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3,12-Dimethoxy-5,6,9,10-tetrahydro-[5]-helicene-7,8-dicarbonitrile

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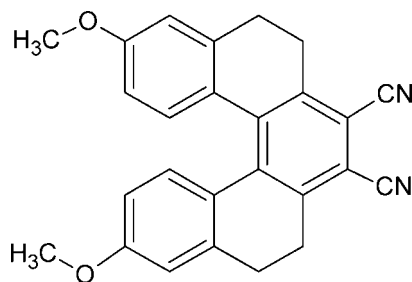
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.042; wR factor = 0.137; data-to-parameter ratio = 16.2.

The complete molecule of the title compound, $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$, is generated by a crystallographic twofold axis. The torsion angle between the terminal and central benzene rings is -32.5 (2)°. The torsion angle along the inner helical rim of the molecule is -18.8 (2)° with each other. The $\text{C}\cdots\text{C}$ distance between the terminal rings is 3.016 (2) Å. In the crystal, weak $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds are observed.

Related literature

For the application of a pentahelicene derivative as an emitter in an organic light-emitting diode, see: Sahasithiwat *et al.* (2010). For related structures, see: McIntosh *et al.* (1954); Wang *et al.* (1997); Stammel *et al.* (1999); Ogawa *et al.* (2003); Rajapakse *et al.* (2011). For the synthesis of the title compound, see: Mandal *et al.* (2006). For general information and applications of helicenes, see: Shen & Chen (2012); Gingras (2013).



Experimental

Crystal data

 $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$ $M_r = 392.44$ Monoclinic, $C2/c$ $a = 17.9533$ (7) Å $b = 13.5533$ (7) Å $c = 8.1417$ (4) Å $\beta = 95.785$ (2)° $V = 1971.00$ (16) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.08$ mm⁻¹
 $T = 296$ K $0.67 \times 0.44 \times 0.26$ mm

Data collection

Bruker APEXII CCD
diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2012)

 $T_{\min} = 0.70$, $T_{\max} = 0.75$

10904 measured reflections

2204 independent reflections

1674 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.042$ $wR(F^2) = 0.137$ $S = 1.07$

2204 reflections

136 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C1}-\text{H1}\cdots\text{N1}^{\text{i}}$	0.93	2.79	3.466 (2)	131
$\text{C4}-\text{H4}\cdots\text{N1}^{\text{ii}}$	0.93	2.86	3.742 (2)	160

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT; program(s) used to solve structure: SHELXS2013 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: WinGX (Farrugia, 2012) and publCIF (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: NR2052).

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supporting information

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3,12-Dimethoxy-5,6,9,10-tetrahydro-[5]helicene-7,8-dicarbonitrile

Somboon Sahasithiwat, Thanasat Sooksimuang, Siriporn Kamtonwong, Waraporn Parnchan and Laongdao Kangkaew

S1. Comment

Helicenes are polycyclic aromatic hydrocarbons (PAHs) that consist of ortho-fused aromatic rings arranged in helical chirality. Applications of helicenes are ranging from catalyst to molecular machines. (Shen *et al.*, 2012; Gingras, 2013). The title compound is a derivative of pentahelicene in which two electron donor and two electron acceptor groups are added into the structure in order to improve its fluorescence quantum yield. Moreover, two rings connected to the central benzene ring are not fully aromatized and in a twist conformation. An application of a similar compound as an emitter for a light-emitting diode was reported (Sahasithiwat *et al.*, 2010).

The geometric parameters of the title molecule agree well with reported similar structures (McIntosh *et al.*, 1954; Wang *et al.*, 1997; Stammel *et al.*, 1999; Rajapakse *et al.*, 2011). Half a molecule of the title compound belongs to asymmetric unit and a molecule is completed by the crystallographic twofold axis as shown in Figure 1. The dihedral angles [C1—C8—C10—C10ⁱ and C1ⁱ—C8ⁱ—C10ⁱ—C10] between a terminal and a central benzene ring are -32.5 (2)°. The two non-fully aromatized rings make a dihedral angle [C8—C10—C10ⁱ—C8ⁱ] of -18.8 (2)° with each other. The distance of the terminal rings as defined by C1...C1ⁱ distance of 3.016 (2)Å is causing by steric repulsion of hydrogens on these carbons.

