Synthesis, resolution and crystal structures of two enantiomeric rhodamine derivatives

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The title molecule, rac-6′-bromo-3′-diethylamino-3H-spiro[2-benzofuran-1,9′-xanthen]-3-one, $C_{24}H_{20}BrNO_3$, was synthesized and the two enantiomers which formed were separated. The structures of all three compounds were determined and compared with those of a variety of related derivatives. A notable feature is the fold of the xanthene portion which ranges from 15.15 (13)° in the racemate to 2.42 (2)° in one molecule of the R enantiomer with that for the S enantiomer having an intermediate value. The differences are attributed to the number and severity of intermolecular interactions which include C—H⋯O hydrogen bonds, C—H⋯π(ring) and, in the S enantiomer, a π-stacking interaction between the carbonyl group and an aromatic ring.

1. Chemical context

The compounds synthesized here are part of ongoing work to form chiral sensors based on the supramolecular interactions of chiral rhodamine derivatives with analytes. Enantiomeric sensing is critical for the efficient and safe formation of chiral pharmaceuticals (LaPlante et al., 2011) since enantiomers may have vastly different biological effects including toxicity (Reist et al., 1998). Most current methods for the detection of enantiomeric purity involve chromatographic techniques that require costly instrumentation (Wang et al., 2006). Chiral supramolecular sensors offer an inexpensive alternative (Chen et al., 2012; Jo et al., 2014; Zhang et al., 2014; Yu & Pu, 2015). Supramolecular sensors, such as modified rhodamine derivatives, have garnered recent interest as sensors with biological applications (Pak et al., 2015; You et al., 2015). Additionally, recent work has shown that rhodamine B can function as a sensor differentiating between diastereomers (Shimizu & Stephenson, 2010). Herein, we report the synthesis, resolution and structures of two asymmetric rhodamine derivatives **4** and **5** which are being investigated for potential as chiral sensors.
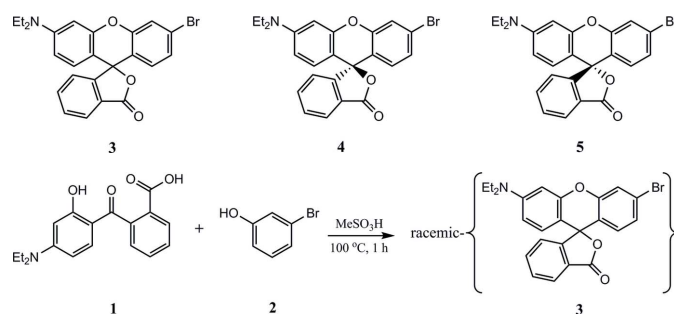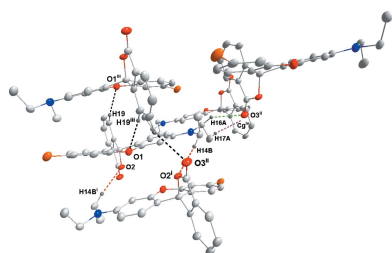
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Table 1
Dihedral angles (°) in selected rhodamine derivatives..

R_1–R_6 positions are defined in Fig. 1.

R_1	R_2	R_3	R_4	R_5	R_6	ring 1–ring 2	ring 3–ring 4	Ref.
H	Et_2N	H	H	Br	H	88.05 (14)	15.15 (13)	*a*
H	Et_2N	H	H	Br	H	88.11 (11)	9.74 (11)	*b*
H	Et_2N	H	H	Br	H	84.2 (2)	6.45 (19)	*c*
H	Et_2N	H	H	Br	H	89.6 (2)	2.4 (2)	*c*
H	Et_2N	H	H	Et_2N	H	89.2 (2)	4.2 (2)	*d*
H	OH	mbz	H	OH	H	88.17 (19)	2.82 (2)	*e*
Cl	OH	CH_2tm	CH_2tm	OH	Cl	90[1]	15.0 (3)	*f*
Cl	OH	CH_2mo	CH_2mo	OH	Cl	90[1]	7.5 (17)	*f*
H	Et_2N	H	H	Et_2N	H	89.59 (5)	7.36 (5)	*g*
H	Et_2n	H	H	Et_2N	H	89.58 (5)	4.59 (5)	*g*
H	Et_2N	H	H	Me	NH(xyl)	88.8 (14)	3.74 (17)	*h*
H	Et_2N	H	H	H	NO_2	89.4 (2)	6.1 (2)	*i*
H	MeO	H	H	OH	H	88.7 (3)	6.3 (3)	*j*
H	Ethm	H	H	Ethm	H	88.64 (17)	14.62 (13)	*k*
NO_2	Ethm	Br	Br	Ethm	NO_2	89.7 (4)	17.5 (5)	*k*
H	OH	H	H	OH	H	89.67 (12)	8.19 (11)	*l*
H	OH	H	H	OH	H	90[1]	4.24 (11)	*l*
H	OH	H	H	OH	H	87.30 (7)	6.25 (7)	*l*
H	OH	H	H	OH	H	90.0 (2)	2.4 (2)	*l*
H	OH	CHO	H	OH	H	89.7 (3)	2.5 (3)	*m*
H	OH	CHO	CHO	OH	H	88.47 (13)	4.68 (12)	*m*
H	Bu_2N	H	H	Me	NHPh	87.08 (13)	13.76 (12)	*n*
H	EtC(O)O	H	H	EtC(O)O	H	89.29 (14)	15.16 (11)	*o*
$MeNH_2$	H	H	H	Et_2N	H	89.1 (3)	6.9 (3)	*p*

