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# (25*R*)-6$\alpha$-Hydroxy-5$\alpha$-spirostan-3$\beta$-yl tosylate

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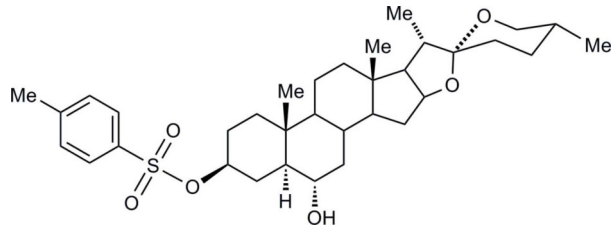
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.036; $wR$ factor = 0.090; data-to-parameter ratio = 16.2.

The title steroid, $C_{34}H_{50}O_6S$, is an intermediate on the synthetic route between diosgenin and brassinosteroids, which possess the $A$ ring modified with the 2$\alpha$,3$\alpha$-diol functionality. The polycyclic spirostan system has the expected conformation, with six-membered rings adopting chair forms and the five-membered rings envelope forms (flap atoms are the methine C atom in the $C$/$D$-ring junction and the spiro C atom connecting rings $E$ and $F$). The 3$\beta$-tosylate group is oriented in such a way that S=O bonds are engaged in intermolecular hydrogen bonds with O—H and C—H donors. Chains of molecules are formed along [100] *via* O—H···O hydrogen bonds, and secondary weak C—H···O interactions connect two neighbouring chains in the [001] direction.

## Related literature

For background to brassinosteroids, see: Asami *et al.* (2005); Kang & Guo (2011); Zullo & Adam (2002). For the hydroboration-oxidation synthetic step used for the preparation of the title compound, see: Smith & Pelter (1991); Brown (1962). For the structure of another steroid functionalized at C-3 with a tosylate group, see: Cox *et al.* (1996).




## Experimental

### Crystal data

$C_{34}H_{50}O_6S$
$M_r$ = 586.80
Orthorhombic, $P2_12_12_1$
$a$ = 6.7653 (8) Å
$b$ = 12.2856 (11) Å
$c$ = 37.943 (4) Å
$V$ = 3153.6 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.15 mm$^{-1}$
$T$ = 296 K
0.6 × 0.5 × 0.4 mm

### Data collection

Bruker P4 diffractometer
Absorption correction: $\psi$ scan (*XSCANS*; Siemens, 1996)
$T_{min}$ = 0.905, $T_{max}$ = 0.943
9218 measured reflections
6167 independent reflections
5274 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.023
3 standard reflections every 97 reflections
intensity decay: 1.5%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.090
$S$ = 1.03
6167 reflections
380 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.16 e Å$^{-3}$
Absolute structure: Flack (1983), 2504 Friedel pairs
Flack parameter: −0.03 (7)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O30—H30···O33$^{i}$ | 0.78 (3) | 2.35 (3) | 3.098 (2) | 159 (3) |
| C40—H40$A$···O34$^{ii}$ | 0.93 | 2.65 | 3.352 (3) | 133 |

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

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2379).

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# supplementary materials

*Acta Cryst.* (2012). E**68**, o3413–o3414 [doi:10.1107/S1600536812046600]

## (25*R*)-6*α*-Hydroxy-5*α*-spirostan-3*β*-yl tosylate

**María A. Fernández-Herrera, Jesús Sandoval-Ramírez, Sylvain Bernès, Maricela Rodríguez-Acosta and María-Guadalupe Hernández Linares**

### Comment

Brassinosteroids (BS) are endogenous plant hormones essential for the regulation of multiple physiological processes required for normal plant growth and development (Asami *et al.*, 2005). Since their discovery, more than 30 years ago, the synthetic chemistry has been extensively developed for obtaining BS and analogs (Zullo & Adam, 2002; Kang & Guo, 2011). The most active BS and analogs possess a 2*α*,3*α*-diol in ring *A* and a ketone at C-6 (or a lactone) in ring *B*. The introduction of the required 6-keto-2*α*,3*α*-diol functionality has been satisfactorily achieved from the 6-hydroxy-3*β*-tosylate framework. The title compound belongs to this line of synthetic approaches to BS analogs. It was synthesized from diosgenin, through a tosylation followed by hydroboration-oxidation (Smith & Pelter, 1991; Brown, 1962). Commonly, the crude product after the hydroboration-oxidation procedure is immediately oxidized in order to obtain the 6-keto derivative; we decided instead, to isolate and properly characterize the 6-hydroxy intermediate.

The compound crystallizes with one molecule in the asymmetric unit (Fig. 1) and the conformation of the *A*-*F* ring system is as expected for a spirostan nucleus. All 6-membered rings have a chair conformation, while 5-membered rings *D* and *E* are envelopes on C14 and C22, respectively. The tosylate group in equatorial position at C3 is oriented in such a way that a potential intramolecular stabilizing O—H···*π* contact could be formed between the hydroxyl group at C6 and the benzene ring of the tosylate. However, this interaction should have an energy approaching zero, because of the too long H···*π* separation, *ca*. 4.4 Å. On the other hand, the tosylate orientation in the title compound is similar to that observed in cholesteryl tosylate (Cox *et al.*, 1996), which has C-6 engaged in a double bond. This suggests that the tosylate orientation results from packing restraints or intermolecular interactions rather than intramolecular contacts.

Regarding the crystal structure, the single feature of interest is the intermolecular hydrogen bond formed between the hydroxyl group and one S═O group in the tosylate. These contacts link molecules in chains oriented in the [100] direction in the crystal. A weak hydrogen bond involving the other S═O group is observed between chains, C40—H40*A*···O34, characterized by a small C—H···O angle of 133° (Fig. 2).

