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# Crystal structure of [1,1′:3′,1″-terphenyl]-2′,3,3″-tricarboxylic acid

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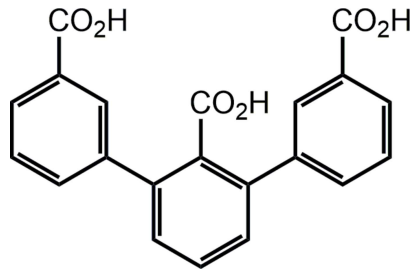
The asymmetric unit of the title compound, $C_{21}H_{14}O_6$, comprises two symmetrically independent molecules that form a locally centrosymmetric hydrogen-bonded dimer, with the planes of the corresponding carboxylic acid groups rotated by 15.8 (1) and 17.5 (1)° relative to those of the adjacent benzene rings. The crystal as a whole, however, exhibits a noncentrosymmetric packing, described by the polar space group $Pca2_1$. The dimers form layers along the *ab* plane, being interconnected by hydrogen bonds involving the remaining carboxylic acid groups. The plane of the central carboxylic acid group forms dihedral angles of 62.5 (1) and 63.0 (1)° with those of the adjacent benzene rings and functions as a hydrogen-bond donor and acceptor. As a donor, it interconnects adjacent layers, while as an acceptor it stabilizes the packing within the layers. The 'distal' carboxylic acid groups are nearly coplanar with the planes of the adjacent benzene rings, forming dihedral angles of 1.8 (1) and 7.1 (1)°. These groups also form intra- and inter-layer hydrogen bonds, but with 'reversed' functionality, as compared with the central carboxylic acid groups.

**Keywords:** crystal structure; hydrogen bonding; meta-terphenyl.

**CCDC reference**: 1418223

## 1. Related literature

For a detailed discussion on local centers of symmetry in the space group $Pca2_1$, see: Marsh *et al.* (1998). For the synthesis of the starting material 3,3″-dimethyl-[1,1′:3′,1″-terphenyl]-2′-carboxylic acid, see: Du *et al.* (1986).




## 2. Experimental

### 2.1. Crystal data

$C_{21}H_{14}O_6$
$M_r$ = 362.32
Orthorhombic, $Pca2_1$
$a$ = 23.1735 (9) Å
$b$ = 7.2480 (2) Å
$c$ = 20.3320 (8) Å
$V$ = 3415.0 (2) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 100 K
0.3 × 0.05 × 0.05 mm

### 2.2. Data collection

Bruker D8 VENTURE DUO diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
$T_{min}$ = 0.695, $T_{max}$ = 0.745
46489 measured reflections
6467 independent reflections
5899 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.028

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.091
$S$ = 1.05
6467 reflections
511 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···O3′$^{i}$ | 0.91 (5) | 1.79 (5) | 2.657 (3) | 159 (4) |
| O4—H4···O1$^{ii}$ | 0.90 (6) | 1.84 (6) | 2.689 (3) | 156 (5) |
| O2′—H2′···O3$^{iii}$ | 0.87 (6) | 1.76 (6) | 2.628 (3) | 171 (5) |
| O4′—H4′···O1′$^{iv}$ | 0.84 (5) | 1.90 (5) | 2.717 (3) | 166 (4) |
| O6′—H6′···O5 | 0.92 (4) | 1.69 (4) | 2.593 (3) | 168 (4) |
| O6—H6···O5′ | 1.01 (3) | 1.58 (3) | 2.581 (3) | 172 (6) |

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

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: LD2133).

## References

Bruker (2012). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Du, C. J. F., Hart, H. & Ng, K. K. D. (1986). *J. Org. Chem.* **51**, 3162–3165.
Marsh, R. E., Schomaker, V. & Herbstein, F. H. (1998). *Acta Cryst.* B**54**, 921–924.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

# supporting information

*Acta Cryst.* (2015). E**71**, o667–o668 [https://doi.org/10.1107/S2056989015015029]

## Crystal structure of [1,1′:3′,1″-terphenyl]-2′,3,3″-tricarboxylic acid

**Daniel A. Decato and Orion B. Berryman**

### S1. Experimental

#### S1.1. Synthesis and crystallization

3,3″-dimethyl-[1,1′:3′,1″-terphenyl]-2′-carboxylic acid (0.432 g, 1.4 mmol) synthesized according to Du *et al.* (1986). The starting material was dissolved in 15 ml pyridine and brought to reflux. $KMnO_4$ (0.50 g, 3.1 mmol) in 1 ml of water was added, and allowed to react for 2 hours. Subsequently, 3 more additions of $KMnO_4$ (0.25 g, 1.6 mmol) in 1.5 ml of water were added every 2 hours for a total of 4 additions. After six hours, 10 ml of water was added and the reaction was refluxed overnight. The reaction mixture was filtered while hot to remove solid $MnO_2$. The filtrate was then concentrated under reduced pressure, and treated by *12M* HCl. The resulting white precipitate was then filtered and purified via silica gel column chromatograph (50/50 hexanes/ethyl acetate with 0.5% acetic acid) to give of the title compound. (0.366 g *Yield 70%*) $^1$H NMR (DMSO, 400 MHz): $\delta$ 7.46 (d, 2H $J$ = 8 Hz), 7.58 (t, 2H, $J$ = 8 Hz), 7.61 (t, 1H, $J$ = 7.2 Hz), 7.68 (d, 2H, $J$ = 8Hz), 7.97 (d, 2H, $J$ = 8 Hz), 8.01 (s, 2H), 13.01 (s, O-H). $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 128.4, 128.7, 129.1, 129.2, 129.3, 130.8, 132.7, 133.9, 138.0, 140.39, 167.0, 169.7. Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of hexane into an ethyl acetate solution of the title compound.

#### S1.2. Refinement

All H atoms were located in difference Fourier maps but finally their positions were determined geometrically, except for the carboxy H atoms that were refined with isotropic thermal parameters. The O6—H6 bond length in the carboxylic acid dimer was restrained at the distance from the corresponding residual electron density peak to the oxygen (0.996 (2)Å) . This was done due to unreasonable lengthening (> 1.4 Å) of the H—O bond during the refinement. All other H atoms were refined using a riding model with fixed isotropic displacement parameters [Uiso(H) = 1.2Ueq(C) for the C(H) groups]. Additional crystal data, data collection and structure refinement details are summarized in Table 1.

