Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 4-(9-Anthryl)-1-(3-bromophenyl)spiro-[azetidine-3,9′-xanthen]-2-one

**Ísmail Çelik,[a] Mehmet Akkurt,[b]* Aliasghar Jarrahpour,[c] Edris Ebrahimi[c] and Orhan Büyükgüngör[d]**

[a]Department of Physics, Faculty of Arts and Sciences, Cumhuriyet University, 58140 Sivas, Turkey, [b]Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey, [c]Department of Chemistry, College of Sciences, Shiraz University, 71454 Shiraz, Iran, and [d]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey
Correspondence e-mail: akkurt@erciyes.edu.tr

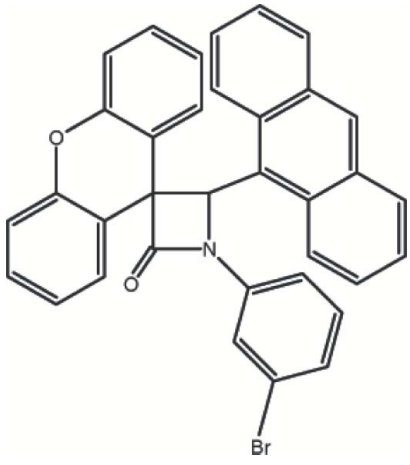
Received 17 September 2009; accepted 18 September 2009

Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.053; $wR$ factor = 0.122; data-to-parameter ratio = 15.4.

In the title molecule, $C_{35}H_{22}BrNO_2$, the four-membered ring of the $\beta$-lactam unit is nearly planar [maximum deviation = 0.003 (3) Å] and makes dihedral angles of 87.07 (15), 59.80 (16) and 20.81 (19)°, respectively, with the xanthene system, the anthracene system and the bromo-substituted benzene ring. The molecular conformation is stabilized by weak intramolecular C—H···O and C—H···N hydrogen bonds. The crystal structure features weak C—H···$\pi$ interactions.

## Related literature

For general background to $\beta$-lactam antibiotics, see: Jarrahpour & Khalili (2007); Landis-Piwowar *et al.* (2006); Palomo *et al.* (2003); Skiles & McNeil (1990); Wu & Tormos (1997). For related structures, see: Akkurt *et al.* (2006, 2007); Akkurt, Jarrahpour *et al.* (2008); Akkurt, Karaca *et al.* (2008); Pınar *et al.* (2006). For geometric analysis, see: Cremer & Pople (1975).




## Experimental

### Crystal data

$C_{35}H_{22}BrNO_2$
$M_r$ = 568.44
Monoclinic, $P2_1/c$
$a$ = 11.1143 (4) Å
$b$ = 19.9412 (5) Å
$c$ = 14.0317 (5) Å
$\beta$ = 122.106 (2)°
$V$ = 2634.28 (16) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.59 mm$^{-1}$
$T$ = 295 K
0.71 × 0.59 × 0.39 mm

### Data collection

Stoe IPDS2 diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min}$ = 0.397, $T_{max}$ = 0.575
39287 measured reflections
5424 independent reflections
4308 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.046

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.122
$S$ = 1.08
5424 reflections
352 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.74 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2···N1 | 0.93 | 2.30 | 2.968 (4) | 128 |
| C31—H31···O2 | 0.93 | 2.46 | 3.073 (4) | 123 |
| C11—H11···$Cg2^{i}$ | 0.93 | 2.75 | 3.653 (5) | 164 |
| C26—H26···$Cg1^{i}$ | 0.93 | 2.96 | 3.616 (4) | 129 |

Symmetry code: (i) $-x+1, -y+1, -z$. $Cg1$ and $Cg2$ are the centroids of the C8–C13 C30–C35 rings, respectively].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS*2* diffractometer (purchased under grant F.279 of the University Research Fund). The authors thank the Cumhuriyet University Research Foundation (CUBAP grant No 2009/F-266) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2462).

## References

Akkurt, M., Jarrahpour, A., Ebrahimi, E., Gençaslan, M. & Büyükgüngör, O. (2008). *Acta Cryst.* E**64**, o2466–o2467.
Akkurt, M., Karaca, S., Jarrahpour, A., Ebrahimi, E. & Büyükgüngör, O. (2008). *Acta Cryst.* E**64**, o902–o903.
Akkurt, M., Karaca, S., Jarrahpour, A. A., Khalili, D. & Büyükgüngör, O. (2006). *Acta Cryst.* E**62**, o866–o868.
Akkurt, M., Yalçın, Ş. P., Jarrahpour, A. A., Nazari, M. & Büyükgüngör, O. (2007). *Acta Cryst.* E**63**, o3729–o3730.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Jarrahpour, A. & Khalili, D. (2007). *Tetrahedron. Lett.* **48**, 7140–7143.
Landis-Piwowar, K. R., Chen, D., Cui, Q. C., Minic, V., Becker, F. F., Banik, B. K. & Dou, Q. P. (2006). *Int. J. Mol Med.* **17**, 931–935.
Palomo, C., Aizpurua, J. M., Benito, A., Miranda, J. I., Fratila, R. M., Matute, C., Domercq, M., Gago, F., Martin-Santamaria, S. & Linden, A. (2003). *J. Am. Chem. Soc*. **125**, 16243–16260.
Pınar, Ş., Akkurt, M., Jarrahpour, A. A., Khalili, D. & Büyükgüngör, O. (2006). *Acta Cryst.* E**62**, o804–o806.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Skiles, J. W. & McNeil, D. (1990). *Tetrahedron Lett.* **31**, 7277–7280.
Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
Wu, G. & Tormos, W. (1997). *J. Org. Chem*. **62**, 6412–6414.

# supporting information

*Acta Cryst.* (2009). E**65**, o2522–o2523 [doi:10.1107/S1600536809037830]

## 4-(9-Anthryl)-1-(3-bromophenyl)spiro[azetidine-3,9′-xanthen]-2-one

**Ísmail Çelik, Mehmet Akkurt, Aliasghar Jarrahpour, Edris Ebrahimi and Orhan Büyükgüngör**

### S1. Comment

The application of spiro-*β*-lactams in peptidomimetic chemistry is well documented, and relevant examples include the development of constrained *β*-turn mimetics (Palomo *et al.*, 2003). Also, spiro-*β*-lactams have received attention in medicinal chemistry owing to their antiviral and antibacterial properties, (Skiles *et al.*, 1990) as well as recognized activity as cholesterol absorption inhibitors (Wu & Tormos, 1997). Syntheses of new spiro-*β*-lactams have been reported in the literature (Jarrahpour & Khalili, 2007). Persistent but relatively limited research has been devoted to the use of compounds related to polycyclic aromatic hydrocarbons (PAH) asanticancer agents. Banik and co-workers have described the cytotoxicity of a number of new and novel PAH against human cancer cell lines (Landis-Piwowar *et al.*, 2006).

