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## Structure Reports

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## 1,3-Diiodoazulene-2-carbonitrile

Sebastian Förster, Wilhelm Seichter and Edwin Weber\*

Institut für Organische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany

Correspondence e-mail: edwin.weber@chemie.tu-freiberg.de

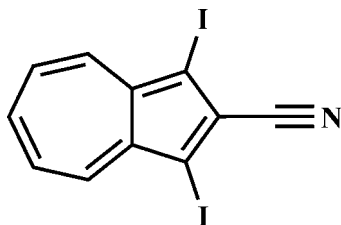
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.024;  $wR$  factor = 0.058; data-to-parameter ratio = 36.3.

In the title compound,  $\text{C}_{11}\text{H}_5\text{I}_2\text{N}$ , the two iodine-atom substituents with their large atomic sizes lead to short intramolecular  $\text{I}\cdots\text{H}$  distances (3.01 Å). In the crystal, the trisubstituted azulene system forms  $\pi$ -stacks [centroid-centroid distance = 3.6343 (11) Å] along the  $a$ -axis direction, showing the characteristic azulene interaction mode between the electron-rich five-membered ring and the electron-deficient seven-membered ring.  $\text{I}\cdots\text{I}$  [3.9129 (2) Å] non-covalent contacts are observed along with weak  $\text{C}-\text{H}\cdots\text{N}$  and  $\text{C}-\text{H}\cdots\pi$  bonds.

## Related literature

For the naphthalene isomer azulene, see: Plattner & Pfau (1937). For the use of azulene derivatives for medical purposes, see: Shi *et al.* (2011). The synthesis of the title compound was performed starting from the azulene derivative 2-cyanoazulene (Nozoe *et al.*, 1962). For the synthesis of related compounds, see Schmitt *et al.* (1998); Suzuka & Yasunami (2008). For related structures, see: Förster *et al.* (2012); Hussain *et al.* (2005); Rahman *et al.* (2004). For halogen interactions in molecular crystal structures, see: Awwadi *et al.* (2006); Metrangolo *et al.* (2008). For weak  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonding, see: Desiraju & Steiner (1999). For  $\text{C}-\text{H}\cdots\pi$  interactions, see: Nishio *et al.* (2009).



## Experimental

## Crystal data

$\text{C}_{11}\text{H}_5\text{I}_2\text{N}$   
 $M_r = 404.96$   
 Monoclinic,  $P2_1/n$

$a = 4.2677$  (1) Å  
 $b = 14.9344$  (4) Å  
 $c = 16.7882$  (4) Å

$\beta = 96.952$  (1)°  
 $V = 1062.14$  (5) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

$\mu = 5.88$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.52 \times 0.07 \times 0.03$  mm

## Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2007)  
 $T_{\min} = 0.150$ ,  $T_{\max} = 0.843$

17691 measured reflections  
 4616 independent reflections  
 3863 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.058$   
 $S = 1.05$   
 4616 reflections

127 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.48$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.32$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

 $\text{Cg}(\text{C11}-\text{N1})$  is the mid-point of the C11–N1 bond.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C8}-\text{H8}\cdots\text{N1}^i$	0.95	2.62	3.400 (3)	139
$\text{C6}-\text{H6}\cdots\text{Cg}(\text{C11}-\text{N1})^i$	0.95	2.76	3.63 (3)	152

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

This work was performed within the Cluster of Excellence Structure Design of Novel High-Performance Materials via Atomic Design and Defect Engineering (ADDE), which is financially supported by the European Union (European Regional Development Fund) and by the Ministry of Science and Art of Saxony (SMWK).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZP2002).

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## supplementary materials

*Acta Cryst.* (2013). E69, o654–o655 [doi:10.1107/S1600536813008301]