## S2. Results and discussion

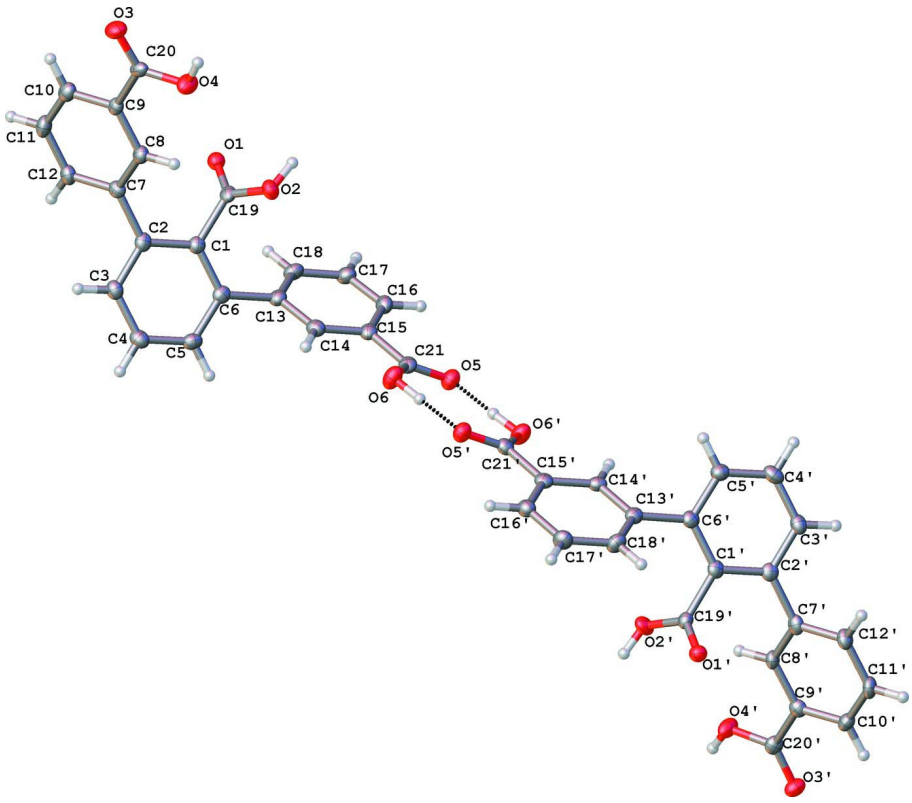


**Figure 1**

The asymmetric unit of the title compound, with displacement elipsoids drawn at 50% probability level. Hydrogen atoms presented by spheres of an arbitrary radius. Intra-dimer hydrogen bonds are represented by dotted lines.

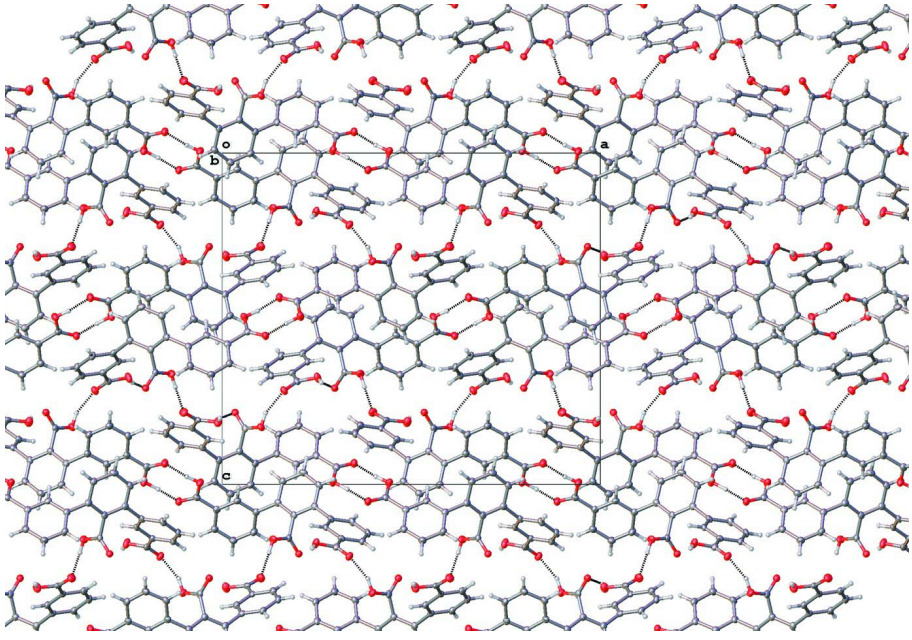

**Figure 2**

Packing view along *b* axis. Hydrogen bonds are represented by dotted lines.

**[1,1′:3′,1″-Terphenyl]-2′,3,3″-tricarboxylic acid**

*Crystal data*

$C_{21}H_{14}O_6$
$M_r$ = 362.32
Orthorhombic, $Pca2_1$
$a$ = 23.1735 (9) Å
$b$ = 7.2480 (2) Å
$c$ = 20.3320 (8) Å
$V$ = 3415.0 (2) Å$^3$
$Z$ = 8
$F(000)$ = 1504
$D_x$ = 1.409 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9141 reflections
$\theta$ = 3.1–25.7°
$\mu$ = 0.10 mm$^{-1}$
$T$ = 100 K
Needle, clear
0.3 × 0.05 × 0.05 mm

*Data collection*

Bruker D8 VENTURE DUO diffractometer
Radiation source: sealed tube, fine-focus
TRIUMPH graphite monochromator
Detector resolution: 10.5 pixels mm$^{-1}$
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
$T_{min}$ = 0.695, $T_{max}$ = 0.745
46489 measured reflections
6467 independent reflections
5899 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.028
$\theta_{max}$ = 25.7°, $\theta_{min}$ = 3.0°
$h$ = −28→28
$k$ = −7→8
$l$ = −24→24

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.091
$S$ = 1.05
6467 reflections
511 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 1.0855P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

*Special details*

**Experimental**. SADABS-2012/1 (Bruker,2012) was used for absorption correction. wR2(int) was 0.0509 before and 0.0455 after correction. The Ratio of minimum to maximum transmission is 0.9326. The $\lambda/2$ correction factor is 0.0015.