In the title compound (I) (Fig. 1), the *β*-lactam ring (N1/C15/C16/C29) is essentially planar with a maximum deviation of 0.003 (3) Å for C29 from the mean plane and its bond lengths and angles are comparable with the values in our previously papers (Akkurt, Jarrahpour *et al.*, 2008; Akkurt, Karaca *et al.*, 2008; Akkurt *et al.*, 2006,2007; Pınar *et al.*, 2006). Atom O2 lies almost in the *β*-lactam plane, with a deviation of -0.032 (2) Å. The dihedral angle between the benzene ring (C30—C35) attached at N1 and the *β*-lactam ring is 20.81 (19)°.

In the xanthene ring system (O1/C17–C28), attached at C16, the benzene rings (C17–C22) and (C23–C28) are almost planar, forming a dihedral angle of 12.84 (16)° with each other. Its central ring, O1/C16/C17/C22/C23/C28, is not planar, with puckering parameters: $Q_T$= 0.198 (3) Å, $\theta$ = 99.3 (9)° and $\varphi$ = 6.5 (9)° (Cremer & Pople, 1975). The mean plane of the xanthene ring system forms the dihedral angles of 87.07 (15)°, and 84.80 (13)°, with the *β*-lactam ring and the benzene ring (C30–C35), respectively.

The anthracene ring system, attached at C15, is almost planar, with maximum deviations of -0.034 (3) Å for C14, 0.032 (3) Å for C13 and 0.031 (4) Å for C1, makes dihedral angle of 59.80 (16)°, 78.58 (13)° and 62.40 (8)°, with the *β*-lactam, benzene and the mean plane of the xanthene ring system, respectively.

Molecular conformation is stabilized by weak intramolecular C—H···O and C—H···N hydrogen bonds. The crystal packing is stabilized by two weak C—H···$\pi$ interactions [Table 1; *Cg*1 and *Cg*2 refer to the ring centroids of the rings (C8–C13) and (C30–C35), respectively]. Fig. 2 shows a view down the *a* axis of the crystal packing of compound (I).

### S2. Experimental

A mixture of (*E*)-*N*-(anthracen-10-ylmethylene)-3-bromobenzenamine (0.30 g, 0.83 mmol) and triethylamine (0.42 g, 4.15 mmol), 9*H*-xanthen-9-carboxylic acid (0.28 g, 1.24 mmol) and tosyl chloride (0.24 g, 1.24 mmol) in $CH_2Cl_2$(15 ml) was stirred at room temperature for 24 h. Then it was washed with HCl 1 N (20 ml) and saturated sodiumbicarbonate solution (20 ml), brine (20 ml), dried ($Na_2SO_4$) and the solvent was evaporated to give the crude product as an orange crystal which was then purified by recrystallization from ethyl acetate (yield: 55%, m.p.: 495–497 K). IR (KBr, $cm^{-1}$): 1755 (CO *β*-lactam). $^1$H-NMR $\delta$ (p.p.m.): 6.18 (s, 1H, H-4), 6.23–8.65 (m, ArH, 21H).$^{13}$C-NMR $\delta$ (p.p.m.): 66.0 (C-3),

75.6 (C-4), 115.7–151.9 (aromatic carbon), 167.7 (CO $\beta$-lactam). Analysis calculated for $C_{35}H_{22}BrNO_2$: C 73.95, H 3.90, N 2.46%. Found: C 73.90, H 3.93, N 2.51%.

### S3. Refinement

H atoms were positioned geometrically and refined a riding model, with the C—H = 0.93 and 0.98 Å and with $U_{iso}$(H) = 1.2$U_{eq}$(C).