[1]Ring 1 lies on a crystallographic mirror. Notes: (*a*) This work (compound **3**); (*b*) this work (compound **4**); (*c*) this work (compound **5**); (*d*) Zhang *et al.* (2015); (*e*) Hou *et al.* (2012) (mbz = PhC(O)NHN≡CH); (*f*) Swamy *et al.* (2009) (tm = thiomorpholino; mo = morpholino); (*g*) Kvick *et al.* (2000) (first line = molecule 1, second line = molecule 2); (*h*) Li *et al.* (2006) (xyl = 2,4-Me$_2$C$_6$H$_3$); (*i*) Liu *et al.* (1995); (*j*) Mchedlov-Petrossyan *et al.* (2015); (*k*) Berscheid *et al.* (1992) (Ethm = OCH$_2$C≡CH); (*l*) Bučar *et al.* (2013); (*m*) Wang *et al.* (2005); (*n*) Okada (1996); (*o*) Wang *et al.* (1990); (*p*) Miao *et al.* (1996).

2. Structural commentary

In general terms, the structures of **3–5** are similar to those of other rhodamine derivatives that have been reported in that the xanthene portion is modestly folded along the O···C axis of the central ring and the benzofuranone unit is nearly perpendicular to the mean plane of the xanthene unit. Of note in the present work is the variation in the fold of the xanthene portion which is largest in **3**, distinctly smaller in **4** and smallest in **5** but with a significant difference in this angle between the two independent molecules (see the first four entries in Table 1Fig. 1). We attribute these differences to the different packing modes for the three structures. In **3** (Fig. 2), the molecules form zigzag stacks with each pair of adjacent molecules related by centers of symmetry. This leads to pairwise H17*C*···C4 separations of 3.04 Å which are only 0.14 Å less than the sum of the van der Waals radii. Were the xanthene portions flatter, these would develop into significant intermolecular contacts. With **4** and **5** (Figs. 3 and 4) in the noncentrosymmetric space group $P2_12_12_1$, this stacking is no longer possible and while in **4** there is a van der Waals contact
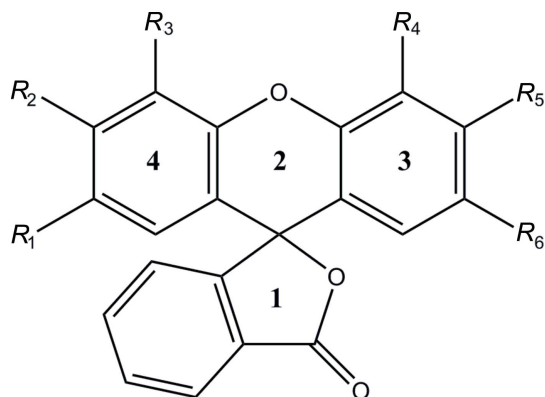
Figure 1
Key for Table 1.

Figure 2
Perspective view of **3**, with the atom-numbering scheme and 50% probability displacement ellipsoids.

Figure 3
Perspective view of **4**, with the atom-numbering scheme and 50% probability displacement ellipsoids.

Table 2
Hydrogen-bond geometry (Å, °) for **3**.