**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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.96578 (9) | 0.7615 (3) | 0.28358 (11) | 0.0228 (5) |
| O2 | 0.89715 (9) | 0.5814 (3) | 0.32756 (11) | 0.0244 (5) |
| H2 | 0.8852 (17) | 0.572 (5) | 0.285 (2) | 0.042 (11)* |

| | | | | |
|---|---|---|---|---|
| O3 | 1.10167 (9) | 0.0388 (3) | 0.28278 (11) | 0.0303 (5) |
| O4 | 1.01069 (10) | 0.0942 (3) | 0.31188 (12) | 0.0306 (5) |
| H4 | 1.006 (2) | −0.025 (8) | 0.301 (3) | 0.085 (18)* |
| O5 | 0.65152 (9) | 0.9096 (3) | 0.43665 (11) | 0.0258 (5) |
| O6 | 0.70682 (9) | 0.7133 (3) | 0.49305 (12) | 0.0285 (5) |
| C1 | 0.95397 (12) | 0.7560 (4) | 0.40061 (15) | 0.0188 (6) |
| C2 | 1.00836 (13) | 0.7148 (4) | 0.42736 (15) | 0.0200 (6) |
| C3 | 1.02024 (14) | 0.7721 (4) | 0.49135 (16) | 0.0214 (7) |
| H3 | 1.0572 | 0.7495 | 0.5098 | 0.026* |
| C4 | 0.97881 (14) | 0.8613 (4) | 0.52817 (16) | 0.0235 (7) |
| H4A | 0.9872 | 0.8968 | 0.5721 | 0.028* |
| C5 | 0.92531 (13) | 0.8995 (4) | 0.50187 (15) | 0.0228 (7) |
| H5 | 0.8969 | 0.9586 | 0.5282 | 0.027* |
| C6 | 0.91246 (13) | 0.8522 (4) | 0.43706 (15) | 0.0197 (6) |
| C7 | 1.05206 (13) | 0.6053 (4) | 0.38977 (15) | 0.0188 (6) |
| C8 | 1.03776 (13) | 0.4318 (4) | 0.36459 (15) | 0.0201 (7) |
| H8 | 0.9999 | 0.3841 | 0.3704 | 0.024* |
| C9 | 1.07890 (13) | 0.3293 (4) | 0.33113 (14) | 0.0178 (6) |
| C10 | 1.13447 (14) | 0.3978 (4) | 0.32208 (16) | 0.0239 (7) |
| H10 | 1.1625 | 0.3272 | 0.2991 | 0.029* |
| C11 | 1.14841 (13) | 0.5694 (4) | 0.34687 (16) | 0.0251 (7) |
| H11 | 1.1861 | 0.6178 | 0.3404 | 0.030* |
| C12 | 1.10790 (13) | 0.6712 (4) | 0.38102 (15) | 0.0221 (6) |
| H12 | 1.1183 | 0.7878 | 0.3988 | 0.026* |
| C13 | 0.85570 (13) | 0.9045 (4) | 0.40774 (15) | 0.0203 (6) |
| C14 | 0.80514 (13) | 0.8518 (4) | 0.43914 (15) | 0.0212 (7) |
| H14 | 0.8072 | 0.7839 | 0.4790 | 0.025* |
| C15 | 0.75168 (13) | 0.8969 (4) | 0.41302 (16) | 0.0205 (6) |
| C16 | 0.74787 (13) | 0.9963 (4) | 0.35433 (16) | 0.0226 (7) |
| H16 | 0.7113 | 1.0245 | 0.3357 | 0.027* |
| C17 | 0.79797 (13) | 1.0528 (4) | 0.32379 (16) | 0.0243 (7) |
| H17 | 0.7959 | 1.1237 | 0.2846 | 0.029* |
| C18 | 0.85140 (13) | 1.0069 (4) | 0.34989 (16) | 0.0233 (7) |
| H18 | 0.8855 | 1.0459 | 0.3280 | 0.028* |
| C19 | 0.94049 (13) | 0.7010 (4) | 0.33133 (15) | 0.0199 (6) |
| C20 | 1.06555 (13) | 0.1399 (4) | 0.30611 (14) | 0.0209 (6) |
| C21 | 0.69880 (13) | 0.8403 (4) | 0.44841 (16) | 0.0220 (6) |
| O1′ | 0.29732 (9) | 0.7389 (3) | 0.70997 (10) | 0.0213 (5) |
| O2′ | 0.36530 (10) | 0.9209 (3) | 0.66648 (12) | 0.0265 (5) |
| H2′ | 0.376 (2) | 0.949 (7) | 0.706 (3) | 0.070 (15)* |
| O3′ | 0.16368 (9) | 1.4521 (3) | 0.71744 (11) | 0.0247 (5) |
| O4′ | 0.25240 (10) | 1.4042 (3) | 0.67837 (12) | 0.0282 (5) |
| H4′ | 0.2621 (18) | 1.507 (7) | 0.693 (2) | 0.054 (13)* |
| O5′ | 0.61435 (9) | 0.6032 (3) | 0.55199 (11) | 0.0247 (5) |
| O6′ | 0.55852 (10) | 0.7980 (3) | 0.49534 (11) | 0.0271 (5) |
| C1′ | 0.31076 (12) | 0.7424 (4) | 0.59342 (15) | 0.0191 (6) |
| C2′ | 0.25613 (13) | 0.7813 (4) | 0.56681 (15) | 0.0193 (6) |
| C3′ | 0.24393 (13) | 0.7237 (4) | 0.50299 (16) | 0.0216 (7) |

