Acta Cryst E STRUCTURE REPORTS

ISSN 1600-5368

Crystal structure of bis[3-methoxy-17β-estra-1,3,5(10)-trien-17-yl] oxalate

William T. A. Harrison,* Lutfun Nahar and Alan B. Turner

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland. *Correspondence e-mail: w.harrison@abdn.ac.uk

Received 1 April 2014
Accepted 24 April 2014

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; oxalate; diester; steroid; conformation

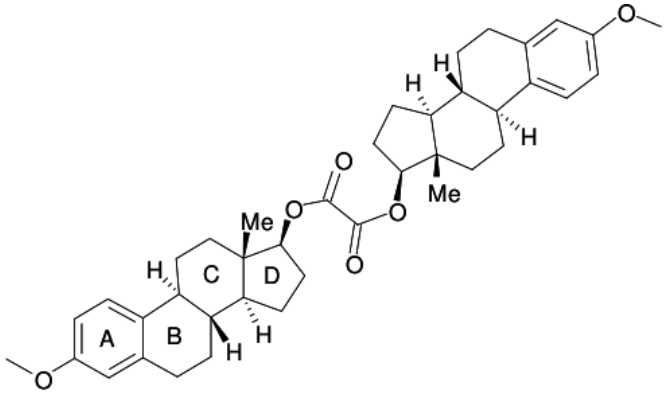
CCDC reference: 1004276

Supporting information: this article has supporting information at journals.iucr.org/e

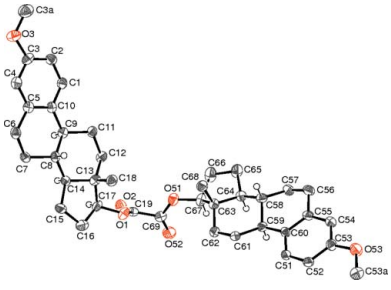
In the title compound, $C_{40}H_{50}O_6$, a symmetrical steroid oxalate diester, the dihedral angle between the CO_2 planes of the oxalate linker is 61.5 (5)° and the C—C bond length is 1.513 (6) Å. The steroid *B*, *C* and *D* rings adopt half-chair, chair and envelope conformations, respectively, in both halves of the molecule, which adopts an overall shallow V-shaped conformation. In the crystal, molecules are linked by weak C—H···O interactions, forming a three-dimensional network.

1. Chemical context

The pyrolysis of esters possessing aliphatic β-hydrogen atoms is a known route to alkenes *via* radical mediated β-elimination (Brown, 1980). As part of our studies in this area (Nahar, 2007), we now describe the crystal structure of the title compound, (I), an oxalate diester of 17-β-estradiol 3-methyl ether (Reck *et al.*, 1986; Schönnecker *et al.*, 2000). Flash-vacuum pyrolysis (FVP) of (I) at 873 K and 0.2 torr led to estratetraene 3-methyl ether in 47% yield.



2. Structural commentary



The atom labelling scheme (Fig. 1) for (I) relates equivalent atoms in the two halves of the molecule by adding 50, *e.g.* C1 and C51. The C19—C69 bond length of 1.513 (6) Å for the oxalate unit is exactly as expected for an sp^2–sp^2 carbon–carbon single bond but significantly shorter than the typical C—C bond length of about 1.57 Å in isolated oxalate ions (Dinnebier *et al.*, 2003). The mean C—O_C bond length is 1.324 Å and the mean C=O bond length is 1.197 Å. The dihedral angle between the C19/O1/O2 and C69/O51/O52 planes of 61.5 (5)° indicates a substantial twist. This leads to an overall shallow V-shaped conformation for the molecule, with the C18 and C68 methyl groups facing each other [C18···C68 = 4.64 Å]. This could be significant in terms of the radical-reactivity of this molecule under FVP (Nahar, 2007).

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

D—H···A	D—H	H···A	D···A	D—H···A
C52—H52···O2^{i}	0.95	2.51	3.161 (5)	126
C53A—H53B···O53^{ii}	0.98	2.51	3.378 (6)	147
C54—H54···O2^{iii}	0.95	2.56	3.309 (5)	136

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

The methoxy carbon atom C3*A* is displaced from the C1–C5/C10 ring plane by −0.114 (7) Å. The C5–C10 ring conformation approximates to a half-chair with C7 and C8 displaced from the C5/C6/C9/C10 plane by 0.287 (7) and −0.477 (7) Å, respectively. The C8/C9/C11–C14 ring is a normal chair. The C13–C17 five-membered ring is an envelope, with C13 displaced from the mean plane of the other four C atoms by −0.735 (6) Å.

These ring conformations are essentially duplicated in the second half of the molecule: C53*A* is displaced from the C51–C55/C60 plane by 0.096 (7) Å. For the C55–C60 ring, atoms C57 and C58 are displaced from the C55/C56/C59/C60 plane by −0.340 (7) and 0.422 (7) Å, respectively. The C58/C59/C61–C64 ring is a normal chair. The C63–C67 ring is an envelope, with C63 displaced from the mean plane of the other four atoms by 0.735 (6) Å.

The stereogenic centres in (I) have the following assumed chiralities: C8 *R*, C9 *S*, C13 *S*, C14 *S*, C17 *S*, C58 *R*, C59 *S*, C63 *S*, C64 *S*, C67 *S* to match the known absolute structure of the starting steroid (Reck *et al.*, 1986).

3. Supramolecular features

In the crystal, molecules are linked by weak C—H···O interactions (Table 1). Interestingly, these three bonds all arise from one 'end' of the molecule. Two of these bonds are accepted by the same oxalate O atom and a three-dimensional network arises.

