Crystal structure and Hirshfeld surface analysis of dimethyl (1R*,3aS*,3a1R*,6aS*,9R*,9aS*)-3a1,5,6,9a-tetrahydro-1H,4H,9H-1,3a:6a,9-di-epoxyphenalene-2,3-dicarboxylate

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The title diepoxyphenalene derivative, C_{17}H_{18}O_{6}, comprises a fused cyclic system containing four five-membered rings (two dihydrofuran and two tetrahydrofuran) and one six-membered ring (cyclohexane). The five-membered dihydrofuran and tetrahydrofuran rings adopt envelope conformations, and the six-membered cyclohexane ring adopts a distorted chair conformation. Two methyl carboxylate groups occupy adjacent positions (2- and 3-) on a tetrahydrofuran ring. In the crystal, two pairs of C–H···O hydrogen bonds link the molecules to form inversion dimers, enclosing two R_{2}^{2}(6) ring motifs, that stack along the a-axis direction and are arranged in layers parallel to the bc plane.

1. Chemical context

Reactions totally depending on thermodynamic and kinetic control are infrequently found in the field of organic synthesis, at the same time such transformations are very perspective and attractive from a practical point of view since they allow the direction of the reaction to be changed radically by varying only one of the reaction parameters (usually the catalyst or temperature).

The first example of kinetic/thermodynamic control in the course of the Diels–Alder reaction was reported in 1948 (Woodward & Baer, 1948). Since then, the reversibility of the [4 + 2] cycloaddition was observed many times for examples of a broad range of dienes and dienophiles, including alkynes and furans (Boutelle & Northrop, 2011; Taffin et al., 2010; White et al., 2000; Marchand et al., 1998; Manoharan & Venuvannalingam, 1997; Bott et al., 1996; Bartlett & Wu, 1985). From this diversity of diene/dienophile combinations, tandem and domino reactions of the [4 + 2] cycloaddition based on acetylenic dienophiles are more interesting for the total synthesis of natural or bioactive products (Sears & Boger, 2016; Parvatkar et al., 2014; Winkler, 1996). However, the range of bis-dienes suitable for such tandem transformations is very limited and, currently, there are only a few published examples of full kinetic/thermodynamic control in the course of the tandem intramolecular [4 + 2] cycloaddition (reactions leading to either kinetically or thermodynamically controlled products, depending on temperature; Marchionni et al., 1996; Oh et al., 2010; Criado et al., 2010; Paquette et al., 1978; Visnick & Battiste, 1985).
The present paper describes the uncommon thermal rearrangement of the ‘pincer-adduct’ (1) into the ‘domino-adduct’ (2) [the terminology and the mechanism of the reaction are given in references Borisova, Nikitina et al. (2018) and Borisova, Kvyatkovskaya et al. (2018); for references of works related to the present paper, see also Lautens & Fillion (1998), Lautens & Fillion (1997) and Domingo et al. (2000)]. The transformation proceeds through the reversible retro-Diels–Alder reaction of the kinetically controlled ‘pincer-adduct’ (1), followed by the repeated intramolecular \([4 + 2]\) cycloaddition in an intermediate, leading to the formation of the thermodynamically controlled ‘domino-adduct’ (2) in an almost quantitative yield.

2. Structural commentary

The molecular structure of compound (2) is illustrated in Fig. 1. It is made up from a fused cyclic system containing four five-membered rings (two dihydrofuran and two tetrahydrofuran) in the usual envelope conformations and a six-membered cyclohexane ring in a distorted chair conformation. The puckering parameters of the five-membered dihydrofuran (A = O1/C1/C2/C5/C6 and B = O2/C1/C6/C7/C10) and tetrahydrofuran (C = O1/C2–C5 and D = O2/C7–C10) rings are \(Q(2) = 0.5230(18)\) Å and \(\theta(2) = 178.1(2)\)° for ring A, \(Q(2) = 0.5492(17)\) Å and \(\theta(2) = 182.3(2)\)° for B, \(Q(2) = 0.5230(18)\) Å and \(\theta(2) = 358.9(2)\)° for C, and \(Q(2) = 0.5303(17)\) Å and \(\phi(2) = 178.2(18)\)° for D. The puckering parameters of the six-membered cyclohexane ring (C1/C2/C10–C13) are \(Q_T = 0.518(2)\) Å, \(\theta = 6.9(2)\)° and \(\phi = 178.2(18)\)°. In positions 2- and 3-, i.e. on atoms C8 and C9 (Fig. 1), there are methyl carboxylate substituents whose mean planes are inclined to the mean plane through atoms C7–C10 by 7.38(13) and in the usual envelope conformations and a six-membered cyclohexane ring in a distorted chair conformation. The puckering parameters of the five-membered dihydrofuran (A = O1/C1/C2/C5/C6 and B = O2/C1/C6/C7/C10) and tetrahydrofuran (C = O1/C2–C5 and D = O2/C7–C10) rings are \(Q(2) = 0.5230(18)\) Å and \(\phi(2) = 178.1(2)\)° for ring A, \(Q(2) = 0.5492(17)\) Å and \(\theta(2) = 182.3(2)\)° for B, \(Q(2) = 0.5230(18)\) Å and \(\phi(2) = 358.9(2)\)° for C, and \(Q(2) = 0.5303(17)\) Å and \(\phi(2) = 178.2(18)\)°. In positions 2- and 3-, i.e. on atoms C8 and C9 (Fig. 1), there are methyl carboxylate substituents whose mean planes are inclined to the mean plane through atoms C7–C10 by 7.38(13) and

