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ISSN 2414-3146

Ethyl 2-(5-bromo-2-iodoanilino)cyclopent-1-ene-1-carboxylate

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Received 29 October 2015
Accepted 16 November 2015

Edited by M. Weil, Vienna University of Technology, Austria

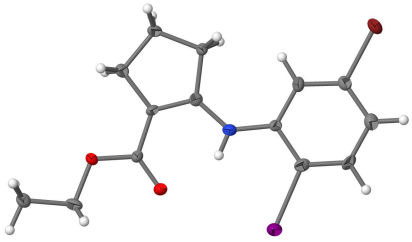
Keywords: Bifurcated hydrogen bond; cyclopentene; C—I···O interaction; crystal structure.

CCDC reference: 1440896

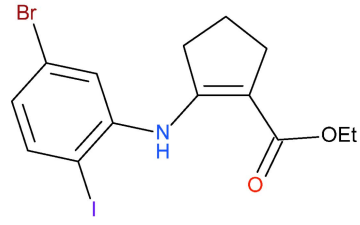
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{14}H_{15}BrINO_2$, the conformation of the C—O—CH_2—CH_3 grouping is *anti* [torsion angle = 173.8 (6)°] and the bond-angle sum at the N atom bridging the two rings is 360°. An unusual intramolecular bifurcated N—H···(O,I) hydrogen bond helps to establish the molecular conformation, in which the I atom and the C═O grouping are *syn*. In the crystal, inversion dimers created by pairs of short intermolecular C—I···O interactions [C—I = 2.080 (7) Å; I···O = 3.211 (5) Å; C—I···O = 152.4 (2)°] occur.

3D view



Chemical scheme



Structure description

The essentially planar cyclopentene ring (r.m.s. deviation = 0.012 Å) subtends a dihedral angle of 4.9 (4)° with the benzene ring. The conformation of the C—O—CH_2—CH_3 grouping is *anti* [torsion angle = 173.8 (6)°] and the bond-angle sum at the N atom bridging the two rings is 360°. The N—C_p (p = cyclopentene) bond [1.368 (9) Å] is slightly shorter than the N—C_b (b = benzene) bond [1.381 (8) Å]. An unusual intramolecular bifurcated N—H···(O,I) hydrogen bond (Fig. 1, Table 1) helps to establish the molecular conformation, in which the I atom and the C═O grouping are *syn*. In the crystal, inversion dimers created by pairs of short intermolecular C—I···O interactions [C—I = 2.080 (7) Å; I···O = 3.211 (5) Å; C—I···O = 152.4 (2)°] occur (Fig. 2).

Background to C—I···O interactions is discussed by Glidewell *et al.* (2005). van der Waals radius data (Bondi, 1964) indicate an expected O···I contact distance of about 3.50 Å. Another compound containing benzene and cyclopentene rings bridged by an NH group and a discussion of resonance contributers to the structure is given by Huang *et al.* (1997).

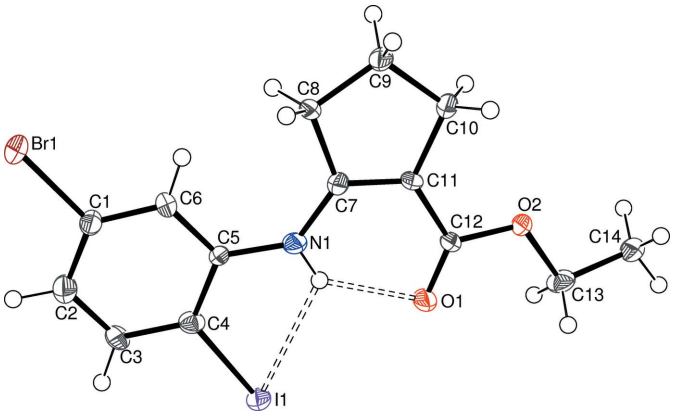


Figure 1
The molecular structure of (I) showing displacement ellipsoids at the 50% probability level. The bifurcated N—H···(O,I) hydrogen bond is indicated by double-dashed lines.