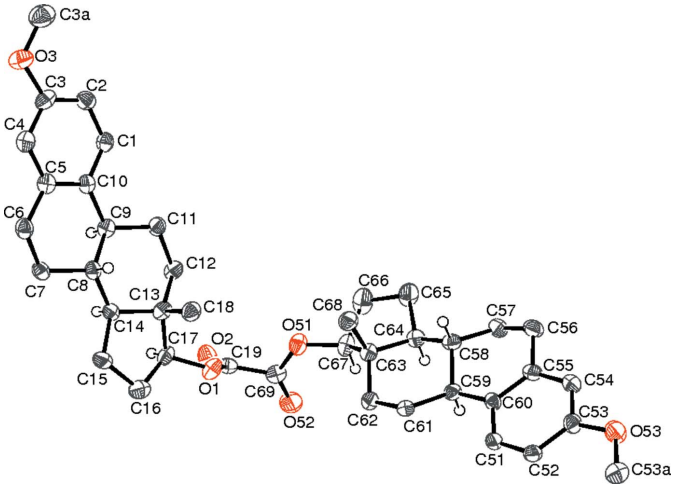


Figure 1
A view of the molecular structure of the title molecule, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. All the H atoms except those bonded to the chiral C atoms have been omitted for clarity.

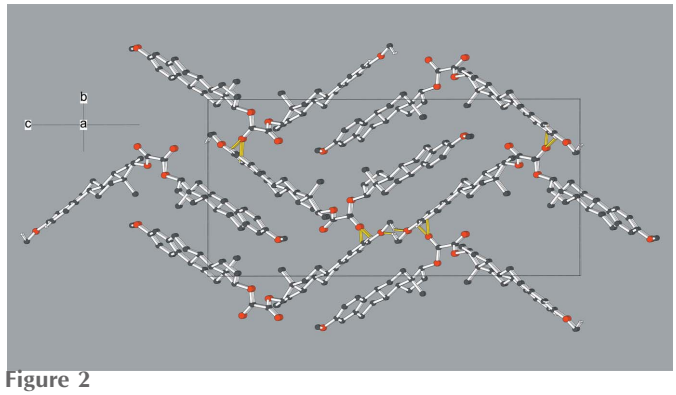


Figure 2
The packing in (I) viewed down [100] with C—H···O hydrogen bonds indicated by yellow lines. All H atoms not involved in such interactions have been omitted for clarity.

4. Database survey

In the closely related dehydroepiandrosterone oxalate diester (Cox *et al.*, 2007), the dihedral angles between the CO_2 planes of the oxalate linkers in the two asymmetric molecules are 24.2 (3) and 51.46 (11)°.

A search of the Cambridge Structural Database (Version 5.31**;** Allen & Motherwell, 2002) revealed four other structures containing an oxalate diester bridge between two fragments connected to the bridge by a secondary carbon atom. In $C_{22}H_{34}O_4$ polymorph-I (Barnes & Weakley, 2004*a*) the dihedral angle between the CO_2 groups in the oxalate fragment is 12.5 (9)° and the bornyl substituents adopt a *syn* orientation. $C_{22}H_{34}O_4$ polymorph-II (Barnes & Weakley, 2004*b*) contains one-and-a-half molecules in the asymmetric unit, with the half-molecule completed by inversion symmetry, hence the oxalate bridge is planar by symmetry; in the complete molecule, the oxalate dihedral angle is 12.2 (5)°. In both molecules, the bornyl substituents are in an anti orientation.

In bis(*cis*-(+)-2-(4-methoxyphenyl)-4-oxo-2,3,4,5-tetrahydro-1,5-benzothiazepin-3-yl) oxalate monohydrate ($C_{34}H_{28}N_2O_8S_2\cdot H_2O$; Kumaradhas *et al.*, 2008), the oxalate dihedral angle is 27.2 (5)° with the substituents in an *anti* disposition. Finally, in bis(di-*t*-butylmethyl)oxalate ($C_{20}H_{38}O_4$; Adiwidjaja & Voss, 1976), the oxalate unit is close to planar [dihedral angle = 5.6 (2)°], but the bulky substituents lie in a *syn* orientation.

5. Synthesis and crystallization

The title compound was prepared by the method of Lotowski & Guzmanski (2005) and recrystallized from dichloromethane/pyridine solution as colourless rods. M.p. 534–535 K; selected ^{1}H NMR δ 0.86 (*s*, 18-Me), 3.74 (*s*, OMe), 4.79 (*m*, 17αH), 6.59 (*d*, 4-H), 6.67 (*dd*, 2-H), 7.16 (*d*, 1-H), ^{13}C NMR δ 12.0, 23.3, 26.2, 27.2, 27.3, 29.7, 36.8, 38.5, 43.3, 43.7, 49.7, 55.2, 85.3, 111.5, 113.8, 126.3,132.3, 137,8, 157.5, 158.2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{40}H_{50}O_6$
M_r	626.80
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	120
a, b, c (Å)	7.8559 (4), 14.1579 (10), 29.888 (2)
V (Å^3)	3324.2 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.25 × 0.08 × 0.06
Data collection	
Diffractometer	Nonius KappaCCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21809, 3674, 2220
R_{int}	0.169
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.075, 0.128, 1.02
No. of reflections	3674
No. of parameters	420
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.31

Computer programs: *COLLECT* (Nonius, 1998), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SORTAV* (Blessing, 1995), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *ORTEP-3 for Windows* (Farrugia, 2012).

6. Refinement

The crystal quality was only fair, which may correlate with the rather high R_{int} value. The H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and refined as riding atoms with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. Experimental details are given in Table 2.

Acknowledgements

We thank the EPSRC National Crystallography Service (University of Southampton) for the data collection.