### Table 1

| Contact | Distance | Symmetry operation |
|---------|----------|--------------------|
| C5—H5—O2 | 1.00 | 2.58 | 3.330 (2) | 132 |
| C7—H7—O1 | 1.00 | 2.52 | 3.351 (2) | 140 |

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

### Table 2

Summary of short interatomic contacts (Å) in the crystal of compound (2).

| Contact | Distance | Symmetry operation |
|---------|----------|--------------------|
| H7···O1 | 2.52 | \(1 - x, 1 - y, 1 - z\) |
| H13B···H17B | 2.49 | \(x, -\frac{1}{2} - y, \frac{1}{2} + z\) |
| H15C···H12A | 2.53 | \(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z\) |
| H15A···H3 | 2.56 | \(-x, 1 - y, 1 - z\) |
| H6···H15B | 2.57 | \(x, \frac{1}{2} - y, -\frac{1}{2} + z\) |
| H17A···O5 | 2.90 | \(-x, 1 - y, 2 - z\) |
| H15B···H6 | 2.57 | \(x, \frac{1}{2} - y, \frac{1}{2} + z\) |
| H5···H17C | 2.48 | \(x, y, -1 + z\) |

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**Figure 1**

The molecular structure of compound (2), with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

**Figure 2**

A viewed along the \(b\) axis of the crystal packing of compound (2), emphasizing the formation of C—H···O hydrogen-bonded dimers. Hydrogen bonds are shown as dashed lines (Table 1).
70.65 (14)° for groups O3/O4/C14/C15 and O5/O6/C16/C17, respectively.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, two pairs of C—H···O hydrogen bonds link the molecules forming inversion dimers, enclosing two $R_2^2(6)$ ring motifs. The dimers stack along the $a$-axis direction and are arranged in layers parallel to the $bc$ plane (Table 1 and Fig. 2). C—H···π and π···π interactions are not observed, but H···H contacts (Tables 2 and 3) dominate in the packing, as detailed in the next section.

4. Hirshfeld surface analysis and two-dimensional fingerprint plots

Hirshfeld surface and fingerprint plots were generated using CrystalExplorer (McKinnon et al., 2007). Hirshfeld surfaces enable the visualization of intermolecular interactions by different colours and colour intensity, representing short or long contacts and indicating the relative strength of the interactions. Fig. 3 shows the Hirshfeld surface of the title compound mapped over $d_{norm}$, where it is evident from the bright-red spots appearing near the O atoms that these atoms play a significant role in the molecular packing. The red spots represent closer contacts and negative $d_{norm}$ values on the surface, corresponding to the C—H···O interactions.

The bright-red spots indicate their roles as the respective donors and/or acceptors; they also appear as blue and red regions corresponding to positive and negative potentials on the Hirshfeld surface mapped over electrostatic potential (Fig. 4; Spackman et al., 2008; Jayatilaka et al., 2005). The blue regions indicate the positive electrostatic potential (hydrogen-bond donors), while the red regions indicate the negative electrostatic potential (hydrogen-bond acceptors). The shape index of the Hirshfeld surface is a tool to visualize the π···π stacking by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue triangles, then there are no π···π interactions. Fig. 5 clearly suggest that no π···π interactions are present in the title compound.

The percentage contributions of various contacts to the total Hirshfeld surface are given in Table 3 and are also shown as two-dimensional (2D) fingerprint plots in Fig. 6. The H···H interactions appear in the middle of the scattered points in the 2D fingerprint plots with an overall contribution to the

| Contact             | Percentage contribution |
|---------------------|-------------------------|
| H···H               | 54.6                    |
| O···H/H···O         | 36.2                    |
| C···H/H···C         | 8.0                     |
| O···O               | 1.1                     |

Table 3
Percentage contributions of interatomic contacts to the Hirshfeld surface of compound (2).

Figure 3
Hirshfeld surface of compound (2) mapped over $d_{norm}$.

Figure 4
View of the three-dimensional Hirshfeld surface of compound (2) plotted over electrostatic potential energy in the range $-0.0500$ to $0.0500$ a.u. using the STO-3 G basis set at the Hartree–Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions around the atoms corresponding to positive and negative potentials, respectively.

