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2,4-Bis[(prop-2-ynyl)oxy]benzaldehyde

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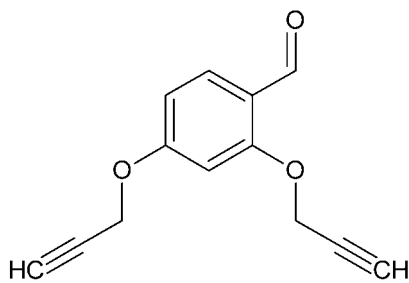
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.113; data-to-parameter ratio = 17.9.

 In the title compound, $\text{C}_{13}\text{H}_{10}\text{O}_3$, two prop-2-ynyloxy groups are attached to the benzaldehyde ring at positions 2 and 6. The crystal packing features $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

 For the biological activity of benzaldehyde derivatives, see: Zhao *et al.* (2007). For related literature, see: Delogu *et al.* (2010); Ley & Bertram (2001). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).


Experimental

Crystal data

 $\text{C}_{13}\text{H}_{10}\text{O}_3$
 $M_r = 214.21$
 Monoclinic, $P2_1/n$
 $a = 4.9219$ (2) Å
 $b = 16.8705$ (7) Å
 $c = 13.4326$ (6) Å

 $\beta = 98.236$ (3)°
 $V = 1103.87$ (8) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 0.09$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

 Bruker SMART APEXII area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.982$, $T_{\max} = 0.982$

 10446 measured reflections
 2754 independent reflections
 2177 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.113$
 $S = 1.04$
 2754 reflections
 154 parameters

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{C6}-\text{H6}\cdots\text{O1}^i$ | 0.93 | 2.48 | 3.3616 (14) | 159 |

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

Data collection: APEX2 (Bruker, 2008); cell refinement: APEX2; data reduction: SAINT (Bruker, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

The authors thank TBI Consultancy, University of Madras, India, for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5961).

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supplementary materials

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2,4-Bis[(prop-2-ynyl)oxy]benzaldehyde

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Comment

The Schiff base derived from amines and substituted benzaldehydes exhibit antibacterial, anticancer and antitumour activities (Zhao *et al.* (2007)). Several benzaldoximes, benzaldehyde-*O*-ethyloximes, and acetophenoximes were synthesized and evaluated as tyrosinase inhibitors (Ley & Bertram (2001)). The bis-salicylaldehydes exhibited greater inhibitory activity than salicylaldehyde (Delogu *et al.* (2010)).

The *ORTEP* plot of the molecule is shown in Fig. 1. The dihedral angles of phenyl ring (C2—C7) attached to prop-2-yn-1-yloxy group at 2, 6-positions (O2/C8/C9/C10) & (O3/C11/C12/C13) are 82.3 (1)° & 71.4 (1)°, respectively. The prop-2-yn-1-yloxy group is in an extended conformation which can be seen from torsion angles O2/C8/C9/C10 = -177.0 (10)° and O3/C11/C12/C13 = 166 (6)°, respectively.

The crystal packing includes an inter-molecular interaction between a terminal ethynyl H atom and an ethynyl group on a glide-related molecule and another interaction between an O-atom-linked methylene H and an ethynyl group of a different glide-related molecule.

The packing of the molecules viewed down *a* axis is shown in Fig. 2. The molecules are stabilized by C—H \cdots π and bifurcated C—H \cdots O types of intra and intermolecular interactions, which form a dimer C8 chain running along the *a* axis (Bernstein *et al.*, 1995).

