

Crystal structure of 9-(3-bromo-5-chloro-2-hydroxyphenyl)-10-(2-hydroxyethyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione

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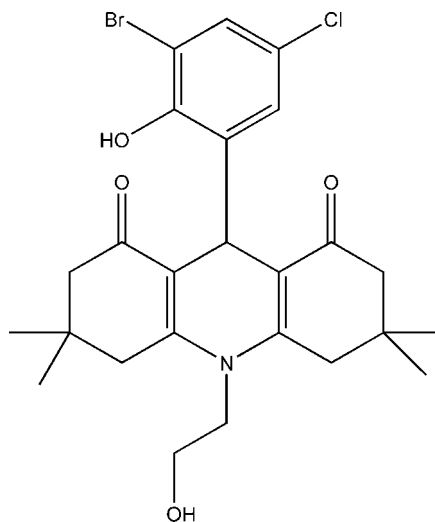
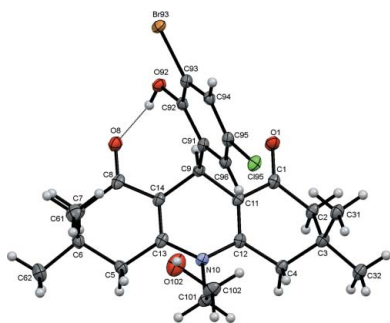
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The title compound $C_{25}H_{29}BrClNO_4$, comprises a 3,3,6,6-tetramethyltetrahydroacridine-1,8-dione ring system that carries a hydroxyethyl substituent on the acridine N atom and a 3-bromo-5-chloro-2-hydroxyphenyl ring on the central methine C atom of the dihydropyridine ring. The benzene ring is inclined to the acridine ring system at an angle of 89.84 (6)° and this conformation is stabilized by an intramolecular O—H...O hydrogen bond between the hydroxy substituent on the benzene ring and one of the carbonyl groups of the acridinedione unit. In the crystal, O—H...O, C—H...O and C—H...Br hydrogen bonds combine to stack molecules in interconnected columns propagating along the *a*-axis direction.

1. Chemical context

Acridine derivatives occupy an important position in medicinal chemistry due to their wide range of biological applications. They exhibit fungicidal (Misra & Bahel, 1984; Srivastava *et al.*, 1985), anti-cancer (Sondhi *et al.*, 2004; Sugaya *et al.*, 1994; Kimura *et al.*, 1993), anti-parasitic (Ngadi *et al.*, 1993), anti-inflammatory and anti-microbial (Shul'ga *et al.*, 1974; Gaiukevich *et al.*, 1973) activity. They are also components of effective analgesics (Taraporewala & Kauffman, 1990; Gaidukevich *et al.*, 1987). Other pharmaceutically active acridine derivatives (*e.g.* Mepacrine, Azacrine, Proflavine, and Aminacrine) also demonstrate antimalarial and antibacterial activity (Denny *et al.*, 1983).



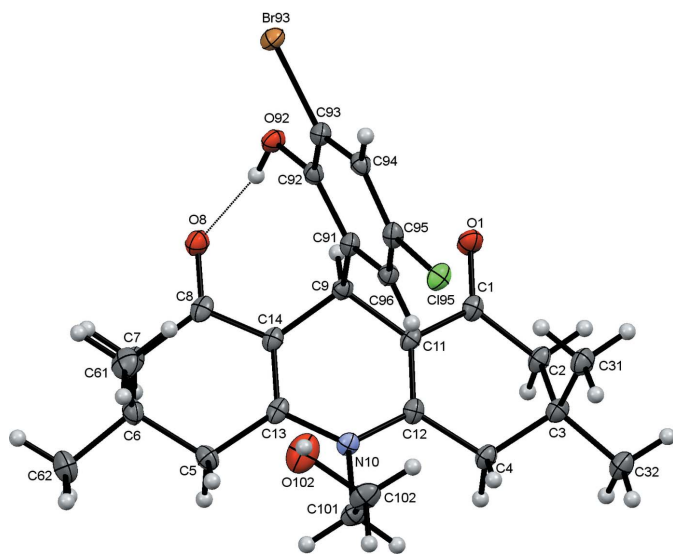


Figure 1
The structure of (1) with ellipsoids drawn at the 50% probability level.

2. Structural commentary

The structure of (1) is shown in Fig. 1. The 3,3,6,6-tetramethyl-tetrahydroacridine-1,8-dione ring system is substituted at the central methine C9 atom by a 3-bromo-5-chloro-2-hydroxyphenyl ring and carries a hydroxyethyl substituent on the acridine N atom. The acridinedione ring system deviates significantly from planarity with an r.m.s. deviation of 0.336 Å for the 13 C atoms and one N atom of the acridine unit. This plane is almost orthogonal to the benzene ring plane [dihedral angle = 89.84 (6)°], a conformation that is stabilized by a strong intramolecular O92—H92···O8 hydrogen bond between the two systems (Table 1). Both the 3-bromo-5-chloro-2-hydroxyphenyl and hydroxyethyl substituents point in the same direction with respect to the acridine plane. Furthermore, one methyl group is axial and the other equatorial with respect to the two outer cyclohexenone rings of the acridinedione and again, the axial methyl substituents are found on the same face of the acridinedione ring system. Overall this ring system is V-shaped with the substituents mentioned above on the convex surface of the shallow V. The outer cyclohexenone rings both adopt flattened chair configurations with the C3 and C6 atoms each 0.646 (4) Å, in the same direction, from the best-fit planes through the remaining

