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# 1,2,3,5-Tetrahydronaphtho[2,1-c]oxepine

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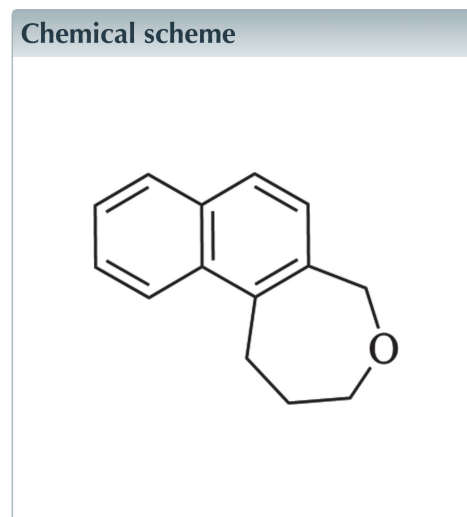
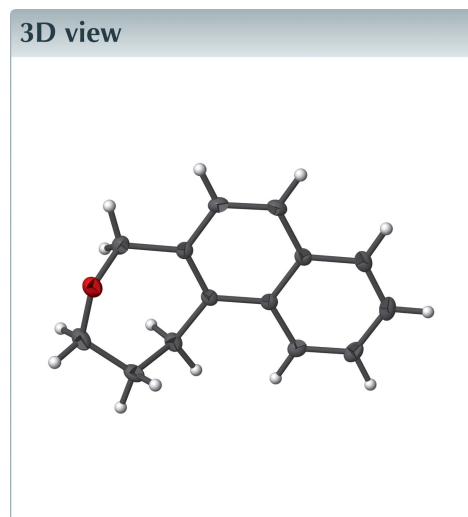
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Keywords: crystal structure; ring-opening reaction; regioisomer; weak hydrogen bonds.

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Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

In the title compound, C<sub>14</sub>H<sub>14</sub>O, the seven-membered ring is in a pseudo-chair conformation. In the crystal, molecules are linked by weak C—H···O hydrogen bonds forming layers parallel to (010). In addition, there are weak  $\pi$ – $\pi$  stacking interactions between inversion-related naphthalene ring systems, with a ring centroid–ring centroid distance of 3.518 (5) Å.



## Structure description

In past years, our research group has investigated the ring-opening reactions of cyclopropanated oxabenzonorbornadienes (CPOBD) (Carlson *et al.*, 2014, 2016, 2018; Tait *et al.*, 2016; Tigchelaar *et al.*, 2014). Recently, we have examined the intramolecular ring-opening of reaction of CPOBD with tethered alcohol nucleophiles (Wicks *et al.*, 2019). Based on previous work done in our research group, we anticipated two possible modes of ring-opening through nucleophilic attack at either the proximal or distal cyclopropyl carbon atom. Reaction of the C<sub>1</sub>-alcohol tethered CPOBD **I** (see Fig. 3) in the presence of *p*-TsOH·H<sub>2</sub>O in toluene afforded the Type 2 **II** and Type 3 **III** ring-opened products in 12% and 59% yields, respectively. The title structure of the Type 2 (**II**) regioisomer was verified by single-crystal X-ray analysis.

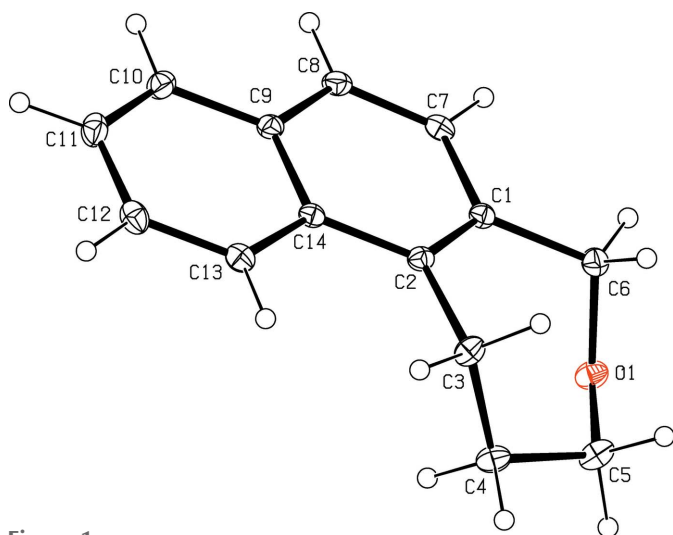
The molecular structure of the title compound is shown in Fig. 1. The seven-membered ring (C1–C6/O1) is in a pseudo-chair conformation. In the crystal, molecules are linked by weak C—H···O hydrogen bonds (Table 1), forming layers parallel to (010) (Fig. 2). In addition, there are weak  $\pi$ – $\pi$  stacking interaction between inversion related naphthalene ring systems (C1/C2/C7–C14) with a ring centroid–ring centroid distance of 3.518 (5) Å.

