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9,10-Bis(iodoethynyl)anthracene

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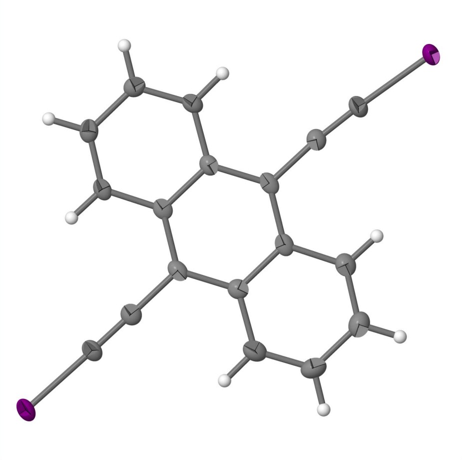
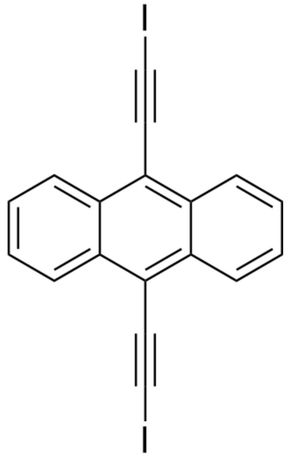
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{18}H_8I_2$, is an ethynyl-substituted anthracene. The C—C—I bond angles deviate from 180°, being affected by intermolecular I···π interactions. These interactions form a two-dimensional supramolecular structure further supported by offset π–π stacking of neighboring anthracene moieties.

3D view



Chemical scheme



Structure description

The flat, stable, and conjugated composition of anthracene derivatives makes them good candidates for two-dimensional molecular crystals. Two-dimensional crystals can have unique properties with applications in electronics, biomedicine, and sensors (Yan *et al.*, 2023). The title compound is an iodoethynyl-substituted anthracene. The iodine functional groups provide the opportunity for halogen-bonding interactions. The synthesis and structure of the title compound are reported here.

The crystal stucture represents the first example of an ethynyl–anthracene halogenated with iodine (Fig. 1). The C—I bonds have an average length of 1.996 (4) Å, similar to that found in 1,4-bis(iodoethynyl)benzene [2.007 (7) Å; Barrès *et al.*, 2008], 4-iodoethnynylanisole [1.990 (3) Å; Dumele *et al.*, 2014], and other iodoethynyl derivatives (Lehnherr *et al.*, 2015). The 180° bond angle expected from the alkynyl C atoms and iodine, C15—C16—I1 and C17—C18—I2, are slightly bent to 177.4 (3) and 178.0 (3)°, respectively. This may be attributed to halogen bonding between C(*sp*)—I moieties and the π-electrons of the adjacent anthracene rings (Fig. 2), where I1 maintains its shortest I···centroid contact to the centroid of the C2–C7 ring (*Cg*1) [I1···*Cg*1 = 3.528 (4) Å and C16—I1···*Cg*1 = 151.2 (3)°] and I2 has a short contact to the centroid of the C9–C14 ring (*Cg*2) [I2···*Cg*2 = 3.767 (4) Å and C18—I2···*Cg*2 = 150.1 (3)°]. The bent nature of the C—I···centroid interactions leads to short I···C contacts ranging from 3.352 (4) to

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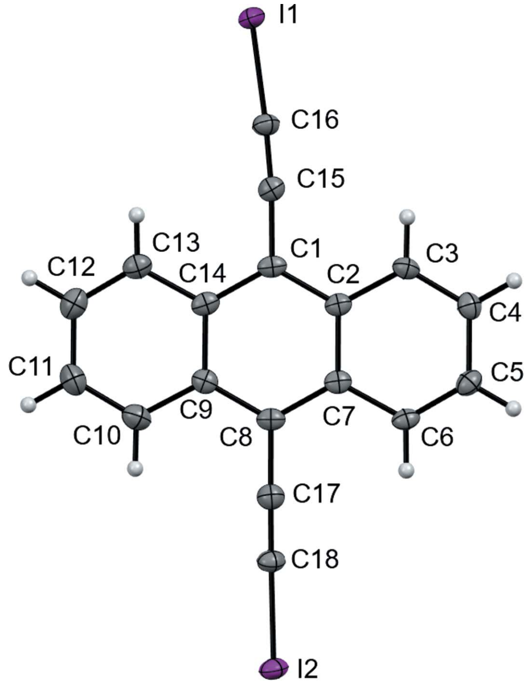

