

10-Methyl-9,11-annulated dibenzobarrelene

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Received 25 July 2018

Accepted 2 August 2018

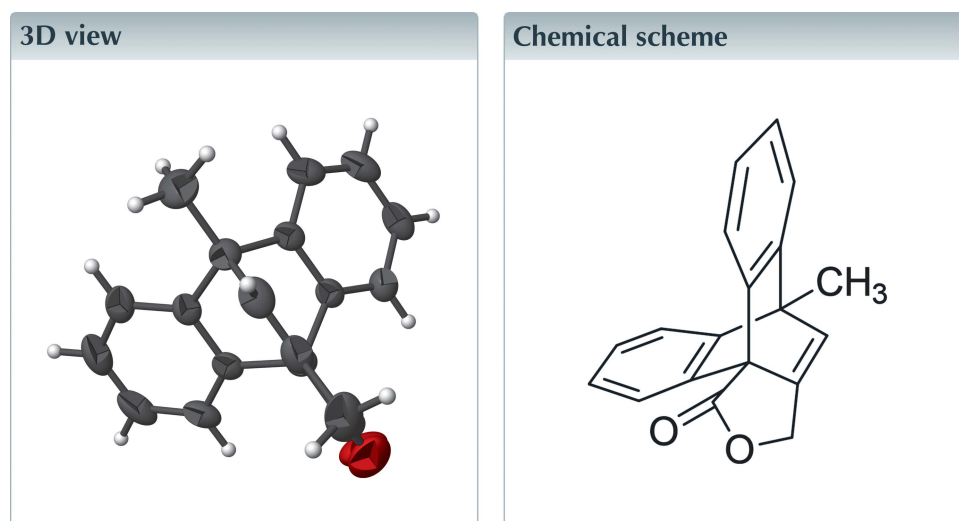
Edited by A. J. Lough, University of Toronto, Canada

Keywords: crystal structure; dibenzobarrelene; 9,11-annulated dibenzobarrelene.

CCDC reference: 1859772

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

In the title compound (systematic name: 8-methyl-16-oxapentacyclo-[6.6.5.0^{1,18}.0^{2,7}.0^{9,14}]nonadeca-2,4,6,9(14),10,12,18-heptaen-15-one), C₁₉H₁₄O₂, the benzene rings form a dihedral angle of 64.84 (7)°. In the crystal, π - π stacking interactions, with a centroid-centroid distance of 3.7695 (8) Å, and weak C—H \cdots π interactions link molecules along the *b*-axis direction.



Structure description

Dibenzobarrelene systems have attracted interest over the years because of their biological (Khalil *et al.*, 2010) and photochemical properties (Zimmerman & Grunewald, 1966). Suitably substituted dibenzobarrelenes exhibit interesting physical properties (Ishii *et al.*, 2016). Mathew *et al.* (2013, 2014) reported two dibenzobarrelene derivatives and discussed their structural features. A recent report highlighted the applications of dibenzobarrelenes in OLEDs and photoluminescent materials (Ishii *et al.*, 2018).

In the present study, an intramolecular Diels–Alder reaction was employed for the synthesis of 9,11-annulated dibenzobarrelenes and their diffraction-quality single crystals could be obtained by crystallization from suitable solvents. The derivatives can be easily modified structurally by using different substituents on the bridgehead positions. In the case of the title compound, the bridgehead position 10 is substituted with a methyl group and we obtained good-quality single crystals by recrystallization from acetonitrile. The molecular structure of the title compound is shown in Fig. 1. The two benzene rings form a dihedral of 64.84 (7)°. These rings form angles of 58.86 (8) and 56.96 (6)°, respectively, with the annulated ring at the vinylic bridge head position.

In the crystal, π - π stacking interactions are present between inversion-related rings (C1–C4/C18/C19) with a centroid-centroid distance of 3.7695 (8) Å. Pairs of weak C—

Table 1

C–H... π interactions (\AA , $^\circ$).

$Cg1$ and $Cg2$ are the centroids of the C6–C9/C16/C17 and C1–C4/C18/C19 rings, respectively.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2 \cdots Cg1^i$	0.93	2.80	3.582 (2)	142
$C11-H11B \cdots Cg2^{ii}$	0.97	2.74	3.675 (2)	163

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$.

H... π interactions are also present between these inversion-related molecules (Table 1, Fig. 2). A further C–H... π interaction links the inversion-related molecules along the b -axis direction (Figs. 2 and 3).