Experimental

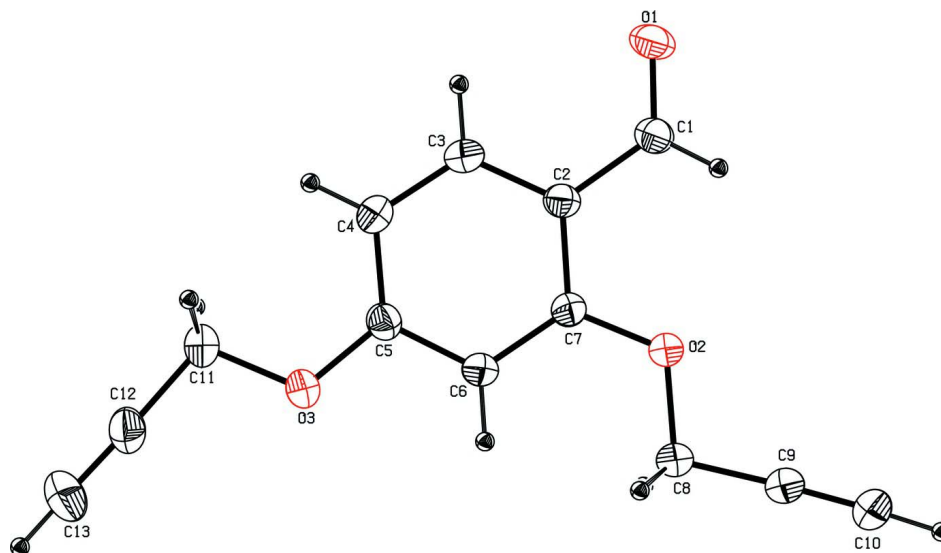
2,4-dihydroxybenzaldehyde (10 mmol), 3-bromopropyne (20 mmol) and potassium carbonate (15 mmol) were suspended in acetonitrile (40 ml) and refluxed for 30 h in presence of KI (0.1 g) as catalyst. The reaction mixture was filtered while hot to remove insoluble impurities, neutralized with dil.HCl (3 N) and extracted with chloroform and dried with Na₂SO₄. The extracts were concentrated to obtain a brown solid which was then purified by column chromatography over SiO₂ by eluting a mixture of 4% ethyl acetate with n-hexane. Evaporation of the purified extract yielded 2, 4-dipropynoxybenzaldehyde in the form of pure white solid. Yield: 85%. Crystals suitable for X-ray analysis were obtained by slow evaporation method.

Refinement

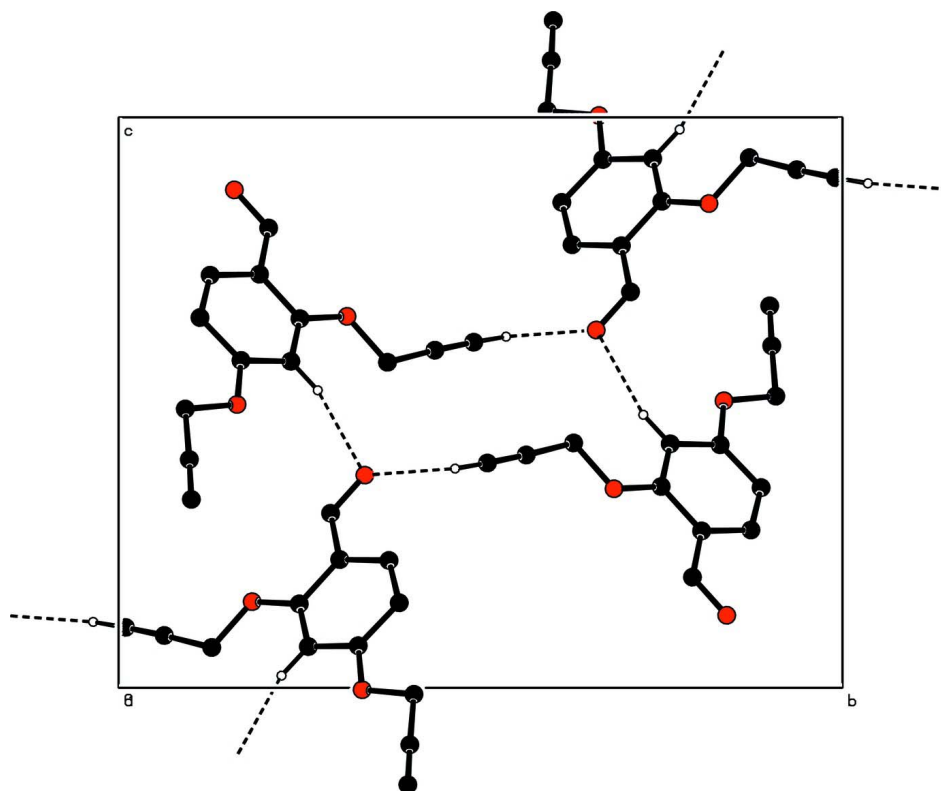
H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *APEX2* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

**Figure 1**

The molecular structure of the title compound, showing the atomic numbering and displacement ellipsoids drawn at 30% probability level.