Figure 1
The title molecule, showing the atom-labeling scheme and with displacement ellipsoids drawn at the 50% probability level.

3.655 (4) Å. The shorter contact between I1 and *Cg*1 appears to influence more significantly the bending of the entire alkynyl substituent [C1—C15—I1 = 173.8 (3)° *versus* C8—C17—I2 = 178.7 (3)°], notably pulling the I1 atom away from the central ring of the neighboring anthracene molecule and toward its C2–C7 centroid.

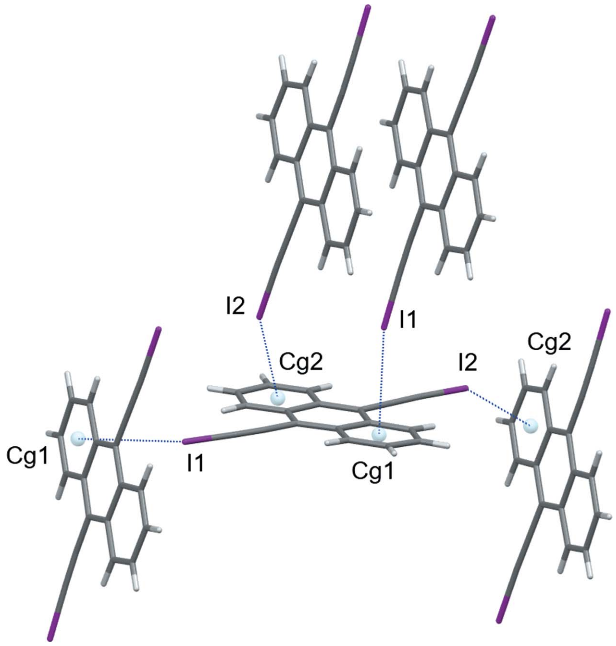

Figure 2
I$\cdots\pi$ interactions (blue dashed lines) occurring to and from a central molecule of the title compound.

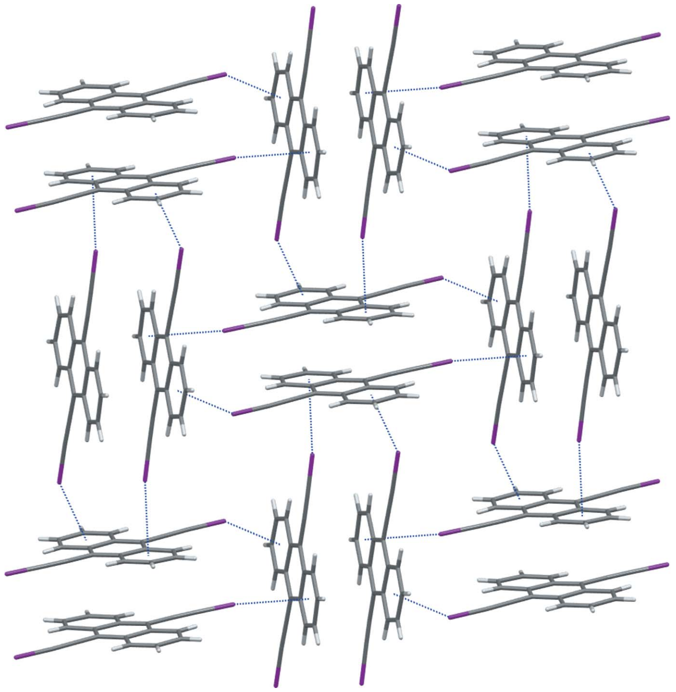

Figure 3
The two-dimensional supramolecular motif formed *via* I$\cdots\pi$ interactions in the title compound.