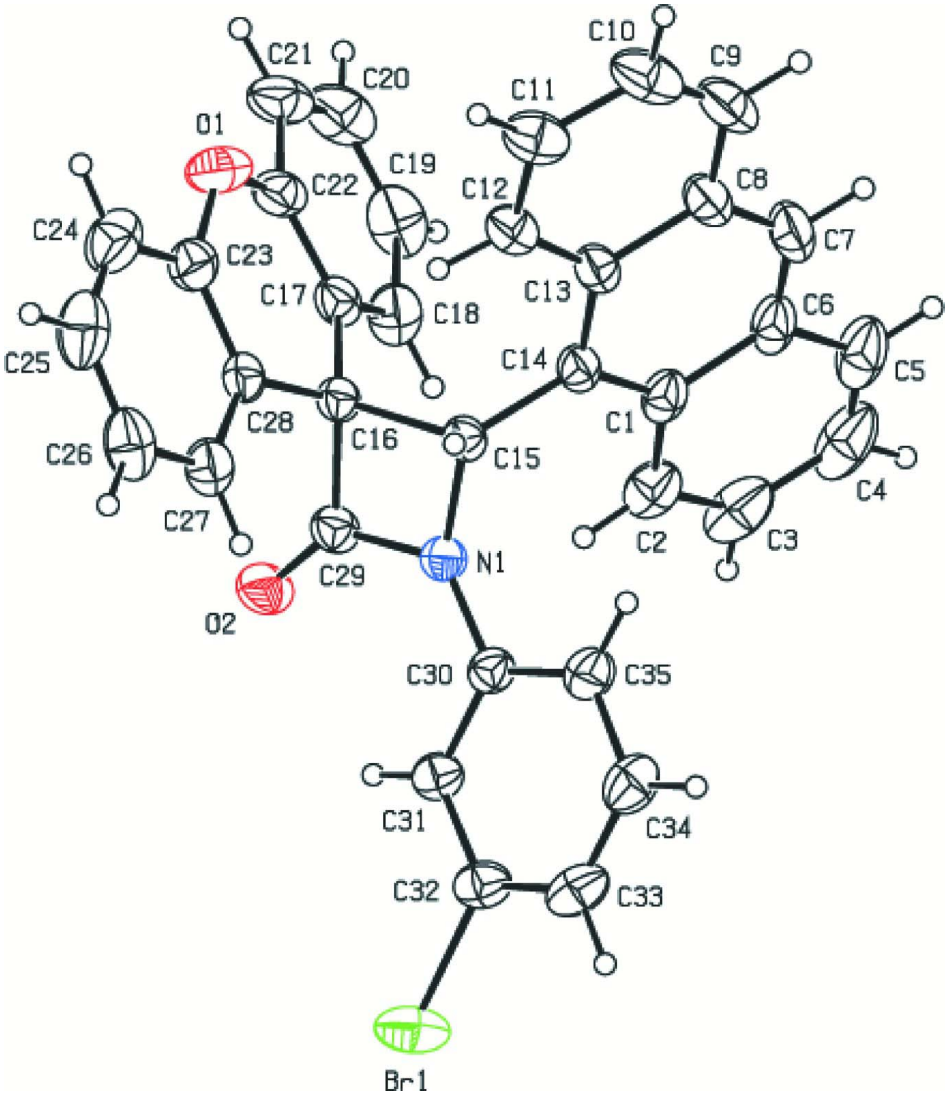



**Figure 1**

The title molecular structure, with the atom-numbering scheme and 30% probability displacement ellipsoids

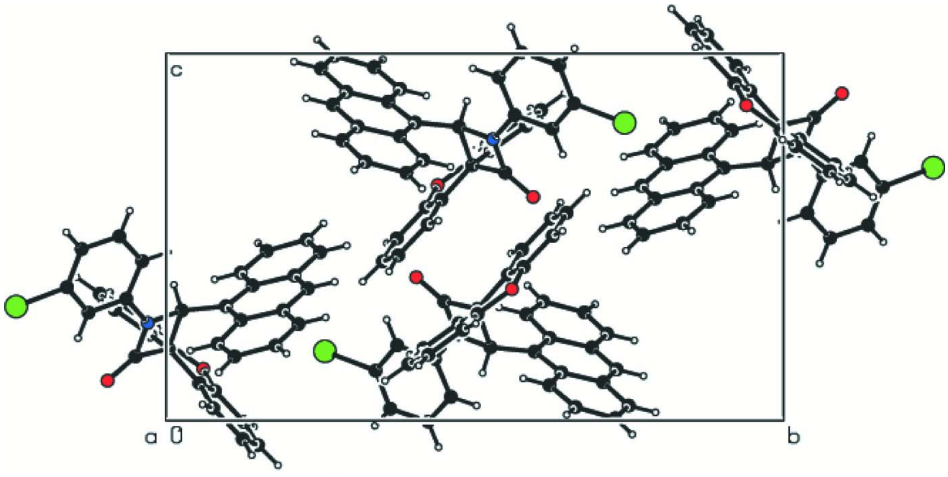



**Figure 2**

A view down the *a* axis of the packing of (I).

**4-(9-Anthryl)-1-(3-bromophenyl)spiro[azetidine-3,9′-xanthen]-2-one**

*Crystal data*

$C_{35}H_{22}BrNO_2$
$M_r = 568.44$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.1143\ (4)$ Å
$b = 19.9412\ (5)$ Å
$c = 14.0317\ (5)$ Å
$\beta = 122.106\ (2)°$
$V = 2634.28\ (16)$ Å$^3$
$Z = 4$
$F(000) = 1160$
$D_x = 1.433$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 43756 reflections
$\theta = 1.7–28.0°$
$\mu = 1.59$ mm$^{-1}$
$T = 295$ K
Block, light yellow
0.71 × 0.59 × 0.39 mm

*Data collection*

Stoe IPDS2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min} = 0.397$, $T_{max} = 0.575$
39287 measured reflections
5424 independent reflections
4308 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 26.5°$, $\theta_{min} = 2.0°$
$h = -13\rightarrow13$
$k = -24\rightarrow24$
$l = -17\rightarrow17$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.122$
$S = 1.08$
5424 reflections
352 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
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 1.4948P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å$^{-3}$
$\Delta\rho_{min} = -0.74$ e Å$^{-3}$

*Special details*

**Geometry**. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement**. Refinement on $F^2$ for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.14849 (5) | 0.25728 (2) | 0.18916 (4) | 0.0883 (2) |
| O1 | 0.9308 (2) | 0.56016 (12) | 0.3586 (2) | 0.0757 (8) |
| O2 | 0.6106 (2) | 0.40529 (10) | 0.39082 (18) | 0.0675 (7) |
| N1 | 0.4500 (2) | 0.47038 (10) | 0.23373 (18) | 0.0475 (7) |
| C1 | 0.3676 (3) | 0.62105 (14) | 0.2257 (2) | 0.0543 (8) |
| C2 | 0.3254 (3) | 0.58361 (19) | 0.2902 (3) | 0.0675 (11) |
| C3 | 0.2423 (4) | 0.6108 (2) | 0.3248 (3) | 0.0878 (14) |
| C4 | 0.1913 (4) | 0.6773 (3) | 0.2953 (4) | 0.1023 (18) |
| C5 | 0.2282 (4) | 0.7145 (2) | 0.2365 (4) | 0.0895 (16) |
| C6 | 0.3177 (3) | 0.68965 (16) | 0.1994 (3) | 0.0668 (10) |
| C7 | 0.3553 (4) | 0.72966 (16) | 0.1396 (3) | 0.0732 (11) |
| C8 | 0.4436 (3) | 0.70807 (14) | 0.1049 (2) | 0.0617 (9) |
| C9 | 0.4806 (4) | 0.74926 (15) | 0.0411 (3) | 0.0798 (13) |
| C10 | 0.5646 (5) | 0.72759 (18) | 0.0068 (3) | 0.0841 (14) |
| C11 | 0.6241 (4) | 0.66303 (17) | 0.0374 (3) | 0.0724 (12) |
| C12 | 0.5919 (3) | 0.62105 (14) | 0.0967 (2) | 0.0562 (9) |
| C13 | 0.4974 (3) | 0.64013 (13) | 0.1315 (2) | 0.0500 (8) |
| C14 | 0.4549 (3) | 0.59686 (12) | 0.1883 (2) | 0.0461 (8) |
| C15 | 0.5078 (3) | 0.52549 (12) | 0.1999 (2) | 0.0429 (7) |
| C16 | 0.6615 (3) | 0.50414 (12) | 0.3045 (2) | 0.0451 (7) |
| C17 | 0.7443 (3) | 0.55389 (13) | 0.3976 (2) | 0.0516 (8) |
| C18 | 0.6972 (4) | 0.57626 (17) | 0.4658 (3) | 0.0684 (11) |
| C19 | 0.7729 (5) | 0.62392 (19) | 0.5495 (3) | 0.0836 (14) |
| C20 | 0.8975 (5) | 0.64880 (19) | 0.5662 (3) | 0.0892 (14) |
| C21 | 0.9491 (4) | 0.62630 (17) | 0.5034 (3) | 0.0784 (11) |
| C22 | 0.8721 (3) | 0.57905 (14) | 0.4188 (2) | 0.0595 (9) |
| C23 | 0.8774 (3) | 0.50458 (15) | 0.2907 (2) | 0.0584 (10) |
| C24 | 0.9551 (4) | 0.4803 (2) | 0.2475 (3) | 0.0804 (14) |
| C25 | 0.9094 (4) | 0.4251 (2) | 0.1796 (3) | 0.0851 (16) |
| C26 | 0.7873 (4) | 0.39262 (19) | 0.1543 (3) | 0.0776 (12) |
| C27 | 0.7097 (3) | 0.41707 (15) | 0.1974 (3) | 0.0610 (10) |
| C28 | 0.7521 (3) | 0.47399 (13) | 0.2655 (2) | 0.0485 (8) |
| C29 | 0.5791 (3) | 0.45045 (13) | 0.3248 (2) | 0.0498 (8) |
| C30 | 0.3212 (3) | 0.43540 (13) | 0.1680 (2) | 0.0460 (8) |
| C31 | 0.3017 (3) | 0.37439 (13) | 0.2052 (2) | 0.0500 (8) |