| | | | | |
|---|---|---|---|---|
| H3′ | 0.2067 | 0.7449 | 0.4850 | 0.026* |
| C4′ | 0.28570 (14) | 0.6353 (4) | 0.46537 (16) | 0.0245 (7) |
| H4′A | 0.2771 | 0.5986 | 0.4216 | 0.029* |
| C5′ | 0.33996 (13) | 0.6003 (4) | 0.49149 (16) | 0.0214 (6) |
| H5′ | 0.3685 | 0.5418 | 0.4652 | 0.026* |
| C6′ | 0.35278 (13) | 0.6504 (4) | 0.55605 (15) | 0.0198 (6) |
| C7′ | 0.21240 (13) | 0.8890 (4) | 0.60456 (16) | 0.0209 (7) |
| C8′ | 0.22618 (12) | 1.0626 (4) | 0.63010 (14) | 0.0183 (6) |
| H8′ | 0.2640 | 1.1105 | 0.6247 | 0.022* |
| C9′ | 0.18463 (13) | 1.1658 (4) | 0.66341 (15) | 0.0198 (6) |
| C10′ | 0.12932 (13) | 1.0961 (4) | 0.67205 (15) | 0.0212 (6) |
| H10′ | 0.1011 | 1.1663 | 0.6949 | 0.025* |
| C11′ | 0.11546 (13) | 0.9241 (4) | 0.64717 (17) | 0.0242 (7) |
| H11′ | 0.0777 | 0.8760 | 0.6532 | 0.029* |
| C12′ | 0.15643 (13) | 0.8211 (4) | 0.61342 (16) | 0.0228 (7) |
| H12′ | 0.1464 | 0.7036 | 0.5962 | 0.027* |
| C13′ | 0.41042 (13) | 0.6027 (4) | 0.58405 (15) | 0.0198 (6) |
| C14′ | 0.46007 (13) | 0.6550 (4) | 0.55043 (15) | 0.0192 (6) |
| H14′ | 0.4569 | 0.7180 | 0.5096 | 0.023* |
| C15′ | 0.51443 (13) | 0.6154 (4) | 0.57626 (15) | 0.0199 (6) |
| C16′ | 0.51981 (13) | 0.5223 (4) | 0.63543 (15) | 0.0231 (7) |
| H16′ | 0.5569 | 0.4950 | 0.6528 | 0.028* |
| C17′ | 0.47048 (13) | 0.4694 (4) | 0.66912 (16) | 0.0252 (7) |
| H17′ | 0.4738 | 0.4067 | 0.7100 | 0.030* |
| C18′ | 0.41620 (13) | 0.5075 (4) | 0.64352 (16) | 0.0252 (7) |
| H18′ | 0.3827 | 0.4685 | 0.6666 | 0.030* |
| C19′ | 0.32344 (12) | 0.7990 (4) | 0.66247 (15) | 0.0183 (6) |
| C20′ | 0.19858 (13) | 1.3529 (4) | 0.68902 (15) | 0.0210 (6) |
| C21′ | 0.56704 (13) | 0.6716 (4) | 0.53989 (14) | 0.0197 (6) |
| H6′ | 0.5939 (17) | 0.824 (6) | 0.477 (2) | 0.045 (12)* |
| H6 | 0.6693 (16) | 0.681 (8) | 0.515 (3) | 0.098 (19)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0208 (11) | 0.0242 (11) | 0.0235 (11) | 0.0006 (8) | −0.0009 (9) | −0.0026 (9) |
| O2 | 0.0228 (12) | 0.0250 (11) | 0.0255 (13) | −0.0031 (9) | −0.0048 (10) | −0.0020 (9) |
| O3 | 0.0304 (12) | 0.0302 (12) | 0.0304 (13) | 0.0075 (10) | 0.0024 (10) | −0.0070 (10) |
| O4 | 0.0275 (13) | 0.0232 (12) | 0.0411 (14) | −0.0028 (10) | 0.0041 (10) | −0.0084 (10) |
| O5 | 0.0209 (11) | 0.0256 (11) | 0.0309 (12) | 0.0030 (9) | 0.0016 (9) | 0.0029 (10) |
| O6 | 0.0221 (12) | 0.0292 (12) | 0.0341 (13) | 0.0023 (10) | 0.0037 (11) | 0.0100 (11) |
| C1 | 0.0199 (15) | 0.0150 (14) | 0.0215 (15) | −0.0009 (11) | −0.0003 (12) | 0.0006 (11) |
| C2 | 0.0192 (15) | 0.0149 (13) | 0.0259 (16) | −0.0022 (11) | −0.0009 (12) | 0.0019 (12) |
| C3 | 0.0224 (16) | 0.0195 (15) | 0.0225 (17) | −0.0004 (12) | −0.0040 (14) | 0.0022 (13) |
| C4 | 0.0287 (18) | 0.0191 (15) | 0.0228 (16) | 0.0006 (13) | −0.0033 (13) | −0.0010 (12) |
| C5 | 0.0252 (17) | 0.0213 (15) | 0.0218 (16) | −0.0007 (12) | 0.0047 (13) | −0.0016 (13) |
| C6 | 0.0207 (15) | 0.0149 (14) | 0.0236 (15) | −0.0017 (12) | 0.0019 (13) | 0.0017 (12) |
| C7 | 0.0217 (16) | 0.0163 (14) | 0.0183 (15) | 0.0021 (12) | −0.0029 (12) | 0.0022 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C8 | 0.0181 (15) | 0.0199 (15) | 0.0222 (16) | 0.0020 (12) | −0.0025 (12) | 0.0011 (12) |
| C9 | 0.0166 (15) | 0.0189 (14) | 0.0178 (14) | 0.0028 (11) | −0.0020 (12) | 0.0042 (11) |
| C10 | 0.0211 (17) | 0.0269 (16) | 0.0235 (16) | 0.0045 (13) | −0.0009 (13) | 0.0041 (13) |
| C11 | 0.0166 (16) | 0.0287 (17) | 0.0299 (18) | −0.0010 (12) | −0.0020 (13) | 0.0061 (14) |
| C12 | 0.0203 (16) | 0.0222 (15) | 0.0237 (16) | −0.0014 (12) | −0.0056 (13) | 0.0025 (12) |
| C13 | 0.0201 (15) | 0.0173 (14) | 0.0234 (16) | 0.0029 (12) | 0.0012 (13) | −0.0033 (12) |
| C14 | 0.0255 (17) | 0.0171 (14) | 0.0211 (16) | 0.0024 (12) | −0.0009 (13) | −0.0009 (12) |
| C15 | 0.0206 (15) | 0.0158 (13) | 0.0250 (16) | 0.0026 (12) | −0.0001 (12) | −0.0050 (12) |
| C16 | 0.0206 (15) | 0.0211 (15) | 0.0262 (17) | 0.0044 (13) | −0.0033 (13) | −0.0026 (13) |
| C17 | 0.0252 (17) | 0.0252 (15) | 0.0225 (17) | 0.0048 (13) | 0.0026 (13) | −0.0007 (13) |
| C18 | 0.0238 (16) | 0.0227 (15) | 0.0234 (17) | 0.0021 (14) | 0.0065 (12) | 0.0007 (13) |
| C19 | 0.0173 (15) | 0.0159 (14) | 0.0264 (16) | 0.0051 (12) | −0.0016 (13) | −0.0044 (12) |
| C20 | 0.0226 (17) | 0.0248 (15) | 0.0153 (14) | 0.0081 (13) | −0.0009 (12) | 0.0002 (12) |
| C21 | 0.0227 (17) | 0.0170 (14) | 0.0261 (16) | 0.0037 (12) | −0.0006 (13) | −0.0049 (12) |
| O1′ | 0.0212 (11) | 0.0221 (11) | 0.0207 (11) | −0.0001 (8) | 0.0011 (9) | −0.0013 (9) |
| O2′ | 0.0268 (12) | 0.0283 (11) | 0.0244 (12) | −0.0108 (9) | −0.0009 (10) | −0.0065 (10) |
| O3′ | 0.0237 (11) | 0.0205 (11) | 0.0301 (12) | 0.0016 (9) | 0.0070 (10) | −0.0003 (9) |
| O4′ | 0.0217 (11) | 0.0201 (11) | 0.0428 (15) | −0.0052 (9) | 0.0083 (10) | −0.0080 (11) |
| O5′ | 0.0205 (12) | 0.0258 (11) | 0.0277 (12) | 0.0002 (9) | 0.0022 (9) | 0.0023 (10) |
| O6′ | 0.0232 (12) | 0.0300 (12) | 0.0280 (12) | 0.0029 (9) | 0.0047 (10) | 0.0076 (10) |
| C1′ | 0.0191 (15) | 0.0141 (13) | 0.0241 (16) | −0.0039 (11) | −0.0004 (13) | 0.0006 (12) |
| C2′ | 0.0209 (16) | 0.0136 (13) | 0.0233 (16) | −0.0028 (11) | −0.0002 (12) | 0.0020 (12) |
| C3′ | 0.0221 (16) | 0.0162 (14) | 0.0264 (17) | −0.0011 (12) | −0.0064 (13) | 0.0002 (12) |
| C4′ | 0.0330 (18) | 0.0204 (16) | 0.0201 (15) | −0.0046 (13) | −0.0039 (13) | −0.0020 (12) |
| C5′ | 0.0235 (17) | 0.0177 (14) | 0.0229 (15) | −0.0012 (12) | 0.0020 (13) | −0.0020 (12) |
| C6′ | 0.0204 (16) | 0.0157 (13) | 0.0234 (15) | −0.0037 (11) | 0.0000 (12) | −0.0017 (12) |
| C7′ | 0.0201 (16) | 0.0197 (14) | 0.0227 (16) | −0.0001 (12) | −0.0060 (13) | 0.0049 (12) |
| C8′ | 0.0140 (15) | 0.0198 (15) | 0.0212 (16) | −0.0025 (11) | −0.0027 (12) | 0.0031 (12) |
| C9′ | 0.0228 (15) | 0.0182 (14) | 0.0185 (14) | −0.0001 (12) | −0.0024 (13) | 0.0029 (12) |
| C10′ | 0.0171 (15) | 0.0237 (15) | 0.0227 (15) | 0.0025 (12) | 0.0018 (13) | 0.0025 (12) |
| C11′ | 0.0151 (16) | 0.0265 (16) | 0.0309 (18) | −0.0040 (12) | −0.0045 (13) | 0.0029 (14) |
| C12′ | 0.0203 (16) | 0.0181 (14) | 0.0301 (17) | −0.0029 (12) | −0.0057 (13) | −0.0005 (12) |
| C13′ | 0.0217 (15) | 0.0152 (13) | 0.0226 (16) | −0.0012 (12) | 0.0011 (12) | −0.0024 (12) |
| C14′ | 0.0240 (16) | 0.0155 (13) | 0.0180 (14) | 0.0003 (11) | 0.0029 (12) | −0.0023 (12) |
| C15′ | 0.0245 (16) | 0.0146 (14) | 0.0205 (15) | 0.0011 (12) | 0.0003 (12) | −0.0041 (12) |
| C16′ | 0.0241 (16) | 0.0230 (15) | 0.0221 (16) | 0.0028 (13) | −0.0014 (12) | −0.0017 (12) |
| C17′ | 0.0275 (17) | 0.0275 (16) | 0.0207 (16) | 0.0011 (13) | −0.0002 (13) | 0.0040 (14) |
| C18′ | 0.0226 (16) | 0.0256 (16) | 0.0272 (18) | 0.0000 (14) | 0.0057 (13) | 0.0026 (14) |
| C19′ | 0.0151 (14) | 0.0174 (13) | 0.0223 (15) | 0.0017 (11) | −0.0002 (13) | −0.0004 (12) |
| C20′ | 0.0211 (16) | 0.0202 (14) | 0.0217 (15) | −0.0021 (13) | 0.0026 (13) | 0.0052 (12) |
| C21′ | 0.0224 (16) | 0.0167 (13) | 0.0198 (15) | −0.0017 (12) | −0.0019 (12) | −0.0023 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C19 | 1.216 (4) | O1′—C19′ | 1.220 (4) |
| O2—H2 | 0.91 (5) | O2′—H2′ | 0.87 (6) |
| O2—C19 | 1.329 (4) | O2′—C19′ | 1.314 (4) |
| O3—C20 | 1.209 (4) | O3′—C20′ | 1.227 (4) |