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O92—H92···O8	0.82 (4)	1.81 (4)	2.613 (3)	166 (4)
O102—H102···O1 ⁱ	0.81 (5)	2.01 (5)	2.808 (3)	167 (5)
C61—H61B···Br93 ⁱⁱ	0.98	2.87	3.720 (3)	146
C31—H31B···O92 ⁱⁱⁱ	0.98	2.65	3.532 (4)	150
C5—H5B···O92 ^{iv}	0.99	2.71	3.479 (4)	135
C7—H7A···O92 ^{iv}	0.99	2.44	3.346 (4)	151
C4—H4A···Cl95 ^{iv}	0.99	2.88	3.868 (3)	173

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

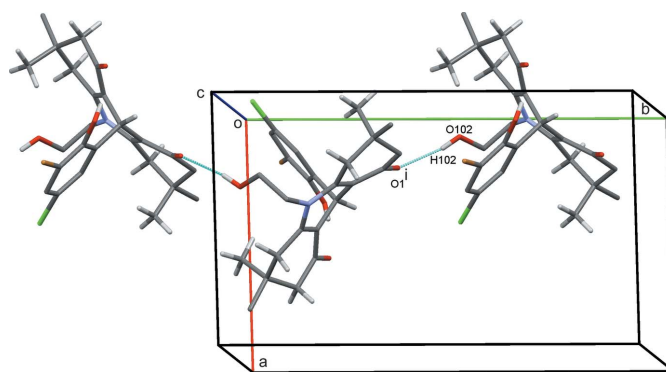


Figure 2
Zigzag chains of (1) parallel to the *b* axis with hydrogen bonds drawn as dashed lines and symmetry operations shown in Table 1. For clarity, H atoms bound to atoms not involved in hydrogen bonding are not shown.

five C atoms. In contrast, the central C9/N10/C11—C14 ring can best be described as a flattened boat with C9 and N10 0.423 (4) and 0.154 (4) Å, respectively, from the best-fit plane through the remaining four C atoms. The bond lengths and angles in the molecule of (1) agree reasonably well with those found in closely related molecules (Abdelhamid *et al.*, 2011; Khalilov *et al.*, 2011).

3. Supramolecular features

The crystal structure of (1) features O102—H102···O1 hydrogen bonds, which link the molecules into zigzag chains parallel to the *b* axis (Fig. 2). Weak C4—H4A···Cl95 together with C5—H5B···O92 and C7—H7A···O92 hydrogen bonds to the same acceptor oxygen atom form $R_2^2(15)$, $R_2^2(13)$ and $R_2^2(6)$ rings. These, combined with weaker inversion-related C61—H61B···Br93 contacts [which in turn generate $R_2^2(22)$ motifs], generate sheets of molecules lying parallel to the $(\bar{4}21)$ plane, as shown in Fig. 3. C31—H31B···O92 hydrogen bonds form additional chains of molecules along the *ac* diagonal

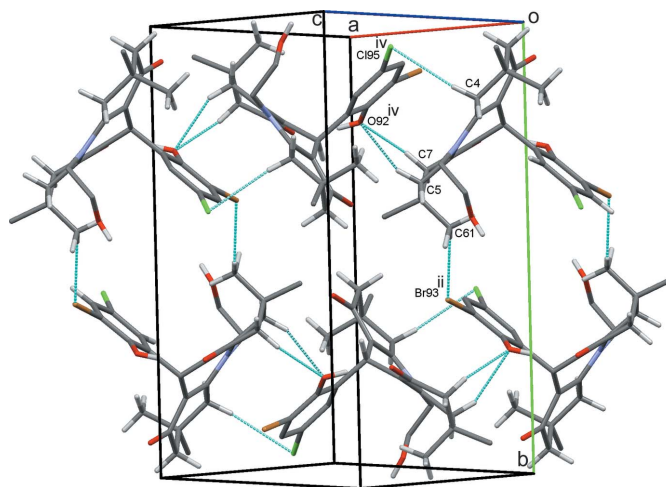


Figure 3
Sheets of molecules of (1) parallel to $(\bar{4}21)$ with hydrogen bonds drawn as dashed lines and symmetry operations shown in Table 1. For clarity, H atoms bound to atoms not involved in hydrogen bonding are not shown.

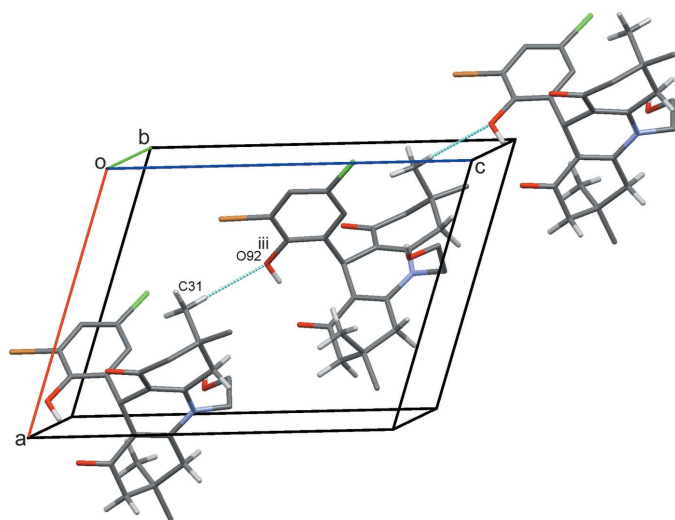


Figure 4
Chains of molecules of (1) along the diagonal of the *ac* plane with hydrogen bonds drawn as dashed lines and symmetry operations shown in Table 1. For clarity, H atoms bound to atoms not involved in hydrogen bonding are not shown.