Cg is the centroid of the C8–C13 ring.

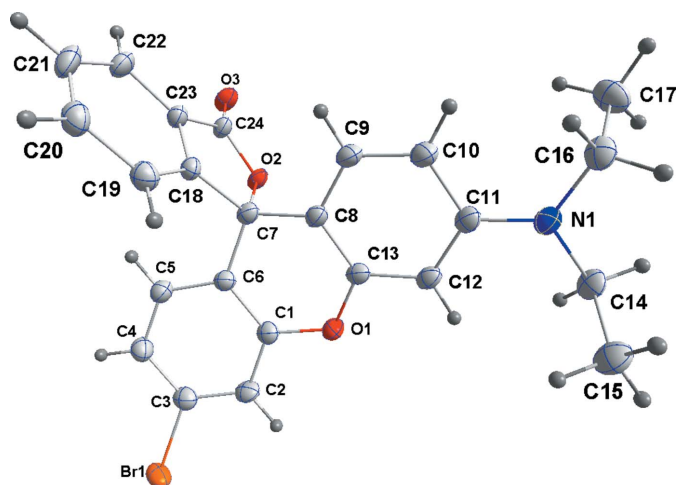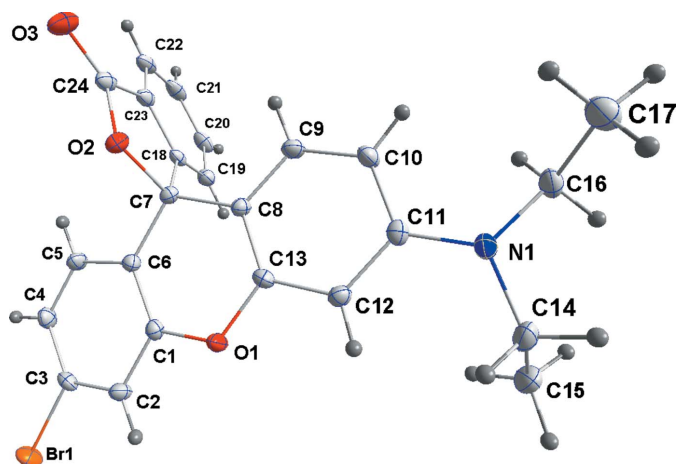| $D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C14—H14B$\cdots$O2[i]	0.99	2.68	3.649 (4)	165
C16—H16A$\cdots$O3[ii]	0.99	2.64	3.522 (3)	148
C16—H16B$\cdots$Br1[iii]	0.99	2.99	3.939 (3)	162
C17—H17A$\cdots$Cg[iv]	0.98	2.75	3.666 (4)	156
C19—H19$\cdots$O1[iii]	0.95	2.57	3.485 (4)	161
C20—H20$\cdots$O3[v]	0.95	2.58	3.421 (3)	148

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

Table 3
Hydrogen-bond geometry (Å, °) for **4**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C14—H14B$\cdots$O3[i]	0.99 (2)	2.68 (2)	3.621 (3)	160.7 (19)
C20—H20$\cdots$O3[ii]	0.94 (2)	2.41 (3)	3.163 (3)	138 (3)

