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(1*R*,4*S*)-(−)-3,3-Ethylenedioxy-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one

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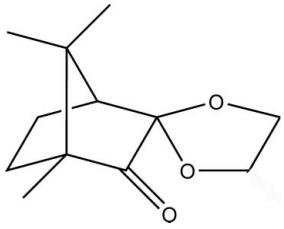
Key indicators: single-crystal X-ray study; T = 223 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.112; data-to-parameter ratio = 11.4.

The title compound, $C_{12}H_{18}O_3$, was synthesized from camphorquinone and ethylene glycol, with the stereochemistry assumed to be unchanged during the reaction. The molecule exhibits several C—C bond lengths that differ significantly from the expected value of 1.54 Å.

Related literature

For related literature, see: Fleming & Woodward (1968); Lachance *et al.* (2005).



Experimental

Crystal data

$C_{12}H_{18}O_3$
M_r = 210.26
Orthorhombic, $P2_12_12_1$
a = 7.2169 (8) Å
b = 11.8122 (14) Å
c = 13.2986 (15) Å
V = 1133.7 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 223 (2) K
0.40 × 0.33 × 0.32 mm

Data collection

Bruker SMART 1K CCD diffractometer
Absorption correction: none
8262 measured reflections
1589 independent reflections
1469 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.112
S = 1.04
1589 reflections
139 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected bond lengths (Å).

C1—C10	1.515 (2)	C3—C4	1.527 (3)
C1—C2	1.520 (2)	C4—C5	1.544 (3)
C1—C6	1.558 (2)	C4—C7	1.562 (3)
C1—C7	1.562 (2)	C5—C6	1.546 (3)
C2—C3	1.555 (2)	C7—C9	1.522 (3)
C2′—C3′	1.502 (3)	C7—C8	1.540 (3)

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2223).

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supplementary materials

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(1*R*,4*S*)-(-)-3,3-Ethylenedioxy-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one

G. A. Boyle, T. Govender, H. G. Kruger and G. E. M. Maguire

Comment

The title compound was synthesized as an intermediate in an ongoing investigation into the synthesis of novel camphor-derived ligands for applications in asymmetric catalysis. The compound was first synthesized in 1968 (Fleming & Woodward, 1968) but the crystal structure has not been reported until now.

The reaction of camphorquinone with ethylene glycol is known to give consistently a 3:1 ratio of the title compound with (1*R*,4*S*)-(-)-1,7,7-Trimethyl-2,2-ethylenedioxybicyclo-[2.2.1] heptan-3-one (Lachance *et al.*, 2005). The crystal analysed contains only the title molecule, with no indication of the other in the structure.

The molecule (Fig. 1) exhibits some C—C bonds that differ significantly from the expected C—C bond length of 1.54 Å (Table 1). The shortest bond is 1.502 (3) Å between C2' and C3'. The camphor skeleton also contains several bonds that are both shorter (*e.g.* 1.520 (3) Å for C1—C2) and longer (1.562 (3) Å for C1—C7) than the expected value. There are numerous short C—H···O and H···H contacts in the structure (Fig. 2): atom O1 interacts with the hydrogen of C4 of one molecule while C2' and C3' interact with O1 of a different neighbouring molecule (Fig. 3). The *exo* hydrogen on C2' interacts with the hydrogen on C5 of a neighbouring molecule and O3' interacts with one of the hydrogen atoms on C10 of a different molecule.

Experimental

A solution of camphorquinone (1 mol eq.), ethylene glycol (1 mol eq.) and *p*-toluenesulphonic acid (catalytic amount) in benzene was refluxed in a Dean-Stark apparatus with water removed azeotropically. When TLC indicated the absence of the starting quinone, the reaction mixture was allowed to cool gradually to ambient temperature and washed sequentially with 10% aqueous $NaHCO_3$ (100 ml), water (100 ml) and brine (100 ml). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified *via* column chromatography on silica gel by eluting with EtOAc-hexane (5:95). The title compound was obtained in 80% yield as a colourless oil which crystallized on standing at room temperature overnight.