## Synthesis and crystallization

To a 6 dram vial open to air were added the alcohol-tethered cyclopropanated oxabenzonorbornadiene **I** (0.3547 g, 1.64 mmol), and *p*-TsOH·H<sub>2</sub>O (57.7 mg, 20 mol%)

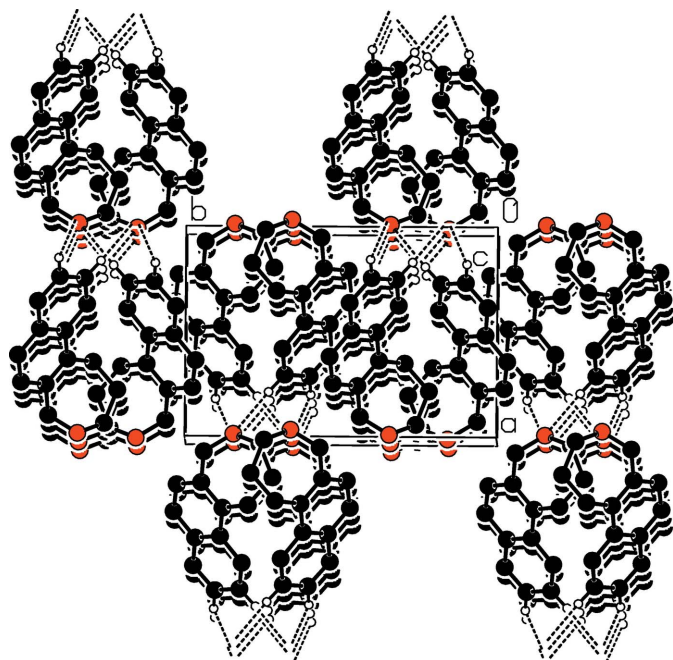


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**Figure 1**  
The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

dissolved in 7 ml of toluene (see Fig. 3). The reaction was left to stir at 333 K for 1.5 h, after which the reaction mixture was cooled and quenched with 10 ml of water. The aqueous layers were combined and back extracted with EtOAc (3 × 5 ml). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography (EtOAc:hexanes, 10: 90) to obtain ring-opened products **II** (38.5 mg, 0.194 mmol, 12%) and **III** (189.8 mg, 0.957 mmol) as a white solid and clear oil, respectively. The title compound **II** was subsequently crystallized from DCM solution by slow evaporation of the solvent to afford colourless blocks.



**Figure 2**  
Part of the crystal structure with weak hydrogen bonds shown as dashed lines. Only H atoms involved in hydrogen bonds are shown.

**Table 1**  
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C11–H11A···O1 <sup>i</sup>	0.970 (16)	2.558 (16)	3.4803 (14)	159.0 (11)
C12–H12A···O1 <sup>ii</sup>	0.976 (15)	2.560 (15)	3.4661 (14)	154.5 (11)

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

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>14</sub> H <sub>14</sub> O
<i>M</i> <sub>r</sub>	198.25
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> / <i>c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.4559 (3), 12.8405 (4), 8.9638 (3)
β (°)	111.445 (1)
<i>V</i> (Å <sup>3</sup> )	1013.02 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.08
Crystal size (mm)	0.37 × 0.26 × 0.25
Data collection	
Diffractometer	Bruker Kappa <i>APEX</i> DUO CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.723, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	21543, 2347, 2055
<i>R</i> <sub>int</sub>	0.021
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.651
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.035, 0.100, 1.07
No. of reflections	2347
No. of parameters	192
H-atom treatment	All H-atom parameters refined
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.30, -0.20

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

## Refinement

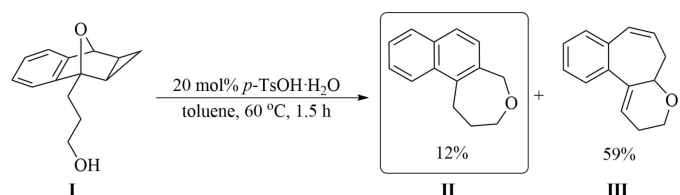
Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

The University of Toronto thanks NSERC for funding.