## 1,3-Diiodoazulene-2-carbonitrile

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### Comment

The naphthalene isomer azulene is a well known blue nonbenzenoid aromatic hydrocarbon (Plattner 1937). Besides the use of azulene derivatives for medical purposes (Shi 2011), special electronic properties and redox behaviour makes them interesting compounds for electronic applications (Förster *et al.* 2012). In this regard, the present trisubstituted azulene derivative is a promising intermediate. In the crystal structure of this compound, the asymmetric unit contains one molecule featuring an almost planar azulene ring system with a maximum deviations of 0.023 (2) and 0.023 (2) Å (Fig.1). Short intramolecular distances (3.01 Å) involving the iodine atoms and their neighboring H atoms (I1···H9, I2···H5) are a further characteristic of the molecular structure. Along the crystallographic *a*-axis, the crystal structure is stabilized by formation of molecular stacks with a distance of 3.46 Å between the planes of the molecules. The parallel orientated azulene ring systems are arranged in an offset *face-to-face* fashion showing  $\pi\cdots\pi$  overlap between the five- and seven-membered ring components in conformity with their dipole character. In direction of the crystallographic *b* and *c* axes, these stacks are connected *via* C—H···N contacts [C8—H8···N1 (3/2+x, 1/2-y, 1/2+z) 2.62 Å, 139.1°] (Desiraju & Steiner, 1999), I···I interactions [I1···I2 (3/2-x, -1/2+y, 1/2-z) 3.91 Å, 91°] (Metrangolo *et al.*, 2008) and C—H··· $\pi$  contacts [C6—H6···center(C11, N1) (1/2-x, -1/2+y, 1/2-z) 2.76 Å, 152.6°] (Nishio *et al.*, 2009) (Fig 2).

### Experimental

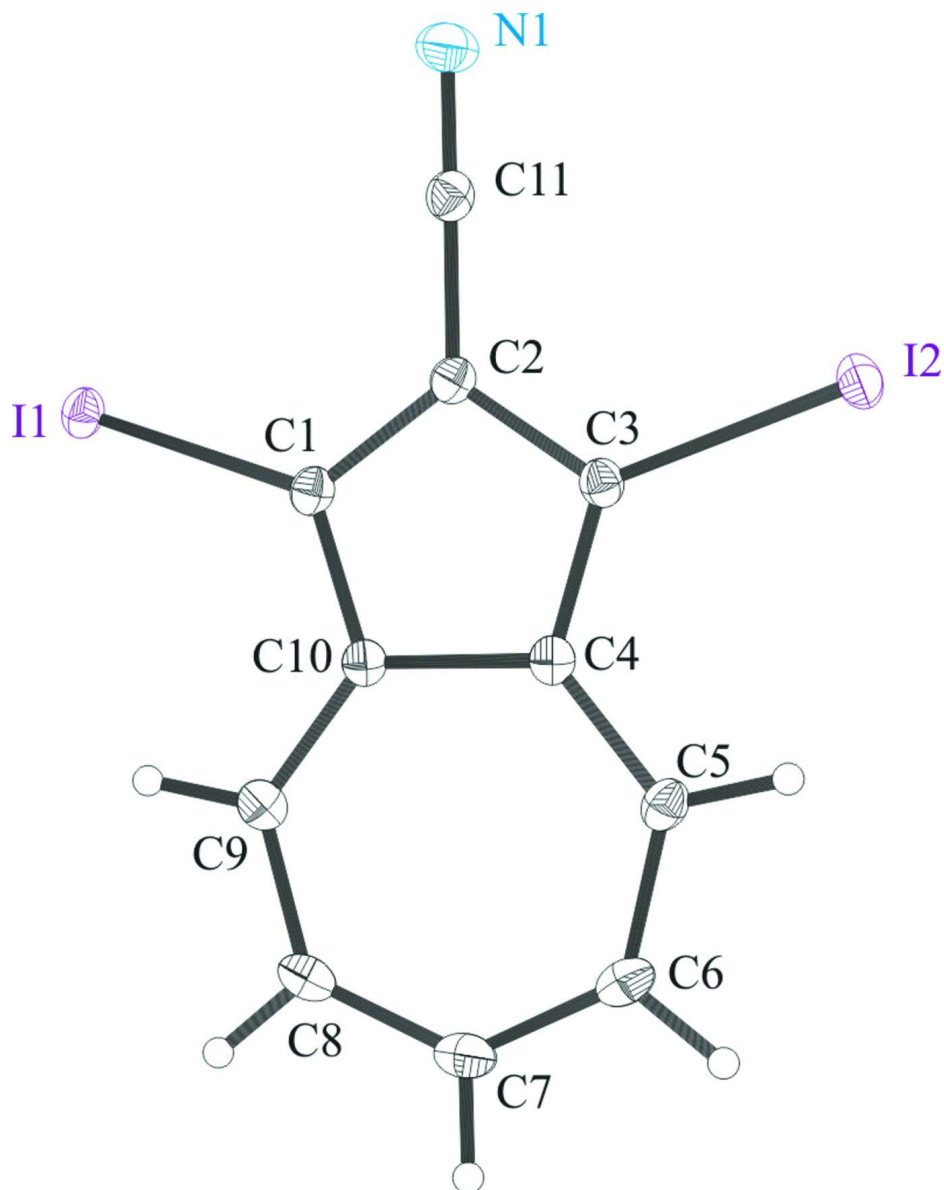
The synthesis of the title compound was done starting from the literature known azulene derivative 2-cyanoazulene (Nozoe *et al.*, 1962). This latter compound (0.1 g, 0.65 mmol) and *N*-iodosuccinimide (0.44 g, 1.96 mmol) were dissolved in 20 ml dichloromethane. The solution was stirred for 8 h under reflux. After removal of the solvent, the residue was purified by column chromatography on SiO<sub>2</sub> [60 F<sub>254</sub> Merck eluent: hexane/ethyl acetate (4:1)] to yield 0.24 g (91%) product as a green solid. Analytical data: mp = 211°C; <sup>1</sup>H-NMR: (CDCl<sub>3</sub>)  $\delta$ /p.p.m. = 7.46 (t, 2 H, ArH, <sup>3</sup>J<sub>HH</sub> = 9.78 Hz), 7.83 (t, 1 H, ArH, <sup>3</sup>J<sub>HH</sub> = 9.85 Hz), 8.30 (d, 2 H, ArH, <sup>3</sup>J<sub>HH</sub> = 9.95 Hz); <sup>13</sup>C-NMR: (CDCl<sub>3</sub>)  $\delta$ /p.p.m. = 78.41(ArC), 117.30(CN), 126.86(ArC), 129.23(ArC), 141.00(ArC), 142.82(ArC), 143.06(ArC); GC/MS calc.: 405; found: 405 [M]<sup>+</sup>. Crystallization by slow evaporation from *n*-hexane yielded suitable crystals.