Refinement

All H atoms were visible in difference Fourier maps but were positioned geometrically with C—H = 0.97–0.99 Å and allowed to ride during refinement with $U_{iso}(H) = 1.2U_{eq}(C)$. In the absence of significant anomalous scattering effects, Friedel pairs have been merged as equivalent data.

Figures

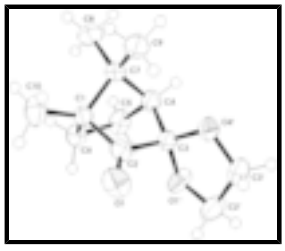

Fig. 1. The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level for non-H atoms

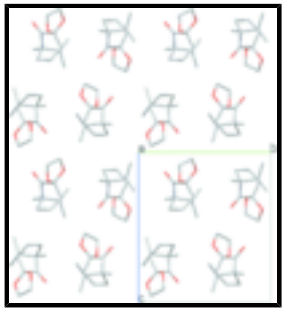

Fig. 2. Packing diagram viewed along the *a* axis. H atoms have been omitted.

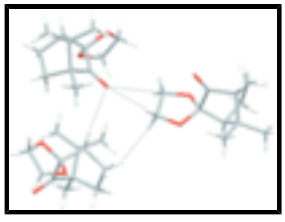

Fig. 3. Some intermolecular interactions involving O1.

(1*R*,4*S*)-(-)-1,7,7-Trimethyl-3,3-ethylenedioxybicyclo- [2.2.1]heptan-2-one

Crystal data

$C_{12}H_{18}O_3$	F_{000} = 456
M_r = 210.26	D_x = 1.232 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 1017 reflections
a = 7.2169 (8) Å	θ = 2.8–28.3º
b = 11.8122 (14) Å	μ = 0.09 mm^{-1}
c = 13.2986 (15) Å	T = 223 (2) K
V = 1133.7 (2) Å^3	Block, colourless
Z = 4	0.40 × 0.33 × 0.32 mm

Data collection

Bruker SMART 1K CCD diffractometer	1469 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.039
Monochromator: graphite	θ_{max} = 28.0º
T = 223(2) K	θ_{min} = 2.3º

φ and ω scans
Absorption correction: none
8262 measured reflections
1589 independent reflections

$h = -9 \rightarrow 9$
$k = -15 \rightarrow 12$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.112$
$S = 1.04$
1589 reflections
139 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.1693P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: none
Absolute structure: In the absence of significant anomalous scattering effects, Friedel pairs have been merged as equivalent data.
Flack parameter: ?
Rogers parameter: ?

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8229 (2)	0.77338 (13)	0.19449 (13)	0.0323 (3)
C2	0.9155 (2)	0.76727 (14)	0.29698 (13)	0.0329 (3)
C2'	1.2832 (3)	0.8104 (2)	0.41436 (16)	0.0573 (6)
H2'A	1.4154	0.8226	0.4272	0.069*
H2'B	1.2461	0.7377	0.4436	0.069*
C3'	1.1691 (4)	0.9056 (2)	0.45635 (16)	0.0567 (6)
H3'A	1.1030	0.8809	0.5169	0.068*
H3'B	1.2484	0.9700	0.4739	0.068*
C3	1.0655 (2)	0.86179 (14)	0.29824 (13)	0.0333 (4)
C4	1.0357 (3)	0.91661 (15)	0.19549 (14)	0.0401 (4)