| | | | |
|---|---|---|---|
| O4—H4 | 0.90 (6) | O4′—H4′ | 0.84 (5) |
| O4—C20 | 1.319 (4) | O4′—C20′ | 1.319 (4) |
| O5—C21 | 1.229 (4) | O5′—C21′ | 1.228 (4) |
| O6—C21 | 1.306 (4) | O6′—C21′ | 1.303 (4) |
| O6—H6 | 1.01 (3) | O6′—H6′ | 0.92 (4) |
| C1—C2 | 1.405 (4) | C1′—C2′ | 1.405 (4) |
| C1—C6 | 1.400 (4) | C1′—C6′ | 1.404 (4) |
| C1—C19 | 1.497 (4) | C1′—C19′ | 1.492 (4) |
| C2—C3 | 1.393 (5) | C2′—C3′ | 1.392 (4) |
| C2—C7 | 1.496 (4) | C2′—C7′ | 1.491 (4) |
| C3—H3 | 0.9500 | C3′—H3′ | 0.9500 |
| C3—C4 | 1.378 (4) | C3′—C4′ | 1.390 (4) |
| C4—H4A | 0.9500 | C4′—H4′A | 0.9500 |
| C4—C5 | 1.378 (4) | C4′—C5′ | 1.388 (4) |
| C5—H5 | 0.9500 | C5′—H5′ | 0.9500 |
| C5—C6 | 1.394 (5) | C5′—C6′ | 1.394 (4) |
| C6—C13 | 1.493 (4) | C6′—C13′ | 1.493 (4) |
| C7—C8 | 1.398 (4) | C7′—C8′ | 1.398 (4) |
| C7—C12 | 1.391 (4) | C7′—C12′ | 1.399 (4) |
| C8—H8 | 0.9500 | C8′—H8′ | 0.9500 |
| C8—C9 | 1.387 (4) | C8′—C9′ | 1.395 (4) |
| C9—C10 | 1.393 (4) | C9′—C10′ | 1.389 (4) |
| C9—C20 | 1.496 (4) | C9′—C20′ | 1.488 (4) |
| C10—H10 | 0.9500 | C10′—H10′ | 0.9500 |
| C10—C11 | 1.380 (5) | C10′—C11′ | 1.384 (4) |
| C11—H11 | 0.9500 | C11′—H11′ | 0.9500 |
| C11—C12 | 1.381 (5) | C11′—C12′ | 1.389 (5) |
| C12—H12 | 0.9500 | C12′—H12′ | 0.9500 |
| C13—C14 | 1.388 (4) | C13′—C14′ | 1.391 (4) |
| C13—C18 | 1.394 (5) | C13′—C18′ | 1.399 (4) |
| C14—H14 | 0.9500 | C14′—H14′ | 0.9500 |
| C14—C15 | 1.387 (4) | C14′—C15′ | 1.394 (4) |
| C15—C16 | 1.397 (5) | C15′—C16′ | 1.385 (4) |
| C15—C21 | 1.479 (5) | C15′—C21′ | 1.483 (4) |
| C16—H16 | 0.9500 | C16′—H16′ | 0.9500 |
| C16—C17 | 1.379 (5) | C16′—C17′ | 1.387 (4) |
| C17—H17 | 0.9500 | C17′—H17′ | 0.9500 |
| C17—C18 | 1.387 (4) | C17′—C18′ | 1.389 (4) |
| C18—H18 | 0.9500 | C18′—H18′ | 0.9500 |
| | | | |
| C19—O2—H2 | 110 (3) | C19′—O2′—H2′ | 115 (3) |
| C20—O4—H4 | 109 (3) | C20′—O4′—H4′ | 117 (3) |
| C21—O6—H6 | 111 (3) | C21′—O6′—H6′ | 107 (3) |
| C2—C1—C19 | 119.7 (3) | C2′—C1′—C19′ | 119.0 (3) |
| C6—C1—C2 | 121.1 (3) | C6′—C1′—C2′ | 120.8 (3) |
| C6—C1—C19 | 119.2 (3) | C6′—C1′—C19′ | 120.2 (3) |
| C1—C2—C7 | 121.5 (3) | C1′—C2′—C7′ | 121.3 (3) |
| C3—C2—C1 | 118.4 (3) | C3′—C2′—C1′ | 118.8 (3) |