### Experimental

Diosgenin (750 mg, 1.8 mmol) was tosylated by means of *p*-TsCl/py/DCM, following the standard procedure, affording diosgenin tosylate quantitatively; the crude was properly washed, dried and immediately submitted to the next reaction. Diosgenin tosylate (1 g, 1.76 mmol) was dissolved in THF (30 ml) and $NaBH_4$ (0.4 g, 10.8 mmol) was added. The system was sealed under Ar atmosphere and then, $BF_3{\cdot}Et_2O$ (0.7 ml, 5.6 mmol) was carefully added. The reaction mixture was kept for 2 h at room temperature, concentrated under reduced pressure, and re-dissolved in a solution of KOH/MeOH (2%, 50 ml), followed by 5 ml of 35% $H_2O_2$. The reaction mixture was stirred for 1 h; then the addition of water produced a precipitate, which was filtered off, washed with cold water, and dried under high vacuum. The resulting white powder was purified by column chromatography with hexanes/EtOAc 7:3 to afford the title compound as a white powder.

It was recrystallized from hexanes/EtOAc 8:2 to obtain 0.72 g (70%) of colourless crystals. *M*.p. 149–150 °C, $[\alpha]_D$ -39° (*c* 1.0, $CHCl_3$). Spectroscopic characterization may be found in the archived CIF.

### Refinement

Hydroxyl H atom H30 was found in a difference map and refined with free coordinates and isotropic *U* parameter. Other H atoms were placed in idealized positions and refined with a riding model and fixed isotropic *U* parameters. C—H bond lengths were fixed to 0.96 (methyl), 0.97 (methylene), or 0.98 Å (methine). Displacement parameters were calculated as $U_{iso}$(H) = $xU_{eq}$(parent C) where $x$ = 1.5 (methyl) or 1.2 (methylene, methine). Anomalous dispersion of the tosylate S atom allowed to refine a Flack parameter (Flack, 1983), which is in agreement with the expected absolute configuration for the molecule.

### Computing details

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS* (Siemens, 1996); data reduction: *XSCANS* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

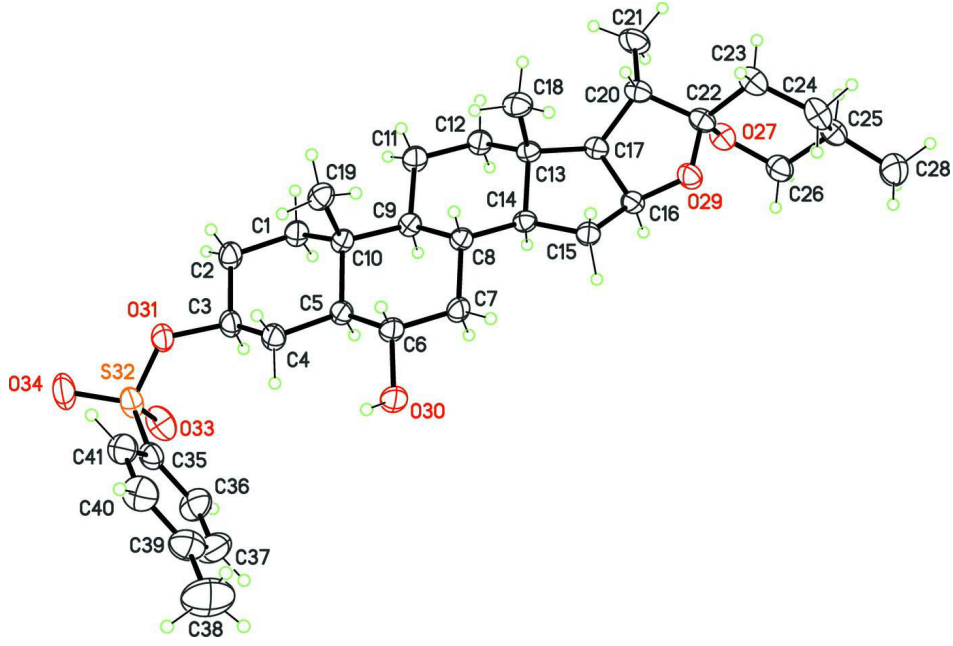


**Figure 1**

*ORTEP* view of the title molecule, with displacement ellipsoids at the 30% probability level.

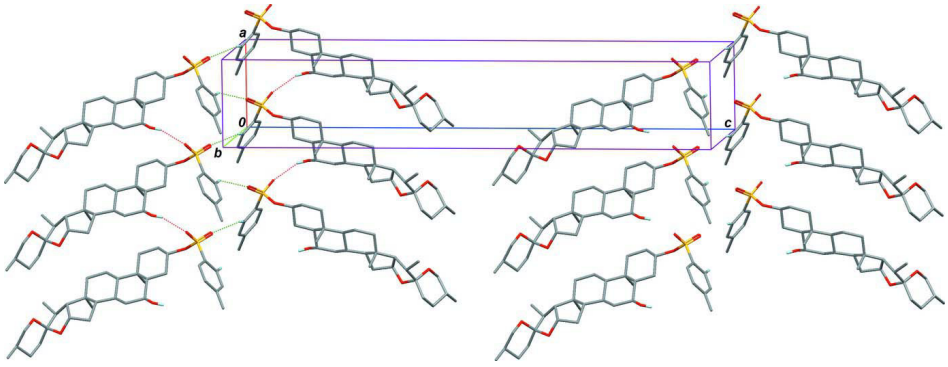


**Figure 2**

Part of the crystal structure of the title compound, showing pairs of chains. On the left stack, intermolecular contacts are depicted with dashed bonds. Red: O—H···O hydrogen bonds; green: interchain C—H···O weak interactions.