H4	1.0829	0.9950	0.1899	0.048*
C5	1.1148 (3)	0.83379 (19)	0.11663 (14)	0.0459 (5)
H5A	1.2399	0.8091	0.1349	0.055*
H5B	1.1181	0.8685	0.0497	0.055*
C6	0.9764 (3)	0.73396 (16)	0.11993 (13)	0.0369 (4)
H6A	1.0369	0.6649	0.1442	0.044*
H6B	0.9242	0.7194	0.0531	0.044*
C7	0.8224 (3)	0.90443 (15)	0.17886 (16)	0.0427 (4)
C8	0.7617 (5)	0.9401 (2)	0.0724 (2)	0.0728 (9)
H8A	0.6289	0.9301	0.0656	0.109*
H8B	0.8250	0.8937	0.0231	0.109*
H8C	0.7929	1.0191	0.0616	0.109*
C9	0.7022 (3)	0.9669 (2)	0.2549 (2)	0.0650 (7)
H9A	0.7214	1.0478	0.2480	0.097*
H9B	0.7358	0.9434	0.3223	0.097*
H9C	0.5729	0.9492	0.2427	0.097*
C10	0.6429 (3)	0.7079 (2)	0.18675 (19)	0.0533 (5)
H10A	0.6666	0.6282	0.1990	0.080*
H10B	0.5912	0.7174	0.1200	0.080*
H10C	0.5559	0.7361	0.2364	0.080*
O1	0.8851 (3)	0.70281 (13)	0.36499 (10)	0.0561 (4)
O1'	1.24417 (18)	0.81368 (14)	0.30867 (11)	0.0475 (4)
O4'	1.0419 (2)	0.93654 (12)	0.38033 (11)	0.0476 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0302 (7)	0.0312 (7)	0.0356 (8)	−0.0006 (6)	−0.0002 (7)	−0.0049 (7)
C2	0.0372 (8)	0.0313 (7)	0.0301 (7)	0.0029 (6)	0.0059 (7)	−0.0033 (6)
C2'	0.0568 (12)	0.0747 (15)	0.0403 (10)	0.0140 (12)	−0.0162 (10)	−0.0062 (10)
C3'	0.0703 (15)	0.0578 (12)	0.0421 (10)	0.0059 (12)	−0.0205 (11)	−0.0124 (9)
C3	0.0336 (8)	0.0341 (8)	0.0322 (8)	0.0018 (6)	−0.0031 (7)	−0.0029 (7)
C4	0.0474 (10)	0.0336 (8)	0.0393 (9)	−0.0089 (8)	−0.0073 (8)	0.0063 (8)
C5	0.0470 (10)	0.0597 (11)	0.0308 (8)	−0.0130 (10)	0.0050 (8)	0.0043 (8)
C6	0.0399 (8)	0.0416 (9)	0.0291 (7)	−0.0003 (7)	0.0033 (7)	−0.0038 (7)
C7	0.0473 (10)	0.0319 (8)	0.0490 (10)	0.0069 (8)	−0.0173 (9)	−0.0017 (8)
C8	0.098 (2)	0.0494 (12)	0.0709 (16)	0.0102 (14)	−0.0461 (16)	0.0083 (12)
C9	0.0532 (13)	0.0539 (12)	0.0878 (18)	0.0232 (11)	−0.0220 (13)	−0.0287 (13)
C10	0.0382 (9)	0.0609 (12)	0.0607 (13)	−0.0116 (9)	0.0042 (10)	−0.0184 (11)
O1	0.0811 (11)	0.0519 (8)	0.0352 (7)	−0.0124 (8)	0.0127 (7)	0.0070 (6)
O1'	0.0347 (6)	0.0703 (10)	0.0375 (7)	0.0123 (7)	−0.0063 (6)	−0.0071 (7)
O4'	0.0559 (8)	0.0447 (7)	0.0421 (7)	0.0105 (6)	−0.0136 (7)	−0.0155 (6)

Geometric parameters (Å, °)