| | | | |
|---|---|---|---|
| C3—C2—C7 | 120.1 (3) | C3′—C2′—C7′ | 119.9 (3) |
| C2—C3—H3 | 119.7 | C2′—C3′—H3′ | 119.7 |
| C4—C3—C2 | 120.6 (3) | C4′—C3′—C2′ | 120.7 (3) |
| C4—C3—H3 | 119.7 | C4′—C3′—H3′ | 119.7 |
| C3—C4—H4A | 119.7 | C3′—C4′—H4′A | 119.9 |
| C5—C4—C3 | 120.7 (3) | C5′—C4′—C3′ | 120.3 (3) |
| C5—C4—H4A | 119.7 | C5′—C4′—H4′A | 119.9 |
| C4—C5—H5 | 119.7 | C4′—C5′—H5′ | 119.8 |
| C4—C5—C6 | 120.6 (3) | C4′—C5′—C6′ | 120.4 (3) |
| C6—C5—H5 | 119.7 | C6′—C5′—H5′ | 119.8 |
| C1—C6—C13 | 121.3 (3) | C1′—C6′—C13′ | 121.6 (3) |
| C5—C6—C1 | 118.4 (3) | C5′—C6′—C1′ | 119.1 (3) |
| C5—C6—C13 | 120.2 (3) | C5′—C6′—C13′ | 119.3 (3) |
| C8—C7—C2 | 120.2 (3) | C8′—C7′—C2′ | 120.5 (3) |
| C12—C7—C2 | 120.9 (3) | C8′—C7′—C12′ | 118.7 (3) |
| C12—C7—C8 | 118.9 (3) | C12′—C7′—C2′ | 120.8 (3) |
| C7—C8—H8 | 120.0 | C7′—C8′—H8′ | 119.8 |
| C9—C8—C7 | 119.9 (3) | C9′—C8′—C7′ | 120.4 (3) |
| C9—C8—H8 | 120.0 | C9′—C8′—H8′ | 119.8 |
| C8—C9—C10 | 120.6 (3) | C8′—C9′—C20′ | 120.6 (3) |
| C8—C9—C20 | 121.1 (3) | C10′—C9′—C8′ | 120.2 (3) |
| C10—C9—C20 | 118.3 (3) | C10′—C9′—C20′ | 119.2 (3) |
| C9—C10—H10 | 120.3 | C9′—C10′—H10′ | 120.1 |
| C11—C10—C9 | 119.3 (3) | C11′—C10′—C9′ | 119.7 (3) |
| C11—C10—H10 | 120.3 | C11′—C10′—H10′ | 120.1 |
| C10—C11—H11 | 119.8 | C10′—C11′—H11′ | 119.8 |
| C10—C11—C12 | 120.4 (3) | C10′—C11′—C12′ | 120.4 (3) |
| C12—C11—H11 | 119.8 | C12′—C11′—H11′ | 119.8 |
| C7—C12—H12 | 119.5 | C7′—C12′—H12′ | 119.7 |
| C11—C12—C7 | 120.9 (3) | C11′—C12′—C7′ | 120.6 (3) |
| C11—C12—H12 | 119.5 | C11′—C12′—H12′ | 119.7 |
| C14—C13—C6 | 119.3 (3) | C14′—C13′—C6′ | 119.3 (3) |
| C14—C13—C18 | 118.3 (3) | C14′—C13′—C18′ | 118.7 (3) |
| C18—C13—C6 | 122.3 (3) | C18′—C13′—C6′ | 122.0 (3) |
| C13—C14—H14 | 119.6 | C13′—C14′—H14′ | 119.8 |
| C15—C14—C13 | 120.9 (3) | C13′—C14′—C15′ | 120.4 (3) |
| C15—C14—H14 | 119.6 | C15′—C14′—H14′ | 119.8 |
| C14—C15—C16 | 120.3 (3) | C14′—C15′—C21′ | 119.9 (3) |
| C14—C15—C21 | 119.2 (3) | C16′—C15′—C14′ | 120.6 (3) |
| C16—C15—C21 | 120.4 (3) | C16′—C15′—C21′ | 119.5 (3) |
| C15—C16—H16 | 120.5 | C15′—C16′—H16′ | 120.3 |
| C17—C16—C15 | 119.0 (3) | C15′—C16′—C17′ | 119.3 (3) |
| C17—C16—H16 | 120.5 | C17′—C16′—H16′ | 120.3 |
| C16—C17—H17 | 119.7 | C16′—C17′—H17′ | 119.8 |
| C16—C17—C18 | 120.5 (3) | C16′—C17′—C18′ | 120.4 (3) |
| C18—C17—H17 | 119.7 | C18′—C17′—H17′ | 119.8 |
| C13—C18—H18 | 119.5 | C13′—C18′—H18′ | 119.7 |
| C17—C18—C13 | 120.9 (3) | C17′—C18′—C13′ | 120.6 (3) |