Propagation of the I$\cdots\pi$ interactions results in a two-dimensional supramolecular structure in the (101) plane (Fig. 3). Interestingly, in 1,4-bis(iodoethynyl)benzene, 4-iodoethnynylanisole, and 1-chloro-4-(iodoethynyl)benzene, the I$\cdots\pi$ interactions occur at a similar distance [for example, the shortest I$\cdots$C contact is 3.427 (7) Å in 1,4-bis(iodoethynyl)benzene, 3.392 (3) Å in 4-iodoethnynylanisole, and 3.417 (4) Å in 1-chloro-4-(iodoethynyl)benzene], but occur to the alkynyl C atoms rather than to the aromatic rings as in the title compound (Barrès *et al.*, 2008; Dumele *et al.*, 2014; Lehnherr *et al.*, 2015). The I atom in (*tert*-butyl)[4-(iodoethynyl)phenyl]carbamate (Kahlfuss *et al.*, 2016) does appear to interact

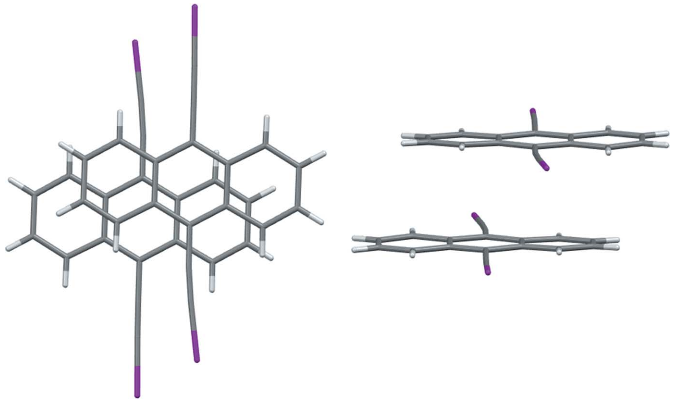

Figure 4
Top (left) and side (right) views of the offset stacking of neighboring molecules in the title compound.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_8I_2$
M_r	478.04
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	8.0022 (3), 15.0735 (7), 12.2506 (5)
β (°)	96.2749 (17)
V (Å^3)	1468.83 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.27
Crystal size (mm)	0.17 × 0.15 × 0.13
Data collection	
Diffractometer	Bruker D8 Venture Photon 2
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.774, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37187, 3373, 3084
R_{int}	0.037
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.063, 1.13
No. of reflections	3373
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, −0.90

Computer programs: *APEX3* (Bruker, 2017), *SAINT* (Bruker, 2016), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

with the aromatic system of a neighboring molecule to form a one-dimensional I···π motif of similar C—I···centroid geometries to the title anthracene derivative. Anthracene portions of adjacent molecules are arranged in an offset stacking arrangement (Fig. 4), with an interplanar separation of 3.377 Å, a shortest C···C distance of 3.436 (5) Å, and a shortest centroid–centroid distance of 3.692 (5) Å. The interplanar spacing of the anthracene scaffold in the title compound is shorter than in the offset stacking in 9,10-diiodoanthracene (3.602 Å; Peters *et al.*, 1996) and similar to that of the offset stacking in monoclinic 9,10-bis(phenylethynyl)anthracene (3.405 Å; Batsanov *et al.*, 2013).

Synthesis and crystallization

The procedure was modeled after an analogous functionalization of an alkynylsilane (Tse *et al.*, 2021). 9,10-Bis(trimethylsilylethynyl)anthracene (0.0325 g, 0.0878 mmol), *N*-iodosuccinimide (0.0531 g, 0.236 mmol) and $AgNO_3$ (0.0022 g, 0.0129 mmol) were added to dry dimethylformamide (5 ml), and the resulting mixture was stirred under nitrogen. After 5 h, the reaction mixture was diluted with EtOAc (30 ml) and washed with H_2O (5 × 30 ml). The organic layer was dried *in vacuo*, resulting in an orange solid. The product was crystallized from the orange solid using vapor–vapor diffusion (CH_2Cl_2/hexanes).