References

Adiwidjaja, G. & Voss, J. (1976). *Chem. Ber.* **109**, 761–768.
Allen, F. H. & Motherwell, W. D. S. (2002). *Acta Cryst.* B**58**, 407–422.
Barnes, J. C. & Weakley, T. J. R. (2004*a*). Private communication (refcode FOGGUE). CCDC, Cambridge, England.
Barnes, J. C. & Weakley, T. J. R. (2004*b*). Private communication (refcode LAKGIO). CCDC, Cambridge, England.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Brown, R. F. C. (1980). *Pyrolytic Methods in Organic Chemistry*, pp. 85–89. New York: Academic Press.
Cox, P. J., Nahar, L., Sarker, S. D. & Turner, A. B. (2007). *Acta Cryst.* E**63**, o3222.
Dinnebier, R. E., Vensky, S., Panthöfer, M. & Jansen, M. (2003). *Inorg. Chem.* **42**, 1499–1507.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Kumaradhas, P., Stephen, A. D., Nirmala, K. A. & Kalyanam, N. (2008). *X-Ray Struct. Anal. Online*, **24**, x113–x114.
Lotowski, L. & Guzmanski, D. (2005). *Monatsh. Chem.* **136**, 153–158.
Nahar, L. (2007). PhD thesis, University of Aberdeen, Scotland.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter, Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Reck, G., Schubert, G. & Bannier, G. (1986). *Cryst. Res. Technol.* **21**, 1313–1319.
Schönnecker, B., Lange, C., Kötteritzsch, M., Günther, W., Weston, J., Anders, E. & Görls, H. (2000). *J. Org. Chem.* **65**, 5487–5497.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2014). E**70**, 62-64 [doi:10.1107/S1600536814009349]

Crystal structure of bis[3-methoxy-17β-estra-1,3,5(10)-trien-17-yl] oxalate

William T. A. Harrison, Lutfun Nahar and Alan B. Turner

Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Bis[3-methoxy-17β-estra-1,3,5(10)-trien-17-yl] oxalate

Crystal data

$C_{40}H_{50}O_6$
M_r = 626.80
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 7.8559 (4) Å
b = 14.1579 (10) Å
c = 29.888 (2) Å
V = 3324.2 (4) Å^3
Z = 4
$F(000)$ = 1352
D_x = 1.252 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4069 reflections
θ = 1.0–27.5°
μ = 0.08 mm^{-1}
T = 120 K
Rod, colourless
0.25 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
21809 measured reflections
3674 independent reflections
2220 reflections with $I > 2\sigma(I)$
R_{int} = 0.169
θ_{max} = 26.0°, θ_{min} = 2.9°
h = −9→8
k = −17→17
l = −35→36

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.075
$wR(F^2)$ = 0.128
S = 1.02
3674 reflections
420 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0132 (14)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1936 (5)	0.1231 (3)	1.09702 (12)	0.0288 (10)
H1	0.1244	0.0772	1.0826	0.035*
C2	0.1253 (6)	0.1738 (3)	1.13226 (13)	0.0320 (11)
H2	0.0108	0.1639	1.1413	0.038*
C3	0.2256 (6)	0.2390 (3)	1.15401 (13)	0.0317 (11)
C3A	0.0043 (6)	0.2884 (3)	1.20355 (15)	0.0525 (14)
H3A	−0.0151	0.3322	1.2285	0.079*
H3B	−0.0228	0.2240	1.2131	0.079*
H3C	−0.0687	0.3060	1.1783	0.079*
C4	0.3910 (6)	0.2540 (3)	1.13966 (13)	0.0308 (11)
H4	0.4600	0.2991	1.1547	0.037*
C5	0.4578 (5)	0.2042 (3)	1.10366 (12)	0.0283 (10)
C6	0.6359 (5)	0.2281 (3)	1.08821 (13)	0.0316 (11)
H6A	0.7095	0.2364	1.1148	0.038*
H6B	0.6328	0.2891	1.0720	0.038*
C7	0.7154 (5)	0.1538 (3)	1.05784 (12)	0.0284 (10)
H7A	0.8183	0.1802	1.0434	0.034*
H7B	0.7503	0.0985	1.0759	0.034*
C8	0.5891 (5)	0.1231 (3)	1.02223 (12)	0.0268 (10)
H8	0.5479	0.1803	1.0059	0.032*
C9	0.4351 (5)	0.0748 (3)	1.04514 (12)	0.0275 (10)
H9	0.4824	0.0180	1.0607	0.033*
C10	0.3587 (5)	0.1362 (3)	1.08178 (13)	0.0259 (10)
C11	0.3043 (5)	0.0365 (3)	1.01134 (13)	0.0323 (10)
H11A	0.2483	0.0902	0.9961	0.039*
H11B	0.2157	0.0006	1.0276	0.039*
C12	0.3877 (5)	−0.0279 (3)	0.97611 (13)	0.0315 (11)
H12A	0.4284	−0.0865	0.9908	0.038*
H12B	0.3019	−0.0458	0.9534	0.038*
C13	0.5359 (6)	0.0206 (3)	0.95328 (12)	0.0276 (10)
C14	0.6641 (5)	0.0544 (3)	0.98867 (12)	0.0253 (10)
H14	0.6981	−0.0029	1.0061	0.030*
C15	0.8217 (5)	0.0831 (3)	0.96073 (13)	0.0347 (11)
H15A	0.9277	0.0744	0.9782	0.042*
H15B	0.8138	0.1499	0.9512	0.042*