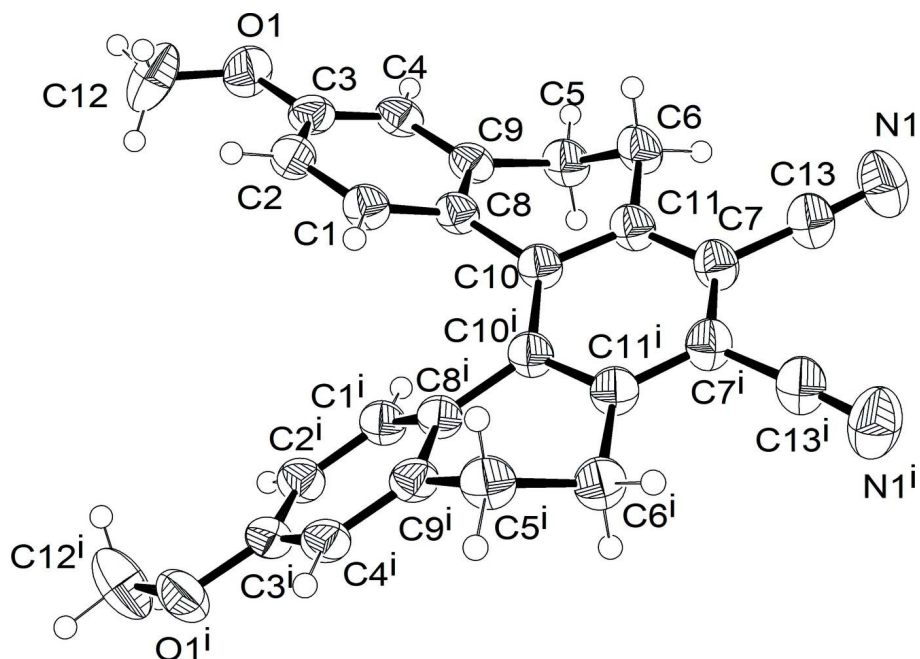
The crystal packing as shown in Figure 2 reveals that the molecules are linked through a network of weak C—H...N [C1—H1...N1(-x,-y,-z)] intermolecular interaction yielding racemic columns. Moreover, the other weak C—H...N [C4—H4...N1(-x+1/2,y,-z+1/2)] intermolecular interactions resulted in holding the columns together as exhibited in Figure 3.

S2. Experimental

A mixture of 6,6'-dimethoxy-3,4,3',4'-tetrahydro[1,1']binaphthalenyl (9.761 g, 30.7 mmol) and fumaronitrile (3.594 g, 46.0 mmol) was stirred and heated at 110 °C under argon atmosphere for 12 h. The resulting mixture was purified by column chromatography (SiO₂, 7734, 3:2 CH₂Cl₂-hexane, 1.8 L) to give a yellow foam of pure Diels-Alder adduct (6.673 g, 55% yield, mp. 139-141 °C). The Diels-Alder product (6.535 g, 16.6 mmol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (8.280 g, 36.5 mmol) and xylene (120 ml) was stirred and refluxed for 6 h. The mixture was cooled to room temperature and filtered off. Filtrate was evaporated to give crude product which was purified by column chromatography (SiO₂, 7734, toluene, 1.2 L) to give a yellow solid product (3.934 g, 61% yield, mp. 263-264 °C). This compound was characterized by FTIR, ¹H-NMR, and ¹³C-NMR. Crystals of the title compound suitable for X-ray analysis was obtained by slow evaporation of a chloroform-hexane solution.