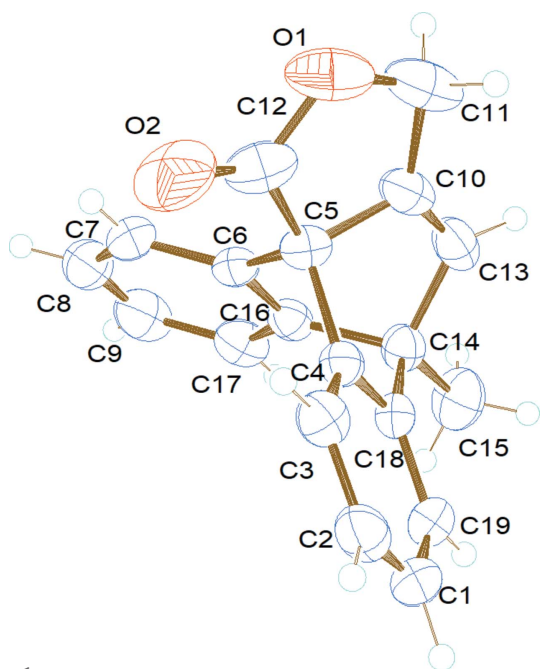


Figure 1

The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

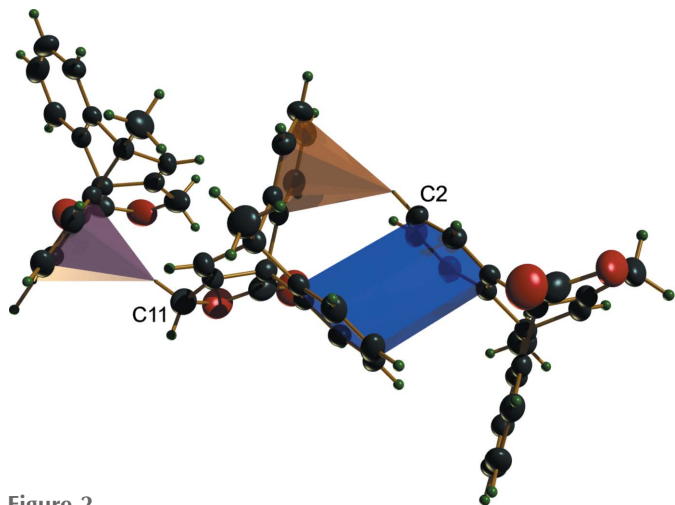


Figure 2

The π - π (blue) and C–H... π (brown) interactions present in the title compound.

Table 2

Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{14}O_2$
M_r	274.30
Crystal system, space group	Orthorhombic, $Pbcn$
Temperature (K)	296
a, b, c (\AA)	19.7403 (10), 9.3294 (3), 15.0595 (7)
V (\AA^3)	2773.4 (2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.40 \times 0.30 \times 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2004)
T_{\min} , T_{\max}	0.967, 0.983
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21513, 3394, 2487
R_{int}	0.030
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.132, 1.04
No. of reflections	3394
No. of parameters	192
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ ($e \text{\AA}^{-3}$)	0.22, -0.25

Computer programs: *APEX2* (Bruker, 2004), *APEX2* and *SAINT* (Bruker, 2004), *SAINT* and *XPREF* (Bruker, 2004), *SHELXT* (Sheldrick, 2015a), *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2010), *SHELXL2018* (Sheldrick, 2015b) and *pubCIF* (Westrip, 2010).

Synthesis and crystallization

The title compound was synthesized by a reported procedure (Ciganek, 1980). 10-Methyl-9-anthracenecarboxylic acid (1.1 g, 5 mmol) was dissolved in acetone and stirred at room