C16	0.8178 (6)	0.0159 (3)	0.91974 (14)	0.0381 (12)
H16A	0.8119	0.0521	0.8915	0.046*
H16B	0.9200	−0.0250	0.9191	0.046*
C17	0.6567 (6)	−0.0427 (3)	0.92658 (12)	0.0313 (11)
H17	0.6848	−0.1001	0.9447	0.038*
C18	0.4706 (6)	0.1014 (3)	0.92326 (13)	0.0335 (11)
H18A	0.5671	0.1314	0.9081	0.050*
H18B	0.4114	0.1483	0.9417	0.050*
H18C	0.3918	0.0758	0.9009	0.050*
C51	0.1276 (5)	0.1300 (3)	0.61705 (12)	0.0272 (10)
H51	0.2452	0.1250	0.6241	0.033*
C52	0.0804 (5)	0.1861 (3)	0.58125 (13)	0.0276 (10)
H52	0.1635	0.2193	0.5643	0.033*
C53	−0.0910 (6)	0.1929 (3)	0.57065 (13)	0.0292 (10)
C53A	−0.0362 (6)	0.3019 (3)	0.51109 (13)	0.0377 (11)
H53A	−0.0958	0.3338	0.4866	0.057*
H53B	0.0542	0.2618	0.4988	0.057*
H53C	0.0137	0.3491	0.5311	0.057*
C54	−0.2088 (6)	0.1447 (3)	0.59550 (13)	0.0323 (10)
H54	−0.3258	0.1494	0.5878	0.039*
C55	−0.1614 (5)	0.0891 (3)	0.63183 (13)	0.0283 (10)
C56	−0.2988 (5)	0.0420 (3)	0.65920 (14)	0.0340 (11)
H56A	−0.3869	0.0169	0.6387	0.041*
H56B	−0.3536	0.0900	0.6785	0.041*
C57	−0.2337 (5)	−0.0382 (3)	0.68852 (14)	0.0332 (11)
H57A	−0.3233	−0.0571	0.7101	0.040*
H57B	−0.2064	−0.0937	0.6696	0.040*
C58	−0.0757 (5)	−0.0071 (3)	0.71376 (13)	0.0287 (10)
H58	−0.1030	0.0519	0.7307	0.034*
C59	0.0704 (5)	0.0145 (3)	0.68065 (12)	0.0269 (10)
H59	0.0982	−0.0469	0.6658	0.032*
C60	0.0123 (5)	0.0806 (3)	0.64322 (12)	0.0248 (10)
C61	0.2325 (5)	0.0455 (3)	0.70446 (12)	0.0304 (10)
H61A	0.2123	0.1068	0.7195	0.037*
H61B	0.3241	0.0546	0.6821	0.037*
C62	0.2897 (6)	−0.0270 (3)	0.73903 (13)	0.0328 (10)
H62A	0.3248	−0.0856	0.7235	0.039*
H62B	0.3898	−0.0022	0.7553	0.039*
C63	0.1492 (5)	−0.0500 (3)	0.77237 (12)	0.0286 (10)
C64	−0.0115 (5)	−0.0810 (3)	0.74658 (13)	0.0303 (10)
H64	0.0239	−0.1363	0.7280	0.036*
C65	−0.1299 (6)	−0.1210 (3)	0.78286 (13)	0.0441 (13)
H65A	−0.2075	−0.1694	0.7703	0.053*
H65B	−0.1984	−0.0703	0.7969	0.053*
C66	−0.0042 (6)	−0.1654 (3)	0.81707 (16)	0.0505 (14)
H66A	−0.0224	−0.1386	0.8473	0.061*
H66B	−0.0191	−0.2347	0.8185	0.061*
C67	0.1733 (6)	−0.1400 (3)	0.79949 (13)	0.0376 (12)