**Figure 2**

The crystal packing of the molecules viewed down *a* axis.

2,4-Bis[(prop-2-ynyl)oxy]benzaldehyde

Crystal data

| | |
|---------------------------------|---|
| $C_{13}H_{10}O_3$ | $F(000) = 448$ |
| $M_r = 214.21$ | $D_x = 1.289 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: $-P 2_1n$ | Cell parameters from 2754 reflections |
| $a = 4.9219 (2) \text{ \AA}$ | $\theta = 2.0\text{--}28.4^\circ$ |
| $b = 16.8705 (7) \text{ \AA}$ | $\mu = 0.09 \text{ mm}^{-1}$ |
| $c = 13.4326 (6) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $\beta = 98.236 (3)^\circ$ | Block, colourless |
| $V = 1103.87 (8) \text{ \AA}^3$ | $0.20 \times 0.20 \times 0.20 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|--|--|
| Bruker SMART APEXII area-detector diffractometer | 10446 measured reflections |
| Radiation source: fine-focus sealed tube | 2754 independent reflections |
| Graphite monochromator | 2177 reflections with $I > 2\sigma(I)$ |
| ω and φ scans | $R_{\text{int}} = 0.025$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2008) | $\theta_{\text{max}} = 28.4^\circ$, $\theta_{\text{min}} = 2.0^\circ$ |
| $T_{\text{min}} = 0.982$, $T_{\text{max}} = 0.982$ | $h = -6 \rightarrow 6$ |
| | $k = -22 \rightarrow 22$ |
| | $l = -16 \rightarrow 17$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.039$ | $w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.1741P]$ |
| $wR(F^2) = 0.113$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.04$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 2754 reflections | $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$ |
| 154 parameters | $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$ |
| 0 restraints | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.035 (4) |
| Secondary atom site location: difference Fourier map | |

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|-------------|-------------|----------------------------------|
| O2 | 0.05286 (17) | 0.31557 (5) | 0.65108 (6) | 0.0445 (2) |
| O3 | 0.68295 (18) | 0.16361 (5) | 0.49674 (7) | 0.0501 (3) |
| O1 | 0.0285 (2) | 0.15987 (5) | 0.87280 (7) | 0.0554 (3) |