C1—C10	1.515 (2)	C4—H4	0.990
C1—C2	1.520 (2)	C5—C6	1.546 (3)
C1—C6	1.558 (2)	C5—H5A	0.980
C1—C7	1.562 (2)	C5—H5B	0.980

C2—O1	1.202 (2)	C6—H6A	0.980
C2—C3	1.555 (2)	C6—H6B	0.980
C2'—O1'	1.434 (3)	C7—C9	1.522 (3)
C2'—C3'	1.502 (3)	C7—C8	1.540 (3)
C2'—H2'A	0.980	C8—H8A	0.970
C2'—H2'B	0.980	C8—H8B	0.970
C3'—O4'	1.413 (3)	C8—H8C	0.970
C3'—H3'A	0.980	C9—H9A	0.970
C3'—H3'B	0.980	C9—H9B	0.970
C3—O4'	1.414 (2)	C9—H9C	0.970
C3—O1'	1.416 (2)	C10—H10A	0.970
C3—C4	1.527 (3)	C10—H10B	0.970
C4—C5	1.544 (3)	C10—H10C	0.970
C4—C7	1.562 (3)		
C10—C1—C2	114.44 (16)	C4—C5—H5B	111.2
C10—C1—C6	114.42 (15)	C6—C5—H5B	111.2
C2—C1—C6	104.10 (13)	H5A—C5—H5B	109.1
C10—C1—C7	119.68 (16)	C5—C6—C1	104.45 (14)
C2—C1—C7	99.64 (13)	C5—C6—H6A	110.9
C6—C1—C7	102.31 (15)	C1—C6—H6A	110.9
O1—C2—C1	128.63 (17)	C5—C6—H6B	110.9
O1—C2—C3	125.01 (17)	C1—C6—H6B	110.9
C1—C2—C3	106.36 (14)	H6A—C6—H6B	108.9
O1'—C2'—C3'	103.67 (18)	C9—C7—C8	108.39 (19)
O1'—C2'—H2'A	111.0	C9—C7—C4	115.01 (17)
C3'—C2'—H2'A	111.0	C8—C7—C4	112.7 (2)
O1'—C2'—H2'B	111.0	C9—C7—C1	113.15 (19)
C3'—C2'—H2'B	111.0	C8—C7—C1	113.22 (17)
H2'A—C2'—H2'B	109.0	C4—C7—C1	94.02 (14)
O4'—C3'—C2'	106.49 (16)	C7—C8—H8A	109.5
O4'—C3'—H3'A	110.4	C7—C8—H8B	109.5
C2'—C3'—H3'A	110.4	H8A—C8—H8B	109.5
O4'—C3'—H3'B	110.4	C7—C8—H8C	109.5
C2'—C3'—H3'B	110.4	H8A—C8—H8C	109.5
H3'A—C3'—H3'B	108.6	H8B—C8—H8C	109.5
O4'—C3—O1'	106.51 (14)	C7—C9—H9A	109.5
O4'—C3—C4	114.15 (14)	C7—C9—H9B	109.5
O1'—C3—C4	112.71 (16)	H9A—C9—H9B	109.5
O4'—C3—C2	111.90 (15)	C7—C9—H9C	109.5
O1'—C3—C2	110.28 (14)	H9A—C9—H9C	109.5
C4—C3—C2	101.35 (14)	H9B—C9—H9C	109.5
C3—C4—C5	106.68 (15)	C1—C10—H10A	109.5
C3—C4—C7	103.09 (16)	C1—C10—H10B	109.5
C5—C4—C7	102.12 (15)	H10A—C10—H10B	109.5
C3—C4—H4	114.5	C1—C10—H10C	109.5
C5—C4—H4	114.5	H10A—C10—H10C	109.5
C7—C4—H4	114.5	H10B—C10—H10C	109.5
C4—C5—C6	103.02 (15)	C3—O1'—C2'	106.62 (15)
C4—C5—H5A	111.2	C3'—O4'—C3	108.23 (15)

C6—C5—H5A	111.2		
C10—C1—C2—O1	15.0 (3)	C7—C1—C6—C5	30.94 (18)
C6—C1—C2—O1	−110.6 (2)	C3—C4—C7—C9	62.7 (2)
C7—C1—C2—O1	144.0 (2)	C5—C4—C7—C9	173.32 (18)
C10—C1—C2—C3	−165.94 (15)	C3—C4—C7—C8	−172.37 (16)
C6—C1—C2—C3	68.44 (16)	C5—C4—C7—C8	−61.8 (2)
C7—C1—C2—C3	−36.97 (17)	C3—C4—C7—C1	−55.13 (17)
O1'—C2'—C3'—O4'	14.3 (3)	C5—C4—C7—C1	55.44 (17)
O1—C2—C3—O4'	−56.3 (2)	C10—C1—C7—C9	60.8 (2)
C1—C2—C3—O4'	124.53 (15)	C2—C1—C7—C9	−64.69 (19)
O1—C2—C3—O1'	62.0 (2)	C6—C1—C7—C9	−171.54 (15)
C1—C2—C3—O1'	−117.10 (15)	C10—C1—C7—C8	−63.1 (3)
O1—C2—C3—C4	−178.37 (18)	C2—C1—C7—C8	171.5 (2)
C1—C2—C3—C4	2.50 (17)	C6—C1—C7—C8	64.6 (2)
O4'—C3—C4—C5	165.71 (15)	C10—C1—C7—C4	−179.83 (17)
O1'—C3—C4—C5	44.03 (19)	C2—C1—C7—C4	54.72 (16)
C2—C3—C4—C5	−73.83 (17)	C6—C1—C7—C4	−52.14 (16)
O4'—C3—C4—C7	−87.15 (18)	O4'—C3—O1'—C2'	29.8 (2)
O1'—C3—C4—C7	151.17 (15)	C4—C3—O1'—C2'	155.70 (17)
C2—C3—C4—C7	33.31 (17)	C2—C3—O1'—C2'	−91.8 (2)
C3—C4—C5—C6	69.78 (18)	C3'—C2'—O1'—C3	−26.8 (2)
C7—C4—C5—C6	−38.04 (19)	C2'—C3'—O4'—C3	3.4 (3)
C4—C5—C6—C1	4.21 (19)	O1'—C3—O4'—C3'	−20.3 (2)
C10—C1—C6—C5	161.92 (17)	C4—C3—O4'—C3'	−145.36 (18)
C2—C1—C6—C5	−72.45 (17)	C2—C3—O4'—C3'	100.3 (2)