| | | | | |
|---|---|---|---|---|
| C32 | 0.1775 (3) | 0.33946 (14) | 0.1364 (3) | 0.0561 (10) |
| C33 | 0.0742 (3) | 0.36319 (18) | 0.0326 (3) | 0.0667 (11) |
| C34 | 0.0942 (3) | 0.42442 (19) | −0.0021 (3) | 0.0703 (11) |
| C35 | 0.2170 (3) | 0.46130 (16) | 0.0651 (2) | 0.0601 (10) |
| H2 | 0.35540 | 0.53940 | 0.30900 | 0.0810* |
| H3 | 0.21890 | 0.58540 | 0.36830 | 0.1050* |
| H4 | 0.13200 | 0.69490 | 0.31710 | 0.1230* |
| H5 | 0.19490 | 0.75840 | 0.21870 | 0.1070* |
| H7 | 0.31960 | 0.77310 | 0.12190 | 0.0880* |
| H9 | 0.44480 | 0.79270 | 0.02290 | 0.0950* |
| H10 | 0.58390 | 0.75500 | −0.03710 | 0.1010* |
| H11 | 0.68670 | 0.64890 | 0.01650 | 0.0870* |
| H12 | 0.63270 | 0.57860 | 0.11530 | 0.0670* |
| H15 | 0.50170 | 0.51280 | 0.13010 | 0.0520* |
| H18 | 0.61330 | 0.55910 | 0.45540 | 0.0820* |
| H19 | 0.73900 | 0.63880 | 0.59370 | 0.1000* |
| H20 | 0.94720 | 0.68130 | 0.62100 | 0.1070* |
| H21 | 1.03530 | 0.64230 | 0.51670 | 0.0940* |
| H24 | 1.03880 | 0.50150 | 0.26460 | 0.0960* |
| H25 | 0.96180 | 0.40930 | 0.15020 | 0.1020* |
| H26 | 0.75710 | 0.35470 | 0.10880 | 0.0930* |
| H27 | 0.62690 | 0.39500 | 0.18060 | 0.0730* |
| H31 | 0.37060 | 0.35740 | 0.27510 | 0.0600* |
| H33 | −0.00770 | 0.33840 | −0.01330 | 0.0800* |
| H34 | 0.02440 | 0.44130 | −0.07170 | 0.0850* |
| H35 | 0.22910 | 0.50290 | 0.04130 | 0.0720* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0990 (3) | 0.0679 (2) | 0.0934 (3) | −0.0370 (2) | 0.0481 (2) | −0.0161 (2) |
| O1 | 0.0685 (14) | 0.0753 (15) | 0.0782 (15) | −0.0261 (11) | 0.0355 (13) | −0.0033 (12) |
| O2 | 0.0671 (13) | 0.0592 (12) | 0.0570 (12) | −0.0049 (10) | 0.0201 (10) | 0.0178 (10) |
| N1 | 0.0440 (11) | 0.0440 (11) | 0.0460 (12) | −0.0020 (9) | 0.0182 (10) | 0.0036 (9) |
| C1 | 0.0395 (13) | 0.0594 (16) | 0.0496 (15) | 0.0022 (11) | 0.0140 (12) | −0.0148 (13) |
| C2 | 0.0560 (17) | 0.082 (2) | 0.0633 (19) | −0.0060 (15) | 0.0310 (16) | −0.0190 (16) |
| C3 | 0.062 (2) | 0.126 (3) | 0.081 (2) | −0.018 (2) | 0.0418 (19) | −0.042 (2) |
| C4 | 0.058 (2) | 0.139 (4) | 0.104 (3) | 0.001 (2) | 0.039 (2) | −0.062 (3) |
| C5 | 0.057 (2) | 0.095 (3) | 0.092 (3) | 0.0152 (19) | 0.023 (2) | −0.041 (2) |
| C6 | 0.0428 (15) | 0.0620 (18) | 0.067 (2) | 0.0086 (13) | 0.0099 (14) | −0.0245 (16) |
| C7 | 0.066 (2) | 0.0451 (16) | 0.072 (2) | 0.0148 (14) | 0.0120 (17) | −0.0073 (15) |
| C8 | 0.0629 (17) | 0.0399 (14) | 0.0537 (17) | 0.0027 (12) | 0.0116 (14) | −0.0003 (12) |
| C9 | 0.095 (3) | 0.0402 (16) | 0.065 (2) | −0.0026 (15) | 0.0160 (19) | 0.0091 (14) |
| C10 | 0.119 (3) | 0.058 (2) | 0.065 (2) | −0.017 (2) | 0.042 (2) | 0.0067 (16) |
| C11 | 0.091 (2) | 0.065 (2) | 0.063 (2) | −0.0138 (17) | 0.0422 (19) | −0.0021 (16) |
| C12 | 0.0659 (17) | 0.0474 (15) | 0.0535 (16) | −0.0011 (12) | 0.0305 (14) | 0.0029 (12) |
| C13 | 0.0519 (14) | 0.0396 (13) | 0.0429 (14) | 0.0033 (11) | 0.0146 (12) | −0.0009 (11) |