(Fig. 4). Overall, these interactions stack the molecules into interconnected columns along the *a*-axis direction (Fig. 5).

4. Database survey

Numerous structures of acridine and its derivatives have been reported previously, with 373 entries in the current database (Version 5.35, November 2013 with 1 update; Allen, 2002). However, far fewer structures of derivatives of the seminal hydroacridine, 3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (Natarajan & Mathews, 2011) are found with only 25 unique structures of derivatives with an aryl substituent on the methine C atom and an alkyl or aryl

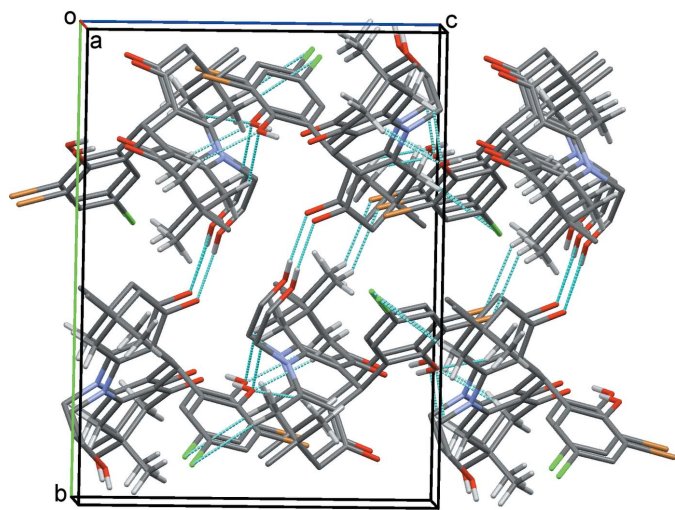


Figure 5
Overall packing for (1) viewed along the *a* axis with hydrogen bonds drawn as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₅ H ₂₉ BrClNO ₄
<i>M_r</i>	522.85
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.5373 (3), 17.1597 (3), 13.7278 (4)
β (°)	107.908 (3)
<i>V</i> (Å ³)	2361.96 (10)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	3.67
Crystal size (mm)	0.19 × 0.07 × 0.06
Data collection	
Diffractometer	Agilent SuperNova (Dual, Cu at zero, Atlas)
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2013)
<i>T</i> _{min} , <i>T</i> _{max}	0.733, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	20233, 4922, 4128
<i>R</i> _{int}	0.076
(sin θ/λ) _{max} (Å ⁻¹)	0.631
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.108, 1.03
No. of reflections	4922
No. of parameters	299
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.67, -0.57

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS97* and *SHELXL2013* (Sheldrick, 2008), *TITAN2000* (Hunter & Simpson, 1999), *Mercury* (Macrae *et al.*, 2008), *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

substituent on the N atom. Of these, aromatic substituents on the N atom predominate with 15 entries (see, for example, Nakhi *et al.* 2013; Shi *et al.* 2008; Wang *et al.* 2003). Two structures, 10-(2-hydroxyethyl)-9-(2-hydroxyphenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (Abdelhamid *et al.*, 2011) and 9-(5-bromo-2-hydroxyphenyl)-10-(2-hydroxypropyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (Khalilov *et al.*, 2011) closely resemble (1), each with 2-hydroxy substituents on the aromatic rings that form intramolecular hydrogen bonds to one of the two keto O atoms in each molecule. In the first instance, the 2-hydroxyethyl substituent on the N atom is identical to that for (1), while the 2-hydroxypropyl substituent in the second analogue is closely related.

5. Synthesis and crystallization

A mixture of 1 mmol (235.5 mg) 3-bromo-5-chloro-2-hydroxybenzaldehyde, 2 mmol (280 mg) 5,5-dimethylcyclohexane-1,3-dione and 1 mmol (61 mg) amino-ethanol in 30 ml of ethanol was refluxed for 12 h. The reaction was monitored by TLC until completion. Excess solvent was evaporated under vacuum and the resulting solid product was recrystallized from a mixture of ethanol/acetone (10:1 *v:v*) to afford yellow needles of the title compound. M.p. 513 K, 82% yield.