### (25*R*)-6*α*-Hydroxy-5*α*-spirostan-3*β*-yl tosylate

*Crystal data*

$C_{34}H_{50}O_6S$
$M_r$ = 586.80
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a$ = 6.7653 (8) Å
$b$ = 12.2856 (11) Å
$c$ = 37.943 (4) Å
$V$ = 3153.6 (6) Å$^3$
$Z$ = 4
$F$(000) = 1272
$D_x$ = 1.236 Mg m$^{-3}$
Melting point: 422 K
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 72 reflections
$\theta$ = 4.6–12.5°
$\mu$ = 0.15 mm$^{-1}$
$T$ = 296 K
Prism, colourless
0.6 × 0.5 × 0.4 mm

*Data collection*

Bruker P4 diffractometer
Radiation source: fine-focus sealed tube, FN4
Graphite monochromator
$\omega$ scans
Absorption correction: $\psi$ scan (*XSCANS*; Siemens, 1996)
$T_{min}$ = 0.905, $T_{max}$ = 0.943
9218 measured reflections
6167 independent reflections
5274 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.023
$\theta_{max}$ = 26.3°, $\theta_{min}$ = 2.0°
$h$ = −8→6
$k$ = −15→15
$l$ = −46→47
3 standard reflections every 97 reflections
intensity decay: 1.5%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.090
$S$ = 1.03
6167 reflections
380 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.5535P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.16 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0058 (5)

Absolute structure: Flack (1983), 2504 Friedel pairs

Flack parameter: −0.03 (7)

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.7277 (3) | 0.76613 (17) | 0.81367 (5) | 0.0487 (5) |
| H1A | 0.7549 | 0.7024 | 0.7994 | 0.058* |
| H1B | 0.8056 | 0.8259 | 0.8044 | 0.058* |
| C2 | 0.7923 (3) | 0.74351 (17) | 0.85158 (5) | 0.0535 (5) |
| H2A | 0.7246 | 0.6793 | 0.8603 | 0.064* |
| H2B | 0.9333 | 0.7293 | 0.8521 | 0.064* |
| C3 | 0.7455 (3) | 0.83933 (17) | 0.87512 (5) | 0.0501 (5) |
| H3A | 0.8291 | 0.9013 | 0.8686 | 0.060* |
| C4 | 0.5302 (3) | 0.87241 (18) | 0.87337 (5) | 0.0510 (5) |
| H4A | 0.5095 | 0.9374 | 0.8874 | 0.061* |
| H4B | 0.4485 | 0.8148 | 0.8830 | 0.061* |
| C5 | 0.4702 (3) | 0.89471 (15) | 0.83500 (4) | 0.0424 (4) |
| H5A | 0.5563 | 0.9532 | 0.8265 | 0.051* |
| C6 | 0.2580 (3) | 0.93700 (16) | 0.83213 (5) | 0.0478 (4) |
| H6A | 0.1664 | 0.8805 | 0.8402 | 0.057* |
| C7 | 0.2094 (3) | 0.96671 (16) | 0.79427 (5) | 0.0484 (5) |
| H7A | 0.2901 | 1.0282 | 0.7872 | 0.058* |
| H7B | 0.0720 | 0.9889 | 0.7929 | 0.058* |
| C8 | 0.2445 (3) | 0.87236 (14) | 0.76861 (4) | 0.0392 (4) |
| H8A | 0.1540 | 0.8130 | 0.7748 | 0.047* |
| C9 | 0.4581 (3) | 0.82992 (14) | 0.77203 (4) | 0.0397 (4) |
| H9A | 0.5443 | 0.8920 | 0.7668 | 0.048* |
| C10 | 0.5071 (3) | 0.79483 (14) | 0.81045 (4) | 0.0398 (4) |
| C11 | 0.5084 (3) | 0.74214 (17) | 0.74437 (5) | 0.0520 (5) |
| H11A | 0.6494 | 0.7280 | 0.7451 | 0.062* |
| H11B | 0.4410 | 0.6752 | 0.7507 | 0.062* |
| C12 | 0.4505 (3) | 0.77331 (17) | 0.70650 (5) | 0.0493 (5) |
| H12A | 0.5339 | 0.8326 | 0.6985 | 0.059* |
| H12B | 0.4723 | 0.7116 | 0.6910 | 0.059* |
| C13 | 0.2344 (3) | 0.80791 (14) | 0.70437 (4) | 0.0392 (4) |
| C14 | 0.2068 (3) | 0.90418 (14) | 0.73031 (4) | 0.0394 (4) |
| H14A | 0.3094 | 0.9573 | 0.7243 | 0.047* |
| C15 | 0.0107 (3) | 0.95550 (16) | 0.71905 (5) | 0.0487 (4) |
| H15A | −0.0063 | 1.0275 | 0.7291 | 0.058* |
| H15B | −0.1011 | 0.9102 | 0.7255 | 0.058* |
| C16 | 0.0397 (3) | 0.96013 (15) | 0.67900 (4) | 0.0444 (4) |
| H16A | 0.1065 | 1.0281 | 0.6726 | 0.053* |
| C17 | 0.1717 (3) | 0.86180 (14) | 0.66890 (4) | 0.0409 (4) |
| H17A | 0.2900 | 0.8885 | 0.6567 | 0.049* |
| C18 | 0.1006 (3) | 0.71110 (16) | 0.71335 (5) | 0.0555 (5) |
| H18A | 0.1350 | 0.6833 | 0.7362 | 0.083* |
| H18B | 0.1178 | 0.6550 | 0.6960 | 0.083* |
| H18C | −0.0348 | 0.7344 | 0.7135 | 0.083* |
| C19 | 0.3831 (3) | 0.69510 (15) | 0.82133 (5) | 0.0517 (5) |