Figure 5
Hirshfeld surface of compound (2) plotted over shape index.
Hirshfeld surface of 54.6% (Fig. 6b). The contribution from the O···H/H···O contacts, corresponding to C—H···O interactions, is represented by a pair of sharp spikes characteristic of a strong hydrogen-bonding interaction (36.2%, Fig. 6c and Tables 2 and 3). The small percentage contributions from the remaining interatomic contacts are summarized in Table 3 and indicated by their fingerprint plots for C···H/H···C (Fig. 6d) and O···O (Fig. 6e). The large number of H···H and O···H/H···O interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar et al., 2015).

Table 4
Experimental details.

| Crystal data       | C17H18O6        |
|--------------------|-----------------|
| Chemical formula   |                 |
| M_r                | 318.31          |
| Crystal system, space group | Monoclinic, P2_1/c |
| Temperature (K)    | 100             |
| a, b, c (Å)        | 9.3903 (19), 14.157 (3), 11.520 (2) |
| β (°)              | 99.032 (3)      |
| V (Å³)             | 1512.5 (5)      |
| Z                  | 4               |
| Radiation type     | Synchrotron, λ = 0.96990 Å |
| µ (mm⁻¹)           | 0.23            |
| Crystal size (mm)  | 0.35 × 0.15 × 0.10 |

Data collection

| Diffractometer      | MAR CCD       |
|---------------------|---------------|
| Absorption correction | Multi-scan (SCALA; Evans, 2006) |
| T_min, T_max        | 0.918, 0.975  |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 17699, 3216, 2464 |
| R_int, (sin θ/λ)max (Å⁻¹) | 0.151, 0.641 |

Refinement

| R[F² > 2σ(F²)], wR(F²), S  | 0.067, 0.192, 1.11 |
| No. of reflections         | 3216             |
| No. of parameters          | 211              |
| H-atom treatment           | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³)       | 0.50, -0.41      |

Computer programs: Automoar (Doyle, 2011), Mosflm (Battye et al., 2011), SHELX97 (Sheldrick, 2008), SHELXL2018 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009).

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, February 2019; Groom et al., 2016) for the di-epoxyphenalen skeleton gave only 2 hits, viz. 9b-acetyl-9a-methoxybenzoyl-1,3a:6a:9-diepoxy-4,5,6,9-tetrahydrophenalen (CSD refcode RUSGOD; Lautens & Fillion, 1997) and 9a-benzensulfonyl-1,3a:6a:9-diepoxy-9b-methoxybenzoyl-4,5,6,9-tetrahydrophenalen (RUSHAO; Lautens & Fillion, 1997). A search for the di-epoxybenzo[de]isoquinoline skeleton gave 8 hits, three of which are very similar to compounds (1) and (2), viz. 2-benzyl-6a,9-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,7,9a-diepoxybenzo[de]isoquinoline (CSD refcode HENLAQ; Borisova, Nikitina et al., 2018), 2-benzyl-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6,7,9a-diepoxybenzo[de]isoquinoline (HENLEU; Borisova, Nikitina et al., 2018) and dimethyl (3aS,6R,6aS,7S)-2-(2,2,2-trifluoroacetyl)-2,3-dihydro-1H,6H,7H-3a,6,7,9a-diepoxybenzo[de]isoquinoline-3a,6a-dicarboxylate (LIRKAB; Atioglu et al., 2018).

In the crystal of HENLAQ, inversion-related molecules are linked by dimers by pairs of C—H···O hydrogen bonds, and the dimers lie in layers parallel to (100). C—H···π interactions are also observed, together with intramolecular F···F contacts. The asymmetric unit of HENLEU contains two independent molecules. In the crystal, molecules are linked by C—H···O and C—H···F hydrogen bonds, forming columns along [010]. Likewise, C—H···π interactions and F···F intramolecular contacts are also present. In the crystal structure of LIRKAB, intermolecular C···O interactions...
involving the O atoms of the carbonyl groups, the oxygen bridgehead atoms and the methoxy O atoms, as well as C—H···F hydrogen bonds, define the crystal packing. These packing features lead to the formation of a supramolecular three-dimensional structure. C—H···π and π···π interactions are not observed, but H···π interactions dominate in the packing. This situation is similar to that in the crystal of the title compound.

