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Hafner^b and Hans J. Lindner^{b*}^aInstitute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warszawa 42, Poland, and ^bInstitut für Organische Chemie, Darmstadt University of Technology, Petersenstrasse 22, D-64287 Darmstadt, Germany

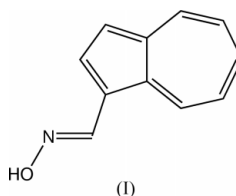
† Research fellow at the Institut für Organische Chemie, Darmstadt University of Technology, July 1–September 1, 2002.

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lindner@oc1.oc.chemie.tu-darmstadt.de**Key indicators**Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.052
wR factor = 0.149
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(*E*)-Azulene-1-carboxaldehyde oxime**

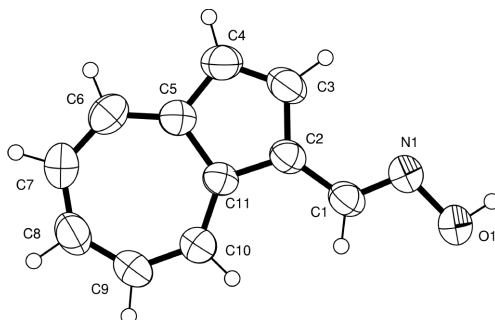
In the title compound, $\text{C}_{11}\text{H}_9\text{NO}$, the azulene moiety is planar with a delocalized 10π -electron perimeter. In the crystal structure, the molecules are connected by hydrogen bonds to form centrosymmetric dimers.

Comment

Azulene-1-carboxaldehyde oxime was first obtained by Hafner & Bernhard (1959) as a crystalline derivative of azulene-1-carbaldehyde. To determine the configuration of the oxime, the synthesis was optimized. The (*E*)-azulene-1-carboxaldehyde oxime, (I), could be separated from the isomer (*Z*)-azulene-1-carboxaldehyde and crystallized. No isomerization could be observed in solution in the absence of acids. The (*E*)-azulene-1-carboxaldehyde oxime shows the expected molecular geometry (see Fig. 1), *viz.* a planar azulene moiety with a delocalized 10π -electron perimeter [mean C–C distance $1.392(4) \text{ \AA}$] and a central bond length of $1.489(4) \text{ \AA}$. The crystal packing is determined by intermolecular hydrogen bonds and π -stacking, as shown in Fig. 2. Hydrogen-bonded centrosymmetric dimers are stacked along the *c* axis.

**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-carbaldehyde (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.

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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. Dark green crystals of (I) were obtained from a toluene solution by evaporation. (*E*)-Azulene-1-carboxaldehyde oxime, (I), m.p. 393–394 K; ^1H NMR (500 MHz, [d_6]DMSO): δ = 10.94 (s, 1H, H11O), 8.92 (*d*, 1H, H8), 8.72 (*s*, 1H, H11), 8.42 (*d*, 1H, H4), 8.13 (*d*, 1H, H2), 7.74 (approx. *t*, 1H, H6), 7.43 (*d*, 1H, H3), 7.32 (approx. *q*, 2H, H5, H7); $J_{2,3}$ = 4.0, $J_{4,5}$ = 9.3, $J_{7,8}$ = 9.8, $J_{5,6}$ = $J_{6,7}$ = 9.8 Hz. ^{13}C NMR (125.75 MHz, [d_6]DMSO): δ = 144.9 (C11), 143.2 (C10), 139.6 (C6), 138.2 (C4), 136.4 (C2), 136.3 (C9), 136.1 (C8), 125.4 (C5), 125.1 (C7), 121.8 (C1), 119.2 (C3).

Crystal data

$\text{C}_{11}\text{H}_9\text{NO}$	$D_x = 1.281 \text{ Mg m}^{-3}$
$M_r = 171.19$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 5481 reflections
$a = 16.931$ (3) Å	$\theta = 3.5\text{--}26.4^\circ$
$b = 6.174$ (2) Å	$\mu = 0.08 \text{ mm}^{-1}$
$c = 17.028$ (5) Å	$T = 293$ (2) K
$\beta = 94.00$ (2)°	Needle, dark green
$V = 1775.6$ (8) Å ³	$0.52 \times 0.28 \times 0.14 \text{ mm}$
$Z = 8$	

Data collection

Oxford Diffraction Excalibur diffractometer with Sapphire CCD detector	815 reflections with $I > 2\sigma(I)$
ω and θ rotation scans	$R_{\text{int}} = 0.066$
Absorption correction: none	$\theta_{\text{max}} = 26.4^\circ$
5481 measured reflections	$h = -21 \rightarrow 21$
1803 independent reflections	$k = -7 \rightarrow 5$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2]$
$wR(F^2) = 0.149$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1803 reflections	$\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$
121 parameters	$\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O11–H11O \cdots N11 ⁱ	0.840 (17)	2.043 (19)	2.841 (3)	158 (3)

Symmetry code: (i) $2 - x, -y, 1 - z$.

The position of the hydroxyl H atom was found in a difference Fourier map and refined. The other H atoms were treated as riding atoms.

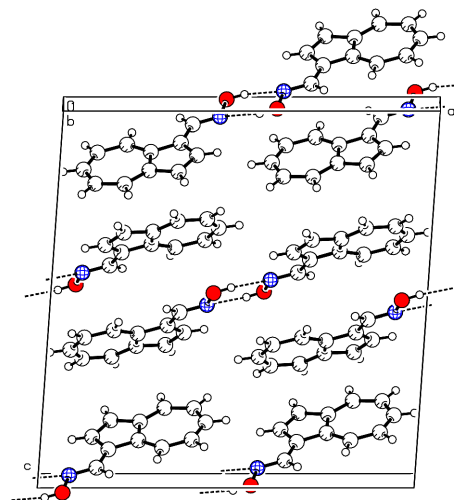


Figure 2
A packing plot of (I), viewed along the b axis.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999) and *ORTEPIII* (Johnson & Burnett, 1998); software used to prepare material for publication: *SHELXL97*, CIF and IUCr *SHELXL97* template.

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