H67	0.2157	−0.1917	0.7795	0.045*
C68	0.1171 (6)	0.0345 (3)	0.80322 (13)	0.0346 (11)
H68A	0.0937	0.0908	0.7851	0.052*
H68B	0.2180	0.0457	0.8218	0.052*
H68C	0.0191	0.0212	0.8225	0.052*
C19	0.5300 (5)	−0.1607 (3)	0.88064 (14)	0.0311 (11)
C69	0.4324 (6)	−0.1782 (3)	0.83780 (14)	0.0327 (11)
O1	0.5808 (4)	−0.07180 (19)	0.88412 (8)	0.0351 (8)
O2	0.5552 (4)	−0.2225 (2)	0.90715 (10)	0.0454 (9)
O3	0.1760 (4)	0.2930 (2)	1.19035 (9)	0.0447 (9)
O51	0.2916 (4)	−0.12707 (19)	0.83696 (9)	0.0375 (8)
O52	0.4778 (4)	−0.2347 (2)	0.81047 (10)	0.0546 (10)
O53	−0.1536 (4)	0.2451 (2)	0.53540 (9)	0.0406 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.032 (3)	0.026 (2)	0.028 (2)	−0.003 (2)	−0.003 (2)	0.0007 (18)
C2	0.030 (3)	0.035 (2)	0.031 (2)	0.000 (2)	0.002 (2)	0.005 (2)
C3	0.046 (3)	0.026 (2)	0.023 (2)	0.009 (2)	0.001 (2)	0.0015 (18)
C3A	0.061 (4)	0.051 (3)	0.046 (3)	0.017 (3)	0.004 (3)	−0.003 (2)
C4	0.037 (3)	0.023 (2)	0.032 (2)	−0.002 (2)	−0.004 (2)	0.0001 (19)
C5	0.034 (3)	0.022 (2)	0.029 (2)	−0.001 (2)	−0.003 (2)	0.0044 (18)
C6	0.032 (3)	0.031 (3)	0.032 (2)	−0.008 (2)	−0.004 (2)	0.0015 (19)
C7	0.024 (3)	0.028 (2)	0.033 (2)	−0.004 (2)	−0.001 (2)	0.0029 (18)
C8	0.026 (3)	0.027 (2)	0.027 (2)	−0.004 (2)	−0.0035 (19)	0.0018 (18)
C9	0.033 (3)	0.023 (2)	0.027 (2)	−0.003 (2)	−0.001 (2)	0.0030 (17)
C10	0.029 (3)	0.022 (2)	0.026 (2)	−0.002 (2)	−0.003 (2)	0.0055 (18)
C11	0.031 (3)	0.037 (2)	0.028 (2)	−0.011 (2)	0.000 (2)	−0.0013 (19)
C12	0.039 (3)	0.027 (2)	0.028 (2)	−0.008 (2)	0.003 (2)	−0.0022 (18)
C13	0.037 (3)	0.022 (2)	0.025 (2)	−0.002 (2)	0.002 (2)	0.0045 (17)
C14	0.024 (3)	0.027 (2)	0.025 (2)	0.0007 (19)	−0.0010 (19)	0.0077 (17)
C15	0.025 (3)	0.041 (3)	0.037 (2)	−0.005 (2)	0.005 (2)	−0.003 (2)
C16	0.040 (3)	0.040 (3)	0.035 (2)	0.005 (2)	0.006 (2)	0.003 (2)
C17	0.042 (3)	0.032 (2)	0.020 (2)	0.006 (2)	−0.003 (2)	0.0003 (18)
C18	0.037 (3)	0.034 (3)	0.029 (2)	0.005 (2)	−0.001 (2)	0.0014 (19)
C51	0.023 (2)	0.032 (2)	0.026 (2)	0.001 (2)	−0.001 (2)	−0.0046 (19)
C52	0.025 (3)	0.032 (2)	0.026 (2)	−0.001 (2)	0.003 (2)	−0.0046 (19)
C53	0.030 (3)	0.029 (2)	0.029 (2)	0.005 (2)	−0.003 (2)	0.0032 (19)
C53A	0.041 (3)	0.036 (3)	0.035 (2)	0.001 (2)	0.004 (2)	0.001 (2)
C54	0.024 (3)	0.040 (3)	0.033 (2)	0.001 (2)	0.000 (2)	0.002 (2)
C55	0.025 (3)	0.029 (2)	0.031 (2)	0.002 (2)	0.004 (2)	−0.0032 (18)
C56	0.026 (3)	0.038 (3)	0.038 (2)	0.004 (2)	0.003 (2)	−0.004 (2)
C57	0.026 (3)	0.037 (3)	0.037 (2)	−0.006 (2)	0.000 (2)	0.000 (2)
C58	0.028 (3)	0.028 (2)	0.030 (2)	−0.001 (2)	0.005 (2)	−0.0043 (18)
C59	0.028 (3)	0.029 (2)	0.024 (2)	−0.001 (2)	0.0016 (19)	−0.0042 (17)
C60	0.022 (3)	0.024 (2)	0.028 (2)	0.000 (2)	−0.003 (2)	−0.0050 (18)
C61	0.025 (3)	0.043 (3)	0.024 (2)	−0.001 (2)	0.003 (2)	0.0011 (19)

C62	0.031 (3)	0.040 (3)	0.027 (2)	0.004 (2)	−0.002 (2)	−0.0039 (19)
C63	0.031 (3)	0.026 (2)	0.028 (2)	0.001 (2)	−0.001 (2)	−0.0004 (18)
C64	0.031 (3)	0.029 (2)	0.031 (2)	−0.001 (2)	0.001 (2)	−0.0008 (18)
C65	0.047 (3)	0.048 (3)	0.037 (3)	−0.015 (2)	−0.003 (2)	0.013 (2)
C66	0.057 (4)	0.049 (3)	0.046 (3)	−0.021 (3)	−0.011 (3)	0.012 (2)
C67	0.046 (3)	0.037 (3)	0.030 (2)	0.000 (2)	−0.009 (2)	−0.001 (2)
C68	0.035 (3)	0.035 (3)	0.033 (2)	−0.001 (2)	0.001 (2)	−0.0058 (19)
C19	0.028 (3)	0.031 (3)	0.034 (2)	0.004 (2)	0.006 (2)	−0.001 (2)
C69	0.039 (3)	0.026 (2)	0.034 (2)	0.000 (2)	0.005 (2)	0.002 (2)
O1	0.052 (2)	0.0255 (16)	0.0274 (15)	−0.0023 (15)	−0.0004 (15)	−0.0002 (12)
O2	0.045 (2)	0.0339 (19)	0.058 (2)	−0.0012 (16)	−0.0153 (18)	0.0103 (16)
O3	0.047 (2)	0.046 (2)	0.0405 (18)	0.0055 (17)	0.0089 (17)	−0.0084 (15)
O51	0.046 (2)	0.0330 (17)	0.0334 (16)	0.0086 (17)	−0.0078 (16)	−0.0033 (14)
O52	0.048 (2)	0.062 (2)	0.054 (2)	0.0107 (19)	0.0021 (18)	−0.0253 (18)
O53	0.0330 (19)	0.0466 (19)	0.0421 (17)	−0.0020 (15)	−0.0014 (16)	0.0135 (15)

Geometric parameters (Å, º)