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**Figure 3**  
The reaction scheme.

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## full crystallographic data

*IUCrData* (2020). 5, x200288 [https://doi.org/10.1107/S2414314620002886]

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*Crystal data*

$C_{14}H_{14}O$	$F(000) = 424$
$M_r = 198.25$	$D_x = 1.300 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 9.4559 (3) \text{ \AA}$	Cell parameters from 9948 reflections
$b = 12.8405 (4) \text{ \AA}$	$\theta = 2.3\text{--}27.5^\circ$
$c = 8.9638 (3) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\beta = 111.445 (1)^\circ$	$T = 150 \text{ K}$
$V = 1013.02 (6) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.37 \times 0.26 \times 0.25 \text{ mm}$

*Data collection*

Bruker Kappa APEX DUO CCD diffractometer	21543 measured reflections
Radiation source: sealed tube with Bruker Triumph monochromator	2347 independent reflections
$\varphi$ and $\omega$ scans	2055 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.723$ , $T_{\text{max}} = 0.746$	$\theta_{\text{max}} = 27.6^\circ$ , $\theta_{\text{min}} = 2.3^\circ$
	$h = -12 \rightarrow 12$
	$k = -16 \rightarrow 16$
	$l = -11 \rightarrow 11$

*Refinement*

Refinement on $F^2$	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	All H-atom parameters refined
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.3073P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
2347 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
192 parameters	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.00150 (8)	0.34280 (6)	0.72056 (9)	0.02263 (19)