| | | | | |
|---|---|---|---|---|
| H19A | 0.4338 | 0.6313 | 0.8099 | 0.078* |
| H19B | 0.2480 | 0.7062 | 0.8145 | 0.078* |
| H19C | 0.3902 | 0.6858 | 0.8464 | 0.078* |
| C20 | 0.0414 (3) | 0.79983 (16) | 0.64246 (5) | 0.0483 (5) |
| H20A | −0.0400 | 0.7484 | 0.6558 | 0.058* |
| C21 | 0.1537 (4) | 0.7352 (2) | 0.61469 (6) | 0.0721 (7) |
| H21A | 0.0614 | 0.7007 | 0.5991 | 0.108* |
| H21B | 0.2333 | 0.6808 | 0.6260 | 0.108* |
| H21C | 0.2373 | 0.7834 | 0.6015 | 0.108* |
| C22 | −0.0941 (3) | 0.88812 (16) | 0.62844 (4) | 0.0471 (4) |
| C23 | −0.2867 (3) | 0.85149 (19) | 0.61189 (5) | 0.0588 (5) |
| H23A | −0.3665 | 0.8151 | 0.6296 | 0.071* |
| H23B | −0.2587 | 0.7995 | 0.5933 | 0.071* |
| C24 | −0.4025 (4) | 0.9461 (2) | 0.59666 (6) | 0.0648 (6) |
| H24A | −0.5165 | 0.9185 | 0.5840 | 0.078* |
| H24B | −0.4499 | 0.9918 | 0.6157 | 0.078* |
| C25 | −0.2772 (4) | 1.01361 (18) | 0.57190 (5) | 0.0593 (5) |
| H25A | −0.2429 | 0.9686 | 0.5515 | 0.071* |
| C26 | −0.0883 (4) | 1.04441 (18) | 0.59073 (5) | 0.0599 (5) |
| H26A | −0.0032 | 1.0834 | 0.5745 | 0.072* |
| H26B | −0.1198 | 1.0932 | 0.6100 | 0.072* |
| O27 | 0.0167 (2) | 0.95231 (12) | 0.60433 (3) | 0.0537 (3) |
| C28 | −0.3833 (4) | 1.1154 (2) | 0.55875 (6) | 0.0824 (7) |
| H28A | −0.2911 | 1.1613 | 0.5465 | 0.124* |
| H28B | −0.4377 | 1.1543 | 0.5784 | 0.124* |
| H28C | −0.4878 | 1.0948 | 0.5430 | 0.124* |
| O29 | −0.1410 (2) | 0.95014 (11) | 0.65939 (3) | 0.0510 (3) |
| O30 | 0.2301 (3) | 1.03360 (13) | 0.85290 (4) | 0.0693 (5) |
| H30 | 0.206 (5) | 1.017 (3) | 0.8723 (8) | 0.107 (12)* |
| O31 | 0.7980 (2) | 0.80181 (12) | 0.91112 (3) | 0.0565 (4) |
| S32 | 0.89495 (8) | 0.88025 (5) | 0.938758 (13) | 0.05819 (15) |
| O33 | 1.0188 (2) | 0.95749 (16) | 0.92101 (4) | 0.0753 (5) |
| O34 | 0.9767 (3) | 0.80926 (16) | 0.96460 (4) | 0.0825 (5) |
| C35 | 0.6942 (3) | 0.94918 (16) | 0.95735 (5) | 0.0506 (5) |
| C36 | 0.6646 (4) | 1.05871 (19) | 0.95077 (7) | 0.0735 (7) |
| H36A | 0.7537 | 1.0974 | 0.9369 | 0.088* |
| C37 | 0.5013 (5) | 1.1100 (2) | 0.96490 (8) | 0.0859 (8) |
| H37A | 0.4812 | 1.1834 | 0.9601 | 0.103* |
| C38 | 0.3682 (4) | 1.0562 (2) | 0.98576 (7) | 0.0763 (7) |
| C39 | 0.4014 (4) | 0.9468 (2) | 0.99195 (6) | 0.0749 (7) |
| H39A | 0.3125 | 0.9084 | 1.0059 | 0.090* |
| C40 | 0.5620 (3) | 0.89296 (19) | 0.97808 (5) | 0.0614 (6) |
| H40A | 0.5811 | 0.8193 | 0.9827 | 0.074* |
| C41 | 0.1927 (6) | 1.1145 (3) | 1.00114 (11) | 0.1337 (14) |
| H41A | 0.1886 | 1.1877 | 0.9923 | 0.201* |
| H41B | 0.2040 | 1.1160 | 1.0264 | 0.201* |
| H41C | 0.0737 | 1.0771 | 0.9946 | 0.201* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0473 (11) | 0.0556 (11) | 0.0431 (10) | 0.0123 (9) | 0.0071 (9) | 0.0001 (9) |
| C2 | 0.0517 (12) | 0.0623 (12) | 0.0465 (10) | 0.0189 (10) | 0.0007 (9) | 0.0011 (9) |
| C3 | 0.0565 (12) | 0.0576 (11) | 0.0362 (9) | 0.0088 (10) | −0.0011 (9) | 0.0058 (8) |
| C4 | 0.0581 (12) | 0.0573 (11) | 0.0378 (9) | 0.0136 (10) | 0.0044 (8) | 0.0005 (9) |
| C5 | 0.0475 (10) | 0.0443 (9) | 0.0355 (8) | 0.0061 (9) | 0.0048 (8) | 0.0013 (7) |
| C6 | 0.0553 (11) | 0.0487 (10) | 0.0394 (9) | 0.0171 (9) | 0.0063 (9) | −0.0048 (8) |
| C7 | 0.0552 (12) | 0.0494 (10) | 0.0407 (9) | 0.0202 (10) | 0.0017 (8) | −0.0024 (8) |
| C8 | 0.0428 (10) | 0.0393 (9) | 0.0356 (8) | 0.0050 (8) | 0.0057 (7) | −0.0007 (7) |
| C9 | 0.0406 (10) | 0.0420 (9) | 0.0367 (8) | 0.0025 (8) | 0.0077 (7) | 0.0027 (7) |
| C10 | 0.0411 (10) | 0.0416 (9) | 0.0369 (8) | 0.0078 (8) | 0.0084 (8) | 0.0022 (7) |
| C11 | 0.0537 (11) | 0.0586 (11) | 0.0436 (10) | 0.0190 (10) | 0.0077 (9) | −0.0053 (9) |
| C12 | 0.0533 (12) | 0.0549 (11) | 0.0397 (9) | 0.0111 (10) | 0.0076 (8) | −0.0040 (9) |
| C13 | 0.0441 (10) | 0.0369 (8) | 0.0366 (8) | −0.0013 (8) | 0.0069 (8) | −0.0022 (7) |
| C14 | 0.0446 (10) | 0.0357 (9) | 0.0380 (8) | −0.0003 (8) | 0.0050 (8) | −0.0008 (7) |
| C15 | 0.0578 (12) | 0.0491 (10) | 0.0393 (9) | 0.0138 (10) | −0.0017 (9) | −0.0074 (8) |
| C16 | 0.0529 (11) | 0.0416 (9) | 0.0387 (9) | −0.0013 (9) | −0.0036 (8) | −0.0019 (8) |
| C17 | 0.0439 (10) | 0.0418 (9) | 0.0371 (8) | −0.0051 (8) | 0.0046 (7) | −0.0016 (7) |
| C18 | 0.0685 (13) | 0.0443 (10) | 0.0536 (11) | −0.0121 (11) | 0.0078 (11) | 0.0016 (9) |
| C19 | 0.0589 (12) | 0.0464 (10) | 0.0498 (10) | 0.0020 (10) | 0.0090 (10) | 0.0082 (9) |
| C20 | 0.0554 (12) | 0.0471 (10) | 0.0424 (9) | −0.0055 (9) | 0.0033 (8) | −0.0089 (8) |
| C21 | 0.0797 (17) | 0.0773 (16) | 0.0594 (13) | 0.0107 (14) | −0.0034 (12) | −0.0307 (12) |
| C22 | 0.0501 (10) | 0.0540 (10) | 0.0373 (8) | −0.0082 (10) | 0.0034 (8) | −0.0058 (8) |
| C23 | 0.0579 (13) | 0.0719 (14) | 0.0468 (11) | −0.0172 (12) | −0.0006 (10) | −0.0029 (10) |
| C24 | 0.0556 (13) | 0.0872 (16) | 0.0516 (11) | −0.0077 (14) | −0.0082 (10) | −0.0018 (11) |
| C25 | 0.0699 (14) | 0.0672 (13) | 0.0409 (10) | −0.0005 (12) | −0.0053 (10) | −0.0072 (9) |
| C26 | 0.0707 (14) | 0.0584 (12) | 0.0506 (11) | −0.0120 (12) | −0.0046 (11) | 0.0041 (10) |
| O27 | 0.0522 (8) | 0.0616 (8) | 0.0472 (7) | −0.0106 (7) | 0.0010 (6) | 0.0036 (7) |
| C28 | 0.0959 (19) | 0.0858 (17) | 0.0654 (14) | 0.0142 (17) | −0.0129 (14) | 0.0027 (14) |
| O29 | 0.0533 (8) | 0.0609 (8) | 0.0387 (6) | 0.0071 (7) | −0.0027 (6) | −0.0085 (6) |
| O30 | 0.0981 (13) | 0.0661 (9) | 0.0435 (8) | 0.0378 (10) | 0.0019 (9) | −0.0110 (7) |
| O31 | 0.0708 (10) | 0.0598 (8) | 0.0390 (6) | 0.0138 (8) | −0.0043 (6) | 0.0051 (6) |
| S32 | 0.0559 (3) | 0.0777 (4) | 0.0410 (2) | 0.0079 (3) | −0.0039 (2) | 0.0055 (2) |
| O33 | 0.0600 (9) | 0.1110 (13) | 0.0551 (9) | −0.0139 (10) | 0.0071 (8) | 0.0017 (9) |
| O34 | 0.0882 (12) | 0.1071 (13) | 0.0521 (8) | 0.0312 (11) | −0.0188 (9) | 0.0102 (9) |
| C35 | 0.0605 (12) | 0.0548 (11) | 0.0365 (9) | −0.0038 (10) | 0.0006 (9) | 0.0038 (9) |
| C36 | 0.0881 (19) | 0.0585 (13) | 0.0740 (15) | −0.0034 (13) | 0.0191 (13) | 0.0177 (12) |
| C37 | 0.108 (2) | 0.0530 (13) | 0.0968 (18) | 0.0096 (16) | 0.0092 (18) | 0.0002 (14) |
| C38 | 0.0751 (17) | 0.0809 (17) | 0.0730 (15) | 0.0027 (15) | 0.0090 (13) | −0.0160 (14) |
| C39 | 0.0727 (16) | 0.0827 (17) | 0.0692 (14) | −0.0126 (15) | 0.0197 (13) | 0.0031 (13) |
| C40 | 0.0720 (15) | 0.0563 (12) | 0.0559 (11) | −0.0085 (12) | 0.0084 (11) | 0.0065 (10) |
| C41 | 0.117 (3) | 0.134 (3) | 0.150 (3) | 0.031 (3) | 0.041 (3) | −0.040 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.528 (3) | C18—H18B | 0.9600 |
| C1—C10 | 1.539 (3) | C18—H18C | 0.9600 |
| C1—H1A | 0.9700 | C19—H19A | 0.9600 |