^{1}H NMR key spectroscopic features as determined from the crude product (400 MHz, chloroform-*d*): δ 8.33 (*d*, J = 9.2 Hz, 4H), 7.82 (*m*, 4H).

Refinement

Crystal data, data collection, and structural refinement details are summarized in Table 1.

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full crystallographic data

IUCrData (2023). **8**, x230553 [https://doi.org/10.1107/S2414314623005539]

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Crystal data

$C_{18}H_8I_2$
$M_r = 478.04$
Monoclinic, $P2_1/n$
$a = 8.0022$ (3) Å
$b = 15.0735$ (7) Å
$c = 12.2506$ (5) Å
$\beta = 96.2749$ (17)°
$V = 1468.83$ (11) Å^3
$Z = 4$
$F(000) = 888$
$D_x = 2.162$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9890 reflections
$\theta = 2.7$–30.6°
$\mu = 4.27$ mm^{-1}
$T = 100$ K
Column, red
0.17 × 0.14 × 0.13 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{\min} = 0.774$, $T_{\max} = 1.000$
37187 measured reflections
3373 independent reflections
3084 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.037$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 2.2°$
$h = -10 \rightarrow 10$
$k = -19 \rightarrow 19$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.063$
$S = 1.13$
3373 reflections
181 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0142P)^2 + 7.1388P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.90$ e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
I1	0.82384 (3)	0.70341 (2)	0.18275 (2)	0.02740 (8)
I2	0.03465 (3)	0.12055 (2)	0.56404 (2)	0.02483 (8)
C1	0.5433 (5)	0.4778 (2)	0.3413 (3)	0.0183 (7)
C2	0.6141 (5)	0.4243 (2)	0.4292 (3)	0.0178 (7)
C3	0.7841 (5)	0.4348 (3)	0.4760 (3)	0.0207 (7)
H3	0.853257	0.477816	0.446422	0.025*
C4	0.8486 (5)	0.3842 (3)	0.5624 (3)	0.0223 (8)
H4	0.961959	0.392364	0.592776	0.027*
C5	0.7470 (5)	0.3190 (3)	0.6078 (3)	0.0230 (8)
H5	0.792490	0.284632	0.668972	0.028*
C6	0.5867 (5)	0.3059 (2)	0.5643 (3)	0.0196 (7)
H6	0.520936	0.261846	0.594840	0.024*
C7	0.5139 (5)	0.3572 (2)	0.4729 (3)	0.0178 (7)
C8	0.3466 (5)	0.3430 (2)	0.4245 (3)	0.0190 (7)
C9	0.2770 (5)	0.3953 (2)	0.3353 (3)	0.0192 (7)
C10	0.1094 (5)	0.3826 (3)	0.2846 (3)	0.0266 (8)
H10	0.042007	0.337285	0.311230	0.032*
C11	0.0440 (5)	0.4340 (3)	0.1990 (4)	0.0297 (9)
H11	−0.067695	0.424074	0.166417	0.036*
C12	0.1413 (6)	0.5018 (3)	0.1588 (3)	0.0282 (9)
H12	0.094835	0.537029	0.098712	0.034*
C13	0.3010 (5)	0.5178 (3)	0.2048 (3)	0.0234 (8)
H13	0.363688	0.564785	0.177326	0.028*
C14	0.3761 (5)	0.4645 (2)	0.2943 (3)	0.0190 (7)
C15	0.6415 (5)	0.5464 (2)	0.2976 (3)	0.0201 (7)
C16	0.7133 (5)	0.6047 (3)	0.2564 (3)	0.0226 (8)
C17	0.2484 (5)	0.2737 (3)	0.4661 (3)	0.0224 (8)
C18	0.1684 (5)	0.2157 (2)	0.5008 (3)	0.0227 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02902 (14)	0.02681 (14)	0.02568 (14)	−0.00824 (10)	−0.00015 (10)	0.01045 (10)
I2	0.03161 (14)	0.01874 (12)	0.02455 (13)	−0.00641 (10)	0.00495 (10)	0.00300 (9)
C1	0.0253 (18)	0.0140 (16)	0.0175 (16)	−0.0007 (14)	0.0104 (14)	−0.0041 (13)
C2	0.0229 (18)	0.0134 (16)	0.0180 (16)	0.0009 (13)	0.0067 (14)	−0.0033 (13)
C3	0.0209 (18)	0.0204 (18)	0.0216 (18)	−0.0032 (14)	0.0061 (14)	−0.0020 (14)
C4	0.0230 (18)	0.0224 (19)	0.0211 (18)	0.0003 (15)	0.0007 (15)	−0.0044 (15)
C5	0.030 (2)	0.0184 (18)	0.0208 (18)	0.0028 (15)	0.0031 (15)	0.0004 (14)
C6	0.0267 (19)	0.0137 (16)	0.0193 (17)	−0.0010 (14)	0.0066 (14)	−0.0018 (13)
C7	0.0238 (18)	0.0136 (16)	0.0171 (16)	0.0001 (13)	0.0066 (14)	−0.0057 (13)
C8	0.0231 (18)	0.0151 (16)	0.0203 (17)	−0.0009 (14)	0.0094 (14)	−0.0038 (13)
C9	0.0209 (17)	0.0172 (17)	0.0200 (17)	0.0009 (14)	0.0052 (14)	−0.0049 (14)
C10	0.026 (2)	0.028 (2)	0.027 (2)	−0.0051 (16)	0.0061 (16)	−0.0027 (16)
C11	0.0226 (19)	0.034 (2)	0.032 (2)	0.0005 (17)	−0.0016 (16)	−0.0029 (18)