### Refinement

Aromatic H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H = 0.95 Å and  $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$ .

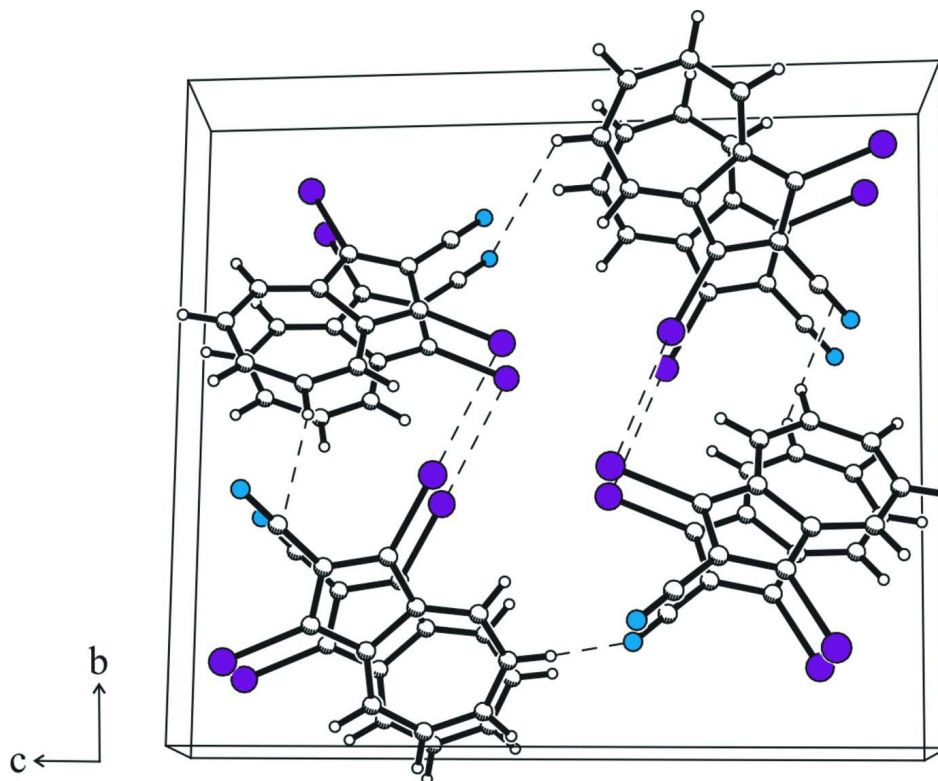
### Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).



**Figure 1**

Asymmetric unit of the title compound, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

A view along the  $a$  axis of the crystal packing of the title compound. Intermolecular interactions are represented as dashed lines.

