Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(*Z*)-Azulene-1-carboxaldehyde oxime

Mariusz Kedziorek,[a]† Klaus Hafner[b] and Hans J. Lindner[b]*

[a]Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warszawa 42, Poland, and [b]Institut für Organische Chemie, Darmstadt University of Technology, Petersenstrasse 22, D-64287 Darmstadt, Germany

† Research fellow at the Institut für Organische Chemie, Darmstadt University of Technology, July 1–September 1, 2002.

Correspondence e-mail:
lindner@oc1.oc.chemie.tu-darmstadt.de

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.058
wR factor = 0.157
Data-to-parameter ratio = 9.9

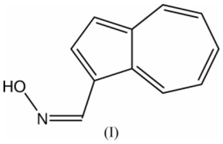
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{11}H_9NO$, the azulene moiety is planar with a delocalized 10π-electron perimeter. In the crystal structure, the molecules are connected by hydrogen bonds and π-stacking to form chains running along the *a* axis.

Received 2 April 2003
Accepted 9 April 2003
Online 23 April 2003

Comment

Azulene-1-carboxaldehyde oxime was first obtained by Hafner & Bernhard (1959) as a crystalline derivative of azulene-1-carboxaldehyde. To determine the configuration of the oxime, the synthesis was optimized. (*Z*)-Azulene-1-carboxaldehyde oxime, (I), was separated from the (*E*)-azulene-1-carboxaldehyde oxime and crystallized. No isomerization could be observed in solution in the absence of acids. Compound (I) shows the expected molecular geometry (see Fig. 1), *viz*. a planar azulene moiety with a delocalized 10π-electron perimeter [mean C—C distance 1.383 (8) Å] and a central bond length of 1.459 (7) Å. The aldoxime group deviates significantly from the azulene plane with a C2—C1—C11—N11 torsion angle of −17.1 (9)°. The crystal packing is determined by intermolecular hydrogen bonds (Table 1) and π-stacking, as shown in Fig. 2. Hydrogen bonds connect the molecules into π-stacked chains running along the *a* axis.



(I)

Experimental

To a mixture of hydroxylammonium chloride (460 mg, 6.6 mmol) and potassium acetate (668 mg, 6.8 mmol) in 40 ml ethanol azulene-1-carboxaldehyde (1.0 g, 6.5 mmol) was added and the mixture was

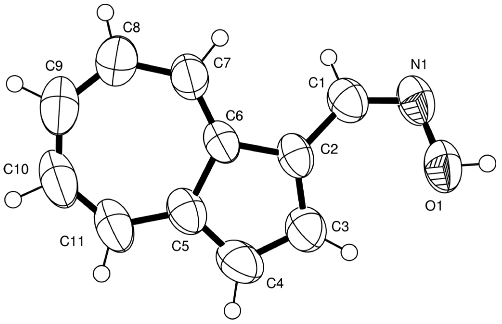


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

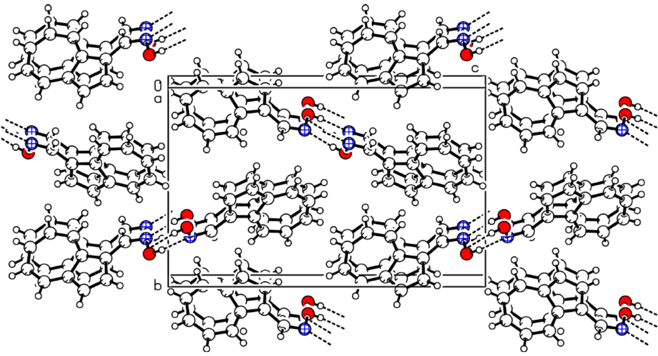


Figure 2
A packing plot of (I), viewed along the *a* axis.

heated to 323 K. After 1.5 h, the solvent was evaporated. Chromatography with silica-gel (hexane/ethyl acetate 4:1) yielded the oxime isomers. Compound (II) crystallized as dark green needles from hexane/ethyl acetate. (*Z*)-Azulene-1-carboxaldehyde oxime, (I), m.p. 391–392 K; ^{1}H NMR (500 MHz, [d_6]DMSO): δ 11.28 (*s*, 1H, H11O), 8.84 (*d*, 1H, H8), 8.80 (*d*, 1H, H2), 8.51 (*d*, 1H, H4), 8.17 (*s*, 1H, H11), 7.82 (approx. *t*, 1H, H6), 7.48 (*d*, 1H, H3), 7.40 (approx. *q*, 2H, H5, H7); $J_{2,3}$ = 4.1, $J_{4,5}$ = 9.6, $J_{7,8}$ = 9.7, $J_{5,6}$ = $J_{6,7}$ = 9.8 Hz. ^{13}C NMR (125.75 MHz, [d_6]DMSO): δ 140.7 (C10), 140.2 (C2), 138.9 (C6), 138.4 (C11), 137.8 (C9), 137.7 (C4), 134.1 (C8), 125.2 (C5), 124.7 (C7), 118.6 (C1), 118.7 (C3).

Crystal data

$C_{11}H_9NO$
$M_r = 171.19$
Orthorhombic, $P2_12_12_1$
$a = 4.631$ (5) Å
$b = 11.068$ (5) Å
$c = 17.487$ (8) Å
$V = 896.3$ (11) Å^3
$Z = 4$
$D_x = 1.269$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6381 reflections
$\theta = 3.9$–27.1°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Needle, dark green
0.55 × 0.10 × 0.08 mm

Data collection

Oxford Diffraction Excalibur diffractometer with Sapphire CCD detector
ω and θ rotation scans
Absorption correction: none
6381 measured reflections
1176 independent reflections
459 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.134$
$\theta_{\rm max} = 27.1^\circ$
$h = -3 \rightarrow 5$
$k = -7 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.157$
$S = 0.93$
1176 reflections
119 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11O···N11$^{\rm i}$	0.82	1.94	2.756 (5)	173

Symmetry code: (i) $\frac{1}{2}+x, -\frac{1}{2}-y, -z$.

The position of the hydroxyl H atom was found in difference Fourier maps and refined. The other H atoms were treated as riding atoms. Friedel pairs were merged; the absolute configuration was not determined.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999) and *ORTEP*III (Johnson & Burnett, 1998); software used to prepare material for publication: *SHELXL*97, CIF and IUCr *SHELXL*97 template.

We thank H. Fuess, Fachgebiet Strukturforschung, TU Darmstadt, for diffractometer time, S. Foro for technical assistance, and the Fonds der Chemischen Industrie for partial funding. MK thanks the Dr Otto Röhm-Gedächtnisstiftung, Darmstadt, for a research fellowship.

References

Hafner, K. & Bernhard, C. (1959). *Liebigs Ann. Chem.* **625**, 108–123.
Johnson, C. K. & Burnett, M. N. (1998). *ORTEP*III. Version 1.0.2. Oak Ridge National Laboratory, Tennessee, USA.
Oxford Diffraction (2001). *CrysAlis CCD* & *CrysAlis RED*. Oxford Diffraction Limited, Oxford, England.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1999). *PLATON*. Version of October 1999. Utrecht University, The Netherlands.

o658 Mariusz Kedziorek *et al.* • $C_{11}H_9NO$ *Acta Cryst.* (2003). E**59**, o657–o658