

The head-to-head photodimer of indenoindene

Heiner Detert,* Nina Jacobs and Dieter Schollmeyer

Johannes Gutenberg University Mainz, Department of Chemistry, Duesbergweg 10-14, 55099 Mainz, Germany.

*Correspondence e-mail: detert@uni-mainz.de

Received 15 February 2020

Accepted 4 March 2020

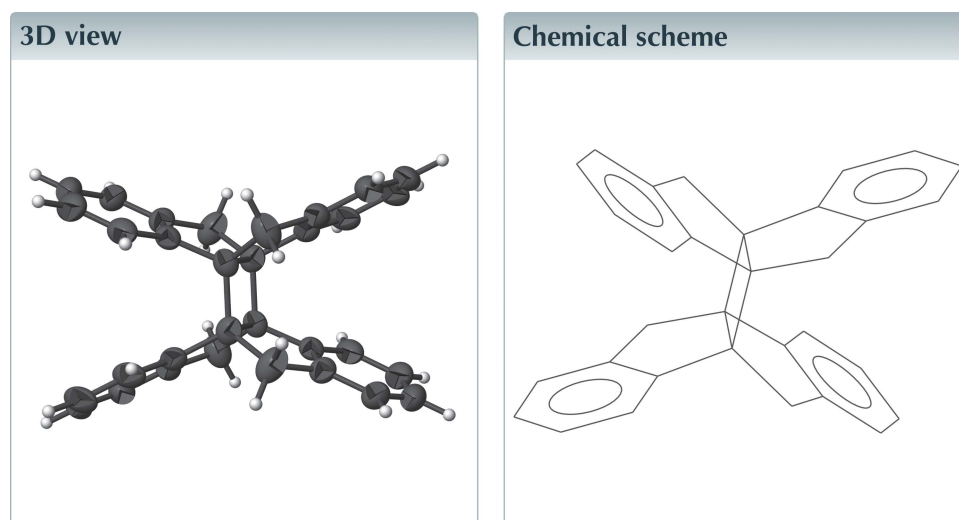
Edited by C. Rizzoli, Università degli Studi di Parma, Italy

Keywords: crystal structure; polycyclic hydrocarbon; strain; cyclobutane.

CCDC reference: 1988066

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

Irradiation of 1-(1-benzocyclobutenylidene)benzocyclobutene gives indenoindene and its head-to-head photodimer nonacyclo[9.7.7.7^{2,10}.0^{1,11}.0^{2,10}.0^{3,8}.0^{12,17}.0^{19,24}.0^{26,31}]dotriaconta-3,5,7,12,14,16,19,21,23,26,28,30-dodecaene, C₃₂H₂₄. The molecule is built from four essentially planar indane units attached to an elongated cyclobutane ring. In the crystal, C—H... π interactions connect molecules into layers parallel to the *bc* plane.



Structure description

The photocycloaddition of 5,10-dihydroindeno[2,1-*a*]indene (Detert & Schollmeyer, 2019) has been studied by Shim (Shim *et al.*, 1983) and Wolff (Wolff *et al.*, 1992). Head-to-head and head-to-tail photodimers have been found in a 1: 2 ratio (Shim & Chae, 1982). As part of a project on strained (Detert *et al.*, 2009; Dobryakov *et al.*, 2016; Krohn *et al.*, 2019) and polycyclic hydrocarbons (Krämer *et al.*, 2009; Detert & Meier, 1997*a,b*), indenoindene was prepared in a photochemical rearrangement of 1-(1-benzocyclobutenylidene)benzocyclobutene; concomitant 2 + 2-cycloaddition of indenoindene produced the title compound as a byproduct.