IR cm^{-1} : OH phenolic 3400, OH alcoholic 3335, Ar 3001, CH-aliphatic 2882, CO 1694, C=C 1591, C—Br 605, C—Cl 738; $^1\text{H NMR}$: δ 10.01 (*s*, 1H, OH phenolic), 7.3 (*d*, 2H, Ar), 6.7 (*d*, 1H, C9), 5.00 (*s*, 1H, OH alcoholic), 4.02 (*t*, 2H, C2), 3.75 (*t*, 2H, C7), 2.95 (*d*, 2H, C4), 2.7 (*d*, 2H, C5), 2.2 (*m*, 4H, ethyl group), 1–1.2 (*m*, 12H, 4 methyl groups); $^{13}\text{C NMR}$: δ 199, 200 (C=O, C1, C8), 145, 132 and 130 (C=C Ar), 110, 112 (C=C, in acridine fused rings), 122 (C—N), 62 (C—Br), 73 (C—Cl), 50 (C—OH), 20, 28, 30 and 32 (C—C of CH_2CH_2 and 4CH_3); MS: *m/z* 522 (100), 523 (30), 524 (100), 525 (30), 443 (56), 363 (39), 271 (42), 175 (29), 94 (74). Analysis calculated for $\text{C}_{25}\text{H}_{29}\text{BrClNO}_4$ (522.85): C 57.43, H 5.59, Br 15.28, Cl 6.78, N 2.68%; found: C 57.41, H 5.60, Br 15.31, Cl 6.81, N 2.71.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms of the two hydroxy substituents were located in an electron density map and their coordinates were freely refined with $U_{\text{iso}} = 1.5U_{\text{eq}}$ (O). All H atoms bound to carbon were refined using a riding model with $d(\text{C—H}) = 0.95 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for aromatic, 0.99 \AA , $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for methylene, 1.00 \AA , $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for methine, and 0.98 \AA , $U_{\text{iso}} = 1.5U_{\text{eq}}$ (C) for methyl H atoms.

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References

- Abdelhamid, A. A., Mohamed, S. K., Khalilov, A. N., Gurbanov, A. V. & Ng, S. W. (2011). *Acta Cryst.* **E67**, o744.
- Agilent (2013). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Denny, W. A., Baguley, B. C., Cain, B. F. & Waring, M. J. (1983). *Antitumor acridines in molecular aspects of anticancer drug action*, edited by S. Neidle & M. J. Waring, pp. 1–34. London: Macmillan.
- Gaidukevich, A. N., Kazakov, G. P., Kravchenko, A. A., Porokhnyak, L. A. & Dinchuk, V. V. (1987). *Khim. Farm. Zh.* **21**, 1067–1070.
- Gaiukevich, N. A., Bashura, G. S., Pestsev, I. M., Pimenov, O. A. & Pyatkop, A. I. (1973). *Farm. Zh.* **28**, 50–54.
- Hunter, K. A. & Simpson, J. (1999). *TITAN2000*. University of Otago, New Zealand.
- Khalilov, A. N., Abdelhamid, A. A., Gurbanov, A. V. & Ng, S. W. (2011). *Acta Cryst.* **E67**, o1146.
- Kimura, M., Okabayashi, I. & Kato, A. (1993). *J. Heterocycl. Chem.* **30**, 1101–1104.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Misra, V. K. & Bahel, S. C. (1984). *J. Indian Chem. Soc.* **61**, 916–918.
- Miyase, G. G., Ali, E., Dogan, R. S., Kevser, E. & Cihat, S. (2009). *Med. Chem. Res.* **18**, 317–325.
- Nakhi, A., Srinivas, P. T. V. A., Rahman, M. S., Kishore, R., Seerapu, G. P. K., Kumar, K. L., Haldar, D., Rao, M. V. B. & Pal, M. (2013). *Bioorg. Med. Chem. Lett.* **23**, 1828–1833.
- Natarajan, S. & Mathews, R. (2011). *J. Chem. Crystallogr.* **41**, 678–683.
- Ngadi, L., Bisri, N. G., Mahamoud, A., Galy, A. M., Galy, J. P., Soyfer, J. C., Barbe, J. & Placidi, M. (1993). *Arzneim. Forsch.* **43**, 480–483.
- Shaikh, B. M., Konda, S. G., Mehare, A. V., Mandawad, G. G., Chobe, S. S. & Dawane, B. S. (2010). *Pharma Chem.* **2**, 25–29.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shi, D.-Q., Ni, S.-N., Fang-Yang, Shi, J.-W., Dou, G.-L., Li, X.-Y. & Wang, X.-S. (2008). *J. Heterocycl. Chem.* **45**, 653–660.
- Shul'ga, I. S., Sukhomlinov, A. K., Goncharov, I. A. & Dikaya, E. M. (1974). *Farm. Zh.* **29**, 27–29.
- Sondhi, S. M., Bhattacharjee, G., Jameel, R. K., Shukla, R., Raghur, R., Lozach, O. & Meijer, L. (2004). *Cent. Eur. J. Chem.* **2**, 1–15.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Srivastava, A., Pathak, R. B. & Bahel, S. C. (1985). *J. Indian Chem. Soc.* **62**, 486–487.
- Sugaya, T., Mimura, Y., Shida, Y., Osawa, Y. & Matsukuma, I. (1994). *J. Med. Chem.* **37**, 1028–1032.
- Taraporewala, I. B. & Kauffman, J. M. (1990). *J. Pharm. Sci.* **79**, 173–178.
- Wang, X., Shi, D. & Tu, S. (2003). *Acta Cryst.* **E59**, o1139–o1140.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

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Crystal structure of 9-(3-bromo-5-chloro-2-hydroxyphenyl)-10-(2-hydroxyethyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *TITAN2000* (Hunter & Simpson, 1999); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008) and *TITAN2000* (Hunter & Simpson, 1999); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Crystal data

$C_{25}H_{29}BrClNO_4$
 $M_r = 522.85$
 Monoclinic, $P2_1/n$
 $a = 10.5373$ (3) Å
 $b = 17.1597$ (3) Å
 $c = 13.7278$ (4) Å
 $\beta = 107.908$ (3)°
 $V = 2361.96$ (10) Å³
 $Z = 4$