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|---|---|---|---|
| C1—H1B | 0.9700 | C19—H19B | 0.9600 |
| C2—C3 | 1.511 (3) | C19—H19C | 0.9600 |
| C2—H2A | 0.9700 | C20—C22 | 1.516 (3) |
| C2—H2B | 0.9700 | C20—C21 | 1.523 (3) |
| C3—O31 | 1.485 (2) | C20—H20A | 0.9800 |
| C3—C4 | 1.514 (3) | C21—H21A | 0.9600 |
| C3—H3A | 0.9800 | C21—H21B | 0.9600 |
| C4—C5 | 1.536 (2) | C21—H21C | 0.9600 |
| C4—H4A | 0.9700 | C22—O27 | 1.422 (2) |
| C4—H4B | 0.9700 | C22—O29 | 1.435 (2) |
| C5—C6 | 1.530 (3) | C22—C23 | 1.515 (3) |
| C5—C10 | 1.561 (2) | C23—C24 | 1.516 (3) |
| C5—H5A | 0.9800 | C23—H23A | 0.9700 |
| C6—O30 | 1.437 (2) | C23—H23B | 0.9700 |
| C6—C7 | 1.518 (2) | C24—C25 | 1.513 (3) |
| C6—H6A | 0.9800 | C24—H24A | 0.9700 |
| C7—C8 | 1.532 (2) | C24—H24B | 0.9700 |
| C7—H7A | 0.9700 | C25—C26 | 1.512 (3) |
| C7—H7B | 0.9700 | C25—C28 | 1.526 (3) |
| C8—C14 | 1.526 (2) | C25—H25A | 0.9800 |
| C8—C9 | 1.542 (2) | C26—O27 | 1.432 (3) |
| C8—H8A | 0.9800 | C26—H26A | 0.9700 |
| C9—C11 | 1.543 (2) | C26—H26B | 0.9700 |
| C9—C10 | 1.556 (2) | C28—H28A | 0.9600 |
| C9—H9A | 0.9800 | C28—H28B | 0.9600 |
| C10—C19 | 1.541 (3) | C28—H28C | 0.9600 |
| C11—C12 | 1.538 (3) | O30—H30 | 0.78 (3) |
| C11—H11A | 0.9700 | O31—S32 | 1.5680 (15) |
| C11—H11B | 0.9700 | S32—O34 | 1.4241 (16) |
| C12—C13 | 1.525 (3) | S32—O33 | 1.4340 (18) |
| C12—H12A | 0.9700 | S32—C35 | 1.749 (2) |
| C12—H12B | 0.9700 | C35—C40 | 1.377 (3) |
| C13—C18 | 1.533 (3) | C35—C36 | 1.383 (3) |
| C13—C14 | 1.550 (2) | C36—C37 | 1.380 (4) |
| C13—C17 | 1.559 (2) | C36—H36A | 0.9300 |
| C14—C15 | 1.529 (3) | C37—C38 | 1.369 (4) |
| C14—H14A | 0.9800 | C37—H37A | 0.9300 |
| C15—C16 | 1.533 (2) | C38—C39 | 1.383 (4) |
| C15—H15A | 0.9700 | C38—C41 | 1.504 (4) |
| C15—H15B | 0.9700 | C39—C40 | 1.377 (3) |
| C16—O29 | 1.436 (2) | C39—H39A | 0.9300 |
| C16—C17 | 1.550 (3) | C40—H40A | 0.9300 |
| C16—H16A | 0.9800 | C41—H41A | 0.9600 |
| C17—C20 | 1.537 (3) | C41—H41B | 0.9600 |
| C17—H17A | 0.9800 | C41—H41C | 0.9600 |
| C18—H18A | 0.9600 | | |