6. Synthesis and crystallization

The synthesis of the title compound (2) is illustrated in the Scheme. Compound (I) (0.89 g, 2.81 mmol) was dissolved in dry α-Me2C6H4 (15 ml) and then heated under reflux for 4 h at ~413 K (thin-layer chromatography monitoring). The reaction mixture was cooled and the solvent removed under reduced pressure. The residue was purified by recrystallization from an EtOAc/hexane mixture (1:1 v/v) to give compound (2) as large colourless prismatic crystals [0.82 g, 2.61 mmol, 93%; m.p. 410.4–411.8 K (hexane/EtOAc)].1H NMR (400 MHz, CDCl3) δ 6.43 (1H, dd, J = 1.8 and 5.6 Hz, H-8), 6.27 (1H, d, J = 5.6 Hz, H-9), 5.09 (1H, s, H-1), 4.88 (1H, d, J = 1.8 Hz, H-9), 3.78 (3H, s, CO2Me), 3.73 (3H, s, CO2Me), 2.22–2.17 (3H, m, H-4A, H-6A and H-9a), 2.00–1.88 (4H, m, H-4B, H-6B, H-5A and H-9b) 1.71–1.68 (1H, m, H-5B).13C NMR (100 MHz, CDCl3): δ 164.7 (CO2Me), 162.6 (CO2Me), 150.6 (C-3), 143.8 (C-2), 140.8 (C-7), 138.5 (C-8), 89.3 (C-3a), 85.8 (C-6a), 81.3 (C-1), 80.5 (C-9), 52.2 (C-9a), 52.0 (2 × CO2Me), 49.8 (C-9b), 26.7 (C-9), 25.0 (C-6), 17.2 (C-5). IR νmax/cm⁻¹ (KBr): 1709, 1628, 1284, 1261. HRMS (ESI−TOF): calculated for C17H18O6 [M + H]+ 318.1103; found 318.1125.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were fixed and allowed to ride on the parent atoms, with C—H = 0.95–1.00 Å, and with Uiso(H) = 1.5Ueq(C) for methyl H atoms and 1.2Ueq(C) for other H atoms.

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Crystal structure and Hirshfeld surface analysis of dimethyl (1$R_*$,3a$S_*$,3a$^1R_*$,6a$S_*$,9$R_*$,9a$S_*$)-3a$^1$,5,6,9a-tetrahydro-1$H$,4$H$,9$H$-1,3a:6a,9-di-epoxyphenalene-2,3-dicarboxylate

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Computing details

Data collection: Automar; cell refinement: iMosflm; data reduction: iMosflm; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2009).

Dimethyl (1$R_*$,3a$S_*$,6a$S_*$,9$R_*$,9a$S_*$,9b$R_*$)-5,6,9a,9b-tetrahydro-1$H$,4$H$,9$H$-1,3a:6a,9-diepoxyphenalene-2,3-dicarboxylate

Crystal data

C$_{17}$H$_{18}$O$_6$

$M_r =$ 318.31

Monoclinic, $P2_1/c$

$a =$ 9.3903 (19) Å

$b =$ 14.157 (3) Å

$c =$ 11.520 (2) Å

$\beta =$ 99.032 (3)$^\circ$

$V =$ 1512.5 (5) Å$^3$

$Z =$ 4

$F(000) =$ 672

$D_x =$ 1.398 Mg m$^{-3}$

Synchrotron radiation, $\lambda =$ 0.96990 Å

Cell parameters from 500 reflections

$\theta =$ 3.5–35.0$^\circ$

$\mu =$ 0.23 mm$^{-1}$

$T =$ 100 K

Prism, colourless

0.35 × 0.15 × 0.10 mm

Data collection

MAR CCD diffractometer

$\theta$ scan

Absorption correction: multi-scan

$\theta_{\text{max}} =$ 38.5$^\circ$, $\theta_{\text{min}} =$ 3.6$^\circ$

$R_{\text{int}} =$ 0.151

$T =$ 0.918, $T_{\text{max}} =$ 0.975

2464 reflections with $I > 2\sigma(I)$

17699 measured reflections

3216 independent reflections

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] =$ 0.067

$wR(F^2) =$ 0.192

$S =$ 1.11

3216 reflections

211 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_c^2) + (0.0746P)^2]$

where $P = (F_c^2 + 2F_s^2)/3$

$(\Delta/\sigma)_{\text{max}} <$ 0.001
$\Delta \rho_{\text{max}} = 0.50 \text{ e Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.40 \text{ e Å}^{-3}$

**Extinction correction:** SHELXL2018 (Sheldrick, 2015), $\text{Fc}^* = \text{kFc}[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$