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

of 2.90 Å between H17A and C4[i] [symmetry code: (i) $\frac{3}{2}-x$, $1-y, -\frac{1}{2}+z$] which could be lessened by a greater folding, this is opposed by a H2$\cdots$H19[ii] [symmetry code: (ii) $-\frac{1}{2}+x, \frac{3}{2}-y, 1-z$] separation of 2.48 (4) Å which is only 0.08 Å greater than the sum of the van der Waals radii. In the case of **5**, the C8–C13 ring experiences the opposing contacts H40B$\cdots$C13 (2.79 Å) and H41B[iii]$\cdots$C11 [2.79 Å; symmetry code: (iii) $1+x$, y, z], both of which are 0.11 Å less than a van der Waals contact and serve to hold this ring in position in the packing. On the other side of this xanthene moiety there is a Br1$\cdots$O6[iv] [symmetry code: (iv) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$] contact of 3.251 (3) Å which is 0.12 Å less than a van der Waals contact and imparts more of a twist than a simple fold to this portion. This can be seen from the dihedral angle of 5.7 (2)° between the C1–C6 ring and the C1/C6/C7/O1 plane. For the second molecule, there are no short intermolecular contacts with either side of the xanthene moiety to influence its conformation.
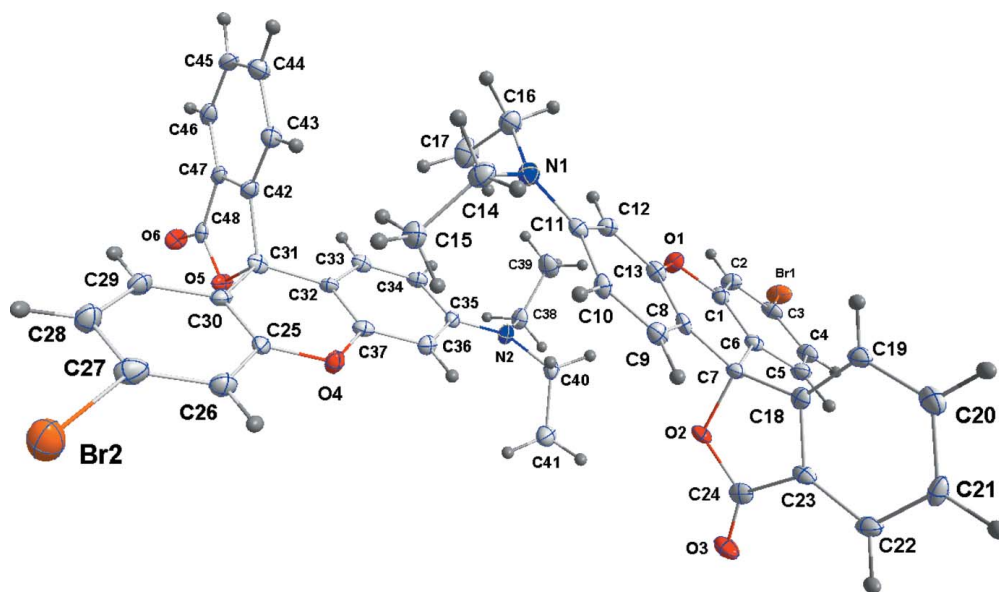
3. Supramolecular features

Fig. 5 illustrates the intermolecular interactions in the crystal of **3** with numerical details given in Table 2. These include two sets of pairwise C—H$\cdots$O hydrogen bonds, two additional sets of C—H$\cdots$O hydrogen bonds and a set of C—H$\cdots\pi$(ring) interactions. The C14$\cdots$H14B$\cdots$O2[i] and C19—H19$\cdots$O1[iii] interactions bind the molecules into stacks along the a-axis direction while the C16—H16A$\cdots$O3[i] and C17—H17A$\cdots\pi$(ring)[iv] interactions tie the stacks together (Fig. 6). Intermolecular interactions are much fewer in the crystal of **4** with C14—H14B$\cdots$O3[v] and C20—H20$\cdots$O3[vi] hydrogen bonds (Table 3) forming zigzag chains (Fig. 7) running approximately along the c-axis direction and arranged to form rectangular channels along the a-axis direction (Fig. 8). In the

Figure 4
The asymmetric unit of **5**, with the atom-numbering scheme and 50% probability displacement ellipsoids.
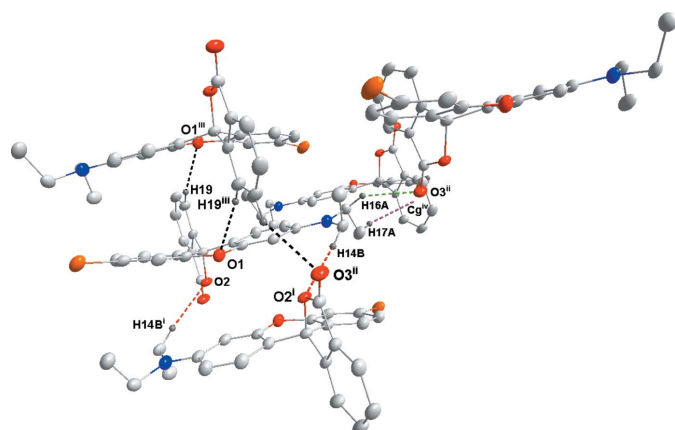
Figure 5
Detail of the intermolecular interactions in **3** with C19—H19···O1^{iii}, C14—H14B···O2^i, and C16—H16A···O3^{ii} hydrogen bonds shown, respectively, as black, red and green dotted lines, while the C17—H17A···Cg^{iv} interaction is given by a purple dotted line. [Symmetry codes: (i) $x, y, -1 + z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, 2 - y, 1 - z$; Cg is the centroid of the indicated ring.]
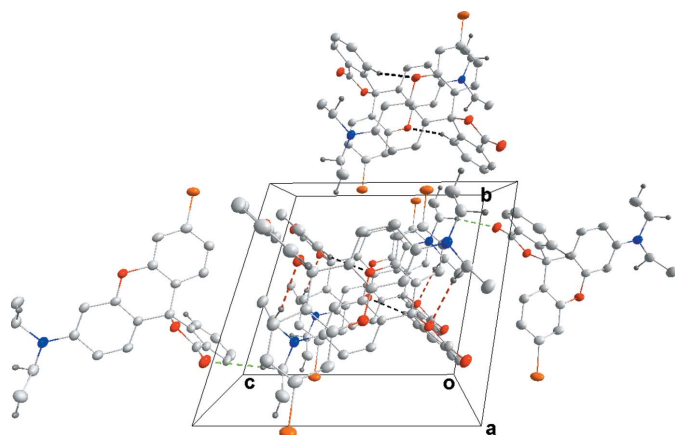
Figure 6
Packing of **3**, viewed along the *a*-axis direction, with the color code for C—H···O interactions as in Fig. 5.