C1—C2	1.383 (5)	C52—C53	1.387 (6)
C1—C10	1.387 (5)	C52—H52	0.9500
C1—H1	0.9500	C53—C54	1.369 (5)
C2—C3	1.376 (6)	C53—O53	1.378 (4)
C2—H2	0.9500	C53A—O53	1.423 (5)
C3—O3	1.384 (5)	C53A—H53A	0.9800
C3—C4	1.385 (6)	C53A—H53B	0.9800
C3A—O3	1.407 (5)	C53A—H53C	0.9800
C3A—H3A	0.9800	C54—C55	1.392 (5)
C3A—H3B	0.9800	C54—H54	0.9500
C3A—H3C	0.9800	C55—C60	1.412 (5)
C4—C5	1.390 (5)	C55—C56	1.509 (6)
C4—H4	0.9500	C56—C57	1.523 (5)
C5—C10	1.400 (5)	C56—H56A	0.9900
C5—C6	1.512 (6)	C56—H56B	0.9900
C6—C7	1.523 (5)	C57—C58	1.518 (5)
C6—H6A	0.9900	C57—H57A	0.9900
C6—H6B	0.9900	C57—H57B	0.9900
C7—C8	1.519 (5)	C58—C64	1.521 (5)
C7—H7A	0.9900	C58—C59	1.546 (6)
C7—H7B	0.9900	C58—H58	1.0000
C8—C14	1.516 (5)	C59—C61	1.524 (5)
C8—C9	1.549 (5)	C59—C60	1.528 (5)
C8—H8	1.0000	C59—H59	1.0000
C9—C10	1.523 (5)	C61—C62	1.524 (5)
C9—C11	1.539 (5)	C61—H61A	0.9900
C9—H9	1.0000	C61—H61B	0.9900
C11—C12	1.540 (5)	C62—C63	1.522 (5)
C11—H11A	0.9900	C62—H62A	0.9900
C11—H11B	0.9900	C62—H62B	0.9900

C12—C13	1.514 (5)	C63—C67	1.523 (5)
C12—H12A	0.9900	C63—C68	1.531 (5)
C12—H12B	0.9900	C63—C64	1.544 (6)
C13—C17	1.530 (5)	C64—C65	1.537 (6)
C13—C14	1.537 (5)	C64—H64	1.0000
C13—C18	1.542 (5)	C65—C66	1.554 (6)
C14—C15	1.547 (5)	C65—H65A	0.9900
C14—H14	1.0000	C65—H65B	0.9900
C15—C16	1.552 (5)	C66—C67	1.533 (6)
C15—H15A	0.9900	C66—H66A	0.9900
C15—H15B	0.9900	C66—H66B	0.9900
C16—C17	1.527 (6)	C67—O51	1.467 (5)
C16—H16A	0.9900	C67—H67	1.0000
C16—H16B	0.9900	C68—H68A	0.9800
C17—O1	1.461 (4)	C68—H68B	0.9800
C17—H17	1.0000	C68—H68C	0.9800
C18—H18A	0.9800	C19—O2	1.197 (5)
C18—H18B	0.9800	C19—O1	1.325 (5)
C18—H18C	0.9800	C19—C69	1.513 (6)
C51—C52	1.383 (5)	C69—O52	1.198 (5)
C51—C60	1.386 (5)	C69—O51	1.322 (5)
C51—H51	0.9500		

C2—C1—C10	122.9 (4)	C53—C52—H52	120.8
C2—C1—H1	118.6	C54—C53—O53	116.2 (4)
C10—C1—H1	118.6	C54—C53—C52	119.9 (4)
C3—C2—C1	119.1 (4)	O53—C53—C52	123.9 (4)
C3—C2—H2	120.5	O53—C53A—H53A	109.5
C1—C2—H2	120.5	O53—C53A—H53B	109.5
C2—C3—O3	125.5 (4)	H53A—C53A—H53B	109.5
C2—C3—C4	119.6 (4)	O53—C53A—H53C	109.5
O3—C3—C4	115.0 (4)	H53A—C53A—H53C	109.5
O3—C3A—H3A	109.5	H53B—C53A—H53C	109.5
O3—C3A—H3B	109.5	C53—C54—C55	121.6 (4)
H3A—C3A—H3B	109.5	C53—C54—H54	119.2
O3—C3A—H3C	109.5	C55—C54—H54	119.2
H3A—C3A—H3C	109.5	C54—C55—C60	119.6 (4)
H3B—C3A—H3C	109.5	C54—C55—C56	118.8 (4)
C3—C4—C5	121.1 (4)	C60—C55—C56	121.5 (4)
C3—C4—H4	119.5	C55—C56—C57	113.6 (3)
C5—C4—H4	119.5	C55—C56—H56A	108.8
C4—C5—C10	120.1 (4)	C57—C56—H56A	108.8
C4—C5—C6	118.2 (4)	C55—C56—H56B	108.8
C10—C5—C6	121.7 (4)	C57—C56—H56B	108.8
C5—C6—C7	114.0 (3)	H56A—C56—H56B	107.7
C5—C6—H6A	108.7	C58—C57—C56	110.1 (3)
C7—C6—H6A	108.7	C58—C57—H57A	109.6
C5—C6—H6B	108.7	C56—C57—H57A	109.6

