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# 9-{[4-(Dimethylamino)benzyl]amino}-5-(3,4,5-trimethoxyphenyl)-5,5a,8a,9-tetrahydrofuro[3′,4′:6,7]naphtho[2,3-*d*][1,3]-dioxol-6(8*H*)-one

**Yan Li,[a]* Huo Wang,[b] Hong Chen,[c,d] Li-Ting Chen[d] and Jing Liu[d]**

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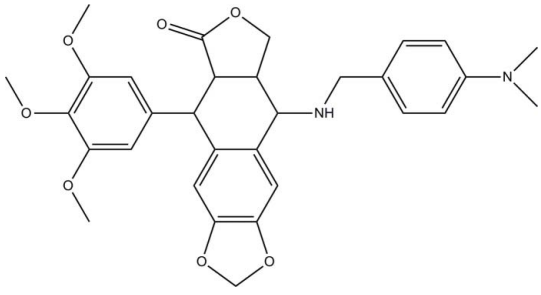
Key indicators: single-crystal X-ray study; $T$ = 113 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.028; $wR$ factor = 0.061; data-to-parameter ratio = 17.1.

In the title compound, $C_{31}H_{34}N_2O_7$, the fused tetrahydrofuran and six-membered rings each display an envelope conformation. The dihedral angles between the benzene ring of the benzo[*d*][1,3]dioxole and the other two benzene rings are 89.68 (3) and 63.38 (2)°. In the crystal, weak intermolecular C—H···O hydrogen bonds link the molecules.

## Related literature

For details of the synthesis and biological activity of podophyllotoxin (systematic name (10*R*,11*R*,15*R*,16*R*)-16-hydroxy-10-(3,4,5-trimethoxyphenyl)-4,6,13-trioxatetracyclo[7.7.0.03,-7.011,15]hexadeca-1,3(7),8-trien-12-one) derivatives, see: Yu *et al.* (2008); Zhao *et al.* (2009); Lu *et al.* (2010). For related structures, see: Zhang *et al.* (1994); Feng *et al.* (2008); Zuo *et al.* (2009).



## Experimental

### Crystal data

$C_{31}H_{34}N_2O_7$
$M_r$ = 546.60
Monoclinic, $P2_1$
$a$ = 10.188 (2) Å
$b$ = 11.530 (3) Å
$c$ = 11.691 (3) Å
$\beta$ = 96.192 (4)°
$V$ = 1365.4 (6) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 113 K
0.20 × 0.18 × 0.12 mm

### Data collection

Rigaku Saturn CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2007)
$T_{min}$ = 0.981, $T_{max}$ = 0.989
17611 measured reflections
6335 independent reflections
4878 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.034

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.061
$S$ = 1.02
6335 reflections
370 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1$B$···O6$^{i}$ | 0.99 | 2.38 | 3.2904 (16) | 153 |
| C21—H21$A$···O6$^{ii}$ | 0.98 | 2.51 | 3.3662 (18) | 145 |
| C22—H22$B$···O3$^{iii}$ | 0.98 | 2.54 | 3.4909 (18) | 162 |
| C29—H29$C$···O1$^{iv}$ | 0.98 | 2.49 | 3.3017 (18) | 140 |

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

Data collection: *CrystalClear* (Rigaku/MSC, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: CV5091).

## References

Feng, M., Zhao, M., Zhang, J., Yang, Z. & Chen, H. (2008). *Acta Cryst.* E**64**, o2339.
Lu, Y. L., Zuo, S., Shi, S. Y., Li, X. C., Zhang, Y., Lv, J. J. & Chen, H. (2010). *Chin. J. Med. Chem.* **20**, 90–95.
Rigaku/MSC (2007). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Yu, P. F., Chen, H., Wang, J., He, C.-X., Cao, B., Li, M., Yang, N., Lei, Z.-Y. & Cheng, M. S. (2008). *Chem. Pharm. Bull.* **56**, 831–834.
Zhang, Y. L., Tropsha, A., McPhail, A. T. & Lee, K. H. (1994). *J. Med. Chem.* **37**, 1460–1464.
Zhao, M., Feng, M., Bai, S. F., Zhang, Y., Bi, W. C. & Chen, H. (2009). *Chin. Chem. Lett.* **20**, 901–904.
Zuo, S., Chen, H., Lu, Y., Cao, B. & Liu, D. (2009). *Acta Cryst.* E**65**, o3257.

# supporting information

*Acta Cryst.* (2011). E**67**, o1538–o1539 [doi:10.1107/S1600536811019234]

# 9-{[4-(Dimethylamino)benzyl]amino}-5-(3,4,5-trimethoxyphenyl)-5,5a,8a,9-tetrahydrofuro[3′,4′:6,7]naphtho[2,3-*d*][1,3]dioxol-6(8*H*)-one

**Yan Li, Huo Wang, Hong Chen, Li-Ting Chen and Jing Liu**

## S1. Comment

Podophyllotoxin and its derivatives are well known as substances with anti-cancer activity. In our group, we synthesize different kinds of Podophyllotoxin compounds in the search for new derivatives with improved bioactivities (Lu *et al.*, 2010; Yu *et al.*, 2008; Zhao *et al.*, 2009). In this paper, we present the crystal structure of the title compound (I).