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|---|---|---|---|
| C2—C1—C10 | 113.18 (16) | C16—C17—C13 | 105.90 (13) |
| C2—C1—H1A | 108.9 | C20—C17—H17A | 109.1 |

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|---|---|---|---|
| C10—C1—H1A | 108.9 | C16—C17—H17A | 109.1 |
| C2—C1—H1B | 108.9 | C13—C17—H17A | 109.1 |
| C10—C1—H1B | 108.9 | C13—C18—H18A | 109.5 |
| H1A—C1—H1B | 107.8 | C13—C18—H18B | 109.5 |
| C3—C2—C1 | 110.78 (16) | H18A—C18—H18B | 109.5 |
| C3—C2—H2A | 109.5 | C13—C18—H18C | 109.5 |
| C1—C2—H2A | 109.5 | H18A—C18—H18C | 109.5 |
| C3—C2—H2B | 109.5 | H18B—C18—H18C | 109.5 |
| C1—C2—H2B | 109.5 | C10—C19—H19A | 109.5 |
| H2A—C2—H2B | 108.1 | C10—C19—H19B | 109.5 |
| O31—C3—C2 | 104.59 (15) | H19A—C19—H19B | 109.5 |
| O31—C3—C4 | 110.72 (16) | C10—C19—H19C | 109.5 |
| C2—C3—C4 | 112.62 (18) | H19A—C19—H19C | 109.5 |
| O31—C3—H3A | 109.6 | H19B—C19—H19C | 109.5 |
| C2—C3—H3A | 109.6 | C22—C20—C21 | 115.60 (17) |
| C4—C3—H3A | 109.6 | C22—C20—C17 | 102.79 (15) |
| C3—C4—C5 | 110.11 (15) | C21—C20—C17 | 115.06 (18) |
| C3—C4—H4A | 109.6 | C22—C20—H20A | 107.6 |
| C5—C4—H4A | 109.6 | C21—C20—H20A | 107.6 |
| C3—C4—H4B | 109.6 | C17—C20—H20A | 107.6 |
| C5—C4—H4B | 109.6 | C20—C21—H21A | 109.5 |
| H4A—C4—H4B | 108.2 | C20—C21—H21B | 109.5 |
| C6—C5—C4 | 112.09 (15) | H21A—C21—H21B | 109.5 |
| C6—C5—C10 | 112.00 (15) | C20—C21—H21C | 109.5 |
| C4—C5—C10 | 112.53 (15) | H21A—C21—H21C | 109.5 |
| C6—C5—H5A | 106.6 | H21B—C21—H21C | 109.5 |
| C4—C5—H5A | 106.6 | O27—C22—O29 | 110.39 (15) |
| C10—C5—H5A | 106.6 | O27—C22—C23 | 110.60 (16) |
| O30—C6—C7 | 106.97 (15) | O29—C22—C23 | 107.87 (16) |
| O30—C6—C5 | 111.38 (17) | O27—C22—C20 | 107.67 (16) |
| C7—C6—C5 | 110.63 (15) | O29—C22—C20 | 103.08 (14) |
| O30—C6—H6A | 109.3 | C23—C22—C20 | 116.93 (18) |
| C7—C6—H6A | 109.3 | C22—C23—C24 | 111.99 (18) |
| C5—C6—H6A | 109.3 | C22—C23—H23A | 109.2 |
| C6—C7—C8 | 112.68 (15) | C24—C23—H23A | 109.2 |
| C6—C7—H7A | 109.1 | C22—C23—H23B | 109.2 |
| C8—C7—H7A | 109.1 | C24—C23—H23B | 109.2 |
| C6—C7—H7B | 109.1 | H23A—C23—H23B | 107.9 |
| C8—C7—H7B | 109.1 | C25—C24—C23 | 111.6 (2) |
| H7A—C7—H7B | 107.8 | C25—C24—H24A | 109.3 |
| C14—C8—C7 | 112.66 (14) | C23—C24—H24A | 109.3 |
| C14—C8—C9 | 108.86 (14) | C25—C24—H24B | 109.3 |
| C7—C8—C9 | 110.35 (15) | C23—C24—H24B | 109.3 |
| C14—C8—H8A | 108.3 | H24A—C24—H24B | 108.0 |
| C7—C8—H8A | 108.3 | C26—C25—C24 | 108.51 (17) |
| C9—C8—H8A | 108.3 | C26—C25—C28 | 110.3 (2) |
| C8—C9—C11 | 112.69 (16) | C24—C25—C28 | 112.9 (2) |
| C8—C9—C10 | 111.83 (14) | C26—C25—H25A | 108.3 |
| C11—C9—C10 | 113.38 (15) | C24—C25—H25A | 108.3 |