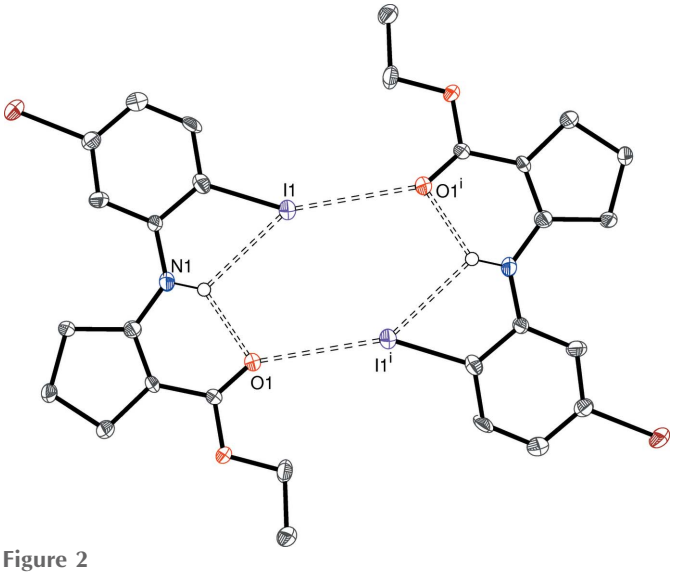


Figure 2
The inversion dimer in (I) arising from a pair of C—I···O interactions (double-dashed lines). All H atoms except H1 omitted for clarity. Symmetry code: (i) $-x, 2-y, 1-z$.

Synthesis and crystallization

For the synthesis, see Barnes & Storey (2015).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

We thank the EPSRC National Crystallography Service (University of Southampton) for the data collection.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.83 (8)	2.03 (8)	2.733 (7)	143 (7)
N1—H1···I1	0.83 (8)	2.77 (8)	3.257 (6)	120 (7)

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{15}BrINO_2$
M_r	436.08
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	120
a, b, c (Å)	7.3066 (4), 7.9672 (4), 12.8467 (7)
α, β, γ (°)	72.994 (3), 86.500 (3), 87.152 (3)
V (Å^3)	713.42 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.04
Crystal size (mm)	0.22 × 0.04 × 0.02
Data collection	
Diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.403, 0.906
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14788, 3285, 2527
R_{int}	0.143
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.133, 1.03
No. of reflections	3285
No. of parameters	177
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.05, −1.71

Computer programs: *COLLECT* (Nonius, 1998), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997) and *SORTAV* (Blessing 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012).

References

Barnes, P. & Storey, J. M. D. (2015). To be published.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Glidewell, C., Low, J. N., Skakle, J. M. S., Wardell, S. M. S. V. & Wardell, J. L. (2005). *Acta Cryst.* B**61**, 227–237.
Huang, K.-S., Stowell, J. G. & Byrn, S. R. (1997). *Acta Cryst.* C**53**, 1717–1719.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter, Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

full crystallographic data

IUCrData (2016). **1**, x152178 [https://doi.org/10.1107/S2414314615021781]

Ethyl 2-(5-bromo-2-iodoanilino)cyclopent-1-ene-1-carboxylate

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Ethyl 2-(5-bromo-2-iodoanilino)cyclopent-1-ene-1-carboxylate