C12	0.033 (2)	0.028 (2)	0.0241 (19)	0.0056 (17)	0.0021 (16)	0.0009 (16)
C13	0.0274 (19)	0.0222 (19)	0.0216 (18)	0.0009 (15)	0.0078 (15)	−0.0011 (15)
C14	0.0268 (18)	0.0157 (16)	0.0158 (16)	0.0012 (14)	0.0086 (14)	−0.0034 (13)
C15	0.0234 (18)	0.0189 (18)	0.0188 (17)	0.0020 (14)	0.0055 (14)	−0.0018 (14)
C16	0.0266 (19)	0.0221 (18)	0.0197 (17)	−0.0043 (15)	0.0055 (15)	0.0016 (14)
C17	0.0251 (19)	0.0199 (18)	0.0225 (18)	0.0003 (15)	0.0046 (15)	−0.0029 (14)
C18	0.0274 (19)	0.0185 (18)	0.0228 (18)	−0.0048 (15)	0.0046 (15)	−0.0012 (14)

Geometric parameters (Å, º)

I1—C16	1.996 (4)	C7—C8	1.420 (5)
I2—C18	1.996 (4)	C8—C9	1.412 (5)
C1—C14	1.413 (5)	C8—C17	1.433 (5)
C1—C2	1.413 (5)	C9—C10	1.428 (6)
C1—C15	1.437 (5)	C9—C14	1.434 (5)
C2—C3	1.426 (5)	C10—C11	1.362 (6)
C2—C7	1.431 (5)	C10—H10	0.9500
C3—C4	1.360 (5)	C11—C12	1.406 (6)
C3—H3	0.9500	C11—H11	0.9500
C4—C5	1.426 (5)	C12—C13	1.360 (6)
C4—H4	0.9500	C12—H12	0.9500
C5—C6	1.349 (6)	C13—C14	1.437 (5)
C5—H5	0.9500	C13—H13	0.9500
C6—C7	1.430 (5)	C15—C16	1.192 (5)
C6—H6	0.9500	C17—C18	1.190 (5)