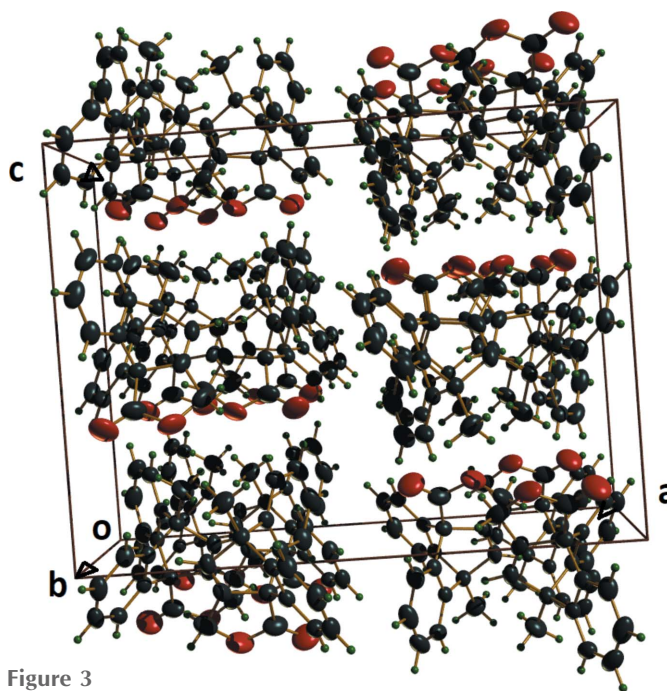


Figure 3

The packing viewed along the b axis.

temperature for 1 h with trimethylamine (0.70 ml, 5 mmol) and cyanuric chloride (0.92 g, 5 mmol). The acid chloride obtained was treated with propargyl alcohol (0.30 ml, 5 mmol) for about 4 h to obtain propargyl-9-anthroate, which underwent an intramolecular Diels–Alder reaction to give the target 9,11-anulated barrelene derivative. The product was purified by silica column chromatography, eluting with a 1:1 DCM–hexane mixture. Recrystallization was carried out in an acetonitrile solvent by slow evaporation.

Refinement

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

Acknowledgements

We acknowledge the Sophisticated Analytical Instruments Facility, Cochin University of Science and Technology, Kochi-22, India, for single-crystal X-ray diffraction measurements.

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full crystallographic data

IUCrData (2018). 3, x181102 [https://doi.org/10.1107/S2414314618011021]

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C₁₉H₁₄O₂

M_r = 274.30

Orthorhombic, *Pbcn*

a = 19.7403 (10) Å

b = 9.3294 (3) Å

c = 15.0595 (7) Å

V = 2773.4 (2) Å³

Z = 8

F(000) = 1152

D_x = 1.314 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 8066 reflections

θ = 4.8–56.3°

μ = 0.08 mm⁻¹

T = 296 K

Block, colorless

0.40 × 0.30 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

ω and φ scan

Absorption correction: multi-scan
(SADABS; Bruker, 2004)

T_{min} = 0.967, *T_{max}* = 0.983

21513 measured reflections

3394 independent reflections

2487 reflections with *I* > 2σ(*I*)

R_{int} = 0.030

θ_{max} = 28.3°, θ_{min} = 2.4°

h = -26→19

k = -9→12

l = -19→18

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.046

wR(*F*²) = 0.132

S = 1.04

3394 reflections

192 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.068*P*)² + 0.5261*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.22 e Å⁻³

Δρ_{min} = -0.25 e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

*F_c** = *kF_c*[1 + 0.001 × *F_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.0118 (12)

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. Carbon bound H atoms were positioned geometrically and refined using a riding model with C—H = 0.93–0.97 Å and with *U*_{iso}(H) = 1.2 *U*_{eq}(C) (1.5 times *U*_{eq}(C) for methyl groups).