Crystal data

$C_{14}H_{15}BrINO_2$
M_r = 436.08
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.3066 (4) Å
b = 7.9672 (4) Å
c = 12.8467 (7) Å
α = 72.994 (3)°
β = 86.500 (3)°
γ = 87.152 (3)°
V = 713.42 (7) Å^3
Z = 2
$F(000)$ = 420
D_x = 2.030 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 14824 reflections
θ = 2.9–27.5°
μ = 5.04 mm^{-1}
T = 120 K
Needle, colourless
0.22 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.403, T_{max} = 0.906
14788 measured reflections
3285 independent reflections
2527 reflections with $I > 2\sigma(I)$
R_{int} = 0.143
θ_{max} = 27.6°, θ_{min} = 3.2°
h = −9→9
k = −10→10
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.133
S = 1.03
3285 reflections
177 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 2.3708P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −1.71 e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0093 (13)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6550 (9)	0.6004 (9)	0.8087 (5)	0.0201 (14)
C2	0.5142 (10)	0.6597 (10)	0.8689 (6)	0.0253 (15)
H2	0.5224	0.6454	0.9446	0.030*
C3	0.3633 (9)	0.7398 (10)	0.8136 (6)	0.0242 (15)
H3	0.2627	0.7768	0.8529	0.029*
C4	0.3530 (9)	0.7681 (9)	0.7028 (6)	0.0204 (14)
C5	0.4978 (8)	0.7090 (9)	0.6414 (5)	0.0172 (13)
C6	0.6508 (9)	0.6245 (10)	0.6984 (5)	0.0220 (15)
H6	0.7514	0.5840	0.6607	0.026*
C7	0.5955 (9)	0.7049 (9)	0.4509 (5)	0.0182 (13)
C8	0.7856 (8)	0.6187 (9)	0.4674 (5)	0.0190 (14)
H8A	0.7792	0.4971	0.5162	0.023*
H8B	0.8650	0.6861	0.4992	0.023*
C9	0.8591 (9)	0.6199 (9)	0.3527 (5)	0.0203 (14)
H9A	0.8836	0.4982	0.3495	0.024*
H9B	0.9752	0.6835	0.3342	0.024*
C10	0.7123 (9)	0.7127 (10)	0.2713 (5)	0.0212 (14)
H10A	0.7589	0.8219	0.2193	0.025*
H10B	0.6732	0.6345	0.2300	0.025*
C11	0.5574 (8)	0.7521 (9)	0.3443 (5)	0.0180 (14)
C12	0.3846 (8)	0.8408 (9)	0.3055 (5)	0.0181 (14)
C13	0.2133 (9)	0.9780 (10)	0.1495 (6)	0.0248 (16)
H13A	0.1904	1.0835	0.1748	0.030*
H13B	0.1063	0.9018	0.1726	0.030*
C14	0.2436 (10)	1.0299 (11)	0.0271 (6)	0.0275 (17)
H14A	0.1353	1.0960	−0.0068	0.041*
H14B	0.2641	0.9242	0.0032	0.041*
H14C	0.3511	1.1034	0.0055	0.041*
N1	0.4806 (8)	0.7386 (8)	0.5310 (5)	0.0197 (12)
H1	0.385 (11)	0.787 (11)	0.504 (7)	0.024*
O1	0.2578 (6)	0.8759 (7)	0.3612 (4)	0.0260 (11)
O2	0.3804 (6)	0.8831 (6)	0.1946 (4)	0.0205 (10)
Br1	0.86744 (10)	0.49046 (11)	0.88327 (6)	0.0289 (2)
I1	0.11622 (6)	0.89708 (6)	0.63303 (4)	0.02154 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.020 (3)	0.022 (3)	0.018 (3)	−0.001 (3)	−0.003 (3)	−0.004 (3)
C2	0.027 (4)	0.029 (4)	0.020 (3)	0.000 (3)	−0.003 (3)	−0.008 (3)
C3	0.022 (3)	0.037 (4)	0.021 (3)	0.003 (3)	0.003 (3)	−0.020 (3)
C4	0.018 (3)	0.021 (3)	0.025 (3)	0.001 (3)	0.001 (3)	−0.011 (3)
C5	0.012 (3)	0.025 (4)	0.016 (3)	0.001 (3)	−0.002 (2)	−0.009 (3)
C6	0.021 (3)	0.031 (4)	0.014 (3)	−0.001 (3)	0.000 (3)	−0.005 (3)
C7	0.017 (3)	0.022 (3)	0.018 (3)	−0.001 (3)	−0.002 (2)	−0.009 (3)
C8	0.015 (3)	0.027 (4)	0.013 (3)	0.001 (3)	0.001 (2)	−0.003 (3)
C9	0.018 (3)	0.023 (4)	0.022 (3)	0.007 (3)	−0.004 (3)	−0.009 (3)
C10	0.019 (3)	0.028 (4)	0.019 (3)	0.002 (3)	−0.005 (3)	−0.010 (3)
C11	0.013 (3)	0.024 (4)	0.017 (3)	0.004 (3)	0.001 (2)	−0.009 (3)
C12	0.015 (3)	0.025 (4)	0.014 (3)	0.002 (3)	0.001 (2)	−0.005 (3)
C13	0.017 (3)	0.026 (4)	0.028 (4)	0.006 (3)	−0.004 (3)	−0.002 (3)
C14	0.019 (3)	0.040 (5)	0.021 (3)	0.001 (3)	−0.004 (3)	−0.006 (3)
N1	0.015 (3)	0.022 (3)	0.020 (3)	0.004 (2)	−0.001 (2)	−0.004 (3)
O1	0.018 (2)	0.040 (3)	0.018 (2)	0.009 (2)	−0.0009 (19)	−0.007 (2)
O2	0.016 (2)	0.030 (3)	0.015 (2)	0.0049 (19)	−0.0036 (18)	−0.005 (2)
Br1	0.0242 (4)	0.0394 (5)	0.0209 (4)	0.0053 (3)	−0.0086 (3)	−0.0047 (3)
I1	0.0173 (2)	0.0250 (3)	0.0225 (3)	0.00316 (16)	−0.00201 (16)	−0.00777 (19)

Geometric parameters (Å, º)