| C14 | 0.0417 (13) | 0.0425 (13) | 0.0392 (13) | 0.0026 (10) | 0.0114 (11) | −0.0028 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C15 | 0.0440 (13) | 0.0397 (12) | 0.0397 (13) | 0.0024 (10) | 0.0186 (11) | 0.0008 (10) |
| C16 | 0.0416 (13) | 0.0400 (12) | 0.0423 (13) | 0.0007 (10) | 0.0146 (11) | 0.0035 (10) |
| C17 | 0.0531 (15) | 0.0422 (13) | 0.0418 (14) | 0.0028 (11) | 0.0133 (12) | 0.0013 (11) |
| C18 | 0.0655 (19) | 0.070 (2) | 0.0535 (17) | 0.0061 (15) | 0.0206 (15) | −0.0107 (15) |
| C19 | 0.100 (3) | 0.077 (2) | 0.0517 (19) | 0.015 (2) | 0.0255 (19) | −0.0099 (17) |
| C20 | 0.109 (3) | 0.064 (2) | 0.053 (2) | −0.014 (2) | 0.015 (2) | −0.0081 (16) |
| C21 | 0.079 (2) | 0.0619 (19) | 0.0574 (19) | −0.0243 (17) | 0.0113 (18) | 0.0043 (16) |
| C22 | 0.0601 (17) | 0.0477 (15) | 0.0503 (16) | −0.0085 (13) | 0.0155 (14) | 0.0069 (12) |
| C23 | 0.0534 (16) | 0.0610 (17) | 0.0547 (17) | 0.0040 (13) | 0.0247 (14) | 0.0127 (13) |
| C24 | 0.061 (2) | 0.106 (3) | 0.078 (2) | 0.0084 (19) | 0.0396 (19) | 0.022 (2) |
| C25 | 0.081 (3) | 0.113 (3) | 0.070 (2) | 0.037 (2) | 0.046 (2) | 0.018 (2) |
| C26 | 0.087 (2) | 0.077 (2) | 0.060 (2) | 0.0271 (19) | 0.0331 (18) | 0.0004 (16) |
| C27 | 0.0577 (17) | 0.0576 (17) | 0.0567 (17) | 0.0084 (13) | 0.0229 (14) | −0.0045 (13) |
| C28 | 0.0445 (13) | 0.0453 (13) | 0.0477 (14) | 0.0081 (11) | 0.0191 (12) | 0.0074 (11) |
| C29 | 0.0524 (15) | 0.0448 (14) | 0.0446 (14) | −0.0014 (11) | 0.0207 (12) | 0.0011 (11) |
| C30 | 0.0424 (13) | 0.0476 (14) | 0.0470 (14) | −0.0026 (10) | 0.0231 (12) | −0.0064 (11) |
| C31 | 0.0509 (14) | 0.0525 (15) | 0.0471 (15) | −0.0047 (11) | 0.0263 (12) | −0.0054 (12) |
| C32 | 0.0595 (17) | 0.0579 (16) | 0.0585 (18) | −0.0134 (13) | 0.0364 (15) | −0.0165 (13) |
| C33 | 0.0526 (17) | 0.087 (2) | 0.0598 (19) | −0.0195 (16) | 0.0294 (15) | −0.0208 (17) |
| C34 | 0.0510 (17) | 0.091 (2) | 0.0540 (18) | −0.0013 (16) | 0.0179 (15) | 0.0008 (17) |
| C35 | 0.0481 (15) | 0.0654 (18) | 0.0539 (17) | −0.0017 (13) | 0.0184 (13) | 0.0013 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C32 | 1.895 (3) | C23—C24 | 1.380 (6) |
| O1—C22 | 1.366 (4) | C23—C28 | 1.383 (5) |
| O1—C23 | 1.374 (4) | C24—C25 | 1.365 (5) |
| O2—C29 | 1.203 (3) | C25—C26 | 1.369 (7) |
| N1—C15 | 1.473 (4) | C26—C27 | 1.379 (6) |
| N1—C29 | 1.379 (4) | C27—C28 | 1.395 (4) |
| N1—C30 | 1.408 (4) | C30—C31 | 1.386 (4) |
| C1—C2 | 1.431 (5) | C30—C35 | 1.384 (4) |
| C1—C6 | 1.448 (4) | C31—C32 | 1.381 (5) |
| C1—C14 | 1.411 (5) | C32—C33 | 1.373 (5) |
| C2—C3 | 1.364 (6) | C33—C34 | 1.376 (5) |
| C3—C4 | 1.415 (7) | C34—C35 | 1.387 (5) |
| C4—C5 | 1.326 (7) | C2—H2 | 0.9300 |
| C5—C6 | 1.434 (6) | C3—H3 | 0.9300 |
| C6—C7 | 1.374 (5) | C4—H4 | 0.9300 |
| C7—C8 | 1.376 (6) | C5—H5 | 0.9300 |
| C8—C9 | 1.427 (5) | C7—H7 | 0.9300 |
| C8—C13 | 1.448 (4) | C9—H9 | 0.9300 |
| C9—C10 | 1.330 (7) | C10—H10 | 0.9300 |
| C10—C11 | 1.406 (5) | C11—H11 | 0.9300 |
| C11—C12 | 1.356 (5) | C12—H12 | 0.9300 |
| C12—C13 | 1.425 (5) | C15—H15 | 0.9800 |
| C13—C14 | 1.415 (4) | C18—H18 | 0.9300 |
| C14—C15 | 1.515 (4) | C19—H19 | 0.9300 |