$F(000) = 1080$
 $D_x = 1.470$ Mg m⁻³
 Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
 Cell parameters from 8397 reflections
 $\theta = 4.3\text{--}76.4^\circ$
 $\mu = 3.67$ mm⁻¹
 $T = 100$ K
 Needle, yellow
 $0.19 \times 0.07 \times 0.06$ mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer
 Radiation source: SuperNova (Cu) X-ray Source
 Detector resolution: 5.1725 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
 $T_{\min} = 0.733$, $T_{\max} = 1.000$

20233 measured reflections
 4922 independent reflections
 4128 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$
 $\theta_{\max} = 76.7^\circ$, $\theta_{\min} = 4.3^\circ$
 $h = -13 \rightarrow 12$
 $k = -21 \rightarrow 21$
 $l = -17 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.108$
 $S = 1.03$
 4922 reflections

299 parameters
 0 restraints
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 3.0935P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.67 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2756 (3)	0.38420 (16)	0.7425 (2)	0.0165 (5)
O1	0.2646 (2)	0.41046 (12)	0.65603 (15)	0.0220 (4)
C2	0.2254 (3)	0.42807 (16)	0.8181 (2)	0.0183 (6)
H2A	0.1555	0.4653	0.7808	0.022*
H2B	0.2996	0.4584	0.8644	0.022*
C3	0.1680 (3)	0.37339 (17)	0.8817 (2)	0.0182 (6)
C31	0.0446 (3)	0.33120 (18)	0.8117 (2)	0.0218 (6)
H31A	-0.0221	0.3697	0.7760	0.033*
H31B	0.0068	0.2973	0.8531	0.033*
H31C	0.0707	0.2997	0.7615	0.033*
C32	0.1278 (3)	0.42057 (18)	0.9624 (2)	0.0224 (6)
H32A	0.2058	0.4486	1.0058	0.034*
H32B	0.0938	0.3852	1.0046	0.034*
H32C	0.0582	0.4580	0.9282	0.034*
C4	0.2757 (3)	0.31371 (16)	0.9365 (2)	0.0169 (5)
H4A	0.3401	0.3394	0.9958	0.020*
H4B	0.2327	0.2709	0.9631	0.020*
C5	0.6375 (3)	0.13867 (17)	0.9129 (2)	0.0187 (6)
H5A	0.5984	0.0944	0.9400	0.022*
H5B	0.6987	0.1665	0.9719	0.022*
C6	0.7183 (3)	0.10665 (17)	0.8456 (2)	0.0199 (6)
C61	0.6375 (3)	0.04386 (18)	0.7733 (2)	0.0272 (7)
H61A	0.6193	0.0006	0.8137	0.041*
H61B	0.6886	0.0247	0.7294	0.041*
H61C	0.5531	0.0661	0.7307	0.041*
C62	0.8489 (3)	0.0709 (2)	0.9150 (3)	0.0284 (7)
H62A	0.8281	0.0300	0.9576	0.043*
H62B	0.9024	0.1115	0.9591	0.043*
H62C	0.8993	0.0483	0.8726	0.043*
C7	0.7509 (3)	0.17336 (18)	0.7830 (2)	0.0210 (6)
H7A	0.8091	0.2117	0.8300	0.025*
H7B	0.8000	0.1525	0.7377	0.025*
C8	0.6261 (3)	0.21319 (16)	0.7195 (2)	0.0179 (5)
O8	0.6181 (2)	0.23890 (12)	0.63285 (15)	0.0211 (4)
C9	0.3948 (3)	0.26576 (16)	0.7015 (2)	0.0146 (5)
H9	0.4202	0.3042	0.6560	0.018*