crystal of **5**, the two independent molecules are associated through C40—H40A···Cg1 and C40—H40B···Cg2 interactions with these units tied together on one side by C16—H16B···Cg^i interactions (Table 4) and on the other by a π–π
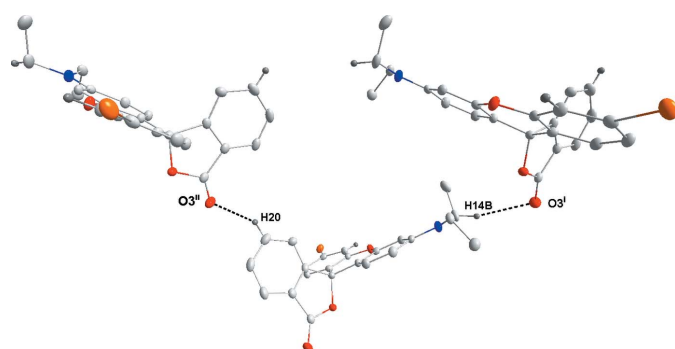
Figure 7
Detail of the intermolecular interactions in **4**. [Symmetry codes: (v) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

Table 4
Hydrogen-bond geometry (Å, °) for **5**.

Cg1 and Cg2 are the centroids of the C8–C13 and O1,C1,C6,C7,C8,C13 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16B···Cg^i	0.99	2.81	3.583 (4)	136
C40—H40A···Cg1	0.99	2.79	3.534 (4)	132
C40—H40B···Cg2	0.99	2.83	3.580 (4)	133

Symmetry code: (i) $x + 1, y, z$.