| | | | |
|---|---|---|---|
| C17—C18—H18 | 119.5 | C17′—C18′—H18′ | 119.7 |
| O1—C19—O2 | 123.6 (3) | O1′—C19′—O2′ | 123.8 (3) |
| O1—C19—C1 | 123.7 (3) | O1′—C19′—C1′ | 123.3 (3) |
| O2—C19—C1 | 112.7 (3) | O2′—C19′—C1′ | 112.9 (3) |
| O3—C20—O4 | 123.3 (3) | O3′—C20′—O4′ | 122.4 (3) |
| O3—C20—C9 | 123.1 (3) | O3′—C20′—C9′ | 123.8 (3) |
| O4—C20—C9 | 113.6 (2) | O4′—C20′—C9′ | 113.9 (3) |
| O5—C21—O6 | 123.4 (3) | O5′—C21′—O6′ | 123.9 (3) |
| O5—C21—C15 | 122.1 (3) | O5′—C21′—C15′ | 121.5 (3) |
| O6—C21—C15 | 114.6 (3) | O6′—C21′—C15′ | 114.5 (3) |
| | | | |
| C1—C2—C3—C4 | 2.2 (4) | C1′—C2′—C3′—C4′ | −2.3 (4) |
| C1—C2—C7—C8 | −54.7 (4) | C1′—C2′—C7′—C8′ | 54.2 (4) |
| C1—C2—C7—C12 | 127.4 (3) | C1′—C2′—C7′—C12′ | −127.7 (3) |
| C1—C6—C13—C14 | 125.4 (3) | C1′—C6′—C13′—C14′ | −127.7 (3) |
| C1—C6—C13—C18 | −55.3 (4) | C1′—C6′—C13′—C18′ | 52.0 (4) |
| C2—C1—C6—C5 | −2.8 (4) | C2′—C1′—C6′—C5′ | 1.0 (4) |
| C2—C1—C6—C13 | 176.9 (3) | C2′—C1′—C6′—C13′ | −178.1 (3) |
| C2—C1—C19—O1 | −63.6 (4) | C2′—C1′—C19′—O1′ | 62.6 (4) |
| C2—C1—C19—O2 | 117.5 (3) | C2′—C1′—C19′—O2′ | −117.0 (3) |
| C2—C3—C4—C5 | −1.6 (5) | C2′—C3′—C4′—C5′ | 1.2 (4) |
| C2—C7—C8—C9 | −178.5 (3) | C2′—C7′—C8′—C9′ | 177.8 (3) |
| C2—C7—C12—C11 | 179.4 (3) | C2′—C7′—C12′—C11′ | −178.3 (3) |
| C3—C2—C7—C8 | 122.8 (3) | C3′—C2′—C7′—C8′ | −123.3 (3) |
| C3—C2—C7—C12 | −55.2 (4) | C3′—C2′—C7′—C12′ | 54.8 (4) |
| C3—C4—C5—C6 | −1.4 (5) | C3′—C4′—C5′—C6′ | 1.1 (4) |
| C4—C5—C6—C1 | 3.5 (4) | C4′—C5′—C6′—C1′ | −2.2 (4) |
| C4—C5—C6—C13 | −176.2 (3) | C4′—C5′—C6′—C13′ | 176.9 (3) |
| C5—C6—C13—C14 | −54.9 (4) | C5′—C6′—C13′—C14′ | 53.2 (4) |
| C5—C6—C13—C18 | 124.4 (3) | C5′—C6′—C13′—C18′ | −127.1 (3) |
| C6—C1—C2—C3 | 0.0 (4) | C6′—C1′—C2′—C3′ | 1.2 (4) |
| C6—C1—C2—C7 | 177.4 (3) | C6′—C1′—C2′—C7′ | −176.3 (3) |
| C6—C1—C19—O1 | 114.7 (3) | C6′—C1′—C19′—O1′ | −116.9 (3) |
| C6—C1—C19—O2 | −64.1 (3) | C6′—C1′—C19′—O2′ | 63.6 (4) |
| C6—C13—C14—C15 | −179.5 (3) | C6′—C13′—C14′—C15′ | 178.7 (3) |
| C6—C13—C18—C17 | 179.8 (3) | C6′—C13′—C18′—C17′ | −178.3 (3) |
| C7—C2—C3—C4 | −175.3 (3) | C7′—C2′—C3′—C4′ | 175.2 (3) |
| C7—C8—C9—C10 | −0.2 (4) | C7′—C8′—C9′—C10′ | 0.6 (4) |
| C7—C8—C9—C20 | 177.4 (3) | C7′—C8′—C9′—C20′ | −178.2 (3) |
| C8—C7—C12—C11 | 1.4 (4) | C8′—C7′—C12′—C11′ | −0.2 (5) |
| C8—C9—C10—C11 | 0.1 (4) | C8′—C9′—C10′—C11′ | −0.3 (4) |
| C8—C9—C20—O3 | −172.2 (3) | C8′—C9′—C20′—O3′ | 178.4 (3) |
| C8—C9—C20—O4 | 7.9 (4) | C8′—C9′—C20′—O4′ | −1.5 (4) |
| C9—C10—C11—C12 | 0.8 (5) | C9′—C10′—C11′—C12′ | −0.3 (5) |
| C10—C9—C20—O3 | 5.5 (4) | C10′—C9′—C20′—O3′ | −0.5 (5) |
| C10—C9—C20—O4 | −174.4 (3) | C10′—C9′—C20′—O4′ | 179.6 (3) |
| C10—C11—C12—C7 | −1.5 (5) | C10′—C11′—C12′—C7′ | 0.5 (5) |
| C12—C7—C8—C9 | −0.5 (4) | C12′—C7′—C8′—C9′ | −0.3 (4) |