Fig. 1

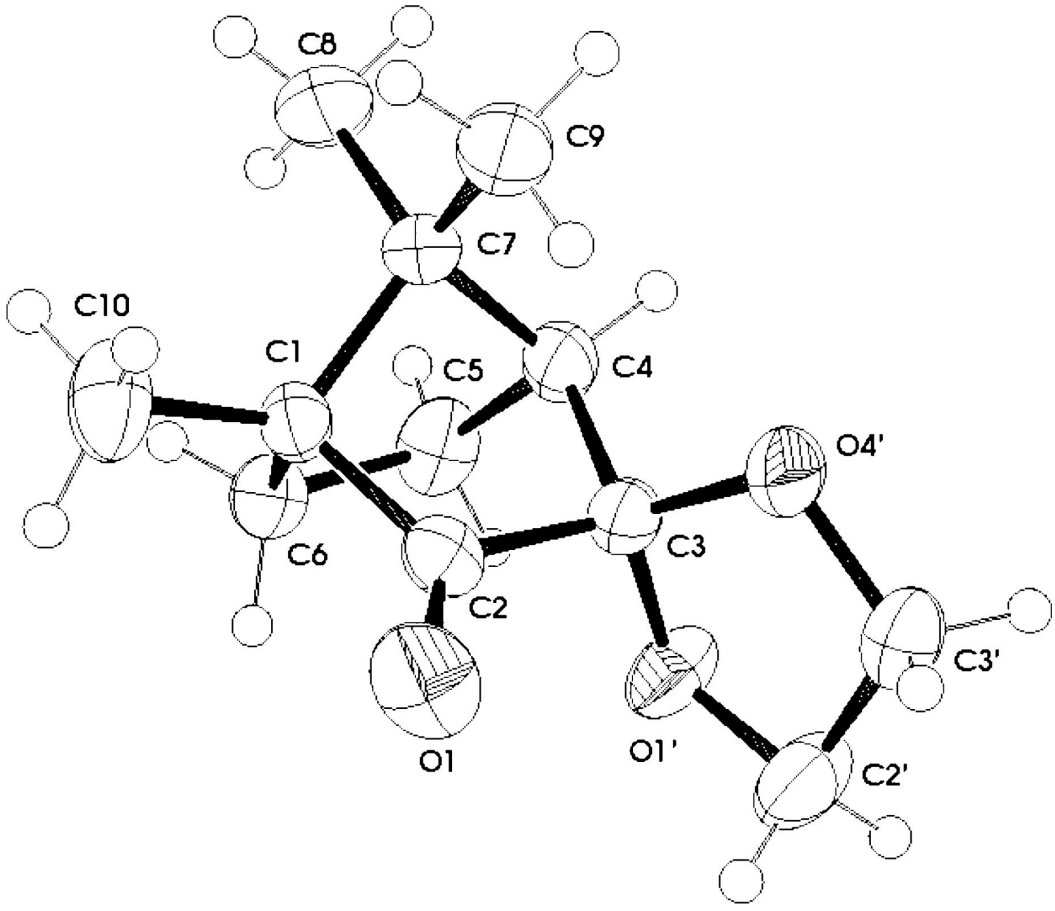