interaction between the C24═O3 bond and the (C18–C23)^{ii} ring [Fig. 9, centroid–centroid distance = 3.349 (3) Å, angle of C═O vector to centroid = 99.5 (3)°]. The result is a more open 3D structure for this enantiomer (Fig. 10).
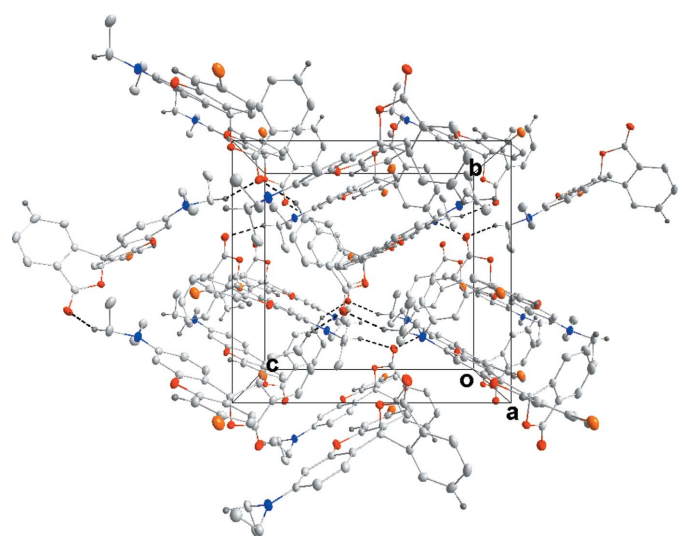
Figure 8
Packing of **4**, viewed along the *a*-axis direction, with C—H···O hydrogen bonds shown as dotted lines.
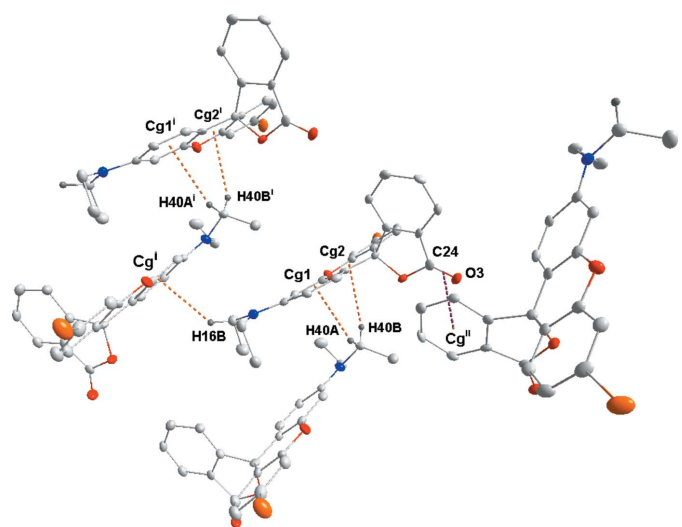
Figure 9
Detail of the intermolecular interactions in **5**. [Symmetry codes: (vii) $1 + x, y, z$; (viii) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.]
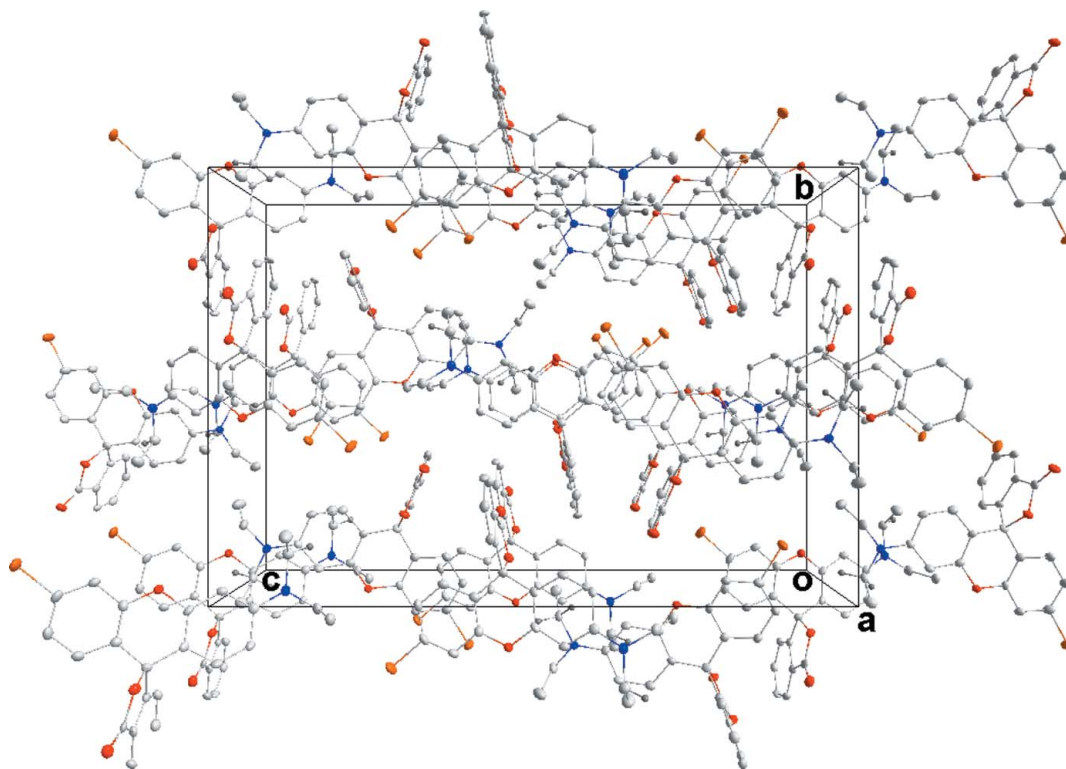
Figure 10
Packing of **5**, viewed along the *a*-axis direction.