| | | | |
|---|---|---|---|
| C13—C14—C15—C16 | 0.1 (4) | C13′—C14′—C15′—C16′ | 0.5 (4) |
| C13—C14—C15—C21 | −179.2 (3) | C13′—C14′—C15′—C21′ | 179.9 (3) |
| C14—C13—C18—C17 | −0.9 (4) | C14′—C13′—C18′—C17′ | 1.4 (4) |
| C14—C15—C16—C17 | −1.7 (4) | C14′—C15′—C16′—C17′ | −0.4 (4) |
| C14—C15—C21—O5 | 163.2 (3) | C14′—C15′—C21′—O5′ | −162.4 (3) |
| C14—C15—C21—O6 | −16.1 (4) | C14′—C15′—C21′—O6′ | 18.1 (4) |
| C15—C16—C17—C18 | 1.9 (5) | C15′—C16′—C17′—C18′ | 0.7 (5) |
| C16—C15—C21—O5 | −16.1 (4) | C16′—C15′—C21′—O5′ | 17.0 (4) |
| C16—C15—C21—O6 | 164.5 (3) | C16′—C15′—C21′—O6′ | −162.6 (3) |
| C16—C17—C18—C13 | −0.6 (5) | C16′—C17′—C18′—C13′ | −1.2 (5) |
| C18—C13—C14—C15 | 1.1 (4) | C18′—C13′—C14′—C15′ | −1.0 (4) |
| C19—C1—C2—C3 | 178.3 (3) | C19′—C1′—C2′—C3′ | −178.2 (3) |
| C19—C1—C2—C7 | −4.2 (4) | C19′—C1′—C2′—C7′ | 4.3 (4) |
| C19—C1—C6—C5 | 178.9 (3) | C19′—C1′—C6′—C5′ | −179.5 (3) |
| C19—C1—C6—C13 | −1.4 (4) | C19′—C1′—C6′—C13′ | 1.3 (4) |
| C20—C9—C10—C11 | −177.6 (3) | C20′—C9′—C10′—C11′ | 178.6 (3) |
| C21—C15—C16—C17 | 177.7 (3) | C21′—C15′—C16′—C17′ | −179.7 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···O3′$^{i}$ | 0.91 (5) | 1.79 (5) | 2.657 (3) | 159 (4) |
| O4—H4···O1$^{ii}$ | 0.90 (6) | 1.84 (6) | 2.689 (3) | 156 (5) |
| O2′—H2′···O3$^{iii}$ | 0.87 (6) | 1.76 (6) | 2.628 (3) | 171 (5) |
| O4′—H4′···O1′$^{iv}$ | 0.84 (5) | 1.90 (5) | 2.717 (3) | 166 (4) |
| O6′—H6′···O5 | 0.92 (4) | 1.69 (4) | 2.593 (3) | 168 (4) |
| O6—H6···O5′ | 1.01 (3) | 1.58 (3) | 2.581 (3) | 172 (6) |

Symmetry codes: (i) −*x*+1, −*y*+2, *z*−1/2; (ii) *x*, *y*−1, *z*; (iii) −*x*+3/2, *y*+1, *z*+1/2; (iv) *x*, *y*+1, *z*.