In (I) (Fig. 1),the bond lengths and angles are normal and in a good agreement with those reported previously for related compounds (Feng *et al.*, 2008; Zhang *et al.*, 1994; Zuo *et al.*, 2009). The tetrahydrofuran ring (C6—C9/O3) and the six-membered ring (C4—C6/C9—C11) fused to it both display envelope conformations. The dihedral angles between the benzene ring (C2—C4/C11—C13) of the benzo[*d*]-[1,3]dioxole and the other two benzene ring (C23—C88 and C15—C20) are 89.68 (3) and 63.38 (2) °, respectively.

Weak intermolecular C—H···O interactions (Table 1) stabilize the crystal packing.

## S2. Experimental

The target compound was synthesized in two steps. 4-(Dimethylamino)benzaldehyde, 4*β*-amino podophyllotoxin, two drops of acetic acid in 95% ethanol was stirred for 6 h. Appropriate amount of $NaBH_4$ was added into the reaction mixture to stirred for 1 h at 273 K. Then add 5% HCl to end off the reaction, the reaction mixture was concentrated *in vacuo*. Add saturated $NaHCO_3$ to adjust PH>7. The reaction mixture was extracted with $CH_2Cl_2$ and dried over $MgSO_4$ and concentrated *in vacuo*. The residue was resolved in a methanol solution and slow evaporation over two weeks at room temperature gave transparent crystals suitable for X-ray analysis.

## S3. Refinement

C-bound H atoms were found on difference maps, but placed in idealized positions with C—H = 0.95–1.00 Å, and refined as riding, with $U_{iso}$(H) = 1.2$U_{eq}$(C) for aryl and methylene H atoms and 1.5$U_{eq}$(C) for the methyl H atoms. N-bound H atoms were located on a difference map and isotropically refined. In the absence of any significant anomalous scatterers in the molecule, the 2920 Friedel pairs were merged before the final refinement.

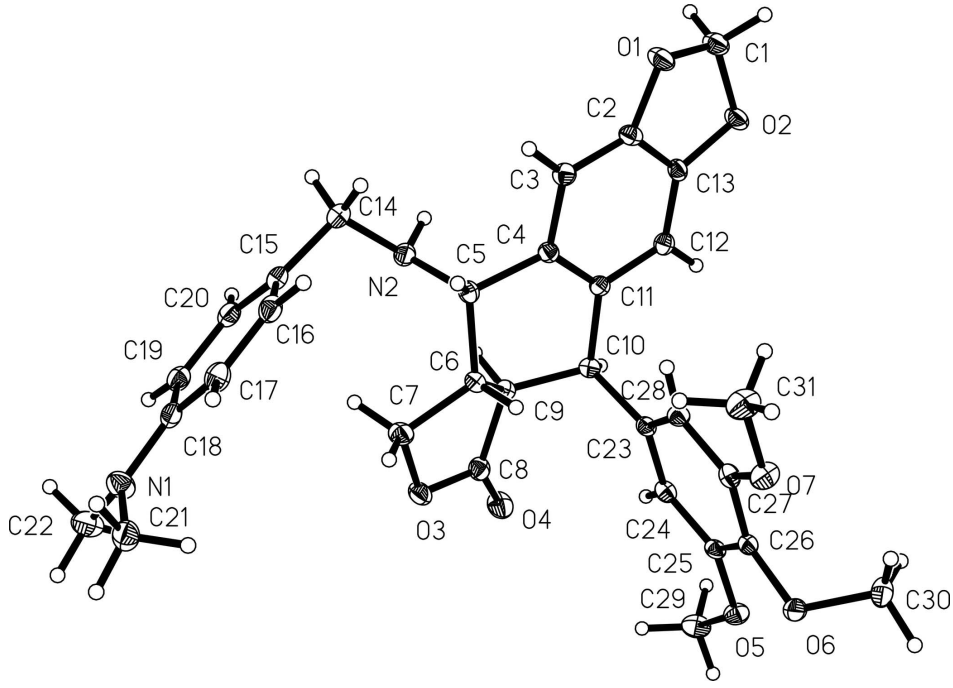


**Figure 1**

View of the title compound, with displacement ellipsoids drawn at the 40% probability level.