| | | | | |
|------|-------------|--------------|--------------|------------|
| C6 | 0.3759 (2) | 0.23786 (7) | 0.57231 (9) | 0.0396 (3) |
| H6 | 0.3799 | 0.2751 | 0.5214 | 0.047* |
| C2 | 0.2097 (2) | 0.19456 (6) | 0.72497 (8) | 0.0376 (3) |
| C3 | 0.3673 (2) | 0.12642 (7) | 0.72331 (9) | 0.0430 (3) |
| H3 | 0.3642 | 0.0890 | 0.7739 | 0.052* |
| C4 | 0.5284 (2) | 0.11234 (7) | 0.64902 (9) | 0.0447 (3) |
| H4 | 0.6320 | 0.0662 | 0.6492 | 0.054* |
| C9 | -0.1318 (3) | 0.43691 (7) | 0.59180 (9) | 0.0447 (3) |
| C7 | 0.2148 (2) | 0.25048 (6) | 0.64716 (8) | 0.0361 (2) |
| C5 | 0.5317 (2) | 0.16901 (7) | 0.57387 (9) | 0.0398 (3) |
| C12 | 0.9705 (3) | 0.09766 (8) | 0.40030 (11) | 0.0554 (3) |
| C1 | 0.0455 (3) | 0.20717 (7) | 0.80598 (9) | 0.0459 (3) |
| H1 | -0.0521 | 0.2544 | 0.8063 | 0.055* |
| C10 | -0.2730 (3) | 0.49054 (8) | 0.60585 (11) | 0.0539 (3) |
| C11 | 0.8314 (3) | 0.09202 (8) | 0.48871 (10) | 0.0495 (3) |
| H11A | 0.7066 | 0.0472 | 0.4822 | 0.059* |
| H11B | 0.9646 | 0.0844 | 0.5485 | 0.059* |
| C8 | 0.0455 (3) | 0.37140 (7) | 0.57073 (9) | 0.0453 (3) |
| H8A | -0.0264 | 0.3465 | 0.5073 | 0.054* |
| H8B | 0.2290 | 0.3907 | 0.5663 | 0.054* |
| C13 | 1.0861 (4) | 0.10046 (11) | 0.33041 (14) | 0.0791 (5) |
| H10 | -0.379 (4) | 0.5352 (11) | 0.6156 (14) | 0.087 (6)* |
| H13 | 1.176 (5) | 0.1042 (13) | 0.2780 (18) | 0.114 (7)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| O2 | 0.0548 (5) | 0.0381 (4) | 0.0443 (5) | 0.0099 (4) | 0.0197 (4) | 0.0088 (3) |
| O3 | 0.0517 (5) | 0.0511 (5) | 0.0520 (5) | 0.0140 (4) | 0.0224 (4) | 0.0074 (4) |
| O1 | 0.0824 (7) | 0.0460 (5) | 0.0421 (5) | -0.0069 (4) | 0.0231 (5) | 0.0041 (4) |
| C6 | 0.0420 (6) | 0.0392 (6) | 0.0391 (6) | 0.0024 (5) | 0.0107 (5) | 0.0070 (5) |
| C2 | 0.0419 (6) | 0.0363 (6) | 0.0351 (5) | -0.0024 (4) | 0.0070 (4) | 0.0019 (4) |
| C3 | 0.0493 (7) | 0.0398 (6) | 0.0400 (6) | 0.0020 (5) | 0.0068 (5) | 0.0085 (5) |
| C4 | 0.0453 (6) | 0.0406 (6) | 0.0484 (7) | 0.0091 (5) | 0.0081 (5) | 0.0052 (5) |
| C9 | 0.0512 (7) | 0.0403 (6) | 0.0432 (6) | 0.0027 (5) | 0.0090 (5) | 0.0061 (5) |
| C7 | 0.0376 (5) | 0.0335 (5) | 0.0377 (6) | 0.0004 (4) | 0.0072 (4) | 0.0020 (4) |
| C5 | 0.0361 (5) | 0.0439 (6) | 0.0402 (6) | 0.0021 (4) | 0.0089 (4) | 0.0009 (5) |
| C12 | 0.0588 (8) | 0.0540 (8) | 0.0555 (8) | 0.0105 (6) | 0.0152 (6) | -0.0073 (6) |
| C1 | 0.0597 (7) | 0.0398 (6) | 0.0409 (6) | -0.0003 (5) | 0.0158 (5) | 0.0017 (5) |
| C10 | 0.0645 (8) | 0.0434 (7) | 0.0551 (8) | 0.0106 (6) | 0.0129 (6) | 0.0036 (6) |
| C11 | 0.0487 (7) | 0.0486 (7) | 0.0533 (7) | 0.0094 (5) | 0.0146 (6) | -0.0023 (6) |
| C8 | 0.0520 (7) | 0.0425 (6) | 0.0437 (6) | 0.0085 (5) | 0.0147 (5) | 0.0105 (5) |
| C13 | 0.0998 (13) | 0.0800 (12) | 0.0659 (10) | 0.0122 (10) | 0.0402 (10) | -0.0076 (9) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-------------|--------|-------------|
| O2—C7 | 1.3622 (13) | C4—C5 | 1.3922 (16) |
| O2—C8 | 1.4292 (14) | C4—H4 | 0.9300 |
| O3—C5 | 1.3626 (13) | C9—C10 | 1.1722 (18) |
| O3—C11 | 1.4235 (14) | C9—C8 | 1.4608 (16) |