### 1,3-Diiodoazulene-2-carbonitrile

#### Crystal data

$C_{11}H_5I_2N$   
 $M_r = 404.96$   
 Monoclinic,  $P2_1/n$   
 Hall symbol: -P 2yn  
 $a = 4.2677$  (1) Å  
 $b = 14.9344$  (4) Å  
 $c = 16.7882$  (4) Å  
 $\beta = 96.952$  (1)°  
 $V = 1062.14$  (5) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 736$   
 $D_x = 2.532$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 7883 reflections  
 $\theta = 2.7$ – $36.5$ °  
 $\mu = 5.88$  mm<sup>-1</sup>  
 $T = 100$  K  
 Needle, green  
 $0.52 \times 0.07 \times 0.03$  mm

#### Data collection

Bruker APEXII CCD area-detector  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 phi and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2007)  
 $T_{\min} = 0.150$ ,  $T_{\max} = 0.843$

17691 measured reflections  
 4616 independent reflections  
 3863 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$   
 $\theta_{\text{max}} = 35.1$ °,  $\theta_{\text{min}} = 1.8$ °  
 $h = -6 \rightarrow 4$   
 $k = -24 \rightarrow 22$   
 $l = -24 \rightarrow 27$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.058$

$S = 1.05$

4616 reflections

127 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.3529P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.48 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -1.32 \text{ e } \text{\AA}^{-3}$

Special details

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.78365 (3)	0.118650 (8)	0.153674 (8)	0.01453 (4)
I2	0.54859 (3)	0.379652 (8)	0.426773 (8)	0.01708 (4)
N1	1.0480 (4)	0.14850 (13)	0.39516 (11)	0.0216 (4)
C1	0.6331 (4)	0.23056 (12)	0.21157 (11)	0.0131 (3)
C2	0.7006 (4)	0.24765 (12)	0.29426 (11)	0.0129 (3)
C3	0.5399 (4)	0.32630 (12)	0.31275 (11)	0.0131 (3)
C4	0.3685 (4)	0.35906 (12)	0.24230 (11)	0.0126 (3)
C10	0.4300 (4)	0.29734 (12)	0.17661 (11)	0.0126 (3)
C9	0.3126 (5)	0.30350 (13)	0.09587 (12)	0.0157 (3)
H9	0.3852	0.2591	0.0620	0.019*
C8	0.1030 (5)	0.36596 (14)	0.05796 (12)	0.0182 (4)
H8	0.0509	0.3581	0.0018	0.022*
C7	-0.0398 (5)	0.43785 (14)	0.09082 (13)	0.0186 (4)
H7	-0.1803	0.4714	0.0540	0.022*
C6	-0.0090 (5)	0.46858 (13)	0.16964 (13)	0.0178 (4)
H6	-0.1279	0.5206	0.1788	0.021*
C5	0.1722 (4)	0.43354 (12)	0.23683 (12)	0.0148 (3)
H5	0.1601	0.4648	0.2856	0.018*
C11	0.8938 (5)	0.19344 (13)	0.35015 (12)	0.0151 (3)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1	0.01660 (6)	0.01155 (6)	0.01611 (6)	0.00045 (4)	0.00466 (4)	-0.00113 (4)
I2	0.02230 (7)	0.01668 (6)	0.01229 (6)	0.00117 (4)	0.00219 (4)	-0.00198 (4)
N1	0.0239 (9)	0.0197 (8)	0.0198 (9)	0.0022 (7)	-0.0036 (7)	0.0007 (7)

C1	0.0144 (7)	0.0101 (7)	0.0152 (8)	-0.0011 (6)	0.0029 (6)	-0.0011 (6)
C2	0.0131 (7)	0.0110 (7)	0.0145 (8)	-0.0006 (6)	0.0020 (6)	0.0001 (6)
C3	0.0150 (8)	0.0117 (7)	0.0127 (8)	-0.0010 (6)	0.0022 (6)	-0.0011 (6)
C4	0.0131 (7)	0.0113 (7)	0.0136 (8)	-0.0022 (6)	0.0027 (6)	-0.0001 (6)
C10	0.0137 (7)	0.0109 (7)	0.0134 (8)	-0.0013 (6)	0.0026 (6)	-0.0001 (6)
C9	0.0177 (8)	0.0147 (8)	0.0146 (8)	-0.0023 (6)	0.0017 (6)	-0.0003 (6)
C8	0.0200 (9)	0.0204 (9)	0.0133 (8)	-0.0017 (7)	-0.0008 (7)	0.0031 (7)
C7	0.0161 (8)	0.0212 (9)	0.0181 (9)	0.0006 (7)	0.0004 (7)	0.0067 (7)
C6	0.0168 (8)	0.0132 (8)	0.0234 (10)	0.0024 (6)	0.0026 (7)	0.0033 (7)
C5	0.0156 (8)	0.0116 (7)	0.0178 (9)	0.0002 (6)	0.0044 (7)	-0.0001 (6)
C11	0.0161 (8)	0.0129 (8)	0.0162 (8)	-0.0009 (6)	0.0017 (6)	-0.0019 (6)