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*Crystal data*

$C_{31}H_{34}N_2O_7$
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Monoclinic, $P2_1$
Hall symbol: P 2yb
$a$ = 10.188 (2) Å
$b$ = 11.530 (3) Å
$c$ = 11.691 (3) Å
$\beta$ = 96.192 (4)°
$V$ = 1365.4 (6) Å$^3$
$Z$ = 2
$F(000)$ = 580
$D_x$ = 1.329 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4484 reflections
$\theta$ = 1.8–28.1°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 113 K
Prism, colourless
0.20 × 0.18 × 0.12 mm

*Data collection*

Rigaku Saturn CCD area-detector diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 14.63 pixels mm$^{-1}$
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2007)
$T_{min}$ = 0.981, $T_{max}$ = 0.989
17611 measured reflections
6335 independent reflections
4878 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.034
$\theta_{max}$ = 27.8°, $\theta_{min}$ = 1.8°
$h$ = −13→13
$k$ = −15→15
$l$ = −15→15

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.061$
$S = 1.02$
6335 reflections
370 parameters
2 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.16$ e Å$^{-3}$
$\Delta\rho_{min} = -0.21$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.52128 (9) | 0.59140 (8) | 0.21947 (8) | 0.0240 (2) |
| O2 | 0.52819 (9) | 0.39712 (8) | 0.27006 (7) | 0.0233 (2) |
| O3 | 0.14528 (9) | 0.64023 (8) | 0.82671 (7) | 0.0235 (2) |
| O4 | 0.14154 (9) | 0.44619 (9) | 0.83314 (8) | 0.0282 (2) |
| O5 | 0.53808 (8) | 0.28789 (8) | 0.99527 (8) | 0.0213 (2) |
| O6 | 0.74780 (8) | 0.42130 (8) | 0.99096 (7) | 0.0214 (2) |
| O7 | 0.77467 (8) | 0.56748 (8) | 0.81392 (8) | 0.0235 (2) |
| N1 | −0.02700 (11) | 1.09298 (11) | 0.83706 (10) | 0.0263 (3) |
| N2 | 0.14526 (11) | 0.72761 (10) | 0.48482 (9) | 0.0210 (3) |
| C1 | 0.53397 (14) | 0.47595 (12) | 0.17577 (12) | 0.0244 (3) |
| H1A | 0.4615 | 0.4596 | 0.1145 | 0.029* |
| H1B | 0.6191 | 0.4675 | 0.1430 | 0.029* |
| C2 | 0.46171 (12) | 0.57629 (12) | 0.31872 (11) | 0.0181 (3) |
| C3 | 0.40468 (12) | 0.65809 (12) | 0.38261 (10) | 0.0187 (3) |
| H3 | 0.3992 | 0.7370 | 0.3591 | 0.022* |
| C4 | 0.35439 (12) | 0.62146 (11) | 0.48439 (10) | 0.0158 (3) |
| C5 | 0.27834 (12) | 0.71177 (11) | 0.54717 (10) | 0.0167 (3) |
| H5 | 0.3268 | 0.7873 | 0.5483 | 0.020* |
| C6 | 0.27250 (13) | 0.67110 (11) | 0.67159 (10) | 0.0166 (3) |
| H6 | 0.3641 | 0.6717 | 0.7122 | 0.020* |
| C7 | 0.18142 (14) | 0.73142 (12) | 0.74730 (11) | 0.0219 (3) |
| H7A | 0.2274 | 0.7963 | 0.7902 | 0.026* |
| H7B | 0.1021 | 0.7620 | 0.7007 | 0.026* |
| C8 | 0.16817 (12) | 0.53318 (12) | 0.78400 (11) | 0.0202 (3) |