Fig. 2

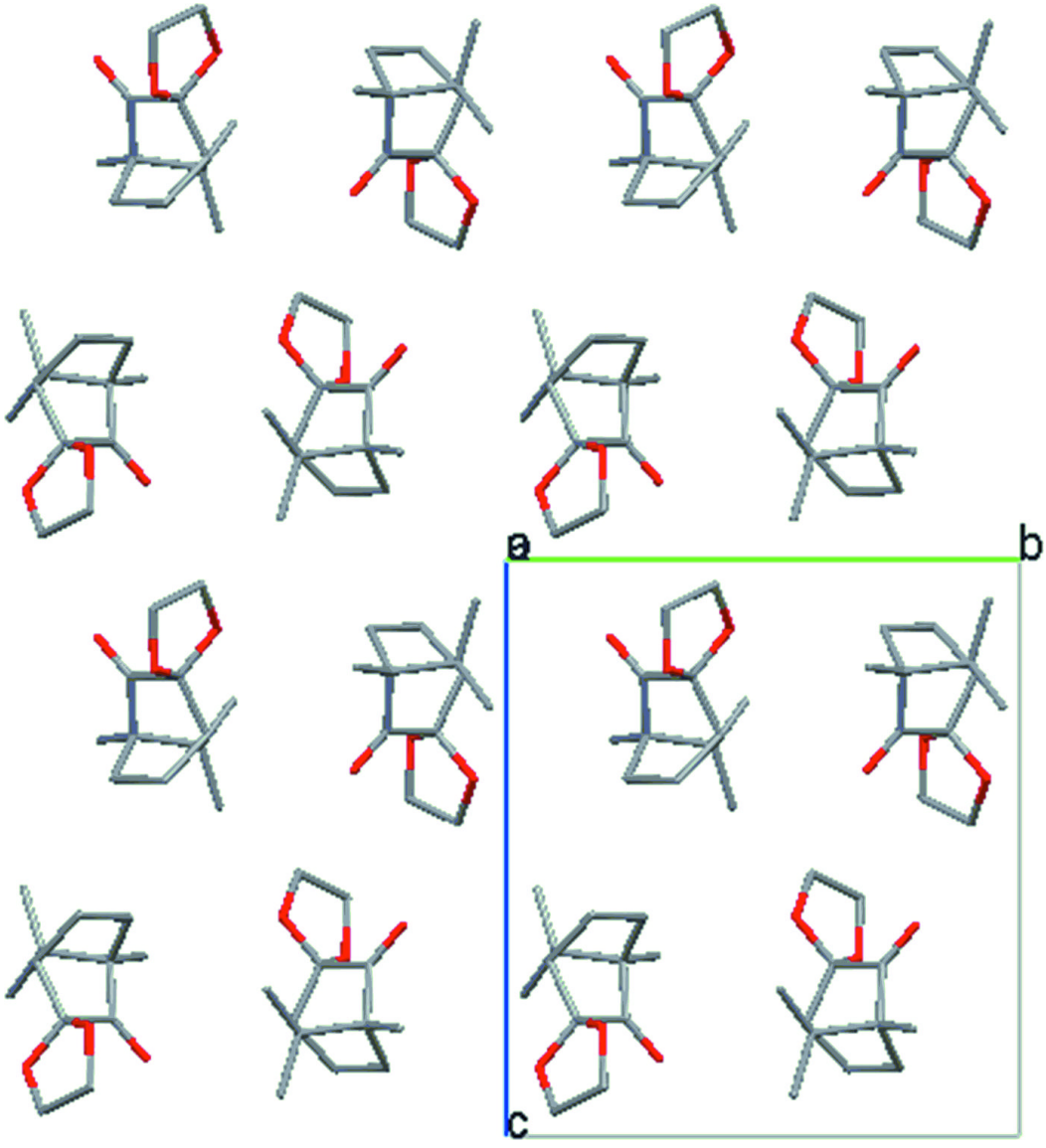

Fig. 3