| | | | |
|---|---|---|---|
| C15—C16 | 1.609 (4) | C20—H20 | 0.9300 |
| C16—C17 | 1.503 (3) | C21—H21 | 0.9300 |
| C16—C28 | 1.504 (5) | C24—H24 | 0.9300 |
| C16—C29 | 1.531 (4) | C25—H25 | 0.9300 |
| C17—C18 | 1.386 (5) | C26—H26 | 0.9300 |
| C17—C22 | 1.382 (5) | C27—H27 | 0.9300 |
| C18—C19 | 1.393 (5) | C31—H31 | 0.9300 |
| C19—C20 | 1.369 (8) | C33—H33 | 0.9300 |
| C20—C21 | 1.358 (7) | C34—H34 | 0.9300 |
| C21—C22 | 1.396 (4) | C35—H35 | 0.9300 |

| | | | |
|---|---|---|---|
| Br1···C21$^{i}$ | 3.491 (4) | C29···H2 | 2.9600 |
| O2···C31 | 3.073 (4) | C30···H2 | 2.7500 |
| O2···H31 | 2.4600 | C30···H11$^{ix}$ | 3.0500 |
| O2···H7$^{i}$ | 2.7800 | C31···H19$^{ii}$ | 3.1000 |
| O2···H9$^{i}$ | 2.7700 | C32···H25$^{vii}$ | 2.8700 |
| O2···H3$^{ii}$ | 2.8700 | C33···H11$^{ix}$ | 3.0900 |
| N1···C2 | 2.968 (4) | C33···H25$^{vii}$ | 2.7100 |
| N1···C27 | 3.359 (5) | C34···H11$^{ix}$ | 2.9400 |
| N1···H2 | 2.3000 | C35···H15 | 2.9700 |
| N1···H27 | 2.8700 | C35···H11$^{ix}$ | 2.9300 |
| C1···C18 | 3.528 (5) | H2···N1 | 2.3000 |
| C2···N1 | 2.968 (4) | H2···C15 | 2.8400 |
| C2···C18 | 3.514 (6) | H2···C29 | 2.9600 |
| C2···C30 | 3.405 (5) | H2···C30 | 2.7500 |
| C4···C9$^{iii}$ | 3.548 (6) | H2···H18 | 2.5200 |
| C9···C4$^{iv}$ | 3.548 (6) | H3···H24$^{vii}$ | 2.4100 |
| C12···C16 | 3.484 (4) | H3···O2$^{ii}$ | 2.8700 |
| C12···C28 | 3.591 (4) | H5···H7 | 2.4200 |
| C14···C35 | 3.525 (4) | H7···H5 | 2.4200 |
| C14···C18 | 3.382 (4) | H7···H9 | 2.4600 |
| C16···C12 | 3.484 (4) | H7···O2$^{vi}$ | 2.7800 |
| C18···C14 | 3.382 (4) | H9···H7 | 2.4600 |
| C18···C2 | 3.514 (6) | H9···O2$^{vi}$ | 2.7700 |
| C18···C1 | 3.528 (5) | H9···C4$^{iv}$ | 2.9900 |
| C19···C24$^{v}$ | 3.524 (6) | H10···C19$^{iv}$ | 3.0000 |
| C20···C25$^{v}$ | 3.371 (5) | H11···C30$^{ix}$ | 3.0500 |
| C20···C24$^{v}$ | 3.405 (5) | H11···C33$^{ix}$ | 3.0900 |
| C21···C23$^{v}$ | 3.599 (4) | H11···C34$^{ix}$ | 2.9400 |
| C21···Br1$^{vi}$ | 3.491 (4) | H11···C35$^{ix}$ | 2.9300 |
| C23···C21$^{v}$ | 3.599 (4) | H12···C15 | 2.4900 |
| C24···C20$^{v}$ | 3.405 (5) | H12···C16 | 2.9100 |
| C24···C19$^{v}$ | 3.524 (6) | H12···C23 | 2.9200 |
| C25···C20$^{v}$ | 3.371 (5) | H12···C28 | 2.7500 |
| C27···N1 | 3.359 (5) | H12···H15 | 2.0500 |
| C28···C12 | 3.591 (4) | H15···C12 | 2.5300 |
| C30···C2 | 3.405 (5) | H15···C27 | 2.7500 |
| C31···O2 | 3.073 (4) | H15···C35 | 2.9700 |

| | | | |
|---|---|---|---|
| C35···C14 | 3.525 (4) | H15···H12 | 2.0500 |
| C2···H18 | 2.8200 | H15···H35 | 2.6000 |
| C3···H24$^{vii}$ | 2.9200 | H18···C2 | 2.8200 |
| C4···H9$^{iii}$ | 2.9900 | H18···C29 | 2.7300 |
| C5···H33$^{viii}$ | 2.9600 | H18···H2 | 2.5200 |
| C6···H33$^{viii}$ | 3.0700 | H19···C31$^{ii}$ | 3.1000 |
| C8···H26$^{ix}$ | 2.9000 | H24···C3$^{x}$ | 2.9200 |
| C9···H31$^{vi}$ | 3.0800 | H24···H3$^{x}$ | 2.4100 |
| C11···H27$^{ix}$ | 3.0700 | H25···C32$^{x}$ | 2.8700 |
| C12···H15 | 2.5300 | H25···C33$^{x}$ | 2.7100 |
| C13···H26$^{ix}$ | 3.0400 | H26···C8$^{ix}$ | 2.9000 |
| C14···H35 | 2.9300 | H26···C13$^{ix}$ | 3.0400 |
| C15···H12 | 2.4900 | H27···N1 | 2.8700 |
| C15···H27 | 3.0000 | H27···C15 | 3.0000 |
| C15···H2 | 2.8400 | H27···C29 | 2.6000 |
| C15···H35 | 2.7200 | H27···C11$^{ix}$ | 3.0700 |
| C16···H12 | 2.9100 | H31···O2 | 2.4600 |
| C19···H10$^{iii}$ | 3.0000 | H31···C29 | 2.7500 |
| C23···H12 | 2.9200 | H31···C9$^{i}$ | 3.0800 |
| C24···H34$^{ix}$ | 3.0300 | H33···C5$^{viii}$ | 2.9600 |
| C25···H35$^{ix}$ | 2.9900 | H33···C6$^{viii}$ | 3.0700 |
| C27···H15 | 2.7500 | H34···C24$^{ix}$ | 3.0300 |
| C28···H12 | 2.7500 | H35···C14 | 2.9300 |
| C29···H27 | 2.6000 | H35···C15 | 2.7200 |
| C29···H18 | 2.7300 | H35···H15 | 2.6000 |
| C29···H31 | 2.7500 | H35···C25$^{ix}$ | 2.9900 |