N10	0.4338 (2)	0.21496 (13)	0.90561 (17)	0.0150 (4)
C101	0.4242 (3)	0.17121 (17)	0.9961 (2)	0.0193 (6)
H10A	0.3974	0.2072	1.0427	0.023*
H10B	0.5128	0.1494	1.0337	0.023*
C102	0.3240 (3)	0.10579 (18)	0.9650 (2)	0.0243 (6)
H10C	0.3186	0.0776	1.0265	0.029*
H10D	0.2347	0.1272	0.9288	0.029*
O102	0.3641 (3)	0.05431 (14)	0.9002 (2)	0.0338 (6)
H102	0.318 (5)	0.015 (3)	0.888 (4)	0.051*
C11	0.3399 (3)	0.30933 (16)	0.7750 (2)	0.0151 (5)
C12	0.3510 (3)	0.27926 (16)	0.8694 (2)	0.0156 (5)
C13	0.5263 (3)	0.19368 (15)	0.8568 (2)	0.0153 (5)
C14	0.5183 (3)	0.22261 (16)	0.7631 (2)	0.0155 (5)
C91	0.2933 (3)	0.20862 (16)	0.6350 (2)	0.0152 (5)
C92	0.2973 (3)	0.18932 (16)	0.5361 (2)	0.0155 (5)
O92	0.3860 (2)	0.22101 (12)	0.49447 (15)	0.0185 (4)
H92	0.453 (4)	0.232 (2)	0.542 (3)	0.028*
C93	0.2039 (3)	0.13599 (17)	0.4773 (2)	0.0167 (5)
Br93	0.20688 (3)	0.10910 (2)	0.34475 (2)	0.01878 (10)
C94	0.1101 (3)	0.10051 (15)	0.5147 (2)	0.0156 (5)
H94	0.0464	0.0652	0.4736	0.019*
C95	0.1116 (3)	0.11794 (16)	0.6140 (2)	0.0165 (5)
Cl95	0.00165 (7)	0.07019 (4)	0.66614 (5)	0.01978 (15)
C96	0.2010 (3)	0.17139 (16)	0.6729 (2)	0.0157 (5)
H96	0.1993	0.1828	0.7402	0.019*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0146 (12)	0.0157 (13)	0.0207 (13)	-0.0030 (10)	0.0075 (10)	-0.0029 (10)
O1	0.0287 (11)	0.0196 (10)	0.0212 (10)	0.0037 (9)	0.0128 (8)	0.0039 (8)
C2	0.0217 (14)	0.0140 (13)	0.0223 (13)	-0.0013 (11)	0.0114 (11)	-0.0024 (11)
C3	0.0179 (13)	0.0196 (13)	0.0190 (13)	-0.0008 (11)	0.0085 (11)	-0.0019 (11)
C31	0.0183 (14)	0.0254 (15)	0.0241 (14)	-0.0015 (12)	0.0100 (11)	-0.0023 (12)
C32	0.0257 (15)	0.0213 (14)	0.0243 (14)	0.0003 (12)	0.0139 (12)	-0.0013 (12)
C4	0.0182 (13)	0.0160 (13)	0.0190 (12)	-0.0009 (11)	0.0094 (10)	-0.0004 (11)
C5	0.0184 (14)	0.0154 (13)	0.0208 (13)	0.0016 (11)	0.0039 (10)	0.0017 (11)
C6	0.0187 (14)	0.0177 (14)	0.0230 (14)	0.0046 (11)	0.0058 (11)	-0.0007 (11)
C61	0.0315 (17)	0.0190 (14)	0.0308 (16)	0.0009 (13)	0.0094 (13)	-0.0066 (13)
C62	0.0243 (16)	0.0259 (16)	0.0339 (17)	0.0087 (13)	0.0070 (13)	0.0032 (13)
C7	0.0176 (14)	0.0244 (15)	0.0235 (14)	0.0034 (12)	0.0099 (11)	-0.0004 (12)
C8	0.0187 (13)	0.0147 (13)	0.0213 (13)	-0.0036 (11)	0.0076 (10)	-0.0067 (11)
O8	0.0183 (10)	0.0254 (11)	0.0215 (10)	-0.0003 (8)	0.0089 (8)	-0.0010 (8)
C9	0.0163 (13)	0.0143 (12)	0.0145 (12)	0.0000 (10)	0.0066 (10)	0.0010 (10)
N10	0.0173 (11)	0.0119 (10)	0.0176 (11)	-0.0013 (9)	0.0082 (9)	0.0013 (9)
C101	0.0253 (14)	0.0169 (13)	0.0178 (13)	-0.0004 (11)	0.0100 (11)	0.0008 (11)
C102	0.0328 (17)	0.0195 (14)	0.0246 (15)	-0.0041 (13)	0.0145 (13)	0.0021 (11)
O102	0.0382 (14)	0.0207 (11)	0.0491 (15)	-0.0109 (10)	0.0232 (11)	-0.0082 (11)

C11	0.0168 (13)	0.0129 (12)	0.0170 (12)	-0.0023 (10)	0.0074 (10)	-0.0034 (10)
C12	0.0145 (13)	0.0132 (12)	0.0205 (13)	-0.0020 (10)	0.0077 (10)	-0.0016 (10)
C13	0.0156 (12)	0.0122 (12)	0.0204 (12)	-0.0055 (10)	0.0087 (10)	-0.0060 (10)
C14	0.0149 (13)	0.0141 (12)	0.0186 (12)	-0.0021 (10)	0.0067 (10)	-0.0037 (10)
C91	0.0148 (12)	0.0143 (12)	0.0176 (12)	0.0014 (10)	0.0067 (10)	-0.0009 (10)
C92	0.0160 (13)	0.0138 (12)	0.0175 (12)	0.0036 (10)	0.0061 (10)	0.0024 (10)
O92	0.0172 (10)	0.0237 (10)	0.0167 (9)	-0.0020 (8)	0.0084 (8)	-0.0001 (8)
C93	0.0160 (13)	0.0177 (13)	0.0169 (12)	0.0026 (11)	0.0058 (10)	-0.0007 (10)
Br93	0.02276 (17)	0.01832 (16)	0.01709 (15)	0.00042 (11)	0.00884 (11)	-0.00280 (10)
C94	0.0146 (13)	0.0133 (12)	0.0177 (12)	0.0010 (10)	0.0034 (10)	-0.0010 (10)
C95	0.0160 (13)	0.0130 (12)	0.0225 (13)	0.0008 (10)	0.0089 (10)	0.0023 (10)
Cl95	0.0189 (3)	0.0198 (3)	0.0234 (3)	-0.0044 (3)	0.0106 (2)	-0.0021 (3)
C96	0.0167 (13)	0.0150 (12)	0.0163 (12)	0.0017 (10)	0.0066 (10)	0.0001 (10)

Geometric parameters (Å, °)