*Geometric parameters (Å, °)*

I1—C1	2.0741 (18)	C10—C9	1.390 (3)
I2—C3	2.0697 (19)	C9—C8	1.392 (3)
N1—C11	1.155 (3)	C9—H9	0.9500
C1—C10	1.403 (3)	C8—C7	1.382 (3)
C1—C2	1.407 (3)	C8—H8	0.9500
C2—C3	1.413 (3)	C7—C6	1.392 (3)
C2—C11	1.424 (3)	C7—H7	0.9500
C3—C4	1.401 (3)	C6—C5	1.390 (3)
C4—C5	1.389 (3)	C6—H6	0.9500
C4—C10	1.485 (3)	C5—H5	0.9500
C10—C1—C2	109.05 (16)	C10—C9—H9	115.6
C10—C1—I1	125.99 (14)	C8—C9—H9	115.6
C2—C1—I1	124.80 (13)	C7—C8—C9	128.91 (19)
C1—C2—C3	108.70 (16)	C7—C8—H8	115.5
C1—C2—C11	125.46 (17)	C9—C8—H8	115.5
C3—C2—C11	125.83 (17)	C8—C7—C6	129.82 (19)
C4—C3—C2	108.81 (16)	C8—C7—H7	115.1
C4—C3—I2	126.53 (14)	C6—C7—H7	115.1
C2—C3—I2	124.62 (13)	C5—C6—C7	128.80 (19)
C5—C4—C3	125.77 (18)	C5—C6—H6	115.6
C5—C4—C10	127.40 (17)	C7—C6—H6	115.6
C3—C4—C10	106.80 (16)	C4—C5—C6	128.82 (19)
C9—C10—C1	125.92 (18)	C4—C5—H5	115.6
C9—C10—C4	127.44 (17)	C6—C5—H5	115.6
C1—C10—C4	106.64 (16)	N1—C11—C2	179.1 (2)
C10—C9—C8	128.76 (19)		
C10—C1—C2—C3	-0.1 (2)	I1—C1—C10—C4	175.27 (13)
I1—C1—C2—C3	-175.66 (13)	C5—C4—C10—C9	2.5 (3)
C10—C1—C2—C11	178.71 (18)	C3—C4—C10—C9	-179.32 (18)
I1—C1—C2—C11	3.2 (3)	C5—C4—C10—C1	-177.67 (18)
C1—C2—C3—C4	0.4 (2)	C3—C4—C10—C1	0.5 (2)
C11—C2—C3—C4	-178.40 (18)	C1—C10—C9—C8	177.6 (2)
C1—C2—C3—I2	178.31 (13)	C4—C10—C9—C8	-2.6 (3)
C11—C2—C3—I2	-0.5 (3)	C10—C9—C8—C7	0.4 (4)

C2—C3—C4—C5	177.63 (18)	C9—C8—C7—C6	1.5 (4)
I2—C3—C4—C5	-0.2 (3)	C8—C7—C6—C5	-1.1 (4)
C2—C3—C4—C10	-0.5 (2)	C3—C4—C5—C6	-178.5 (2)
I2—C3—C4—C10	-178.39 (13)	C10—C4—C5—C6	-0.8 (3)
C2—C1—C10—C9	179.57 (18)	C7—C6—C5—C4	0.1 (4)
I1—C1—C10—C9	-4.9 (3)	C1—C2—C11—N1	-55 (15)
C2—C1—C10—C4	-0.2 (2)	C3—C2—C11—N1	123 (15)

*Hydrogen-bond geometry (Å, °)*

Cg(C11—N1) is the mid-point of the C11—N1 bond.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8—H8...N1 <sup>i</sup>	0.95	2.62	3.400 (3)	139
C6—H6...Cg(C11—N1) <sup>i</sup>	0.95	2.76	3.63 (3)	152

Symmetry code: (i)  $x-3/2, -y+1/2, z-1/2$ .