**Extinction coefficient:** 0.038 (4)

**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 ($\text{Å}^2$)**

|     | $x$   | $y$   | $z$   | $U_{\text{iso}}$/$U_{\text{eq}}$ |
|-----|-------|-------|-------|-------------------------------|
| C1  | 0.20277 (19) | 0.59385 (13) | 0.59498 (15) | 0.0155 (5) |
| H1  | 0.106665 | 0.591973 | 0.621979 | 0.019* |
| C2  | 0.21999 (18) | 0.67977 (14) | 0.51388 (16) | 0.0177 (5) |
| C3  | 0.0861 (2) | 0.67729 (14) | 0.41833 (16) | 0.0195 (5) |
| H3  | 0.006228 | 0.719276 | 0.409799 | 0.023* |
| C4  | 0.1054 (2) | 0.60374 (14) | 0.34962 (16) | 0.0214 (5) |
| H4  | 0.041452 | 0.582144 | 0.282721 | 0.026* |
| C5  | 0.25131 (19) | 0.56171 (14) | 0.40095 (15) | 0.0173 (5) |
| H5  | 0.299224 | 0.523974 | 0.344653 | 0.021* |
| C6  | 0.22826 (19) | 0.50832 (14) | 0.51569 (15) | 0.0163 (5) |
| H6  | 0.144221 | 0.464107 | 0.502585 | 0.020* |
| C7  | 0.36433 (19) | 0.46304 (13) | 0.58988 (15) | 0.0157 (5) |
| H7  | 0.419362 | 0.418266 | 0.546483 | 0.019* |
| C8  | 0.31304 (18) | 0.42263 (13) | 0.69973 (15) | 0.0156 (5) |
| C9  | 0.29437 (19) | 0.49717 (13) | 0.76792 (16) | 0.0160 (5) |
| C10 | 0.33216 (18) | 0.58488 (13) | 0.69840 (15) | 0.0141 (5) |
| C11 | 0.3755 (2) | 0.67670 (13) | 0.76102 (16) | 0.0194 (5) |
| H11A| 0.465992 | 0.667147 | 0.816594 | 0.023* |
| H11B| 0.299650 | 0.695990 | 0.806996 | 0.023* |
| C12 | 0.3976 (2) | 0.75571 (15) | 0.67394 (17) | 0.0198 (5) |
| H12A| 0.481612 | 0.739906 | 0.635317 | 0.024* |
| H12B| 0.419398 | 0.815491 | 0.717708 | 0.024* |
| C13 | 0.2644 (2) | 0.77010 (14) | 0.57926 (17) | 0.0202 (5) |
| H13A| 0.183317 | 0.793440 | 0.616846 | 0.024* |
| H13B| 0.286127 | 0.818677 | 0.522740 | 0.024* |
| C14 | 0.27146 (19) | 0.32255 (14) | 0.71005 (16) | 0.0159 (5) |
| C15 | 0.1868 (2) | 0.20708 (15) | 0.83169 (18) | 0.0268 (5) |
| H15A| 0.104113 | 0.188440 | 0.773336 | 0.040* |
| H15B| 0.162026 | 0.200255 | 0.910798 | 0.040* |
| H15C| 0.269400 | 0.166559 | 0.823982 | 0.040* |
| C16 | 0.22323 (19) | 0.50325 (14) | 0.87480 (16) | 0.0163 (5) |
| C17 | 0.2451 (3) | 0.46966 (17) | 1.07828 (17) | 0.0322 (6) |
| H17A| 0.179303 | 0.415658 | 1.075185 | 0.048* |
| H17B| 0.191531 | 0.528174 | 1.085776 | 0.048* |
| H17C| 0.321654 | 0.463002 | 1.146134 | 0.048* |
supporting information

O1  0.32913 (13)  0.64562 (9)  0.44759 (10)  0.0165 (4)
O2  0.44470 (13)  0.54506 (9)  0.64055 (10)  0.0160 (4)
O3  0.27815 (14)  0.26386 (10)  0.63425 (11)  0.0211 (4)
O4  0.22345 (14)  0.30455 (10)  0.81243 (11)  0.0216 (4)
O5  0.10290 (15)  0.53573 (11)  0.87145 (11)  0.0287 (4)
O6  0.30886 (14)  0.47284 (10)  0.97057 (11)  0.0231 (4)

