C2	87.14 (16)	O2—C4—C1	112.97 (18)
C3—N1—N2—O3	−4.1 (3)	C3—N1—C1—C2	−2.68 (17)
C1—N1—N2—O3	−177.16 (19)	N1—C1—C2—C3	2.54 (16)
N2—N1—C1—C4	−69.7 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O3^{i}	0.85	1.73	2.575 (2)	169
C3—H32···O1^{ii}	0.96	2.48	3.376 (3)	156

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

All H atoms were located in difference maps. H-atom distances were standarized to 0.85 and 0.96 Å for O—H and C—H bonds, respectively. In the refinement process, H atoms were treated as

riding, with $U_{iso} = 1.2U_{eq}$ of the parent atom. Since the Flack (1983) parameter was found to be meaningless due to the presence of weak anomalous scatterers, Friedel pairs were merged before refinement. The *S* configuration at C1 was adopted on the basis of the configuration of the azetidine-2-carboxylic acid used for the synthesis of (I).

Data collection: *KM*-4 *Software* (Kuma, 1991); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL*97.

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