| | | | |
|---|---|---|---|
| C22—O1—C23 | 118.6 (3) | O2—C29—C16 | 135.1 (3) |
| C15—N1—C29 | 95.5 (2) | N1—C29—C16 | 93.3 (2) |
| C15—N1—C30 | 128.6 (2) | N1—C30—C31 | 119.8 (2) |
| C29—N1—C30 | 131.2 (2) | N1—C30—C35 | 119.6 (3) |
| C2—C1—C6 | 116.4 (3) | C31—C30—C35 | 120.6 (3) |
| C2—C1—C14 | 125.3 (3) | C30—C31—C32 | 118.6 (3) |
| C6—C1—C14 | 118.3 (3) | Br1—C32—C31 | 118.5 (2) |
| C1—C2—C3 | 122.0 (3) | Br1—C32—C33 | 119.5 (3) |
| C2—C3—C4 | 120.7 (4) | C31—C32—C33 | 122.0 (3) |
| C3—C4—C5 | 119.9 (5) | C32—C33—C34 | 118.7 (3) |
| C4—C5—C6 | 122.4 (4) | C33—C34—C35 | 121.0 (3) |
| C1—C6—C5 | 118.7 (3) | C30—C35—C34 | 119.1 (3) |
| C1—C6—C7 | 120.3 (3) | C1—C2—H2 | 119.00 |
| C5—C6—C7 | 121.1 (3) | C3—C2—H2 | 119.00 |
| C6—C7—C8 | 122.7 (3) | C2—C3—H3 | 120.00 |
| C7—C8—C9 | 122.6 (3) | C4—C3—H3 | 120.00 |
| C7—C8—C13 | 118.4 (3) | C3—C4—H4 | 120.00 |
| C9—C8—C13 | 118.9 (3) | C5—C4—H4 | 120.00 |
| C8—C9—C10 | 122.1 (3) | C4—C5—H5 | 119.00 |
| C9—C10—C11 | 119.6 (4) | C6—C5—H5 | 119.00 |
| C10—C11—C12 | 121.2 (4) | C6—C7—H7 | 119.00 |

| | | | |
|---|---|---|---|
| C11—C12—C13 | 121.9 (3) | C8—C7—H7 | 119.00 |
| C8—C13—C12 | 116.1 (3) | C8—C9—H9 | 119.00 |
| C8—C13—C14 | 120.0 (3) | C10—C9—H9 | 119.00 |
| C12—C13—C14 | 123.9 (3) | C9—C10—H10 | 120.00 |
| C1—C14—C13 | 120.2 (2) | C11—C10—H10 | 120.00 |
| C1—C14—C15 | 125.8 (3) | C10—C11—H11 | 119.00 |
| C13—C14—C15 | 114.0 (3) | C12—C11—H11 | 119.00 |
| N1—C15—C14 | 121.6 (3) | C11—C12—H12 | 119.00 |
| N1—C15—C16 | 86.68 (19) | C13—C12—H12 | 119.00 |
| C14—C15—C16 | 120.7 (2) | N1—C15—H15 | 109.00 |
| C15—C16—C17 | 118.7 (2) | C14—C15—H15 | 109.00 |
| C15—C16—C28 | 111.4 (2) | C16—C15—H15 | 109.00 |
| C15—C16—C29 | 84.5 (2) | C17—C18—H18 | 119.00 |
| C17—C16—C28 | 111.2 (3) | C19—C18—H18 | 119.00 |
| C17—C16—C29 | 116.8 (2) | C18—C19—H19 | 120.00 |
| C28—C16—C29 | 111.8 (2) | C20—C19—H19 | 120.00 |
| C16—C17—C18 | 122.1 (3) | C19—C20—H20 | 120.00 |
| C16—C17—C22 | 120.8 (3) | C21—C20—H20 | 120.00 |
| C18—C17—C22 | 117.2 (3) | C20—C21—H21 | 120.00 |
| C17—C18—C19 | 121.4 (4) | C22—C21—H21 | 120.00 |
| C18—C19—C20 | 119.6 (5) | C23—C24—H24 | 120.00 |
| C19—C20—C21 | 120.5 (4) | C25—C24—H24 | 120.00 |
| C20—C21—C22 | 119.7 (4) | C24—C25—H25 | 120.00 |
| O1—C22—C17 | 122.7 (2) | C26—C25—H25 | 120.00 |
| O1—C22—C21 | 115.7 (3) | C25—C26—H26 | 121.00 |
| C17—C22—C21 | 121.6 (3) | C27—C26—H26 | 120.00 |
| O1—C23—C24 | 116.6 (3) | C26—C27—H27 | 119.00 |
| O1—C23—C28 | 122.6 (3) | C28—C27—H27 | 119.00 |
| C24—C23—C28 | 120.9 (3) | C30—C31—H31 | 121.00 |
| C23—C24—C25 | 120.1 (4) | C32—C31—H31 | 121.00 |
| C24—C25—C26 | 120.8 (4) | C32—C33—H33 | 121.00 |
| C25—C26—C27 | 118.9 (3) | C34—C33—H33 | 121.00 |
| C26—C27—C28 | 121.7 (4) | C33—C34—H34 | 119.00 |
| C16—C28—C23 | 120.6 (2) | C35—C34—H34 | 120.00 |
| C16—C28—C27 | 121.8 (3) | C30—C35—H35 | 120.00 |
| C23—C28—C27 | 117.5 (3) | C34—C35—H35 | 120.00 |
| O2—C29—N1 | 131.5 (3) | | |

| | | | |
|---|---|---|---|
| C23—O1—C22—C21 | 166.8 (3) | C14—C15—C16—C17 | 7.2 (4) |
| C22—O1—C23—C24 | −168.8 (3) | N1—C15—C16—C17 | −118.0 (3) |
| C22—O1—C23—C28 | 11.5 (4) | N1—C15—C16—C28 | 110.9 (2) |
| C23—O1—C22—C17 | −13.8 (4) | C14—C15—C16—C29 | 124.8 (3) |
| C29—N1—C30—C31 | 13.3 (5) | C14—C15—C16—C28 | −123.9 (3) |
| C29—N1—C30—C35 | −164.7 (3) | C29—C16—C28—C27 | 33.9 (3) |
| C29—N1—C15—C16 | 0.4 (2) | C29—C16—C28—C23 | −150.1 (2) |
| C15—N1—C30—C35 | −14.9 (5) | C15—C16—C28—C27 | −58.7 (3) |
| C30—N1—C15—C14 | 78.4 (3) | C15—C16—C29—O2 | 177.7 (4) |
| C15—N1—C29—C16 | −0.4 (2) | C15—C16—C28—C23 | 117.3 (3) |