| Atomic displacement parameters (Å²) |
|-------------------------------------|
|          | \(U^{11}\)  | \(U^{22}\)  | \(U^{33}\)  | \(U^{12}\)  | \(U^{13}\)  | \(U^{23}\)  |
| C1       | 0.0115 (9)  | 0.0231 (12) | 0.0132 (9)  | 0.0005 (7)  | 0.0054 (7)  | 0.0011 (8)  |
| C2       | 0.0127 (9)  | 0.0273 (12) | 0.0140 (9)  | 0.0018 (8)  | 0.0053 (7)  | 0.0002 (8)  |
| C3       | 0.0177 (10) | 0.0258 (12) | 0.0155 (9)  | 0.0009 (8)  | 0.0043 (7)  | 0.0040 (8)  |
| C4       | 0.0182 (10) | 0.0328 (13) | 0.0131 (9)  | −0.0008 (8) | 0.0028 (7)  | 0.0055 (8)  |
| C5       | 0.0180 (10) | 0.0214 (11) | 0.0133 (9)  | −0.0026 (8) | 0.0051 (7)  | −0.0039 (8) |
| C6       | 0.0135 (9)  | 0.0236 (12) | 0.0129 (9)  | −0.0010 (8) | 0.0054 (7)  | −0.0002 (8) |
| C7       | 0.0148 (9)  | 0.0193 (11) | 0.0140 (9)  | 0.0003 (7)  | 0.0057 (7)  | −0.0032 (8) |
| C8       | 0.0126 (9)  | 0.0216 (12) | 0.0134 (9)  | 0.0003 (8)  | 0.0047 (7)  | 0.0015 (8)  |
| C9       | 0.0129 (9)  | 0.0236 (12) | 0.0120 (9)  | −0.0001 (8) | 0.0037 (7)  | 0.0020 (8)  |
| C10      | 0.0125 (9)  | 0.0199 (11) | 0.0112 (9)  | 0.0025 (7)  | 0.0055 (7)  | −0.0007 (7) |
| C11      | 0.0164 (10) | 0.0270 (12) | 0.0156 (9)  | −0.0019 (8) | 0.0055 (7)  | −0.0015 (8) |
| C12      | 0.0195 (10) | 0.0208 (12) | 0.0197 (10) | −0.0042 (8) | 0.0051 (7)  | −0.0025 (8) |
| C13      | 0.0213 (10) | 0.0221 (12) | 0.0186 (10) | 0.0012 (8)  | 0.0072 (7)  | −0.0008 (8) |
| C14      | 0.0119 (9)  | 0.0220 (12) | 0.0143 (9)  | 0.0026 (7)  | 0.0032 (7)  | 0.0010 (8)  |
| C15      | 0.0328 (12) | 0.0273 (13) | 0.0219 (10) | −0.0056 (10)| 0.0088 (9)  | 0.0049 (9)  |
| C16      | 0.0183 (10) | 0.0167 (11) | 0.0146 (9)  | −0.0027 (7) | 0.0048 (7)  | −0.0013 (7) |
| C17      | 0.0488 (15) | 0.0368 (14) | 0.0141 (10) | 0.0058 (11) | 0.0148 (9)  | 0.0028 (10)|
| O1       | 0.0154 (7)  | 0.0210 (8)  | 0.0148 (7)  | −0.0006 (5) | 0.0070 (5)  | −0.0011 (6) |
| O2       | 0.0128 (7)  | 0.0214 (8)  | 0.0151 (7)  | −0.0006 (5) | 0.0060 (5)  | −0.0033 (5) |
| O3       | 0.0236 (8)  | 0.0228 (9)  | 0.0177 (7)  | 0.0006 (6)  | 0.0057 (6)  | −0.0018 (6) |
| O4       | 0.0282 (8)  | 0.0212 (8)  | 0.0175 (7)  | −0.0017 (6) | 0.0099 (6)  | 0.0028 (6)  |
| O5       | 0.0204 (8)  | 0.0479 (11) | 0.0198 (8)  | 0.0063 (7)  | 0.0094 (6)  | −0.0001 (7) |
| O6       | 0.0283 (8)  | 0.0319 (9)  | 0.0100 (7)  | 0.0043 (6)  | 0.0054 (6)  | 0.0023 (6)  |

Geometric parameters (Å, °)

|          | C1—C2  | C1—C6  | C1—C10 | C1—H1  | C2—O1  | C2—C3  | C3—C4  | C3—H3  | C4—C5  | C4—H4  | C5—O1  |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|          | 1.558 (3) | 1.558 (3) | 1.568 (2) | 1.0000 | 1.454 (2) | 1.536 (3) | 1.337 (3) | 0.9500 | 1.525 (3) | 0.9500 | 1.453 (2) |
|          | 1.449 (2) | 1.511 (2) | 1.538 (3) | 0.9900 | 0.9900  | 0.9900  | 0.9900  | 0.9900  | 0.9900  | 1.214 (2) | 1.351 (2) |

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| Bond                  | Length (Å) | Bond                  | Length (Å) | Bond                  | Length (Å) |
|----------------------|------------|----------------------|------------|----------------------|------------|
| C5—C6                | 1.567 (2)  | C15—O4               | 1.448 (2)  | C15—H15A             | 0.9800     |
| C5—H5                | 1.0000     | C15—H15B             | 0.9800     | C15—H15C             | 0.9800     |
| C6—C7                | 1.559 (3)  | C6—C7                | 1.559 (3)  | C6—C7                | 1.559 (3)  |
| C6—H6                | 1.0000     | C6—H6                | 1.0000     | C6—H6                | 1.0000     |
| C7—O2                | 1.456 (2)  | C7—O2                | 1.456 (2)  | C7—O2                | 1.456 (2)  |
| C7—C8                | 1.534 (2)  | C7—C8                | 1.534 (2)  | C7—C8                | 1.534 (2)  |
| C7—H7                | 1.0000     | C7—H7                | 1.0000     | C7—H7                | 1.0000     |
| C8—C9                | 1.343 (3)  | C8—C9                | 1.343 (3)  | C8—C9                | 1.343 (3)  |
| C8—C14               | 1.479 (3)  | C8—C14               | 1.479 (3)  | C8—C14               | 1.479 (3)  |
| C9—C16               | 1.493 (2)  | C9—C16               | 1.493 (2)  | C9—C16               | 1.493 (2)  |
| C9—C10               | 1.549 (3)  | C9—C10               | 1.549 (3)  | C9—C10               | 1.549 (3)  |