| | | | | |
|---|---|---|---|---|
| C9 | 0.22116 (12) | 0.54719 (12) | 0.66907 (11) | 0.0164 (3) |
| H9 | 0.1437 | 0.5439 | 0.6088 | 0.020* |
| C10 | 0.32353 (12) | 0.46168 (11) | 0.63313 (10) | 0.0160 (3) |
| H10 | 0.2802 | 0.3843 | 0.6197 | 0.019* |
| C11 | 0.36598 (12) | 0.50503 (12) | 0.51885 (10) | 0.0160 (3) |
| C12 | 0.42322 (12) | 0.42254 (12) | 0.45006 (11) | 0.0179 (3) |
| H12 | 0.4305 | 0.3433 | 0.4723 | 0.022* |
| C13 | 0.46778 (12) | 0.46049 (12) | 0.35037 (11) | 0.0177 (3) |
| C14 | 0.11461 (15) | 0.84675 (13) | 0.44324 (12) | 0.0265 (3) |
| H14A | 0.0420 | 0.8443 | 0.3797 | 0.032* |
| H14B | 0.1932 | 0.8807 | 0.4130 | 0.032* |
| C15 | 0.07453 (13) | 0.92169 (12) | 0.53913 (11) | 0.0218 (3) |
| C16 | 0.15867 (13) | 1.00166 (12) | 0.59750 (12) | 0.0234 (3) |
| H16 | 0.2414 | 1.0168 | 0.5701 | 0.028* |
| C17 | 0.12671 (13) | 1.06049 (13) | 0.69451 (12) | 0.0240 (3) |
| H17 | 0.1869 | 1.1151 | 0.7314 | 0.029* |
| C18 | 0.00521 (12) | 1.03947 (12) | 0.73842 (11) | 0.0204 (3) |
| C19 | −0.08234 (13) | 0.96224 (12) | 0.67618 (11) | 0.0217 (3) |
| H19 | −0.1670 | 0.9491 | 0.7008 | 0.026* |
| C20 | −0.04779 (13) | 0.90515 (12) | 0.58008 (11) | 0.0216 (3) |
| H20 | −0.1091 | 0.8530 | 0.5406 | 0.026* |
| C21 | 0.07587 (14) | 1.15428 (13) | 0.91019 (12) | 0.0274 (3) |
| H21A | 0.1551 | 1.1057 | 0.9220 | 0.041* |
| H21B | 0.0443 | 1.1713 | 0.9847 | 0.041* |
| H21C | 0.0972 | 1.2270 | 0.8730 | 0.041* |
| C22 | −0.14462 (14) | 1.05611 (15) | 0.88653 (12) | 0.0321 (4) |
| H22A | −0.2228 | 1.0745 | 0.8333 | 0.048* |
| H22B | −0.1499 | 1.0966 | 0.9596 | 0.048* |
| H22C | −0.1407 | 0.9723 | 0.9002 | 0.048* |
| C23 | 0.44248 (12) | 0.44741 (11) | 0.72446 (10) | 0.0160 (3) |
| C24 | 0.43331 (13) | 0.37052 (11) | 0.81531 (11) | 0.0175 (3) |
| H24 | 0.3558 | 0.3252 | 0.8181 | 0.021* |
| C25 | 0.53765 (12) | 0.36013 (11) | 0.90182 (11) | 0.0164 (3) |
| C26 | 0.65162 (12) | 0.42673 (12) | 0.89914 (10) | 0.0163 (3) |
| C27 | 0.66085 (12) | 0.50269 (11) | 0.80689 (11) | 0.0176 (3) |
| C28 | 0.55777 (12) | 0.51155 (11) | 0.71925 (11) | 0.0168 (3) |
| H28 | 0.5658 | 0.5614 | 0.6557 | 0.020* |
| C29 | 0.41589 (13) | 0.23341 (13) | 1.01374 (11) | 0.0260 (3) |
| H29A | 0.3478 | 0.2928 | 1.0183 | 0.039* |
| H29B | 0.4272 | 0.1894 | 1.0858 | 0.039* |
| H29C | 0.3890 | 0.1807 | 0.9497 | 0.039* |
| C30 | 0.87104 (13) | 0.37267 (14) | 0.96535 (13) | 0.0309 (4) |
| H30A | 0.8542 | 0.3019 | 0.9197 | 0.046* |
| H30B | 0.9254 | 0.3539 | 1.0373 | 0.046* |
| H30C | 0.9176 | 0.4290 | 0.9216 | 0.046* |
| C31 | 0.78655 (14) | 0.65140 (14) | 0.72551 (12) | 0.0301 (4) |
| H31A | 0.7865 | 0.6119 | 0.6513 | 0.045* |
| H31B | 0.8693 | 0.6944 | 0.7426 | 0.045* |