The monoclinic unit cell of the title compound (Fig. 1) contains two centrosymmetrical molecules. The indane units, though containing sp^3 carbons, are essentially planar with a maximum deviation of 0.043 (2) Å at C16 from the mean plane. An angle of 51.53 (5)° is opened by the least-squares planes of indanes annulated to the cyclobutane [C8, C16, C8ⁱ, C16ⁱ; symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*], nearly identical to the angle of 52.28 (8)° between the planes of indanes on opposite sides of the cyclobutane. The C—C bonds in the central cyclobutane ring are largely elongated, the C8—C16 bond is 1.569 (3) Å long and the C8—C16ⁱ bond, connecting the indanoindane units, is even more stretched to 1.597 (3) Å. This is due to the eclipsed conformation of vicinal methylene groups, the minimal distance between C7—H and C15ⁱ—H is 1.95 Å, lower than the sum of the van der Waals radii. Bond angles in the cyclobutane are close to orthogonal, C8—C16—C8ⁱ =

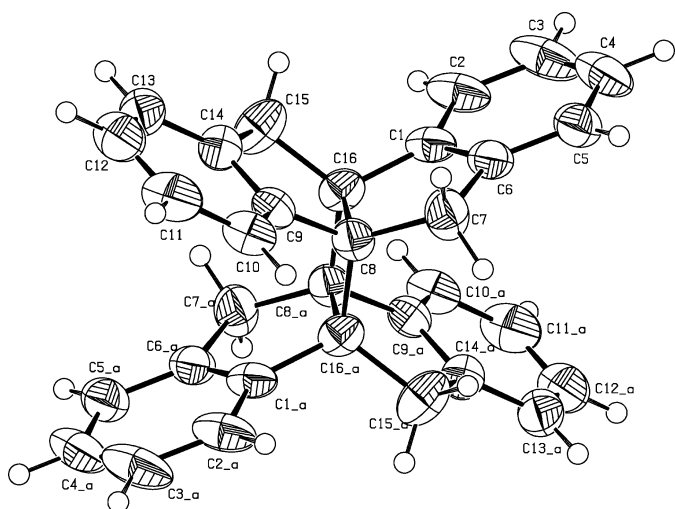


Figure 1
Perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level. The second part of the molecule is generated by the symmetry operation $1 - x, 1 - y, 1 - z$.

90.41 (15) and $C16-C8-C16^i = 89.59 (15)^\circ$. Bond angles on the cyclobutane are much larger, $C1-C16-C8^i = 115.12 (17)$, $C1-C16-C15 = 116.65 (19)^\circ$ and $C15-C16-C8^i = 118.80 (19)^\circ$. In the crystal, molecules are linked by $C-H \cdots \pi$ interactions (Fig. 2, Table 1), forming layers parallel to the bc plane.

Synthesis and crystallization

Indeno[2,1-*a*]indene (Detert & Schollmeyer, 2019) was prepared from benzocyclobutenone (Schiess & Heitzmann, 1977), according to literature procedures (Detert & Schollmeyer, 2018; Oelgemöller *et al.*, 2002). The photochemical rearrangement was performed in a falling film photoreactor (Normag, Ilmenau) equipped with a medium pressure mercury lamp (TQ 718) in a diluted solution (0.1%) in

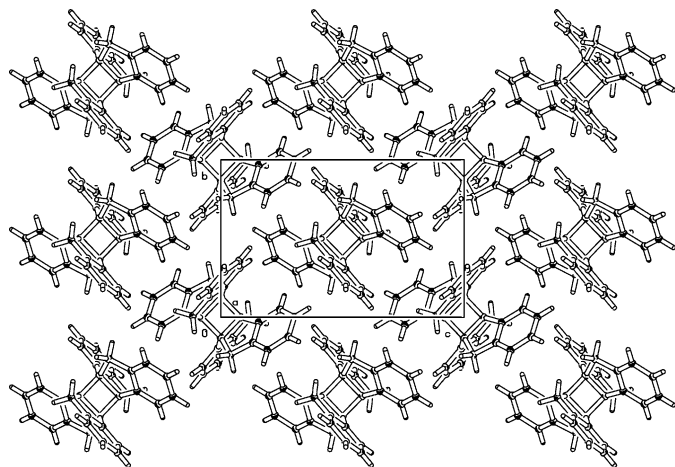


Figure 2
Partial packing diagram of the title compound. View along the a axis.