**Bond Angles:**

| Bond                  | Angle (°) | Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|----------------------|-----------|
| C2—C1—C6             | 102.44 (14)| C11—C10—C9          | 120.61 (15)| C11—C10—C9          | 120.61 (15)|
| C2—C1—C10            | 112.21 (14)| C11—C10—C1          | 102.48 (13)| C11—C10—C1          | 102.48 (13)|
| C2—C1—H1             | 102.16 (13)| C9—C10—C1           | 114.30 (14)| C9—C10—C1           | 114.30 (14)|
| C6—C1—H1             | 113.0     | C9—C10—C1           | 104.17 (14)| C9—C10—C1           | 104.17 (14)|
| C10—C1—H1            | 113.0     | C10—C11—C12         | 111.59 (15)| C10—C11—C12         | 111.59 (15)|
| O1—C2—C13            | 112.43 (15)| C10—C11—C11—H11A   | 109.3     | C10—C11—C11—H11A   | 109.3     |
| O1—C2—C3             | 100.43 (13)| C12—C11—C11—H11B   | 109.3     | C12—C11—C11—H11B   | 109.3     |
| O1—C2—C3             | 120.53 (16)| C12—C11—H11B       | 109.3     | C12—C11—H11B       | 109.3     |
| O1—C2—C1             | 101.74 (14)| H11A—C11—C11—H11B  | 109.1     | H11A—C11—C11—H11B  | 109.1     |
| C3—C2—C1             | 114.14 (15)| C11—C12—C12         | 112.36 (15)| C11—C12—C12         | 112.36 (15)|
| C3—C2—C1             | 105.17 (14)| C12—C12—C12—H12A   | 109.1     | C12—C12—C12—H12A   | 109.1     |
| C3—C3—C2             | 105.69 (16)| C13—C12—H12A       | 109.1     | C13—C12—H12A       | 109.1     |
| C3—C3—H3             | 127.2     | C13—C12—H12B       | 109.1     | C13—C12—H12B       | 109.1     |
| C3—C4—C5             | 127.1     | H12A—C12—H12B      | 107.9     | H12A—C12—H12B      | 107.9     |
| C4—C4—H4             | 127.1     | C2—C13—C12         | 111.82 (16)| C2—C13—C12         | 111.82 (16)|
| C5—C5—C4             | 101.15 (15)| C2—C13—H13A       | 109.3     | C2—C13—H13A       | 109.3     |
| C6—C5—C4             | 102.15 (13)| C2—C13—H13B       | 109.3     | C2—C13—H13B       | 109.3     |
| C6—C5—C6             | 106.29 (14)| C12—C13—H13B      | 109.3     | C12—C13—H13B      | 109.3     |
| C6—C6—C7             | 115.2     | H13A—C13—H13B     | 107.9     | H13A—C13—H13B     | 107.9     |
| C6—C6—C7             | 115.2     | O3—C14—O4         | 124.10 (17)| O3—C14—O4         | 124.10 (17)|
| C6—C7—O2             | 115.2     | O3—C14—C8         | 123.61 (16)| O3—C14—C8         | 123.61 (16)|
| C6—C7—C8             | 115.5     | O4—C15—H15A       | 109.5     | O4—C15—H15A       | 109.5     |
| C6—C7—C8             | 115.5     | O4—C15—H15B       | 109.5     | O4—C15—H15B       | 109.5     |
| C6—C7—H7             | 115.5     | H15A—C15—H15B   | 109.5     | H15A—C15—H15B   | 109.5     |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| C9—C8—C14           | 130.17 (16)  | H17A—C17—H17B       | 109.5        |
| C9—C8—C7            | 106.03 (16)  | O6—C17—H17C         | 109.5        |
| C14—C8—C7           | 123.00 (15)  | H17A—C17—H17C       | 109.5        |
| C8—C9—C16           | 130.09 (17)  | H17B—C17—H17C       | 109.5        |
| C8—C9—C10           | 105.42 (15)  | C5—O1—C2            | 96.38 (13)   |
| C16—C9—C10          | 123.29 (15)  | C10—O2—C7           | 97.18 (12)   |