| | | | |
|--------------|--------------|----------------|--------------|
| O1—C1 | 1.2127 (14) | C12—C13 | 1.166 (2) |
| C6—C7 | 1.3832 (15) | C12—C11 | 1.4565 (18) |
| C6—C5 | 1.3905 (15) | C1—H1 | 0.9300 |
| C6—H6 | 0.9300 | C10—H10 | 0.935 (19) |
| C2—C3 | 1.3886 (16) | C11—H11A | 0.9700 |
| C2—C7 | 1.4109 (15) | C11—H11B | 0.9700 |
| C2—C1 | 1.4611 (15) | C8—H8A | 0.9700 |
| C3—C4 | 1.3814 (17) | C8—H8B | 0.9700 |
| C3—H3 | 0.9300 | C13—H13 | 0.89 (2) |
| | | | |
| C7—O2—C8 | 116.99 (8) | C6—C5—C4 | 121.39 (10) |
| C5—O3—C11 | 117.16 (9) | C13—C12—C11 | 178.21 (17) |
| C7—C6—C5 | 119.35 (10) | O1—C1—C2 | 124.02 (11) |
| C7—C6—H6 | 120.3 | O1—C1—H1 | 118.0 |
| C5—C6—H6 | 120.3 | C2—C1—H1 | 118.0 |
| C3—C2—C7 | 118.20 (10) | C9—C10—H10 | 176.8 (12) |
| C3—C2—C1 | 120.16 (10) | O3—C11—C12 | 108.22 (11) |
| C7—C2—C1 | 121.65 (10) | O3—C11—H11A | 110.1 |
| C4—C3—C2 | 122.26 (11) | C12—C11—H11A | 110.1 |
| C4—C3—H3 | 118.9 | O3—C11—H11B | 110.1 |
| C2—C3—H3 | 118.9 | C12—C11—H11B | 110.1 |
| C3—C4—C5 | 118.25 (11) | H11A—C11—H11B | 108.4 |
| C3—C4—H4 | 120.9 | O2—C8—C9 | 107.67 (9) |
| C5—C4—H4 | 120.9 | O2—C8—H8A | 110.2 |
| C10—C9—C8 | 177.88 (13) | C9—C8—H8A | 110.2 |
| O2—C7—C6 | 123.48 (9) | O2—C8—H8B | 110.2 |
| O2—C7—C2 | 115.97 (9) | C9—C8—H8B | 110.2 |
| C6—C7—C2 | 120.55 (10) | H8A—C8—H8B | 108.5 |
| O3—C5—C6 | 113.87 (10) | C12—C13—H13 | 178.1 (16) |
| O3—C5—C4 | 124.74 (10) | | |
| | | | |
| C7—C2—C3—C4 | 0.52 (18) | C11—O3—C5—C4 | 4.98 (17) |
| C1—C2—C3—C4 | -179.18 (11) | C7—C6—C5—O3 | -179.57 (10) |
| C2—C3—C4—C5 | 0.20 (19) | C7—C6—C5—C4 | 0.22 (18) |
| C8—O2—C7—C6 | 2.28 (16) | C3—C4—C5—O3 | 179.19 (11) |
| C8—O2—C7—C2 | -177.39 (10) | C3—C4—C5—C6 | -0.58 (18) |
| C5—C6—C7—O2 | -179.13 (10) | C3—C2—C1—O1 | -2.48 (19) |
| C5—C6—C7—C2 | 0.53 (17) | C7—C2—C1—O1 | 177.83 (12) |
| C3—C2—C7—O2 | 178.80 (10) | C5—O3—C11—C12 | 178.25 (10) |
| C1—C2—C7—O2 | -1.51 (16) | C13—C12—C11—O3 | 166 (6) |
| C3—C2—C7—C6 | -0.89 (16) | C7—O2—C8—C9 | -178.20 (10) |
| C1—C2—C7—C6 | 178.81 (11) | C10—C9—C8—O2 | -177 (100) |
| C11—O3—C5—C6 | -175.24 (11) | | |

Hydrogen-bond geometry (Å, °)

| <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> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C6—H6 \cdots O1 ⁱ | 0.93 | 2.48 | 3.3616 (14) | 159 |

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