C14—C1—C2	120.9 (3)	C7—C8—C17	119.3 (3)
C14—C1—C15	118.8 (3)	C8—C9—C10	122.3 (3)
C2—C1—C15	120.3 (3)	C8—C9—C14	119.4 (3)
C1—C2—C3	121.9 (3)	C10—C9—C14	118.3 (3)
C1—C2—C7	119.6 (3)	C11—C10—C9	121.5 (4)
C3—C2—C7	118.5 (3)	C11—C10—H10	119.3
C4—C3—C2	121.0 (3)	C9—C10—H10	119.3
C4—C3—H3	119.5	C10—C11—C12	120.1 (4)
C2—C3—H3	119.5	C10—C11—H11	119.9
C3—C4—C5	120.4 (4)	C12—C11—H11	119.9
C3—C4—H4	119.8	C13—C12—C11	121.0 (4)
C5—C4—H4	119.8	C13—C12—H12	119.5
C6—C5—C4	120.3 (4)	C11—C12—H12	119.5
C6—C5—H5	119.9	C12—C13—C14	120.8 (4)
C4—C5—H5	119.9	C12—C13—H13	119.6
C5—C6—C7	121.3 (3)	C14—C13—H13	119.6
C5—C6—H6	119.4	C1—C14—C9	119.7 (3)
C7—C6—H6	119.4	C1—C14—C13	122.0 (3)
C8—C7—C6	122.1 (3)	C9—C14—C13	118.2 (3)
C8—C7—C2	119.4 (3)	C16—C15—C1	175.4 (4)
C6—C7—C2	118.5 (3)	C15—C16—I1	177.4 (4)
C9—C8—C7	120.9 (3)	C18—C17—C8	179.3 (4)

C9—C8—C17	119.8 (3)	C17—C18—I2	178.0 (3)
C14—C1—C2—C3	178.2 (3)	C7—C8—C9—C10	179.9 (3)
C15—C1—C2—C3	−1.1 (5)	C17—C8—C9—C10	0.7 (5)
C14—C1—C2—C7	−1.6 (5)	C7—C8—C9—C14	−0.9 (5)
C15—C1—C2—C7	179.0 (3)	C17—C8—C9—C14	180.0 (3)
C1—C2—C3—C4	178.2 (3)	C8—C9—C10—C11	179.7 (4)
C7—C2—C3—C4	−1.9 (5)	C14—C9—C10—C11	0.4 (6)
C2—C3—C4—C5	0.3 (6)	C9—C10—C11—C12	−0.4 (6)
C3—C4—C5—C6	1.1 (6)	C10—C11—C12—C13	−0.5 (6)
C4—C5—C6—C7	−0.6 (5)	C11—C12—C13—C14	1.3 (6)
C5—C6—C7—C8	178.6 (3)	C2—C1—C14—C9	−0.5 (5)
C5—C6—C7—C2	−1.0 (5)	C15—C1—C14—C9	178.8 (3)
C1—C2—C7—C8	2.5 (5)	C2—C1—C14—C13	−179.9 (3)
C3—C2—C7—C8	−177.3 (3)	C15—C1—C14—C13	−0.5 (5)
C1—C2—C7—C6	−177.9 (3)	C8—C9—C14—C1	1.8 (5)
C3—C2—C7—C6	2.3 (5)	C10—C9—C14—C1	−178.9 (3)
C6—C7—C8—C9	179.1 (3)	C8—C9—C14—C13	−178.9 (3)
C2—C7—C8—C9	−1.3 (5)	C10—C9—C14—C13	0.4 (5)
C6—C7—C8—C17	−1.7 (5)	C12—C13—C14—C1	178.0 (4)
C2—C7—C8—C17	177.9 (3)	C12—C13—C14—C9	−1.3 (5)