| O2—C10—C11          | 113.16 (14)  | C14—O4—C15          | 115.69 (15)  |
| O2—C10—C9           | 99.72 (14)   | C16—O6—C17          | 116.06 (15)  |
| C6—C1—C2—O1         | −33.60 (15)  | C16—C9—C10—C1      | −96.67 (18)  |
| C10—C1—C2—O1        | 75.25 (16)   | C2—C1—C10—O2       | −76.85 (16)  |
| C6—C1—C2—C13        | −154.94 (14) | C6—C1—C10—O2       | 32.17 (16)   |
| C10—C1—C2—C13       | −46.10 (19)  | C2—C1—C10—C11      | 45.96 (19)   |
| C6—C1—C2—C3         | 70.76 (16)   | C6—C1—C10—C11      | 154.98 (14)  |
| C10—C1—C2—C3        | 179.61 (14)  | C2—C1—C10—C9       | 179.61 (14)  |
| O1—C2—C3—C4         | 33.34 (19)   | C6—C1—C10—C9       | −71.37 (16)  |
| C13—C2—C3—C4        | 157.33 (17)  | O2—C10—C11—C12     | 66.21 (19)   |
| C1—C2—C3—C4         | −71.98 (18)  | C9—C10—C11—C12     | −176.00 (15) |
| C2—C3—C4—C5         | −0.86 (19)   | C1—C10—C11—C12     | −50.6 (2)    |
| C3—C4—C5—O1         | −31.98 (18)  | C10—C11—C12—C13    | 55.1 (2)     |
| C3—C4—C5—C6         | 74.35 (19)   | O1—C2—C13—C12      | −64.1 (2)    |
| C2—C1—C6—C7         | 118.41 (14)  | C3—C2—C13—C12      | 177.84 (15)  |
| C10—C1—C6—C7        | 2.08 (16)    | C1—C2—C13—C12      | 51.2 (2)     |
| C2—C1—C6—C5         | −1.57 (15)   | C11—C12—C13—C2     | −55.4 (2)    |
| C10—C1—C6—C5        | −117.90 (14) | C9—C8—C14—O3       | 170.32 (18)  |
| O1—C5—C6—C1         | 36.44 (15)   | C7—C8—C14—O3       | 2.1 (3)      |
| C4—C5—C6—C1         | −69.17 (17)  | C9—C8—C14—O4       | −8.8 (3)     |
| O1—C5—C6—C7         | −71.09 (18)  | C7—C8—C14—O4       | −177.03 (14) |
| C4—C5—C6—C7         | −176.70 (16) | C8—C9—C16—O5       | −102.8 (2)   |
| C1—C6—C7—O2         | −35.69 (15)  | C10—C9—C16—O5      | 62.9 (3)     |
| C5—C6—C7—O2         | 71.42 (17)   | C8—C9—C16—O6       | 79.6 (2)     |
| C1—C6—C7—C8         | 68.87 (17)   | C10—C9—C16—O6      | −114.78 (19) |
| C5—C6—C7—C8         | 175.98 (15)  | C4—C5—O1—C2        | 51.11 (15)   |
| O2—C7—C8—C9         | 31.95 (17)   | C6—C5—O1—C2        | −58.46 (15)  |
| C6—C7—C8—C9         | −74.48 (17)  | C13—C2—O1—C5       | 179.32 (15)  |
| O2—C7—C8—C14        | −157.37 (15) | C3—C2—O1—C5        | −51.27 (15)  |
| C6—C7—C8—C14        | 96.20 (19)   | C1—C2—O1—C5        | 56.79 (14)   |
| C14—C8—C9—C16       | −1.3 (3)     | C11—C10—O2—C7      | −178.39 (14) |
| C7—C8—C9—C16        | 168.50 (18)  | C9—C10—O2—C7       | 52.18 (14)   |
| C14—C8—C9—C10       | −168.84 (17) | C1—C10—O2—C7       | −54.81 (15)  |
| C7—C8—C9—C10        | 0.92 (17)    | C8—C7—O2—C10       | −51.89 (15)  |
| C8—C9—C10—O2        | −33.65 (17)  | C6—C7—O2—C10       | 56.83 (14)   |
| C16—C9—C10—O2       | 157.70 (15)  | O3—C14—O4—C15      | 3.6 (3)      |
| C8—C9—C10—C11       | −158.04 (16) | C8—C14—O4—C15      | −177.27 (15) |
| C16—C9—C10—C11      | 33.3 (2)     | O5—C16—O6—C17      | 6.7 (3)      |
| C8—C9—C10—C1        | 71.98 (16)   | C9—C16—O6—C17      | −175.75 (15) |
Hydrogen-bond geometry (Å, º)

| D—H···A     | D—H | H···A | D···A   | D—H···A |
|-------------|------|-------|---------|---------|
| C5—H5···O2i | 1.00 | 2.58  | 3.330 (2) | 132     |
| C7—H7···O1i | 1.00 | 2.52  | 3.351 (2) | 140     |

Symmetry code: (i) −x+1, −y+1, −z+1.