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$Cg1$ is the centroid of the $C9-C14$ ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C3-H3 \cdots Cg1^i$	0.95	2.77	3.713 (3)	171

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{32}H_{24}$
M_r	408.51
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	193
a, b, c (\AA)	9.3106 (11), 8.7232 (8), 13.4776 (12)
β ($^\circ$)	91.959 (8)
V (\AA^3)	1093.99 (19)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.40 \times 0.32 \times 0.17
Data collection	
Diffractometer	Stoe <i>IPDS</i> 2T
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5905, 2604, 1416
R_{int}	0.051
$(\sin \theta/\lambda)_{max}$ (\AA^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.061, 0.196, 0.97
No. of reflections	2604
No. of parameters	145
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ ($e \text{\AA}^{-3}$)	0.19, -0.22

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 1996), *SIR2004* (Burla *et al.*, 2005), *SHELXL2018/3* (Sheldrick, 2015) and *PLATON* (Spek, 2020).

petroleum ether. Contrary to the irradiation of indenoindene in benzene (Shim & Chae, 1982), the head-to-head isomer was the main dimerization product. Crystals were obtained by slow evaporation of a petroleum ether solution.

Refinement

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

References

- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Detert, H., Lenoir, D. & Zipse, H. (2009). *Eur. J. Org. Chem.* **2009**, 1181–1190.
- Detert, H. & Meier, H. (1997). *Liebigs Ann. Recl.* **1997**, 1557–1563.
- Detert, H. & Meier, H. (1997). *Liebigs Ann. Recl.* **1997**, 1565–1570.
- Detert, H. & Schollmeyer, D. (2018). *IUCrData*, **3**, x181550.
- Detert, H. & Schollmeyer, D. (2019). *IUCrData*, **4**, x191179.
- Dobryakov, A., Quick, M., Lenoir, D., Detert, H., Ernsting, N. & Kovalenko, S. A. (2016). *Chem. Phys. Lett.* **652**, 225–229.
- Krämer, G., Detert, H. & Meier, H. (2009). *Tetrahedron Lett.* **50**, 4810–4812.

- Krohn, O., Quick, M., Ioffe, I., Mazaleva, O., Lenoir, D., Detert, H. & Kovalenko, S. (2019). *J. Phys. Chem. B*, **123**, 4291–4300.
- Oelgemöller, M., Brem, B., Frank, R., Schneider, S., Lenoir, D., Hertkorn, N., Origane, Y., Lemmen, P., Lex, J. & Inoue, Y. (2002). *J. Chem. Soc. Perkin Trans. 2*, pp. 1760–1771.
- Schiess, P. & Heitzmann, M. (1977). *Angew. Chem.* **89**, 485–485.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Shim, S. C. & Chae, J. S. (1982). *Bull. Chem. Soc. Jpn*, **55**, 1310–1312.
- Shim, S. C., Chae, J. S. & Choi, J. H. (1983). *J. Org. Chem.* **48**, 417–421.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Stoe & Cie (1996). *X-RED and X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Wolff, T., Schmidt, F. & Volz, P. (1992). *J. Org. Chem.* **57**, 4255–4262.

full crystallographic data

IUCrData (2020). 5, x200307 [https://doi.org/10.1107/S2414314620003077]

The head-to-head photodimer of indenoindene

Heiner Detert, Nina Jacobs and Dieter Schollmeyer

Nonacyclo[9.7.7.7^{2,10}.0^{1,11}.0^{2,10}.0^{3,8}.0^{12,17}.0^{19,24}.0^{26,31}]dotriaconta-3,5,7,12,14,16,19,21,23,26,28,30-dodecaene

Crystal data

$C_{32}H_{24}$	$F(000) = 432$
$M_r = 408.51$	$D_x = 1.240 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 9.3106 (11) \text{ \AA}$	Cell parameters from 4760 reflections
$b = 8.7232 (8) \text{ \AA}$	$\theta = 2.8\text{--}28.4^\circ$
$c = 13.4776 (12) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$\beta = 91.959 (8)^\circ$	$T = 193 \text{ K}$
$V = 1093.99 (19) \text{ \AA}^3$	Block, colourless
$Z = 2$	$0.40 \times 0.32 \times 0.17 \text{ mm}$