| | | | |
|---|---|---|---|
| C30—N1—C15—C16 | −157.3 (3) | C28—C16—C17—C18 | −164.1 (3) |
| C29—N1—C15—C14 | −123.9 (2) | C28—C16—C17—C22 | 15.6 (3) |
| C30—N1—C29—C16 | 156.3 (3) | C29—C16—C17—C18 | −34.3 (4) |
| C15—N1—C30—C31 | 163.1 (3) | C29—C16—C17—C22 | 145.5 (3) |
| C15—N1—C29—O2 | −177.8 (3) | C15—C16—C17—C18 | 64.6 (4) |
| C30—N1—C29—O2 | −21.1 (5) | C17—C16—C28—C23 | −17.7 (3) |
| C2—C1—C14—C13 | −175.7 (3) | C17—C16—C28—C27 | 166.4 (3) |
| C2—C1—C6—C7 | 178.8 (3) | C15—C16—C29—N1 | 0.4 (2) |
| C6—C1—C14—C15 | −175.1 (3) | C15—C16—C17—C22 | −115.6 (3) |
| C14—C1—C6—C5 | 179.6 (3) | C28—C16—C29—N1 | −110.5 (2) |
| C2—C1—C6—C5 | −1.5 (5) | C28—C16—C29—O2 | 66.7 (4) |
| C14—C1—C6—C7 | −0.1 (5) | C17—C16—C29—O2 | −62.8 (5) |
| C14—C1—C2—C3 | 179.0 (3) | C17—C16—C29—N1 | 119.9 (3) |
| C6—C1—C14—C13 | 3.1 (4) | C16—C17—C22—C21 | 178.7 (3) |
| C6—C1—C2—C3 | 0.2 (5) | C22—C17—C18—C19 | 2.3 (5) |
| C2—C1—C14—C15 | 6.2 (5) | C18—C17—C22—O1 | 179.0 (3) |
| C1—C2—C3—C4 | 1.6 (6) | C16—C17—C18—C19 | −178.0 (3) |
| C2—C3—C4—C5 | −2.2 (7) | C18—C17—C22—C21 | −1.6 (4) |
| C3—C4—C5—C6 | 0.9 (7) | C16—C17—C22—O1 | −0.7 (4) |
| C4—C5—C6—C1 | 1.0 (6) | C17—C18—C19—C20 | −0.8 (5) |
| C4—C5—C6—C7 | −179.3 (4) | C18—C19—C20—C21 | −1.4 (6) |
| C1—C6—C7—C8 | −1.9 (5) | C19—C20—C21—C22 | 2.1 (5) |
| C5—C6—C7—C8 | 178.4 (4) | C20—C21—C22—C17 | −0.6 (5) |
| C6—C7—C8—C13 | 0.8 (5) | C20—C21—C22—O1 | 178.9 (3) |
| C6—C7—C8—C9 | 178.9 (3) | O1—C23—C24—C25 | 179.8 (3) |
| C7—C8—C13—C14 | 2.3 (4) | C28—C23—C24—C25 | −0.5 (5) |
| C7—C8—C9—C10 | −179.1 (4) | O1—C23—C28—C16 | 5.1 (4) |
| C13—C8—C9—C10 | −1.1 (5) | C24—C23—C28—C16 | −174.6 (3) |
| C9—C8—C13—C12 | 3.7 (4) | C24—C23—C28—C27 | 1.5 (4) |
| C7—C8—C13—C12 | −178.1 (3) | O1—C23—C28—C27 | −178.8 (3) |
| C9—C8—C13—C14 | −175.9 (3) | C23—C24—C25—C26 | −0.7 (6) |
| C8—C9—C10—C11 | −2.5 (6) | C24—C25—C26—C27 | 0.8 (6) |
| C9—C10—C11—C12 | 3.3 (6) | C25—C26—C27—C28 | 0.3 (5) |
| C10—C11—C12—C13 | −0.4 (5) | C26—C27—C28—C16 | 174.7 (3) |
| C11—C12—C13—C8 | −3.1 (4) | C26—C27—C28—C23 | −1.4 (5) |
| C11—C12—C13—C14 | 176.6 (3) | N1—C30—C31—C32 | −176.6 (3) |
| C12—C13—C14—C15 | −5.5 (4) | C35—C30—C31—C32 | 1.3 (5) |
| C8—C13—C14—C15 | 174.2 (2) | N1—C30—C35—C34 | 176.0 (3) |
| C12—C13—C14—C1 | 176.2 (3) | C31—C30—C35—C34 | −1.9 (5) |
| C8—C13—C14—C1 | −4.2 (4) | C30—C31—C32—Br1 | −178.2 (3) |
| C1—C14—C15—N1 | 11.7 (4) | C30—C31—C32—C33 | 0.5 (5) |
| C1—C14—C15—C16 | −94.9 (4) | Br1—C32—C33—C34 | 177.0 (3) |
| C13—C14—C15—C16 | 86.9 (3) | C31—C32—C33—C34 | −1.7 (6) |
| C13—C14—C15—N1 | −166.5 (2) | C32—C33—C34—C35 | 1.1 (6) |
| N1—C15—C16—C29 | −0.37 (19) | C33—C34—C35—C30 | 0.7 (5) |

Symmetry codes: (i) $-x+1, y-1/2, -z+1/2$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, -y+3/2, z+1/2$; (iv) $x, -y+3/2, z-1/2$; (v) $-x+2, -y+1, -z+1$; (vi) $-x+1, y+1/2, -z+1/2$; (vii) $x-1, y, z$; (viii) $-x, -y+1, -z$; (ix) $-x+1, -y+1, -z$; (x) $x+1, y, z$.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2···N1 | 0.93 | 2.30 | 2.968 (4) | 128 |
| C31—H31···O2 | 0.93 | 2.46 | 3.073 (4) | 123 |
| C11—H11···*Cg*2$^{ix}$ | 0.93 | 2.75 | 3.653 (5) | 164 |
| C26—H26···*Cg*1$^{ix}$ | 0.93 | 2.96 | 3.616 (4) | 129 |

Symmetry code: (ix) −*x*+1, −*y*+1, −*z*.