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| C8—C9—H9A | 106.1 | C28—C25—H25A | 108.3 |
| C11—C9—H9A | 106.1 | O27—C26—C25 | 113.06 (17) |
| C10—C9—H9A | 106.1 | O27—C26—H26A | 109.0 |
| C1—C10—C19 | 108.94 (16) | C25—C26—H26A | 109.0 |
| C1—C10—C9 | 110.15 (14) | O27—C26—H26B | 109.0 |
| C19—C10—C9 | 110.82 (16) | C25—C26—H26B | 109.0 |
| C1—C10—C5 | 106.74 (16) | H26A—C26—H26B | 107.8 |
| C19—C10—C5 | 112.22 (14) | C22—O27—C26 | 114.12 (16) |
| C9—C10—C5 | 107.90 (14) | C25—C28—H28A | 109.5 |
| C12—C11—C9 | 113.93 (15) | C25—C28—H28B | 109.5 |
| C12—C11—H11A | 108.8 | H28A—C28—H28B | 109.5 |
| C9—C11—H11A | 108.8 | C25—C28—H28C | 109.5 |
| C12—C11—H11B | 108.8 | H28A—C28—H28C | 109.5 |
| C9—C11—H11B | 108.8 | H28B—C28—H28C | 109.5 |
| H11A—C11—H11B | 107.7 | C22—O29—C16 | 106.34 (13) |
| C13—C12—C11 | 111.28 (15) | C6—O30—H30 | 109 (2) |
| C13—C12—H12A | 109.4 | C3—O31—S32 | 121.63 (13) |
| C11—C12—H12A | 109.4 | O34—S32—O33 | 120.11 (12) |
| C13—C12—H12B | 109.4 | O34—S32—O31 | 104.27 (10) |
| C11—C12—H12B | 109.4 | O33—S32—O31 | 109.71 (9) |
| H12A—C12—H12B | 108.0 | O34—S32—C35 | 108.69 (10) |
| C12—C13—C18 | 109.76 (16) | O33—S32—C35 | 108.83 (11) |
| C12—C13—C14 | 107.14 (15) | O31—S32—C35 | 104.03 (9) |
| C18—C13—C14 | 112.31 (14) | C40—C35—C36 | 119.8 (2) |
| C12—C13—C17 | 115.15 (15) | C40—C35—S32 | 119.47 (16) |
| C18—C13—C17 | 111.15 (16) | C36—C35—S32 | 120.73 (17) |
| C14—C13—C17 | 101.04 (13) | C37—C36—C35 | 119.4 (2) |
| C8—C14—C15 | 121.10 (15) | C37—C36—H36A | 120.3 |
| C8—C14—C13 | 112.90 (14) | C35—C36—H36A | 120.3 |
| C15—C14—C13 | 103.99 (14) | C38—C37—C36 | 122.1 (2) |
| C8—C14—H14A | 105.9 | C38—C37—H37A | 119.0 |
| C15—C14—H14A | 105.9 | C36—C37—H37A | 119.0 |
| C13—C14—H14A | 105.9 | C37—C38—C39 | 117.4 (2) |
| C14—C15—C16 | 100.44 (15) | C37—C38—C41 | 120.9 (3) |
| C14—C15—H15A | 111.7 | C39—C38—C41 | 121.7 (3) |
| C16—C15—H15A | 111.7 | C40—C39—C38 | 122.0 (2) |
| C14—C15—H15B | 111.7 | C40—C39—H39A | 119.0 |
| C16—C15—H15B | 111.7 | C38—C39—H39A | 119.0 |
| H15A—C15—H15B | 109.5 | C39—C40—C35 | 119.4 (2) |
| O29—C16—C15 | 113.67 (16) | C39—C40—H40A | 120.3 |
| O29—C16—C17 | 107.18 (14) | C35—C40—H40A | 120.3 |
| C15—C16—C17 | 106.85 (14) | C38—C41—H41A | 109.5 |
| O29—C16—H16A | 109.7 | C38—C41—H41B | 109.5 |
| C15—C16—H16A | 109.7 | H41A—C41—H41B | 109.5 |
| C17—C16—H16A | 109.7 | C38—C41—H41C | 109.5 |
| C20—C17—C16 | 102.53 (15) | H41A—C41—H41C | 109.5 |
| C20—C17—C13 | 120.61 (15) | H41B—C41—H41C | 109.5 |
| | | | |
| C10—C1—C2—C3 | −56.5 (2) | O29—C16—C17—C13 | −127.69 (15) |