| | | | | |
|---|---|---|---|---|
| H31C | 0.7120 | 0.7054 | 0.7221 | 0.045* |
| H2 | 0.1326 (14) | 0.6802 (12) | 0.4235 (10) | 0.033 (4)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0322 (6) | 0.0216 (5) | 0.0202 (5) | 0.0008 (4) | 0.0114 (4) | −0.0022 (4) |
| O2 | 0.0307 (5) | 0.0213 (5) | 0.0195 (5) | 0.0047 (4) | 0.0098 (4) | −0.0025 (4) |
| O3 | 0.0282 (5) | 0.0229 (5) | 0.0212 (5) | 0.0033 (4) | 0.0106 (4) | 0.0016 (4) |
| O4 | 0.0291 (6) | 0.0260 (6) | 0.0319 (6) | −0.0013 (5) | 0.0136 (5) | 0.0057 (5) |
| O5 | 0.0240 (5) | 0.0214 (5) | 0.0187 (5) | −0.0029 (4) | 0.0036 (4) | 0.0054 (4) |
| O6 | 0.0164 (5) | 0.0301 (6) | 0.0177 (5) | 0.0007 (4) | 0.0017 (4) | 0.0006 (4) |
| O7 | 0.0188 (5) | 0.0261 (6) | 0.0253 (5) | −0.0074 (4) | 0.0013 (4) | 0.0065 (4) |
| N1 | 0.0224 (6) | 0.0318 (7) | 0.0243 (6) | −0.0011 (5) | 0.0013 (5) | −0.0075 (6) |
| N2 | 0.0236 (6) | 0.0206 (6) | 0.0179 (6) | 0.0047 (5) | −0.0019 (5) | −0.0031 (5) |
| C1 | 0.0325 (8) | 0.0221 (8) | 0.0198 (7) | 0.0017 (7) | 0.0087 (6) | −0.0015 (6) |
| C2 | 0.0170 (6) | 0.0225 (8) | 0.0153 (6) | −0.0025 (6) | 0.0033 (5) | −0.0005 (6) |
| C3 | 0.0218 (7) | 0.0157 (7) | 0.0185 (7) | −0.0005 (6) | 0.0024 (6) | 0.0003 (6) |
| C4 | 0.0149 (6) | 0.0174 (7) | 0.0151 (6) | −0.0003 (5) | 0.0012 (5) | −0.0014 (5) |
| C5 | 0.0166 (6) | 0.0155 (7) | 0.0181 (7) | −0.0001 (6) | 0.0026 (5) | −0.0017 (6) |
| C6 | 0.0172 (6) | 0.0172 (7) | 0.0157 (6) | 0.0002 (6) | 0.0035 (5) | −0.0017 (6) |
| C7 | 0.0276 (8) | 0.0190 (7) | 0.0203 (7) | −0.0006 (6) | 0.0077 (6) | 0.0033 (6) |
| C8 | 0.0162 (6) | 0.0223 (8) | 0.0225 (7) | 0.0003 (6) | 0.0042 (5) | 0.0018 (6) |
| C9 | 0.0145 (6) | 0.0187 (7) | 0.0160 (6) | −0.0017 (6) | 0.0018 (5) | −0.0010 (6) |
| C10 | 0.0176 (7) | 0.0148 (7) | 0.0156 (6) | −0.0020 (6) | 0.0022 (5) | −0.0002 (5) |
| C11 | 0.0135 (6) | 0.0194 (7) | 0.0149 (6) | −0.0008 (6) | 0.0003 (5) | −0.0016 (6) |
| C12 | 0.0182 (7) | 0.0158 (7) | 0.0197 (7) | 0.0007 (6) | 0.0014 (5) | 0.0001 (6) |
| C13 | 0.0158 (6) | 0.0205 (7) | 0.0165 (7) | 0.0026 (6) | 0.0009 (5) | −0.0048 (6) |
| C14 | 0.0296 (8) | 0.0280 (8) | 0.0215 (7) | 0.0096 (7) | 0.0008 (6) | 0.0042 (6) |
| C15 | 0.0252 (7) | 0.0199 (7) | 0.0202 (7) | 0.0073 (6) | 0.0018 (6) | 0.0051 (6) |
| C16 | 0.0211 (7) | 0.0220 (8) | 0.0278 (8) | 0.0037 (6) | 0.0055 (6) | 0.0080 (6) |
| C17 | 0.0215 (7) | 0.0202 (8) | 0.0296 (8) | −0.0006 (6) | 0.0000 (6) | 0.0023 (6) |
| C18 | 0.0200 (7) | 0.0182 (7) | 0.0224 (7) | 0.0044 (6) | −0.0006 (5) | 0.0023 (6) |
| C19 | 0.0173 (7) | 0.0243 (8) | 0.0230 (7) | 0.0019 (6) | 0.0007 (6) | 0.0047 (6) |
| C20 | 0.0222 (7) | 0.0198 (7) | 0.0214 (7) | 0.0025 (6) | −0.0041 (6) | 0.0010 (6) |
| C21 | 0.0271 (8) | 0.0246 (8) | 0.0292 (8) | 0.0025 (7) | −0.0030 (6) | −0.0054 (7) |
| C22 | 0.0289 (8) | 0.0447 (10) | 0.0230 (7) | −0.0014 (8) | 0.0040 (6) | −0.0040 (7) |
| C23 | 0.0185 (6) | 0.0152 (7) | 0.0147 (6) | 0.0017 (5) | 0.0039 (5) | −0.0012 (5) |
| C24 | 0.0185 (7) | 0.0154 (7) | 0.0193 (7) | −0.0021 (5) | 0.0059 (5) | −0.0012 (6) |
| C25 | 0.0217 (7) | 0.0138 (7) | 0.0146 (6) | 0.0014 (6) | 0.0067 (5) | 0.0020 (5) |
| C26 | 0.0160 (6) | 0.0181 (7) | 0.0148 (6) | 0.0022 (5) | 0.0017 (5) | −0.0026 (6) |
| C27 | 0.0161 (6) | 0.0164 (7) | 0.0209 (7) | −0.0006 (5) | 0.0052 (5) | −0.0013 (6) |
| C28 | 0.0204 (7) | 0.0145 (7) | 0.0160 (6) | −0.0002 (5) | 0.0048 (5) | 0.0028 (6) |
| C29 | 0.0313 (8) | 0.0253 (8) | 0.0225 (7) | −0.0079 (7) | 0.0088 (6) | 0.0050 (6) |
| C30 | 0.0242 (8) | 0.0364 (9) | 0.0311 (8) | 0.0124 (7) | −0.0007 (6) | −0.0026 (7) |
| C31 | 0.0271 (8) | 0.0318 (9) | 0.0316 (8) | −0.0096 (7) | 0.0041 (7) | 0.0113 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C2 | 1.3773 (15) | C11—C12 | 1.4118 (18) |
| O1—C1 | 1.4367 (17) | C12—C13 | 1.3676 (17) |
| O2—C13 | 1.3852 (15) | C12—H12 | 0.9500 |
| O2—C1 | 1.4349 (16) | C14—C15 | 1.5063 (19) |
| O3—C8 | 1.3610 (16) | C14—H14A | 0.9900 |
| O3—C7 | 1.4753 (15) | C14—H14B | 0.9900 |
| O4—C8 | 1.2014 (16) | C15—C16 | 1.387 (2) |
| O5—C25 | 1.3734 (15) | C15—C20 | 1.3955 (18) |
| O5—C29 | 1.4314 (15) | C16—C17 | 1.3901 (19) |
| O6—C26 | 1.3746 (15) | C16—H16 | 0.9500 |
| O6—C30 | 1.4359 (16) | C17—C18 | 1.4113 (18) |
| O7—C27 | 1.3744 (15) | C17—H17 | 0.9500 |
| O7—C31 | 1.4305 (16) | C18—C19 | 1.4064 (19) |
| N1—C18 | 1.3784 (16) | C19—C20 | 1.3802 (18) |
| N1—C22 | 1.4494 (17) | C19—H19 | 0.9500 |
| N1—C21 | 1.4615 (17) | C20—H20 | 0.9500 |
| N2—C14 | 1.4792 (18) | C21—H21A | 0.9800 |
| N2—C5 | 1.4798 (16) | C21—H21B | 0.9800 |
| N2—H2 | 0.900 (9) | C21—H21C | 0.9800 |
| C1—H1A | 0.9900 | C22—H22A | 0.9800 |
| C1—H1B | 0.9900 | C22—H22B | 0.9800 |
| C2—C3 | 1.3707 (18) | C22—H22C | 0.9800 |
| C2—C13 | 1.3851 (19) | C23—C24 | 1.3945 (17) |
| C3—C4 | 1.4100 (17) | C23—C28 | 1.3949 (18) |
| C3—H3 | 0.9500 | C24—C25 | 1.3912 (17) |
| C4—C11 | 1.4030 (18) | C24—H24 | 0.9500 |
| C4—C5 | 1.5317 (18) | C25—C26 | 1.3954 (18) |
| C5—C6 | 1.5356 (17) | C26—C27 | 1.4004 (17) |
| C5—H5 | 1.0000 | C27—C28 | 1.3896 (17) |
| C6—C7 | 1.5184 (17) | C28—H28 | 0.9500 |
| C6—C9 | 1.5206 (18) | C29—H29A | 0.9800 |
| C6—H6 | 1.0000 | C29—H29B | 0.9800 |
| C7—H7A | 0.9900 | C29—H29C | 0.9800 |
| C7—H7B | 0.9900 | C30—H30A | 0.9800 |
| C8—C9 | 1.5098 (18) | C30—H30B | 0.9800 |
| C9—C10 | 1.5268 (17) | C30—H30C | 0.9800 |
| C9—H9 | 1.0000 | C31—H31A | 0.9800 |
| C10—C11 | 1.5319 (16) | C31—H31B | 0.9800 |
| C10—C23 | 1.5351 (17) | C31—H31C | 0.9800 |
| C10—H10 | 1.0000 | | |
| | | | |
| C2—O1—C1 | 104.30 (10) | C15—C14—H14A | 109.5 |
| C13—O2—C1 | 104.16 (10) | N2—C14—H14B | 109.5 |
| C8—O3—C7 | 110.56 (9) | C15—C14—H14B | 109.5 |
| C25—O5—C29 | 117.25 (10) | H14A—C14—H14B | 108.1 |
| C26—O6—C30 | 114.88 (9) | C16—C15—C20 | 116.70 (12) |