C1—O1	1.242 (3)	C7—H7A	0.9900
C1—C11	1.457 (4)	C7—H7B	0.9900
C1—C2	1.504 (4)	C8—O8	1.247 (4)
C2—C3	1.527 (4)	C8—C14	1.447 (4)
C2—H2A	0.9900	C9—C11	1.506 (4)
C2—H2B	0.9900	C9—C14	1.510 (4)
C3—C32	1.532 (4)	C9—C91	1.529 (4)
C3—C31	1.539 (4)	C9—H9	1.0000
C3—C4	1.542 (4)	N10—C13	1.392 (3)
C31—H31A	0.9800	N10—C12	1.399 (4)
C31—H31B	0.9800	N10—C101	1.481 (3)
C31—H31C	0.9800	C101—C102	1.510 (4)
C32—H32A	0.9800	C101—H10A	0.9900
C32—H32B	0.9800	C101—H10B	0.9900
C32—H32C	0.9800	C102—O102	1.408 (4)
C4—C12	1.508 (4)	C102—H10C	0.9900
C4—H4A	0.9900	C102—H10D	0.9900
C4—H4B	0.9900	O102—H102	0.81 (5)
C5—C13	1.517 (4)	C11—C12	1.367 (4)
C5—C6	1.538 (4)	C13—C14	1.357 (4)
C5—H5A	0.9900	C91—C96	1.392 (4)
C5—H5B	0.9900	C91—C92	1.410 (4)
C6—C7	1.532 (4)	C92—O92	1.351 (3)
C6—C61	1.533 (4)	C92—C93	1.403 (4)
C6—C62	1.541 (4)	O92—H92	0.82 (4)
C61—H61A	0.9800	C93—C94	1.387 (4)
C61—H61B	0.9800	C93—Br93	1.887 (3)
C61—H61C	0.9800	C94—C95	1.390 (4)
C62—H62A	0.9800	C94—H94	0.9500
C62—H62B	0.9800	C95—C96	1.384 (4)
C62—H62C	0.9800	C95—Cl95	1.742 (3)
C7—C8	1.501 (4)	C96—H96	0.9500

O1—C1—C11	120.7 (3)	C8—C7—H7B	109.4
O1—C1—C2	121.9 (3)	C6—C7—H7B	109.4
C11—C1—C2	117.4 (2)	H7A—C7—H7B	108.0
C1—C2—C3	111.8 (2)	O8—C8—C14	121.5 (3)
C1—C2—H2A	109.2	O8—C8—C7	120.4 (3)
C3—C2—H2A	109.2	C14—C8—C7	118.0 (2)
C1—C2—H2B	109.2	C11—C9—C14	108.1 (2)
C3—C2—H2B	109.2	C11—C9—C91	112.1 (2)
H2A—C2—H2B	107.9	C14—C9—C91	110.1 (2)
C2—C3—C32	109.5 (2)	C11—C9—H9	108.8
C2—C3—C31	109.8 (2)	C14—C9—H9	108.8
C32—C3—C31	109.4 (2)	C91—C9—H9	108.8
C2—C3—C4	109.0 (2)	C13—N10—C12	119.2 (2)
C32—C3—C4	108.9 (2)	C13—N10—C101	120.6 (2)
C31—C3—C4	110.2 (2)	C12—N10—C101	120.1 (2)
C3—C31—H31A	109.5	N10—C101—C102	111.2 (2)
C3—C31—H31B	109.5	N10—C101—H10A	109.4
H31A—C31—H31B	109.5	C102—C101—H10A	109.4
C3—C31—H31C	109.5	N10—C101—H10B	109.4
H31A—C31—H31C	109.5	C102—C101—H10B	109.4
H31B—C31—H31C	109.5	H10A—C101—H10B	108.0
C3—C32—H32A	109.5	O102—C102—C101	109.0 (3)
C3—C32—H32B	109.5	O102—C102—H10C	109.9
H32A—C32—H32B	109.5	C101—C102—H10C	109.9
C3—C32—H32C	109.5	O102—C102—H10D	109.9
H32A—C32—H32C	109.5	C101—C102—H10D	109.9
H32B—C32—H32C	109.5	H10C—C102—H10D	108.3
C12—C4—C3	114.2 (2)	C102—O102—H102	112 (3)
C12—C4—H4A	108.7	C12—C11—C1	121.3 (2)
C3—C4—H4A	108.7	C12—C11—C9	120.6 (2)
C12—C4—H4B	108.7	C1—C11—C9	118.1 (2)
C3—C4—H4B	108.7	C11—C12—N10	119.8 (2)
H4A—C4—H4B	107.6	C11—C12—C4	121.5 (2)
C13—C5—C6	113.6 (2)	N10—C12—C4	118.7 (2)
C13—C5—H5A	108.8	C14—C13—N10	120.8 (3)
C6—C5—H5A	108.8	C14—C13—C5	121.5 (3)
C13—C5—H5B	108.8	N10—C13—C5	117.7 (2)
C6—C5—H5B	108.8	C13—C14—C8	121.5 (3)
H5A—C5—H5B	107.7	C13—C14—C9	120.1 (2)
C7—C6—C61	109.8 (2)	C8—C14—C9	118.3 (2)
C7—C6—C5	109.3 (2)	C96—C91—C92	118.9 (2)
C61—C6—C5	109.9 (2)	C96—C91—C9	120.8 (2)
C7—C6—C62	109.4 (3)	C92—C91—C9	120.2 (2)
C61—C6—C62	109.4 (2)	O92—C92—C93	118.2 (2)
C5—C6—C62	109.0 (2)	O92—C92—C91	122.8 (2)
C6—C61—H61A	109.5	C93—C92—C91	118.9 (3)
C6—C61—H61B	109.5	C92—O92—H92	107 (3)