Data collection

Stoe IPDS 2T diffractometer	2604 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	1416 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{\text{int}} = 0.051$
rotation method scans	$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 2.8^\circ$
5905 measured reflections	$h = -12 \rightarrow 12$
	$k = -11 \rightarrow 11$
	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.061$	H-atom parameters constrained
$wR(F^2) = 0.196$	$w = 1/[\sigma^2(F_o^2) + (0.1156P)^2]$
$S = 0.97$	where $P = (F_o^2 + 2F_c^2)/3$
2604 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
145 parameters	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

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.

Refinement. Hydrogen atoms attached to carbons were placed at calculated positions and were refined in the riding-model approximation with C–H = 0.95–0.99 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4266 (2)	0.5319 (2)	0.65609 (14)	0.0434 (5)
C2	0.3996 (3)	0.4508 (3)	0.74264 (16)	0.0586 (7)
H2	0.455901	0.363472	0.760360	0.070*
C3	0.2908 (4)	0.4981 (3)	0.80229 (18)	0.0738 (9)
H3	0.271851	0.442967	0.861199	0.089*
C4	0.2099 (3)	0.6238 (4)	0.77730 (18)	0.0675 (8)
H4	0.134797	0.654571	0.818923	0.081*
C5	0.2357 (3)	0.7075 (3)	0.69200 (18)	0.0566 (7)
H5	0.179057	0.794881	0.675228	0.068*
C6	0.3453 (2)	0.6613 (3)	0.63188 (15)	0.0450 (5)
C7	0.3945 (3)	0.7366 (3)	0.53776 (17)	0.0553 (6)
H7A	0.435041	0.839524	0.551922	0.066*
H7B	0.313791	0.746705	0.488456	0.066*
C8	0.5100 (2)	0.6283 (2)	0.49985 (14)	0.0399 (5)
C9	0.6561 (2)	0.6969 (2)	0.48827 (14)	0.0384 (5)
C10	0.6955 (3)	0.8137 (2)	0.42436 (16)	0.0490 (6)
H10	0.625938	0.861017	0.381202	0.059*
C11	0.8370 (3)	0.8597 (3)	0.42464 (19)	0.0635 (7)
H11	0.865113	0.939744	0.381628	0.076*
C12	0.9381 (3)	0.7905 (3)	0.48689 (19)	0.0618 (7)
H12	1.035286	0.823562	0.486287	0.074*
C13	0.9004 (3)	0.6743 (3)	0.54978 (18)	0.0521 (6)
H13	0.970946	0.626587	0.591988	0.063*
C14	0.7580 (2)	0.6277 (2)	0.55081 (16)	0.0429 (5)
C15	0.6931 (3)	0.5091 (3)	0.6165 (2)	0.0581 (7)
H15A	0.700371	0.541016	0.686992	0.070*
H15B	0.741669	0.408951	0.609403	0.070*
C16	0.5354 (2)	0.4997 (2)	0.57990 (15)	0.0419 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0536 (13)	0.0476 (12)	0.0287 (10)	−0.0135 (10)	−0.0022 (8)	0.0010 (9)
C2	0.091 (2)	0.0540 (14)	0.0302 (11)	−0.0209 (13)	0.0020 (11)	0.0007 (10)
C3	0.120 (3)	0.0679 (18)	0.0344 (12)	−0.0366 (18)	0.0200 (14)	−0.0072 (13)
C4	0.081 (2)	0.0788 (19)	0.0440 (13)	−0.0325 (16)	0.0233 (13)	−0.0229 (13)
C5	0.0526 (15)	0.0684 (16)	0.0492 (13)	−0.0105 (12)	0.0069 (11)	−0.0150 (12)
C6	0.0465 (13)	0.0534 (13)	0.0350 (10)	−0.0082 (10)	0.0017 (9)	−0.0040 (9)
C7	0.0527 (15)	0.0652 (15)	0.0483 (12)	0.0166 (12)	0.0070 (10)	0.0127 (11)
C8	0.0440 (12)	0.0416 (11)	0.0342 (10)	0.0045 (9)	0.0033 (8)	0.0083 (9)
C9	0.0483 (13)	0.0309 (10)	0.0363 (10)	0.0003 (9)	0.0061 (8)	−0.0011 (8)
C10	0.0686 (17)	0.0380 (11)	0.0406 (11)	−0.0071 (11)	0.0058 (10)	0.0011 (9)
C11	0.082 (2)	0.0577 (15)	0.0518 (14)	−0.0284 (14)	0.0125 (13)	−0.0015 (12)
C12	0.0597 (17)	0.0669 (16)	0.0597 (15)	−0.0245 (13)	0.0148 (12)	−0.0135 (12)
C13	0.0468 (14)	0.0509 (13)	0.0587 (14)	−0.0052 (11)	0.0030 (11)	−0.0090 (11)