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| C27—O7—C31 | 117.45 (10) | C16—C15—C14 | 123.00 (13) |
| C18—N1—C22 | 118.96 (12) | C20—C15—C14 | 120.05 (13) |
| C18—N1—C21 | 119.05 (11) | C15—C16—C17 | 122.62 (12) |
| C22—N1—C21 | 118.69 (11) | C15—C16—H16 | 118.7 |
| C14—N2—C5 | 115.23 (11) | C17—C16—H16 | 118.7 |
| C14—N2—H2 | 107.1 (10) | C16—C17—C18 | 120.32 (13) |
| C5—N2—H2 | 111.3 (10) | C16—C17—H17 | 119.8 |
| O2—C1—O1 | 107.52 (10) | C18—C17—H17 | 119.8 |
| O2—C1—H1A | 110.2 | N1—C18—C19 | 121.42 (12) |
| O1—C1—H1A | 110.2 | N1—C18—C17 | 121.65 (12) |
| O2—C1—H1B | 110.2 | C19—C18—C17 | 116.92 (12) |
| O1—C1—H1B | 110.2 | C20—C19—C18 | 121.33 (12) |
| H1A—C1—H1B | 108.5 | C20—C19—H19 | 119.3 |
| C3—C2—O1 | 128.56 (12) | C18—C19—H19 | 119.3 |
| C3—C2—C13 | 121.80 (12) | C19—C20—C15 | 121.99 (13) |
| O1—C2—C13 | 109.63 (11) | C19—C20—H20 | 119.0 |
| C2—C3—C4 | 117.89 (12) | C15—C20—H20 | 119.0 |
| C2—C3—H3 | 121.1 | N1—C21—H21A | 109.5 |
| C4—C3—H3 | 121.1 | N1—C21—H21B | 109.5 |
| C11—C4—C3 | 120.13 (12) | H21A—C21—H21B | 109.5 |
| C11—C4—C5 | 122.96 (11) | N1—C21—H21C | 109.5 |
| C3—C4—C5 | 116.71 (12) | H21A—C21—H21C | 109.5 |
| N2—C5—C4 | 109.38 (10) | H21B—C21—H21C | 109.5 |
| N2—C5—C6 | 112.16 (10) | N1—C22—H22A | 109.5 |
| C4—C5—C6 | 108.64 (10) | N1—C22—H22B | 109.5 |
| N2—C5—H5 | 108.9 | H22A—C22—H22B | 109.5 |
| C4—C5—H5 | 108.9 | N1—C22—H22C | 109.5 |
| C6—C5—H5 | 108.9 | H22A—C22—H22C | 109.5 |
| C7—C6—C9 | 102.19 (10) | H22B—C22—H22C | 109.5 |
| C7—C6—C5 | 120.06 (11) | C24—C23—C28 | 119.75 (12) |
| C9—C6—C5 | 108.48 (10) | C24—C23—C10 | 119.03 (11) |
| C7—C6—H6 | 108.5 | C28—C23—C10 | 121.21 (11) |
| C9—C6—H6 | 108.5 | C25—C24—C23 | 119.99 (12) |
| C5—C6—H6 | 108.5 | C25—C24—H24 | 120.0 |
| O3—C7—C6 | 104.48 (10) | C23—C24—H24 | 120.0 |
| O3—C7—H7A | 110.9 | O5—C25—C24 | 124.55 (12) |
| C6—C7—H7A | 110.9 | O5—C25—C26 | 114.86 (11) |
| O3—C7—H7B | 110.9 | C24—C25—C26 | 120.58 (12) |
| C6—C7—H7B | 110.9 | O6—C26—C25 | 118.83 (11) |
| H7A—C7—H7B | 108.9 | O6—C26—C27 | 121.91 (12) |
| O4—C8—O3 | 121.68 (11) | C25—C26—C27 | 119.12 (11) |
| O4—C8—C9 | 129.48 (13) | O7—C27—C28 | 124.74 (12) |
| O3—C8—C9 | 108.74 (11) | O7—C27—C26 | 114.84 (11) |
| C8—C9—C6 | 103.80 (10) | C28—C27—C26 | 120.38 (11) |
| C8—C9—C10 | 119.75 (11) | C27—C28—C23 | 120.12 (12) |
| C6—C9—C10 | 111.61 (10) | C27—C28—H28 | 119.9 |
| C8—C9—H9 | 107.0 | C23—C28—H28 | 119.9 |
| C6—C9—H9 | 107.0 | O5—C29—H29A | 109.5 |