C1	0.77678 (11)	0.44489 (7)	0.56216 (11)	0.0171 (2)
C2	0.65678 (11)	0.37620 (7)	0.53419 (11)	0.0163 (2)
C3	0.66501 (11)	0.29413 (8)	0.65822 (12)	0.0209 (2)
H3A	0.5679 (16)	0.2539 (11)	0.6272 (16)	0.029 (3)*
H3B	0.6758 (16)	0.3299 (11)	0.7608 (17)	0.031 (3)*
C4	0.79563 (12)	0.21581 (8)	0.68926 (13)	0.0235 (2)
H4A	0.7759 (16)	0.1550 (11)	0.7461 (16)	0.029 (3)*
H4B	0.7980 (16)	0.1911 (12)	0.5840 (18)	0.035 (4)*
C5	0.95069 (12)	0.25805 (9)	0.79119 (14)	0.0254 (2)
H5A	0.9486 (16)	0.2824 (11)	0.8993 (18)	0.033 (4)*
H5B	1.0304 (15)	0.2034 (10)	0.8079 (16)	0.025 (3)*
C6	0.91744 (11)	0.43684 (8)	0.71202 (13)	0.0214 (2)
H6A	0.9889 (14)	0.4953 (11)	0.7133 (14)	0.023 (3)*
H6B	0.8913 (15)	0.4415 (10)	0.8106 (17)	0.028 (3)*
C7	0.77109 (12)	0.52380 (7)	0.45040 (12)	0.0194 (2)
H7A	0.8559 (16)	0.5724 (11)	0.4711 (16)	0.029 (3)*
C8	0.64771 (12)	0.53392 (7)	0.31122 (12)	0.0198 (2)
H8A	0.6454 (15)	0.5891 (11)	0.2355 (16)	0.027 (3)*
C9	0.52464 (11)	0.46395 (7)	0.27548 (11)	0.0172 (2)
C10	0.39883 (12)	0.47042 (8)	0.12770 (12)	0.0218 (2)
H10A	0.4011 (15)	0.5267 (11)	0.0541 (16)	0.026 (3)*
C11	0.28267 (12)	0.40005 (9)	0.08940 (13)	0.0248 (2)
H11A	0.1987 (17)	0.4037 (11)	-0.0128 (19)	0.036 (4)*
C12	0.28495 (12)	0.32073 (9)	0.19878 (13)	0.0236 (2)
H12A	0.2036 (16)	0.2691 (11)	0.1702 (16)	0.031 (3)*
C13	0.40269 (11)	0.31364 (8)	0.34385 (12)	0.0201 (2)
H13A	0.4012 (15)	0.2577 (11)	0.4170 (16)	0.027 (3)*
C14	0.52804 (10)	0.38377 (7)	0.38733 (11)	0.0157 (2)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0183 (4)	0.0229 (4)	0.0269 (4)	0.0028 (3)	0.0085 (3)	0.0040 (3)
C1	0.0174 (4)	0.0164 (4)	0.0174 (5)	0.0016 (3)	0.0064 (4)	-0.0017 (3)
C2	0.0178 (4)	0.0157 (4)	0.0168 (4)	0.0018 (3)	0.0080 (4)	0.0008 (3)
C3	0.0190 (5)	0.0241 (5)	0.0207 (5)	0.0002 (4)	0.0086 (4)	0.0058 (4)
C4	0.0254 (5)	0.0193 (5)	0.0274 (5)	0.0016 (4)	0.0115 (4)	0.0069 (4)
C5	0.0217 (5)	0.0276 (6)	0.0268 (5)	0.0052 (4)	0.0088 (4)	0.0092 (4)
C6	0.0197 (5)	0.0203 (5)	0.0215 (5)	0.0003 (4)	0.0043 (4)	-0.0025 (4)
C7	0.0215 (5)	0.0142 (4)	0.0239 (5)	-0.0025 (4)	0.0099 (4)	-0.0024 (4)
C8	0.0260 (5)	0.0143 (4)	0.0207 (5)	0.0010 (4)	0.0105 (4)	0.0016 (4)
C9	0.0190 (5)	0.0160 (4)	0.0175 (5)	0.0034 (4)	0.0077 (4)	-0.0004 (3)
C10	0.0231 (5)	0.0234 (5)	0.0185 (5)	0.0061 (4)	0.0070 (4)	0.0015 (4)
C11	0.0192 (5)	0.0324 (6)	0.0197 (5)	0.0048 (4)	0.0035 (4)	-0.0043 (4)
C12	0.0177 (5)	0.0265 (5)	0.0265 (5)	-0.0023 (4)	0.0080 (4)	-0.0074 (4)
C13	0.0194 (5)	0.0195 (5)	0.0231 (5)	-0.0011 (4)	0.0099 (4)	-0.0025 (4)
C14	0.0167 (4)	0.0151 (4)	0.0170 (4)	0.0017 (3)	0.0081 (4)	-0.0016 (3)