C14	0.0435 (13)	0.0358 (11)	0.0494 (12)	-0.0013 (9)	0.0017 (9)	-0.0015 (9)
C15	0.0492 (14)	0.0524 (14)	0.0719 (16)	-0.0063 (12)	-0.0124 (12)	0.0219 (12)
C16	0.0439 (12)	0.0439 (11)	0.0377 (11)	-0.0032 (9)	-0.0024 (9)	0.0117 (9)

Geometric parameters (Å, °)

C1—C6	1.392 (3)	C8—C16	1.569 (3)
C1—C2	1.395 (3)	C8—C16 ⁱ	1.597 (3)
C1—C16	1.494 (3)	C9—C14	1.386 (3)
C2—C3	1.379 (4)	C9—C10	1.392 (3)
C2—H2	0.9500	C10—C11	1.376 (4)
C3—C4	1.366 (4)	C10—H10	0.9500
C3—H3	0.9500	C11—C12	1.379 (4)
C4—C5	1.389 (4)	C11—H11	0.9500
C4—H4	0.9500	C12—C13	1.374 (3)
C5—C6	1.384 (3)	C12—H12	0.9500
C5—H5	0.9500	C13—C14	1.388 (3)
C6—C7	1.513 (3)	C13—H13	0.9500
C7—C8	1.532 (3)	C14—C15	1.501 (3)
C7—H7A	0.9900	C15—C16	1.535 (3)
C7—H7B	0.9900	C15—H15A	0.9900
C8—C9	1.500 (3)	C15—H15B	0.9900
C6—C1—C2	119.7 (2)	C14—C9—C10	120.4 (2)
C6—C1—C16	111.58 (18)	C14—C9—C8	111.53 (17)
C2—C1—C16	128.7 (2)	C10—C9—C8	128.0 (2)
C3—C2—C1	119.5 (3)	C11—C10—C9	119.0 (2)
C3—C2—H2	120.3	C11—C10—H10	120.5
C1—C2—H2	120.3	C9—C10—H10	120.5
C4—C3—C2	120.5 (2)	C10—C11—C12	120.5 (2)
C4—C3—H3	119.8	C10—C11—H11	119.8
C2—C3—H3	119.8	C12—C11—H11	119.8
C3—C4—C5	121.1 (3)	C13—C12—C11	121.0 (2)
C3—C4—H4	119.5	C13—C12—H12	119.5
C5—C4—H4	119.5	C11—C12—H12	119.5
C6—C5—C4	118.9 (3)	C12—C13—C14	119.1 (2)
C6—C5—H5	120.5	C12—C13—H13	120.4
C4—C5—H5	120.5	C14—C13—H13	120.4
C5—C6—C1	120.3 (2)	C9—C14—C13	120.0 (2)
C5—C6—C7	128.0 (2)	C9—C14—C15	112.24 (19)
C1—C6—C7	111.7 (2)	C13—C14—C15	127.7 (2)
C6—C7—C8	104.37 (18)	C14—C15—C16	104.30 (17)
C6—C7—H7A	110.9	C14—C15—H15A	110.9
C8—C7—H7A	110.9	C16—C15—H15A	110.9
C6—C7—H7B	110.9	C14—C15—H15B	110.9
C8—C7—H7B	110.9	C16—C15—H15B	110.9
H7A—C7—H7B	108.9	H15A—C15—H15B	108.9
C9—C8—C7	115.99 (18)	C1—C16—C15	115.65 (19)