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| C10—C9—H9 | 107.0 | O5—C29—H29B | 109.5 |
| C9—C10—C11 | 107.14 (10) | H29A—C29—H29B | 109.5 |
| C9—C10—C23 | 112.91 (10) | O5—C29—H29C | 109.5 |
| C11—C10—C23 | 111.45 (10) | H29A—C29—H29C | 109.5 |
| C9—C10—H10 | 108.4 | H29B—C29—H29C | 109.5 |
| C11—C10—H10 | 108.4 | O6—C30—H30A | 109.5 |
| C23—C10—H10 | 108.4 | O6—C30—H30B | 109.5 |
| C4—C11—C12 | 120.54 (11) | H30A—C30—H30B | 109.5 |
| C4—C11—C10 | 122.67 (11) | O6—C30—H30C | 109.5 |
| C12—C11—C10 | 116.74 (12) | H30A—C30—H30C | 109.5 |
| C13—C12—C11 | 117.74 (12) | H30B—C30—H30C | 109.5 |
| C13—C12—H12 | 121.1 | O7—C31—H31A | 109.5 |
| C11—C12—H12 | 121.1 | O7—C31—H31B | 109.5 |
| C12—C13—O2 | 128.42 (12) | H31A—C31—H31B | 109.5 |
| C12—C13—C2 | 121.79 (12) | O7—C31—H31C | 109.5 |
| O2—C13—C2 | 109.74 (11) | H31A—C31—H31C | 109.5 |
| N2—C14—C15 | 110.65 (11) | H31B—C31—H31C | 109.5 |
| N2—C14—H14A | 109.5 | | |