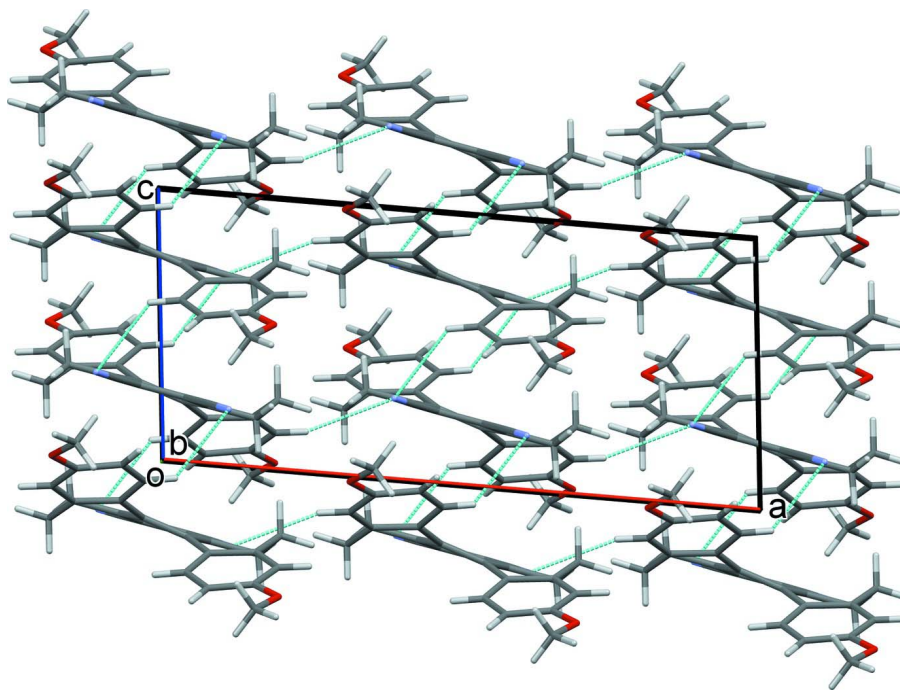
S2.1. Refinement

All hydrogen atoms were placed in calculated positions and treated as riding atoms with C—H distances of 0.93 Å, 0.97 Å, and 0.96 Å for aryl, methylene, and methyl H atoms, respectively. The H atoms were assigned U_{iso} = 1.2 U_{eq}(C) for aryl H, U_{iso} = 1.2 U_{eq}(C) for methylene H, and U_{iso} = 1.5 U_{eq}(C) for methyl H.

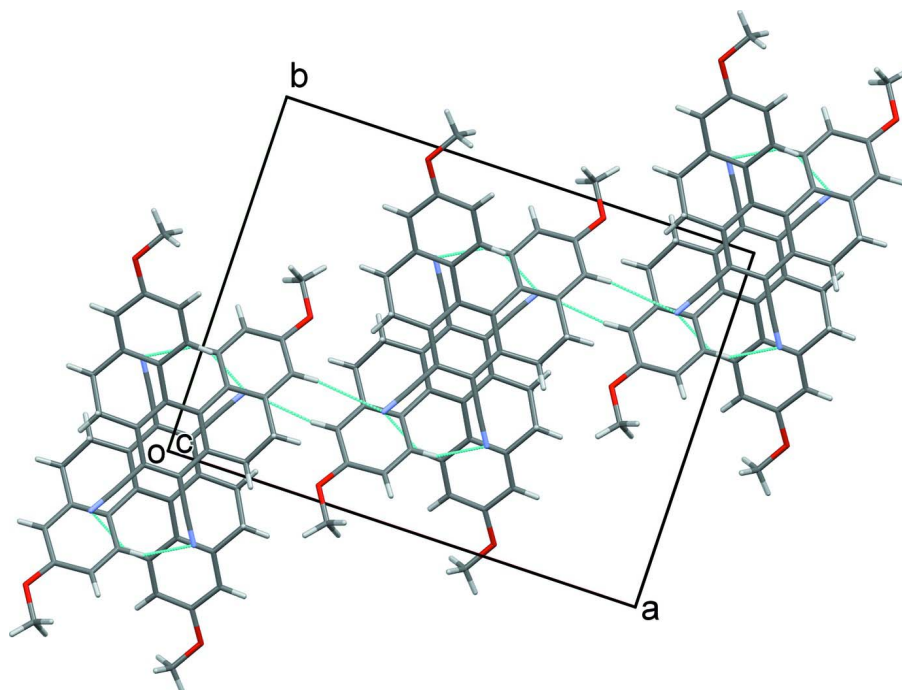
**Figure 1**

The molecular structure of the title compound showing 50% probability displacement ellipsoids for non-H atoms.

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

**Figure 2**

Packing diagram of the title compound projected down the b axis showing hydrogen bonds as dashed lines.

**Figure 3**

Packing diagram of the title compound projected down the *c* axis showing hydrogen bonds as dashed lines.

3,12-Dimethoxy-5,6,9,10-tetrahydro-[5]helicene-7,8-dicarbonitrile

Crystal data

$C_{26}H_{20}N_2O_2$
 $M_r = 392.44$
 Monoclinic, $C2/c$
 $a = 17.9533 (7) \text{ \AA}$
 $b = 13.5533 (7) \text{ \AA}$
 $c = 8.1417 (4) \text{ \AA}$
 $\beta = 95.785 (2)^\circ$
 $V = 1971.00 (16) \text{ \AA}^3$
 $Z = 4$

$F(000) = 824$
 $D_x = 1.322 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 3787 reflections
 $\theta = 2.3\text{--}27.1^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Block, green
 $0.67 \times 0.44 \times 0.26 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: sealed tube
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2012)
 $T_{\min} = 0.70$, $T_{\max} = 0.75$
 10904 measured reflections

2204 independent reflections
 1674 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 27.3^\circ$, $\theta_{\min} = 2.3^\circ$
 $h = -23 \rightarrow 21$
 $k = -17 \rightarrow 17$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.137$
 $S = 1.07$