C1—C6	1.376 (9)	C9—C10	1.548 (9)
C1—C2	1.395 (10)	C9—H9A	0.9900
C1—Br1	1.910 (7)	C9—H9B	0.9900
C2—C3	1.374 (10)	C10—C11	1.506 (9)
C2—H2	0.9500	C10—H10A	0.9900
C3—C4	1.381 (10)	C10—H10B	0.9900
C3—H3	0.9500	C11—C12	1.458 (9)
C4—C5	1.424 (9)	C12—O1	1.208 (8)
C4—I1	2.080 (7)	C12—O2	1.366 (8)
C5—N1	1.381 (8)	C13—O2	1.462 (8)
C5—C6	1.406 (9)	C13—C14	1.509 (10)
C6—H6	0.9500	C13—H13A	0.9900
C7—C11	1.352 (9)	C13—H13B	0.9900
C7—N1	1.368 (9)	C14—H14A	0.9800
C7—C8	1.517 (9)	C14—H14B	0.9800
C8—C9	1.534 (9)	C14—H14C	0.9800
C8—H8A	0.9900	N1—H1	0.83 (8)
C8—H8B	0.9900		
C6—C1—C2	123.1 (6)	C10—C9—H9B	110.1
C6—C1—Br1	119.0 (5)	H9A—C9—H9B	108.4
C2—C1—Br1	117.8 (5)	C11—C10—C9	103.0 (5)
C3—C2—C1	116.9 (6)	C11—C10—H10A	111.2

C3—C2—H2	121.6	C9—C10—H10A	111.2
C1—C2—H2	121.6	C11—C10—H10B	111.2
C2—C3—C4	122.2 (6)	C9—C10—H10B	111.2
C2—C3—H3	118.9	H10A—C10—H10B	109.1
C4—C3—H3	118.9	C7—C11—C12	122.0 (6)
C3—C4—C5	120.8 (6)	C7—C11—C10	113.8 (6)
C3—C4—I1	116.5 (5)	C12—C11—C10	124.2 (6)
C5—C4—I1	122.7 (5)	O1—C12—O2	122.2 (6)
N1—C5—C6	124.3 (6)	O1—C12—C11	126.2 (6)
N1—C5—C4	118.7 (6)	O2—C12—C11	111.6 (5)
C6—C5—C4	117.0 (6)	O2—C13—C14	106.6 (5)
C1—C6—C5	120.0 (6)	O2—C13—H13A	110.4
C1—C6—H6	120.0	C14—C13—H13A	110.4
C5—C6—H6	120.0	O2—C13—H13B	110.4
C11—C7—N1	124.1 (6)	C14—C13—H13B	110.4
C11—C7—C8	110.6 (6)	H13A—C13—H13B	108.6
N1—C7—C8	125.3 (6)	C13—C14—H14A	109.5
C7—C8—C9	104.6 (5)	C13—C14—H14B	109.5
C7—C8—H8A	110.8	H14A—C14—H14B	109.5
C9—C8—H8A	110.8	C13—C14—H14C	109.5
C7—C8—H8B	110.8	H14A—C14—H14C	109.5
C9—C8—H8B	110.8	H14B—C14—H14C	109.5
H8A—C8—H8B	108.9	C7—N1—C5	132.6 (6)
C8—C9—C10	108.0 (5)	C7—N1—H1	109 (6)
C8—C9—H9A	110.1	C5—N1—H1	118 (6)
C10—C9—H9A	110.1	C12—O2—C13	114.7 (5)
C8—C9—H9B	110.1		

C6—C1—C2—C3	2.4 (11)	N1—C7—C11—C12	−1.7 (11)
Br1—C1—C2—C3	179.5 (5)	C8—C7—C11—C12	−178.8 (6)
C1—C2—C3—C4	−2.8 (12)	N1—C7—C11—C10	175.4 (6)
C2—C3—C4—C5	2.3 (12)	C8—C7—C11—C10	−1.7 (9)
C2—C3—C4—I1	−178.4 (6)	C9—C10—C11—C7	2.8 (8)
C3—C4—C5—N1	179.3 (7)	C9—C10—C11—C12	179.8 (6)
I1—C4—C5—N1	0.1 (9)	C7—C11—C12—O1	−2.7 (12)
C3—C4—C5—C6	−1.1 (11)	C10—C11—C12—O1	−179.4 (7)
I1—C4—C5—C6	179.6 (5)	C7—C11—C12—O2	177.0 (7)
C2—C1—C6—C5	−1.4 (12)	C10—C11—C12—O2	0.3 (10)
Br1—C1—C6—C5	−178.4 (5)	C11—C7—N1—C5	−176.6 (7)
N1—C5—C6—C1	−179.7 (7)	C8—C7—N1—C5	0.1 (12)
C4—C5—C6—C1	0.7 (11)	C6—C5—N1—C7	−2.4 (12)
C11—C7—C8—C9	−0.2 (8)	C4—C5—N1—C7	177.1 (7)
N1—C7—C8—C9	−177.2 (7)	O1—C12—O2—C13	1.7 (10)
C7—C8—C9—C10	1.9 (7)	C11—C12—O2—C13	−178.0 (6)
C8—C9—C10—C11	−2.7 (8)	C14—C13—O2—C12	173.8 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.83 (8)	2.03 (8)	2.733 (7)	143 (7)
N1—H1···I1	0.83 (8)	2.77 (8)	3.257 (6)	120 (7)