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|---|---|---|---|
| C1—C2—C3—O31 | 174.77 (17) | C15—C16—C17—C13 | −5.49 (19) |
| C1—C2—C3—C4 | 54.5 (2) | C12—C13—C17—C20 | 107.2 (2) |
| O31—C3—C4—C5 | −171.61 (16) | C18—C13—C17—C20 | −18.4 (2) |
| C2—C3—C4—C5 | −54.9 (2) | C14—C13—C17—C20 | −137.79 (17) |
| C3—C4—C5—C6 | −175.57 (17) | C12—C13—C17—C16 | −137.32 (16) |
| C3—C4—C5—C10 | 57.1 (2) | C18—C13—C17—C16 | 97.08 (17) |
| C4—C5—C6—O30 | 56.6 (2) | C14—C13—C17—C16 | −22.27 (17) |
| C10—C5—C6—O30 | −175.81 (15) | C16—C17—C20—C22 | 24.43 (18) |
| C4—C5—C6—C7 | 175.44 (17) | C13—C17—C20—C22 | 141.67 (16) |
| C10—C5—C6—C7 | −57.0 (2) | C16—C17—C20—C21 | 150.96 (18) |
| O30—C6—C7—C8 | 176.66 (17) | C13—C17—C20—C21 | −91.8 (2) |
| C5—C6—C7—C8 | 55.2 (2) | C21—C20—C22—O27 | −50.2 (2) |
| C6—C7—C8—C14 | −176.75 (17) | C17—C20—C22—O27 | 76.01 (17) |
| C6—C7—C8—C9 | −54.8 (2) | C21—C20—C22—O29 | −166.88 (18) |
| C14—C8—C9—C11 | −50.40 (19) | C17—C20—C22—O29 | −40.70 (18) |
| C7—C8—C9—C11 | −174.53 (15) | C21—C20—C22—C23 | 75.0 (2) |
| C14—C8—C9—C10 | −179.51 (15) | C17—C20—C22—C23 | −158.82 (16) |
| C7—C8—C9—C10 | 56.36 (19) | O27—C22—C23—C24 | −52.4 (2) |
| C2—C1—C10—C19 | −64.9 (2) | O29—C22—C23—C24 | 68.4 (2) |
| C2—C1—C10—C9 | 173.36 (16) | C20—C22—C23—C24 | −176.07 (17) |
| C2—C1—C10—C5 | 56.5 (2) | C22—C23—C24—C25 | 52.5 (2) |
| C8—C9—C10—C1 | −173.24 (15) | C23—C24—C25—C26 | −52.1 (2) |
| C11—C9—C10—C1 | 58.0 (2) | C23—C24—C25—C28 | −174.71 (18) |
| C8—C9—C10—C19 | 66.14 (19) | C24—C25—C26—O27 | 54.8 (2) |
| C11—C9—C10—C19 | −62.6 (2) | C28—C25—C26—O27 | 178.89 (18) |
| C8—C9—C10—C5 | −57.08 (19) | O29—C22—O27—C26 | −63.9 (2) |
| C11—C9—C10—C5 | 174.17 (16) | C23—C22—O27—C26 | 55.4 (2) |
| C6—C5—C10—C1 | 175.76 (15) | C20—C22—O27—C26 | −175.73 (15) |
| C4—C5—C10—C1 | −56.9 (2) | C25—C26—O27—C22 | −58.3 (2) |
| C6—C5—C10—C19 | −65.0 (2) | O27—C22—O29—C16 | −73.14 (18) |
| C4—C5—C10—C19 | 62.4 (2) | C23—C22—O29—C16 | 165.92 (16) |
| C6—C5—C10—C9 | 57.39 (19) | C20—C22—O29—C16 | 41.62 (18) |
| C4—C5—C10—C9 | −175.26 (16) | C15—C16—O29—C22 | −143.50 (16) |
| C8—C9—C11—C12 | 48.6 (2) | C17—C16—O29—C22 | −25.66 (18) |
| C10—C9—C11—C12 | 176.91 (17) | C2—C3—O31—S32 | 142.58 (15) |
| C9—C11—C12—C13 | −52.6 (2) | C4—C3—O31—S32 | −95.9 (2) |
| C11—C12—C13—C18 | −64.8 (2) | C3—O31—S32—O34 | −162.55 (15) |
| C11—C12—C13—C14 | 57.4 (2) | C3—O31—S32—O33 | −32.69 (18) |
| C11—C12—C13—C17 | 168.88 (15) | C3—O31—S32—C35 | 83.60 (16) |
| C7—C8—C14—C15 | −53.7 (2) | O34—S32—C35—C40 | −42.7 (2) |
| C9—C8—C14—C15 | −176.44 (16) | O33—S32—C35—C40 | −175.16 (17) |
| C7—C8—C14—C13 | −177.83 (15) | O31—S32—C35—C40 | 67.93 (18) |
| C9—C8—C14—C13 | 59.4 (2) | O34—S32—C35—C36 | 138.8 (2) |
| C12—C13—C14—C8 | −63.21 (19) | O33—S32—C35—C36 | 6.4 (2) |
| C18—C13—C14—C8 | 57.4 (2) | O31—S32—C35—C36 | −110.5 (2) |
| C17—C13—C14—C8 | 175.91 (15) | C40—C35—C36—C37 | −0.5 (4) |
| C12—C13—C14—C15 | 163.71 (15) | S32—C35—C36—C37 | 177.9 (2) |
| C18—C13—C14—C15 | −75.69 (18) | C35—C36—C37—C38 | 0.9 (4) |
| C17—C13—C14—C15 | 42.83 (17) | C36—C37—C38—C39 | −0.8 (4) |

| | | | |
|---|---|---|---|
| C8—C14—C15—C16 | −174.43 (16) | C36—C37—C38—C41 | 179.3 (3) |
| C13—C14—C15—C16 | −46.22 (17) | C37—C38—C39—C40 | 0.4 (4) |
| C14—C15—C16—O29 | 149.34 (15) | C41—C38—C39—C40 | −179.7 (3) |
| C14—C15—C16—C17 | 31.31 (18) | C38—C39—C40—C35 | −0.1 (4) |
| O29—C16—C17—C20 | −0.41 (18) | C36—C35—C40—C39 | 0.1 (3) |
| C15—C16—C17—C20 | 121.79 (16) | S32—C35—C40—C39 | −178.35 (18) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O30—H30···O33$^{i}$ | 0.78 (3) | 2.35 (3) | 3.098 (2) | 159 (3) |
| C40—H40*A*···O34$^{ii}$ | 0.93 | 2.65 | 3.352 (3) | 133 |

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