2204 reflections
 136 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 0.772P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C4	0.18794 (7)	0.30146 (11)	0.13412 (18)	0.0409 (3)
H4	0.2399	0.3047	0.1479	0.049*
C10	0.03622 (7)	0.12362 (10)	0.22237 (18)	0.0374 (3)
C2	0.06956 (8)	0.37374 (11)	0.03575 (19)	0.0419 (4)
H2	0.0421	0.4247	-0.0174	0.050*
C8	0.07336 (7)	0.21339 (10)	0.16691 (17)	0.0370 (3)
O1	0.18785 (6)	0.46083 (8)	0.02479 (16)	0.0572 (3)
C9	0.15209 (7)	0.21797 (10)	0.18425 (17)	0.0382 (3)
C1	0.03382 (7)	0.29099 (10)	0.08781 (18)	0.0399 (3)
H1	-0.0181	0.2870	0.0695	0.048*
C6	0.15632 (8)	0.03662 (11)	0.1795 (2)	0.0465 (4)
H6A	0.1598	0.0358	0.0613	0.056*
H6B	0.1819	-0.0213	0.2269	0.056*
C7	0.03793 (8)	-0.05492 (10)	0.23454 (19)	0.0416 (4)
C3	0.14727 (8)	0.38012 (10)	0.06373 (18)	0.0416 (4)
C11	0.07496 (7)	0.03379 (10)	0.21240 (19)	0.0401 (3)
C5	0.19390 (7)	0.12912 (11)	0.2542 (2)	0.0465 (4)
H5A	0.1937	0.1280	0.3733	0.056*
H5B	0.2455	0.1318	0.2287	0.056*
C13	0.07734 (8)	-0.14666 (11)	0.2179 (2)	0.0476 (4)
N1	0.11026 (8)	-0.21725 (10)	0.2016 (2)	0.0659 (5)
C12	0.14758 (12)	0.54725 (14)	-0.0283 (3)	0.0749 (6)
H12A	0.1822	0.5981	-0.0518	0.112*
H12B	0.1184	0.5692	0.0572	0.112*
H12C	0.1150	0.5328	-0.1262	0.112*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C4	0.0256 (6)	0.0491 (8)	0.0494 (8)	-0.0029 (6)	0.0100 (6)	-0.0070 (6)
C10	0.0260 (6)	0.0394 (7)	0.0466 (8)	-0.0002 (5)	0.0033 (5)	-0.0005 (6)
C2	0.0353 (7)	0.0443 (8)	0.0465 (8)	0.0021 (6)	0.0060 (6)	0.0025 (6)
C8	0.0259 (6)	0.0396 (7)	0.0460 (8)	0.0002 (5)	0.0068 (5)	-0.0018 (6)
O1	0.0440 (6)	0.0520 (7)	0.0778 (8)	-0.0107 (5)	0.0166 (6)	0.0084 (6)
C9	0.0268 (6)	0.0440 (8)	0.0446 (8)	0.0016 (5)	0.0068 (5)	-0.0044 (6)
C1	0.0266 (6)	0.0443 (7)	0.0489 (8)	0.0001 (6)	0.0043 (6)	-0.0007 (6)

C6	0.0294 (7)	0.0446 (8)	0.0664 (10)	0.0074 (6)	0.0086 (7)	-0.0007 (7)
C7	0.0345 (7)	0.0388 (7)	0.0507 (9)	0.0031 (6)	-0.0002 (6)	-0.0011 (6)
C3	0.0370 (7)	0.0448 (8)	0.0447 (8)	-0.0063 (6)	0.0128 (6)	-0.0021 (6)
C11	0.0284 (7)	0.0420 (8)	0.0497 (8)	0.0032 (5)	0.0028 (6)	-0.0007 (6)
C5	0.0251 (6)	0.0520 (9)	0.0623 (10)	0.0043 (6)	0.0043 (6)	0.0005 (7)
C13	0.0370 (8)	0.0427 (8)	0.0618 (10)	0.0005 (6)	-0.0008 (7)	-0.0022 (7)
N1	0.0529 (9)	0.0487 (8)	0.0946 (12)	0.0102 (7)	-0.0004 (8)	-0.0082 (8)
C12	0.0666 (12)	0.0661 (12)	0.0881 (15)	-0.0194 (9)	-0.0103 (10)	0.0366 (11)

Geometric parameters (Å, °)