*Geometric parameters (Å, °)*

O1—C5	1.4277 (13)	C6—H6B	1.003 (14)
O1—C6	1.4323 (12)	C7—C8	1.3675 (14)
C1—C2	1.3858 (13)	C7—H7A	0.979 (14)
C1—C7	1.4120 (14)	C8—C9	1.4112 (14)
C1—C6	1.5092 (13)	C8—H8A	0.975 (14)
C2—C14	1.4327 (13)	C9—C10	1.4229 (13)
C2—C3	1.5131 (13)	C9—C14	1.4292 (13)
C3—C4	1.5372 (14)	C10—C11	1.3657 (16)
C3—H3A	1.000 (14)	C10—H10A	0.984 (14)
C3—H3B	0.999 (14)	C11—C12	1.4084 (16)
C4—C5	1.5163 (15)	C11—H11A	0.969 (15)
C4—H4A	0.987 (14)	C12—C13	1.3712 (15)
C4—H4B	1.004 (15)	C12—H12A	0.976 (14)
C5—H5A	1.025 (15)	C13—C14	1.4248 (13)
C5—H5B	1.000 (13)	C13—H13A	0.977 (14)
C6—H6A	1.007 (13)		
C5—O1—C6	113.34 (8)	O1—C6—H6B	108.3 (8)
C2—C1—C7	120.80 (9)	C1—C6—H6B	111.0 (8)
C2—C1—C6	120.95 (9)	H6A—C6—H6B	109.0 (10)
C7—C1—C6	118.24 (9)	C8—C7—C1	120.93 (9)
C1—C2—C14	119.18 (9)	C8—C7—H7A	118.6 (8)
C1—C2—C3	119.45 (9)	C1—C7—H7A	120.5 (8)
C14—C2—C3	121.38 (8)	C7—C8—C9	120.28 (9)
C2—C3—C4	114.25 (8)	C7—C8—H8A	119.9 (8)
C2—C3—H3A	111.1 (8)	C9—C8—H8A	119.8 (8)
C4—C3—H3A	107.9 (8)	C8—C9—C10	120.90 (9)
C2—C3—H3B	108.5 (8)	C8—C9—C14	119.61 (9)
C4—C3—H3B	109.2 (8)	C10—C9—C14	119.47 (9)
H3A—C3—H3B	105.5 (11)	C11—C10—C9	121.14 (10)
C5—C4—C3	114.27 (9)	C11—C10—H10A	122.0 (8)
C5—C4—H4A	107.2 (8)	C9—C10—H10A	116.8 (8)
C3—C4—H4A	108.7 (8)	C10—C11—C12	119.82 (10)
C5—C4—H4B	109.3 (8)	C10—C11—H11A	120.8 (9)
C3—C4—H4B	109.2 (8)	C12—C11—H11A	119.4 (9)
H4A—C4—H4B	108.0 (12)	C13—C12—C11	120.57 (10)
O1—C5—C4	114.42 (9)	C13—C12—H12A	119.5 (8)
O1—C5—H5A	108.2 (8)	C11—C12—H12A	119.9 (8)
C4—C5—H5A	109.3 (8)	C12—C13—C14	121.55 (10)
O1—C5—H5B	104.1 (8)	C12—C13—H13A	118.7 (8)
C4—C5—H5B	110.4 (8)	C14—C13—H13A	119.7 (8)
H5A—C5—H5B	110.3 (11)	C13—C14—C9	117.41 (9)
O1—C6—C1	113.36 (8)	C13—C14—C2	123.42 (9)
O1—C6—H6A	105.7 (7)	C9—C14—C2	119.15 (8)
C1—C6—H6A	109.2 (7)		

C7—C1—C2—C14	2.09 (14)	C7—C8—C9—C14	1.43 (14)
C6—C1—C2—C14	-177.41 (8)	C8—C9—C10—C11	177.03 (9)
C7—C1—C2—C3	-178.58 (9)	C14—C9—C10—C11	-1.35 (15)
C6—C1—C2—C3	1.92 (14)	C9—C10—C11—C12	1.34 (15)
C1—C2—C3—C4	-62.32 (12)	C10—C11—C12—C13	0.19 (16)
C14—C2—C3—C4	117.00 (10)	C11—C12—C13—C14	-1.72 (15)
C2—C3—C4—C5	76.33 (12)	C12—C13—C14—C9	1.66 (14)
C6—O1—C5—C4	69.71 (12)	C12—C13—C14—C2	-176.93 (9)
C3—C4—C5—O1	-63.49 (12)	C8—C9—C14—C13	-178.54 (9)
C5—O1—C6—C1	-87.27 (10)	C10—C9—C14—C13	-0.14 (13)
C2—C1—C6—O1	65.29 (12)	C8—C9—C14—C2	0.11 (13)
C7—C1—C6—O1	-114.22 (10)	C10—C9—C14—C2	178.51 (8)
C2—C1—C7—C8	-0.56 (15)	C1—C2—C14—C13	176.72 (9)
C6—C1—C7—C8	178.95 (9)	C3—C2—C14—C13	-2.60 (14)
C1—C7—C8—C9	-1.23 (15)	C1—C2—C14—C9	-1.84 (13)
C7—C8—C9—C10	-176.95 (9)	C3—C2—C14—C9	178.83 (8)

*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>
C11—H11 <i>A</i> $\cdots$ O1 <sup>i</sup>	0.970 (16)	2.558 (16)	3.4803 (14)	159.0 (11)
C12—H12 <i>A</i> $\cdots$ O1 <sup>ii</sup>	0.976 (15)	2.560 (15)	3.4661 (14)	154.5 (11)

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