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| C13—O2—C1—O1 | 20.33 (13) | C1—O2—C13—C2 | −11.56 (14) |
| C2—O1—C1—O2 | −21.44 (14) | C3—C2—C13—C12 | −3.4 (2) |
| C1—O1—C2—C3 | −166.58 (13) | O1—C2—C13—C12 | 175.82 (11) |
| C1—O1—C2—C13 | 14.31 (14) | C3—C2—C13—O2 | 179.03 (11) |
| O1—C2—C3—C4 | −177.49 (12) | O1—C2—C13—O2 | −1.79 (15) |
| C13—C2—C3—C4 | 1.52 (19) | C5—N2—C14—C15 | −80.58 (14) |
| C2—C3—C4—C11 | 1.34 (19) | N2—C14—C15—C16 | 102.22 (16) |
| C2—C3—C4—C5 | −173.71 (11) | N2—C14—C15—C20 | −71.91 (16) |
| C14—N2—C5—C4 | −120.42 (12) | C20—C15—C16—C17 | 2.2 (2) |
| C14—N2—C5—C6 | 118.97 (12) | C14—C15—C16—C17 | −172.16 (13) |
| C11—C4—C5—N2 | −98.96 (14) | C15—C16—C17—C18 | 0.6 (2) |
| C3—C4—C5—N2 | 75.94 (14) | C22—N1—C18—C19 | 9.1 (2) |
| C11—C4—C5—C6 | 23.77 (16) | C21—N1—C18—C19 | 168.32 (13) |
| C3—C4—C5—C6 | −161.34 (11) | C22—N1—C18—C17 | −171.60 (13) |
| N2—C5—C6—C7 | −47.32 (16) | C21—N1—C18—C17 | −12.38 (19) |
| C4—C5—C6—C7 | −168.35 (11) | C16—C17—C18—N1 | 177.37 (12) |
| N2—C5—C6—C9 | 69.46 (13) | C16—C17—C18—C19 | −3.3 (2) |
| C4—C5—C6—C9 | −51.57 (13) | N1—C18—C19—C20 | −177.35 (12) |
| C8—O3—C7—C6 | −19.07 (13) | C17—C18—C19—C20 | 3.3 (2) |
| C9—C6—C7—O3 | 30.09 (13) | C18—C19—C20—C15 | −0.6 (2) |
| C5—C6—C7—O3 | 150.07 (11) | C16—C15—C20—C19 | −2.2 (2) |
| C7—O3—C8—O4 | −177.51 (12) | C14—C15—C20—C19 | 172.34 (12) |
| C7—O3—C8—C9 | −0.70 (14) | C9—C10—C23—C24 | 83.46 (14) |
| O4—C8—C9—C6 | −163.42 (13) | C11—C10—C23—C24 | −155.89 (11) |
| O3—C8—C9—C6 | 20.10 (13) | C9—C10—C23—C28 | −95.20 (13) |
| O4—C8—C9—C10 | −38.2 (2) | C11—C10—C23—C28 | 25.45 (16) |
| O3—C8—C9—C10 | 145.35 (11) | C28—C23—C24—C25 | 1.60 (18) |
| C7—C6—C9—C8 | −30.27 (13) | C10—C23—C24—C25 | −177.08 (11) |
| C5—C6—C9—C8 | −158.04 (10) | C29—O5—C25—C24 | −10.00 (18) |

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| C7—C6—C9—C10 | −160.58 (10) | C29—O5—C25—C26 | 169.00 (11) |
| C5—C6—C9—C10 | 71.65 (13) | C23—C24—C25—O5 | 179.42 (12) |
| C8—C9—C10—C11 | −175.07 (11) | C23—C24—C25—C26 | 0.46 (18) |
| C6—C9—C10—C11 | −53.61 (13) | C30—O6—C26—C25 | 114.96 (13) |
| C8—C9—C10—C23 | −51.99 (15) | C30—O6—C26—C27 | −69.35 (16) |
| C6—C9—C10—C23 | 69.47 (13) | O5—C25—C26—O6 | −4.51 (17) |
| C3—C4—C11—C12 | −2.49 (19) | C24—C25—C26—O6 | 174.54 (11) |
| C5—C4—C11—C12 | 172.24 (11) | O5—C25—C26—C27 | 179.68 (11) |
| C3—C4—C11—C10 | 174.96 (11) | C24—C25—C26—C27 | −1.27 (18) |
| C5—C4—C11—C10 | −10.31 (19) | C31—O7—C27—C28 | 1.12 (18) |
| C9—C10—C11—C4 | 23.65 (16) | C31—O7—C27—C26 | −176.55 (11) |
| C23—C10—C11—C4 | −100.33 (14) | O6—C26—C27—O7 | 2.12 (17) |
| C9—C10—C11—C12 | −158.81 (11) | C25—C26—C27—O7 | 177.80 (11) |
| C23—C10—C11—C12 | 77.21 (14) | O6—C26—C27—C28 | −175.65 (11) |
| C4—C11—C12—C13 | 0.75 (18) | C25—C26—C27—C28 | 0.02 (18) |
| C10—C11—C12—C13 | −176.85 (11) | O7—C27—C28—C23 | −175.51 (12) |
| C11—C12—C13—O2 | 179.26 (12) | C26—C27—C28—C23 | 2.04 (19) |
| C11—C12—C13—C2 | 2.13 (19) | C24—C23—C28—C27 | −2.84 (18) |
| C1—O2—C13—C12 | 171.03 (13) | C10—C23—C28—C27 | 175.81 (11) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1*A*···O5$^{i}$ | 0.99 | 2.59 | 3.0292 (18) | 107 |
| C1—H1*B*···O6$^{i}$ | 0.99 | 2.38 | 3.2904 (16) | 153 |
| C21—H21*A*···O6$^{ii}$ | 0.98 | 2.51 | 3.3662 (18) | 145 |
| C22—H22*B*···O3$^{iii}$ | 0.98 | 2.54 | 3.4909 (18) | 162 |
| C29—H29*C*···O1$^{iv}$ | 0.98 | 2.49 | 3.3017 (18) | 140 |

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