C4—C3	1.383 (2)	C1—H1	0.9300
C4—C9	1.3836 (19)	C6—C11	1.5120 (19)
C4—H4	0.9300	C6—C5	1.521 (2)
C10—C11	1.4085 (18)	C6—H6A	0.9700
C10—C10 ⁱ	1.418 (3)	C6—H6B	0.9700
C10—C8	1.4796 (19)	C7—C11	1.3943 (19)
C2—C1	1.3798 (19)	C7—C7 ⁱ	1.410 (3)
C2—C3	1.393 (2)	C7—C13	1.444 (2)
C2—H2	0.9300	C5—H5A	0.9700
C8—C1	1.3903 (19)	C5—H5B	0.9700
C8—C9	1.4076 (18)	C13—N1	1.1392 (19)
O1—C3	1.3692 (17)	C12—H12A	0.9600
O1—C12	1.421 (2)	C12—H12B	0.9600
C9—C5	1.5005 (19)	C12—H12C	0.9600
C3—C4—C9	120.71 (12)	H6A—C6—H6B	108.1
C3—C4—H4	119.6	C11—C7—C7 ⁱ	120.32 (8)
C9—C4—H4	119.6	C11—C7—C13	119.08 (13)
C11—C10—C10 ⁱ	119.48 (8)	C7 ⁱ —C7—C13	120.54 (8)
C11—C10—C8	116.93 (12)	O1—C3—C4	116.15 (12)
C10 ⁱ —C10—C8	123.54 (7)	O1—C3—C2	123.99 (14)
C1—C2—C3	119.29 (13)	C4—C3—C2	119.85 (13)
C1—C2—H2	120.4	C7—C11—C10	119.56 (12)
C3—C2—H2	120.4	C7—C11—C6	121.77 (12)
C1—C8—C9	118.28 (12)	C10—C11—C6	118.67 (12)
C1—C8—C10	122.59 (12)	C9—C5—C6	108.96 (12)
C9—C8—C10	118.98 (12)	C9—C5—H5A	109.9
C3—O1—C12	117.57 (12)	C6—C5—H5A	109.9
C4—C9—C8	119.92 (13)	C9—C5—H5B	109.9
C4—C9—C5	122.58 (12)	C6—C5—H5B	109.9
C8—C9—C5	117.49 (12)	H5A—C5—H5B	108.3
C2—C1—C8	121.71 (13)	N1—C13—C7	177.50 (18)
C2—C1—H1	119.1	O1—C12—H12A	109.5
C8—C1—H1	119.1	O1—C12—H12B	109.5
C11—C6—C5	110.32 (12)	H12A—C12—H12B	109.5
C11—C6—H6A	109.6	O1—C12—H12C	109.5
C5—C6—H6A	109.6	H12A—C12—H12C	109.5

C11—C6—H6B	109.6	H12B—C12—H12C	109.5
C5—C6—H6B	109.6		
C11—C10—C8—C1	145.00 (15)	C9—C4—C3—C2	-3.0 (2)
C10 ⁱ —C10—C8—C1	-32.5 (3)	C1—C2—C3—O1	-176.54 (14)
C11—C10—C8—C9	-30.49 (19)	C1—C2—C3—C4	3.8 (2)
C10 ⁱ —C10—C8—C9	152.05 (18)	C7 ⁱ —C7—C11—C10	0.5 (3)
C3—C4—C9—C8	-1.3 (2)	C13—C7—C11—C10	177.68 (15)
C3—C4—C9—C5	177.21 (14)	C7 ⁱ —C7—C11—C6	179.84 (17)
C1—C8—C9—C4	4.7 (2)	C13—C7—C11—C6	-3.0 (2)
C10—C8—C9—C4	-179.60 (13)	C10 ⁱ —C10—C11—C7	8.9 (3)
C1—C8—C9—C5	-173.89 (13)	C8—C10—C11—C7	-168.68 (14)
C10—C8—C9—C5	1.79 (19)	C10 ⁱ —C10—C11—C6	-170.49 (16)
C3—C2—C1—C8	-0.3 (2)	C8—C10—C11—C6	11.9 (2)
C9—C8—C1—C2	-3.9 (2)	C5—C6—C11—C7	-147.72 (15)
C10—C8—C1—C2	-179.43 (13)	C5—C6—C11—C10	31.6 (2)
C12—O1—C3—C4	-172.31 (16)	C4—C9—C5—C6	-136.89 (14)
C12—O1—C3—C2	8.0 (2)	C8—C9—C5—C6	41.68 (18)
C9—C4—C3—O1	177.34 (13)	C11—C6—C5—C9	-57.20 (17)

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

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

<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>
C1—H1 \cdots N1 ⁱⁱ	0.93	2.79	3.466 (2)	131
C4—H4 \cdots N1 ⁱⁱⁱ	0.93	2.86	3.742 (2)	160

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