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.29033 (7)	0.80423 (15)	-0.15003 (8)	0.0740 (4)
O2	0.40199 (8)	0.83530 (16)	-0.15059 (9)	0.0827 (5)
C1	0.44196 (8)	0.28888 (15)	-0.00666 (12)	0.0503 (4)
H1	0.461537	0.199210	0.001693	0.060*
C2	0.45800 (7)	0.36683 (16)	-0.08067 (11)	0.0483 (4)
H2	0.487959	0.329543	-0.122356	0.058*
C3	0.42961 (7)	0.50186 (15)	-0.09380 (9)	0.0410 (3)
H3	0.440680	0.555812	-0.143655	0.049*
C4	0.38498 (6)	0.55377 (13)	-0.03171 (8)	0.0331 (3)
C5	0.34901 (7)	0.69910 (14)	-0.03169 (9)	0.0368 (3)
C6	0.37181 (6)	0.77210 (13)	0.05361 (9)	0.0348 (3)
C7	0.40604 (7)	0.90020 (15)	0.06192 (11)	0.0461 (4)
H7	0.417357	0.953570	0.011919	0.055*
C8	0.42329 (8)	0.94811 (17)	0.14604 (13)	0.0574 (5)
H8	0.446029	1.034771	0.152578	0.069*
C9	0.40712 (8)	0.86881 (18)	0.21974 (12)	0.0569 (5)
H9	0.419167	0.901980	0.275796	0.068*
C10	0.27445 (7)	0.66803 (16)	-0.02136 (10)	0.0432 (3)
C11	0.23853 (9)	0.7332 (2)	-0.09881 (11)	0.0650 (5)
H11A	0.216396	0.659710	-0.133955	0.078*
H11B	0.204683	0.801348	-0.078902	0.078*
C12	0.35311 (10)	0.78600 (18)	-0.11548 (11)	0.0561 (4)
C13	0.25779 (7)	0.59227 (16)	0.04863 (10)	0.0449 (4)
H13	0.213399	0.566592	0.061862	0.054*
C14	0.31846 (6)	0.55000 (14)	0.10663 (9)	0.0371 (3)
C15	0.29780 (9)	0.46275 (18)	0.18740 (11)	0.0576 (4)
H15A	0.267777	0.518400	0.223819	0.086*
H15B	0.337410	0.437734	0.220981	0.086*
H15C	0.275158	0.376981	0.168433	0.086*
C16	0.35485 (6)	0.69107 (14)	0.12803 (9)	0.0345 (3)
C17	0.37298 (7)	0.73966 (17)	0.21144 (10)	0.0456 (4)
H17	0.362351	0.686079	0.261617	0.055*
C18	0.36800 (6)	0.47459 (13)	0.04359 (9)	0.0336 (3)
C19	0.39709 (7)	0.34135 (15)	0.05595 (11)	0.0445 (4)
H19	0.386568	0.287351	0.105994	0.053*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0880 (9)	0.0844 (9)	0.0496 (7)	0.0323 (8)	-0.0154 (6)	0.0128 (6)
O2	0.0991 (11)	0.0788 (9)	0.0700 (9)	0.0036 (8)	0.0134 (8)	0.0381 (7)
C1	0.0412 (7)	0.0315 (7)	0.0783 (11)	0.0040 (5)	-0.0036 (7)	-0.0066 (7)
C2	0.0359 (7)	0.0475 (8)	0.0614 (10)	0.0043 (6)	-0.0002 (6)	-0.0193 (7)
C3	0.0391 (7)	0.0451 (8)	0.0388 (7)	-0.0007 (6)	0.0002 (5)	-0.0058 (6)
C4	0.0316 (6)	0.0313 (6)	0.0364 (7)	0.0003 (5)	-0.0044 (5)	-0.0038 (5)

C5	0.0402 (7)	0.0349 (7)	0.0354 (7)	0.0055 (5)	-0.0019 (5)	0.0024 (5)
C6	0.0326 (6)	0.0292 (6)	0.0427 (7)	0.0065 (5)	-0.0021 (5)	-0.0009 (5)
C7	0.0433 (7)	0.0285 (7)	0.0663 (10)	0.0049 (5)	-0.0029 (7)	0.0012 (6)
C8	0.0497 (9)	0.0350 (8)	0.0876 (13)	0.0030 (6)	-0.0151 (8)	-0.0172 (8)
C9	0.0541 (9)	0.0559 (10)	0.0607 (11)	0.0107 (7)	-0.0162 (8)	-0.0271 (8)
C10	0.0376 (7)	0.0464 (8)	0.0457 (8)	0.0108 (6)	-0.0099 (6)	-0.0113 (7)
C11	0.0595 (10)	0.0828 (13)	0.0526 (10)	0.0290 (9)	-0.0197 (8)	-0.0119 (9)
C12	0.0744 (11)	0.0493 (9)	0.0447 (9)	0.0154 (8)	-0.0008 (8)	0.0096 (7)
C13	0.0294 (6)	0.0511 (8)	0.0541 (9)	-0.0009 (6)	-0.0009 (6)	-0.0109 (7)
C14	0.0345 (6)	0.0381 (7)	0.0386 (7)	-0.0030 (5)	0.0024 (5)	0.0016 (5)
C15	0.0599 (9)	0.0592 (10)	0.0536 (10)	-0.0109 (8)	0.0153 (8)	0.0074 (8)
C16	0.0294 (6)	0.0366 (7)	0.0376 (7)	0.0051 (5)	-0.0006 (5)	-0.0051 (5)
C17	0.0433 (7)	0.0536 (8)	0.0399 (8)	0.0096 (6)	-0.0013 (6)	-0.0090 (6)
C18	0.0305 (6)	0.0298 (6)	0.0404 (7)	-0.0036 (5)	-0.0032 (5)	-0.0018 (5)
C19	0.0420 (7)	0.0320 (7)	0.0594 (9)	-0.0034 (6)	-0.0030 (6)	0.0061 (6)

Geometric parameters (Å, °)