H61A—C61—H61B	109.5	C94—C93—C92	121.8 (3)
C6—C61—H61C	109.5	C94—C93—Br93	118.4 (2)
H61A—C61—H61C	109.5	C92—C93—Br93	119.8 (2)
H61B—C61—H61C	109.5	C93—C94—C95	118.3 (2)
C6—C62—H62A	109.5	C93—C94—H94	120.9
C6—C62—H62B	109.5	C95—C94—H94	120.9
H62A—C62—H62B	109.5	C96—C95—C94	121.1 (3)
C6—C62—H62C	109.5	C96—C95—C195	119.4 (2)
H62A—C62—H62C	109.5	C94—C95—C195	119.5 (2)
H62B—C62—H62C	109.5	C95—C96—C91	120.9 (3)
C8—C7—C6	111.0 (2)	C95—C96—H96	119.5
C8—C7—H7A	109.4	C91—C96—H96	119.5
C6—C7—H7A	109.4		
O1—C1—C2—C3	143.8 (3)	C101—N10—C13—C14	166.6 (2)
C11—C1—C2—C3	-36.9 (3)	C12—N10—C13—C5	164.2 (2)
C1—C2—C3—C32	175.9 (2)	C101—N10—C13—C5	-14.7 (4)
C1—C2—C3—C31	-63.9 (3)	C6—C5—C13—C14	-12.2 (4)
C1—C2—C3—C4	56.9 (3)	C6—C5—C13—N10	169.1 (2)
C2—C3—C4—C12	-44.4 (3)	N10—C13—C14—C8	168.2 (2)
C32—C3—C4—C12	-163.8 (2)	C5—C13—C14—C8	-10.4 (4)
C31—C3—C4—C12	76.1 (3)	N10—C13—C14—C9	-11.8 (4)
C13—C5—C6—C7	45.1 (3)	C5—C13—C14—C9	169.5 (2)
C13—C5—C6—C61	-75.5 (3)	O8—C8—C14—C13	179.1 (3)
C13—C5—C6—C62	164.6 (2)	C7—C8—C14—C13	-2.7 (4)
C61—C6—C7—C8	63.6 (3)	O8—C8—C14—C9	-0.9 (4)
C5—C6—C7—C8	-57.0 (3)	C7—C8—C14—C9	177.3 (2)
C62—C6—C7—C8	-176.2 (2)	C11—C9—C14—C13	33.7 (3)
C6—C7—C8—O8	-144.6 (3)	C91—C9—C14—C13	-89.1 (3)
C6—C7—C8—C14	37.2 (3)	C11—C9—C14—C8	-146.4 (2)
C13—N10—C101—C102	-91.2 (3)	C91—C9—C14—C8	90.8 (3)
C12—N10—C101—C102	89.9 (3)	C11—C9—C91—C96	-32.5 (3)
N10—C101—C102—O102	60.0 (3)	C14—C9—C91—C96	87.9 (3)
O1—C1—C11—C12	-179.1 (3)	C11—C9—C91—C92	151.4 (2)
C2—C1—C11—C12	1.6 (4)	C14—C9—C91—C92	-88.2 (3)
O1—C1—C11—C9	1.2 (4)	C96—C91—C92—O92	-178.2 (2)
C2—C1—C11—C9	-178.1 (2)	C9—C91—C92—O92	-1.9 (4)
C14—C9—C11—C12	-33.5 (3)	C96—C91—C92—C93	3.0 (4)
C91—C9—C11—C12	88.1 (3)	C9—C91—C92—C93	179.2 (2)
C14—C9—C11—C1	146.2 (2)	O92—C92—C93—C94	179.6 (2)
C91—C9—C11—C1	-92.2 (3)	C91—C92—C93—C94	-1.5 (4)
C1—C11—C12—N10	-168.3 (2)	O92—C92—C93—Br93	1.1 (3)
C9—C11—C12—N10	11.4 (4)	C91—C92—C93—Br93	180.0 (2)
C1—C11—C12—C4	11.8 (4)	C92—C93—C94—C95	-1.1 (4)
C9—C11—C12—C4	-168.5 (2)	Br93—C93—C94—C95	177.4 (2)
C13—N10—C12—C11	14.7 (4)	C93—C94—C95—C96	2.3 (4)
C101—N10—C12—C11	-166.4 (2)	C93—C94—C95—C195	-176.3 (2)
C13—N10—C12—C4	-165.4 (2)	C94—C95—C96—C91	-0.8 (4)

C101—N10—C12—C4	13.5 (4)	C195—C95—C96—C91	177.8 (2)
C3—C4—C12—C11	11.1 (4)	C92—C91—C96—C95	-1.9 (4)
C3—C4—C12—N10	-168.8 (2)	C9—C91—C96—C95	-178.1 (2)
C12—N10—C13—C14	-14.5 (4)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O92—H92...O8	0.82 (4)	1.81 (4)	2.613 (3)	166 (4)
O102—H102...O1 ⁱ	0.81 (5)	2.01 (5)	2.808 (3)	167 (5)
C61—H61B...Br93 ⁱⁱ	0.98	2.87	3.720 (3)	146
C31—H31B...O92 ⁱⁱⁱ	0.98	2.65	3.532 (4)	150
C5—H5B...O92 ^{iv}	0.99	2.71	3.479 (4)	135
C7—H7A...O92 ^{iv}	0.99	2.44	3.346 (4)	151
C4—H4A...Cl95 ^{iv}	0.99	2.88	3.868 (3)	173

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