C9—C8—C16	103.94 (16)	C1—C16—C8	104.37 (17)
C7—C8—C16	107.62 (17)	C15—C16—C8	107.63 (17)
C9—C8—C16 ⁱ	115.41 (17)	C1—C16—C8 ⁱ	115.12 (17)
C7—C8—C16 ⁱ	118.91 (19)	C15—C16—C8 ⁱ	118.80 (19)
C16—C8—C16 ⁱ	89.59 (15)	C8—C16—C8 ⁱ	90.41 (15)
C6—C1—C2—C3	1.2 (3)	C10—C9—C14—C13	-0.2 (3)
C16—C1—C2—C3	-178.4 (2)	C8—C9—C14—C13	179.10 (18)
C1—C2—C3—C4	-0.2 (4)	C10—C9—C14—C15	177.7 (2)
C2—C3—C4—C5	-0.5 (4)	C8—C9—C14—C15	-3.0 (3)
C3—C4—C5—C6	0.1 (4)	C12—C13—C14—C9	0.6 (3)
C4—C5—C6—C1	0.9 (3)	C12—C13—C14—C15	-176.9 (2)
C4—C5—C6—C7	-178.3 (2)	C9—C14—C15—C16	5.6 (3)
C2—C1—C6—C5	-1.6 (3)	C13—C14—C15—C16	-176.7 (2)
C16—C1—C6—C5	178.12 (19)	C6—C1—C16—C15	116.9 (2)
C2—C1—C6—C7	177.8 (2)	C2—C1—C16—C15	-63.4 (3)
C16—C1—C6—C7	-2.5 (3)	C6—C1—C16—C8	-1.1 (2)
C5—C6—C7—C8	-175.6 (2)	C2—C1—C16—C8	178.6 (2)
C1—C6—C7—C8	5.1 (3)	C6—C1—C16—C8 ⁱ	-98.5 (2)
C6—C7—C8—C9	-121.4 (2)	C2—C1—C16—C8 ⁱ	81.2 (3)
C6—C7—C8—C16	-5.5 (2)	C14—C15—C16—C1	-122.1 (2)
C6—C7—C8—C16 ⁱ	94.1 (2)	C14—C15—C16—C8	-6.0 (2)
C7—C8—C9—C14	116.93 (19)	C14—C15—C16—C8 ⁱ	94.6 (2)
C16—C8—C9—C14	-1.0 (2)	C9—C8—C16—C1	127.77 (17)
C16 ⁱ —C8—C9—C14	-97.3 (2)	C7—C8—C16—C1	4.2 (2)
C7—C8—C9—C10	-63.9 (3)	C16 ⁱ —C8—C16—C1	-116.11 (18)
C16—C8—C9—C10	178.2 (2)	C9—C8—C16—C15	4.4 (2)
C16 ⁱ —C8—C9—C10	81.9 (3)	C7—C8—C16—C15	-119.2 (2)
C14—C9—C10—C11	-0.3 (3)	C16 ⁱ —C8—C16—C15	120.5 (2)
C8—C9—C10—C11	-179.5 (2)	C9—C8—C16—C8 ⁱ	-116.13 (18)
C9—C10—C11—C12	0.4 (4)	C7—C8—C16—C8 ⁱ	120.3 (2)
C10—C11—C12—C13	0.1 (4)	C16 ⁱ —C8—C16—C8 ⁱ	-0.002 (1)
C11—C12—C13—C14	-0.6 (4)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 is the centroid of the C9—C14 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots Cg1 ⁱⁱ	0.95	2.77	3.713 (3)	171

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