O1—C12	1.355 (2)	C8—H8	0.9300
O1—C11	1.442 (3)	C9—C17	1.386 (2)
O2—C12	1.193 (2)	C9—H9	0.9300
C1—C2	1.368 (2)	C10—C13	1.311 (2)
C1—C19	1.383 (2)	C10—C11	1.494 (2)
C1—H1	0.9300	C11—H11A	0.9700
C2—C3	1.393 (2)	C11—H11B	0.9700
C2—H2	0.9300	C13—C14	1.5339 (19)
C3—C4	1.3730 (18)	C13—H13	0.9300
C3—H3	0.9300	C14—C15	1.5194 (19)
C4—C18	1.3943 (18)	C14—C16	1.5336 (18)
C4—C5	1.5305 (17)	C14—C18	1.5338 (18)
C5—C12	1.502 (2)	C15—H15A	0.9600
C5—C10	1.5081 (19)	C15—H15B	0.9600
C5—C6	1.5220 (18)	C15—H15C	0.9600
C6—C7	1.3786 (19)	C16—C17	1.3825 (19)
C6—C16	1.3927 (19)	C17—H17	0.9300
C7—C8	1.386 (2)	C18—C19	1.3819 (18)
C7—H7	0.9300	C19—H19	0.9300
C8—C9	1.372 (3)		
C12—O1—C11	112.66 (13)	O1—C11—H11A	110.6
C2—C1—C19	121.02 (13)	C10—C11—H11A	110.6
C2—C1—H1	119.5	O1—C11—H11B	110.6
C19—C1—H1	119.5	C10—C11—H11B	110.6
C1—C2—C3	120.22 (13)	H11A—C11—H11B	108.8
C1—C2—H2	119.9	O2—C12—O1	121.43 (16)
C3—C2—H2	119.9	O2—C12—C5	128.62 (17)
C4—C3—C2	118.72 (14)	O1—C12—C5	109.95 (15)
C4—C3—H3	120.6	C10—C13—C14	113.61 (12)

C2—C3—H3	120.6	C10—C13—H13	123.2
C3—C4—C18	121.41 (12)	C14—C13—H13	123.2
C3—C4—C5	127.61 (12)	C15—C14—C16	114.66 (12)
C18—C4—C5	110.96 (10)	C15—C14—C18	114.89 (12)
C12—C5—C10	104.06 (12)	C16—C14—C18	103.01 (9)
C12—C5—C6	116.85 (12)	C15—C14—C13	112.58 (12)
C10—C5—C6	106.71 (11)	C16—C14—C13	105.35 (11)
C12—C5—C4	116.94 (11)	C18—C14—C13	105.27 (10)
C10—C5—C4	106.41 (11)	C14—C15—H15A	109.5
C6—C5—C4	105.03 (10)	C14—C15—H15B	109.5
C7—C6—C16	121.02 (13)	H15A—C15—H15B	109.5
C7—C6—C5	127.55 (13)	C14—C15—H15C	109.5
C16—C6—C5	111.42 (11)	H15A—C15—H15C	109.5
C6—C7—C8	118.88 (15)	H15B—C15—H15C	109.5
C6—C7—H7	120.6	C17—C16—C6	119.40 (13)
C8—C7—H7	120.6	C17—C16—C14	126.41 (12)
C9—C8—C7	120.57 (14)	C6—C16—C14	114.16 (11)
C9—C8—H8	119.7	C16—C17—C9	119.53 (15)
C7—C8—H8	119.7	C16—C17—H17	120.2
C8—C9—C17	120.60 (15)	C9—C17—H17	120.2
C8—C9—H9	119.7	C19—C18—C4	119.09 (12)
C17—C9—H9	119.7	C19—C18—C14	126.46 (12)
C13—C10—C11	136.70 (15)	C4—C18—C14	114.43 (10)
C13—C10—C5	115.56 (12)	C18—C19—C1	119.52 (14)
C11—C10—C5	107.72 (13)	C18—C19—H19	120.2
O1—C11—C10	105.55 (13)	C1—C19—H19	120.2

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

*Cg*1 and *Cg*2 are the centroids of the C6—C9/C16/C17 and C1—C4/C18/C19 rings, respectively.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C2—H2 \cdots <i>Cg</i> 1 ⁱ	0.93	2.80	3.582 (2)	142
C11—H11 <i>B</i> \cdots <i>Cg</i> 2 ⁱⁱ	0.97	2.74	3.675 (2)	163

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1/2, y+1/2, z$.