C7—C6—H6B	108.7	C58—C57—H57B	109.6
H6A—C6—H6B	107.6	C56—C57—H57B	109.6
C8—C7—C6	110.3 (3)	H57A—C57—H57B	108.2
C8—C7—H7A	109.6	C57—C58—C64	113.0 (3)
C6—C7—H7A	109.6	C57—C58—C59	110.3 (3)
C8—C7—H7B	109.6	C64—C58—C59	107.6 (3)
C6—C7—H7B	109.6	C57—C58—H58	108.6
H7A—C7—H7B	108.1	C64—C58—H58	108.6
C14—C8—C7	113.2 (3)	C59—C58—H58	108.6
C14—C8—C9	108.2 (3)	C61—C59—C60	114.5 (3)
C7—C8—C9	109.1 (3)	C61—C59—C58	112.2 (3)
C14—C8—H8	108.8	C60—C59—C58	111.6 (3)
C7—C8—H8	108.8	C61—C59—H59	105.9
C9—C8—H8	108.8	C60—C59—H59	105.9
C10—C9—C11	114.2 (3)	C58—C59—H59	105.9
C10—C9—C8	111.9 (3)	C51—C60—C55	116.9 (4)
C11—C9—C8	112.7 (3)	C51—C60—C59	121.8 (4)
C10—C9—H9	105.7	C55—C60—C59	121.1 (4)
C11—C9—H9	105.7	C59—C61—C62	111.7 (3)
C8—C9—H9	105.7	C59—C61—H61A	109.3
C1—C10—C5	117.3 (4)	C62—C61—H61A	109.3
C1—C10—C9	121.9 (4)	C59—C61—H61B	109.3
C5—C10—C9	120.6 (4)	C62—C61—H61B	109.3
C9—C11—C12	111.9 (3)	H61A—C61—H61B	107.9
C9—C11—H11A	109.2	C63—C62—C61	111.9 (3)
C12—C11—H11A	109.2	C63—C62—H62A	109.2
C9—C11—H11B	109.2	C61—C62—H62A	109.2
C12—C11—H11B	109.2	C63—C62—H62B	109.2
H11A—C11—H11B	107.9	C61—C62—H62B	109.2
C13—C12—C11	111.5 (3)	H62A—C62—H62B	107.9
C13—C12—H12A	109.3	C62—C63—C67	115.9 (3)
C11—C12—H12A	109.3	C62—C63—C68	110.3 (3)
C13—C12—H12B	109.3	C67—C63—C68	110.8 (3)
C11—C12—H12B	109.3	C62—C63—C64	109.1 (3)
H12A—C12—H12B	108.0	C67—C63—C64	97.4 (3)
C12—C13—C17	116.5 (3)	C68—C63—C64	112.9 (3)
C12—C13—C14	109.6 (3)	C58—C64—C65	120.5 (4)
C17—C13—C14	97.8 (3)	C58—C64—C63	113.4 (3)
C12—C13—C18	110.1 (4)	C65—C64—C63	104.3 (3)
C17—C13—C18	109.7 (3)	C58—C64—H64	105.8
C14—C13—C18	112.8 (3)	C65—C64—H64	105.8
C8—C14—C13	113.6 (3)	C63—C64—H64	105.8
C8—C14—C15	120.0 (3)	C64—C65—C66	103.2 (4)
C13—C14—C15	103.6 (3)	C64—C65—H65A	111.1
C8—C14—H14	106.2	C66—C65—H65A	111.1
C13—C14—H14	106.2	C64—C65—H65B	111.1
C15—C14—H14	106.2	C66—C65—H65B	111.1
C14—C15—C16	104.4 (3)	H65A—C65—H65B	109.1

C14—C15—H15A	110.9	C67—C66—C65	105.0 (3)
C16—C15—H15A	110.9	C67—C66—H66A	110.8
C14—C15—H15B	110.9	C65—C66—H66A	110.8
C16—C15—H15B	110.9	C67—C66—H66B	110.8
H15A—C15—H15B	108.9	C65—C66—H66B	110.8
C17—C16—C15	104.1 (3)	H66A—C66—H66B	108.8
C17—C16—H16A	110.9	O51—C67—C63	112.4 (3)
C15—C16—H16A	110.9	O51—C67—C66	110.1 (3)
C17—C16—H16B	110.9	C63—C67—C66	105.4 (4)
C15—C16—H16B	110.9	O51—C67—H67	109.6
H16A—C16—H16B	109.0	C63—C67—H67	109.6
O1—C17—C16	112.0 (3)	C66—C67—H67	109.6
O1—C17—C13	111.4 (3)	C63—C68—H68A	109.5
C16—C17—C13	105.4 (3)	C63—C68—H68B	109.5
O1—C17—H17	109.3	H68A—C68—H68B	109.5
C16—C17—H17	109.3	C63—C68—H68C	109.5
C13—C17—H17	109.3	H68A—C68—H68C	109.5
C13—C18—H18A	109.5	H68B—C68—H68C	109.5
C13—C18—H18B	109.5	O2—C19—O1	126.4 (4)
H18A—C18—H18B	109.5	O2—C19—C69	121.7 (4)
C13—C18—H18C	109.5	O1—C19—C69	112.0 (3)
H18A—C18—H18C	109.5	O52—C69—O51	127.0 (4)
H18B—C18—H18C	109.5	O52—C69—C19	122.4 (4)
C52—C51—C60	123.4 (4)	O51—C69—C19	110.5 (4)
C52—C51—H51	118.3	C19—O1—C17	117.3 (3)
C60—C51—H51	118.3	C3—O3—C3A	117.7 (4)
C51—C52—C53	118.5 (4)	C69—O51—C67	118.4 (3)
C51—C52—H52	120.8	C53—O53—C53A	117.5 (3)

C10—C1—C2—C3	−1.5 (6)	C60—C55—C56—C57	−19.4 (5)
C1—C2—C3—O3	−178.3 (3)	C55—C56—C57—C58	47.5 (4)
C1—C2—C3—C4	1.4 (6)	C56—C57—C58—C64	175.4 (3)
C2—C3—C4—C5	−0.1 (6)	C56—C57—C58—C59	−64.0 (4)
O3—C3—C4—C5	179.7 (3)	C57—C58—C59—C61	−179.6 (3)
C3—C4—C5—C10	−1.2 (6)	C64—C58—C59—C61	−55.9 (4)
C3—C4—C5—C6	176.7 (4)	C57—C58—C59—C60	50.3 (4)
C4—C5—C6—C7	164.2 (3)	C64—C58—C59—C60	174.0 (3)
C10—C5—C6—C7	−18.0 (5)	C52—C51—C60—C55	0.3 (6)
C5—C6—C7—C8	45.8 (4)	C52—C51—C60—C59	176.1 (3)
C6—C7—C8—C14	175.7 (3)	C54—C55—C60—C51	0.4 (6)
C6—C7—C8—C9	−63.7 (4)	C56—C55—C60—C51	−177.3 (4)
C14—C8—C9—C10	176.1 (3)	C54—C55—C60—C59	−175.4 (3)
C7—C8—C9—C10	52.6 (4)	C56—C55—C60—C59	6.9 (6)
C14—C8—C9—C11	−53.5 (4)	C61—C59—C60—C51	33.3 (5)
C7—C8—C9—C11	−177.0 (3)	C58—C59—C60—C51	162.2 (3)
C2—C1—C10—C5	0.1 (6)	C61—C59—C60—C55	−151.1 (4)
C2—C1—C10—C9	175.6 (4)	C58—C59—C60—C55	−22.2 (5)
C4—C5—C10—C1	1.2 (5)	C60—C59—C61—C62	−176.0 (3)

C6—C5—C10—C1	−176.6 (4)	C58—C59—C61—C62	55.5 (4)
C4—C5—C10—C9	−174.3 (3)	C59—C61—C62—C63	−54.6 (4)
C6—C5—C10—C9	7.9 (5)	C61—C62—C63—C67	163.1 (3)
C11—C9—C10—C1	29.8 (5)	C61—C62—C63—C68	−70.1 (4)
C8—C9—C10—C1	159.4 (3)	C61—C62—C63—C64	54.4 (4)
C11—C9—C10—C5	−154.9 (3)	C57—C58—C64—C65	−55.4 (5)
C8—C9—C10—C5	−25.3 (5)	C59—C58—C64—C65	−177.4 (3)
C10—C9—C11—C12	−178.0 (3)	C57—C58—C64—C63	180.0 (3)
C8—C9—C11—C12	52.8 (4)	C59—C58—C64—C63	57.9 (4)
C9—C11—C12—C13	−53.5 (4)	C62—C63—C64—C58	−58.0 (4)
C11—C12—C13—C17	165.0 (3)	C67—C63—C64—C58	−178.8 (3)
C11—C12—C13—C14	55.3 (4)	C68—C63—C64—C58	64.9 (4)
C11—C12—C13—C18	−69.3 (4)	C62—C63—C64—C65	168.9 (3)
C7—C8—C14—C13	178.3 (3)	C67—C63—C64—C65	48.2 (4)
C9—C8—C14—C13	57.3 (4)	C68—C63—C64—C65	−68.1 (4)
C7—C8—C14—C15	−58.4 (5)	C58—C64—C65—C66	−161.9 (4)
C9—C8—C14—C15	−179.5 (3)	C63—C64—C65—C66	−33.1 (4)
C12—C13—C14—C8	−59.3 (4)	C64—C65—C66—C67	4.5 (4)
C17—C13—C14—C8	178.9 (3)	C62—C63—C67—O51	79.5 (4)
C18—C13—C14—C8	63.7 (4)	C68—C63—C67—O51	−47.2 (5)
C12—C13—C14—C15	168.9 (3)	C64—C63—C67—O51	−165.1 (3)
C17—C13—C14—C15	47.1 (4)	C62—C63—C67—C66	−160.6 (4)
C18—C13—C14—C15	−68.2 (4)	C68—C63—C67—C66	72.8 (4)
C8—C14—C15—C16	−159.1 (3)	C64—C63—C67—C66	−45.2 (4)
C13—C14—C15—C16	−31.1 (4)	C65—C66—C67—O51	147.5 (3)
C14—C15—C16—C17	1.9 (4)	C65—C66—C67—C63	26.2 (4)
C15—C16—C17—O1	149.6 (3)	O2—C19—C69—O52	−59.3 (6)
C15—C16—C17—C13	28.2 (4)	O1—C19—C69—O52	120.6 (4)
C12—C13—C17—O1	75.2 (4)	O2—C19—C69—O51	117.4 (4)
C14—C13—C17—O1	−168.3 (3)	O1—C19—C69—O51	−62.8 (4)
C18—C13—C17—O1	−50.7 (4)	O2—C19—O1—C17	−8.1 (6)
C12—C13—C17—C16	−163.1 (3)	C69—C19—O1—C17	172.1 (3)
C14—C13—C17—C16	−46.6 (3)	C16—C17—O1—C19	135.1 (4)
C18—C13—C17—C16	71.0 (4)	C13—C17—O1—C19	−107.1 (4)
C60—C51—C52—C53	−0.6 (6)	C2—C3—O3—C3A	−6.8 (6)
C51—C52—C53—C54	0.1 (6)	C4—C3—O3—C3A	173.4 (4)
C51—C52—C53—O53	−178.9 (3)	O52—C69—O51—C67	1.1 (6)
O53—C53—C54—C55	179.7 (4)	C19—C69—O51—C67	−175.3 (3)
C52—C53—C54—C55	0.6 (6)	C63—C67—O51—C69	−118.8 (4)
C53—C54—C55—C60	−0.9 (6)	C66—C67—O51—C69	124.1 (4)
C53—C54—C55—C56	176.9 (4)	C54—C53—O53—C53A	175.1 (4)
C54—C55—C56—C57	162.9 (3)	C52—C53—O53—C53A	−5.9 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C52—H52···O2^{i}	0.95	2.51	3.161 (5)	126

C53*A*—H53*B*···O53^{ii}	0.98	2.51	3.378 (6)	147
C54—H54···O2^{iii}	0.95	2.56	3.309 (5)	136

Symmetry codes: (i) $-x+1, y+1/2, -z+3/2$; (ii) $x+1/2, -y+1/2, -z+1$; (iii) $-x, y+1/2, -z+3/2$.