4. Database survey

There are 71 structures of rhodamine derivatives in the literature, although many are considerably more substituted than **4** and **5** and include a variety of fused-ring systems. Table 1 lists, in addition to those reported here, 20 other structures which are most nearly comparable to those of this work. In all of these, the lactone ring (ring 1, Fig. 1) is nearly perpendicular to the mean plane of the central pyran ring (ring 2, Fig. 1) with dihedral angles ranging from 87.08 (13) to 90.0 (2)° and with three structures having the lactone ring on a crystallographic mirror (Table 1). In all cases, the xanthene moiety is folded across the O···C axis, with the majority having a dihedral angle between rings 3 and 4 (Fig. 1) in the range 2.42 (3)–7.36 (5)°, but there are six having angles up to 17.5 (5)° (Table 1). In this latter group, those with the largest angles involve a twist of the xanthene moiety as well as a fold, and this is seen in both symmetrically and unsymmetrically substituted examples. Inspection of intermolecular contact calculations indicates that the largest dihedral angles correlate with intermolecular contacts at or somewhat less than the sums of the relevant van der Waals radii.

5. Synthesis and crystallization

As outlined in the scheme, compound **1** (2.00 g, 6.73 mmol) was mixed with compound **2** (1.10g, 6.35 mmol) in 16 mL of methylsulfonic acid. The mixture was stirred and heated for 1 h at 373 K. The cooled solution was poured over ice and then extracted with dicholoromethane. A crude yield of the race-mate **3** was obtained. A portion of the crude product (1.343 g) was purified on a flash column with 15% ethyl acetate in hexanes followed by 100% ethyl acetate. The fractions containing the product were combined and left in a beaker covered with a tissue and the solvent was allowed to evaporate slowly. After about two weeks, the purified racemate yielded a mixture of long needle-shaped as well as plate-shaped crystals (0.293 g, 0.651 mmol, 21.8% yield). Thin layer chromatography demonstrated that both crystal shapes were the desired product (racemate **3**), but only the needles provided a well-refined structure. The melting point range was found to be 420.6–428.9 K for the needles and 415.9–429.8 K for the plates. An NMR spectrum of compound **3** was also obtained (Figs. S1 and S2).

To separate the enantiomers a mobile phase of 70% hexanes, 29.97% ethanol and 0.03% diethylamine was used. A 4 mg mL^{-1} solution of the racemic bromo-rhodamine derivative, **3** was dissolved in the mobile phase. A two-pump system, both Shimadzu LC-20AD pumps, was utilized for moving the mobile phase through the column. Pump A pumped hexanes and Pump B pumped the mixture of 95% ethanol and 0.5% diethylamine at a flow rate of 3.0 mL min^{-1} for a total of 16 minutes. The sample was placed in a Shimadzu SIL-20AC autosampler, which injected 400 μL of the sample into the mobile phase. A Shimadzu CTO-20A oven, set at 298 k, held the ChiralPak AD-H column whose stationary phase is amylose tris (3,5-dimethylphenylcarbamate) coated on 5 μm silica-gel. The compounds were eluted and then detected with a Shimadzu SPD-20A UV photodiode array detector with a deuterium lamp set at 230 nm. Each enantiomer was collected

Table 5
Experimental details.

	3	4	5
Crystal data			
Chemical formula	$C_{24}H_{20}BrNO_3$	$C_{24}H_{20}BrNO_3$	$C_{24}H_{20}BrNO_3$
M_r	450.32	450.32	450.32
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	150	100	100
a, b, c (Å)	8.3074 (4), 11.1871 (5), 11.7693 (6)	11.0772 (6), 13.0582 (8), 13.8966 (8)	8.1529 (13), 18.185 (3), 26.860 (4)
α, β, γ (°)	102.384 (2), 91.106 (2), 109.581 (2)	90, 90, 90	90, 90, 90
V (Å^3)	1001.60 (8)	2010.1 (2)	3982.3 (11)
Z	2	4	8
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	3.01	2.07	2.09
Crystal size (mm)	$0.11 \times 0.07 \times 0.06$	$0.31 \times 0.12 \times 0.10$	$0.26 \times 0.06 \times 0.04$
Data collection			
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS	Bruker *SMART APEX* CCD	Bruker *SMART APEX* CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)	Multi-scan (*SADABS*; Bruker, 2016)	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.59, 0.84	0.69, 0.82	0.70, 0.92
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7525, 3725, 3415	39006, 5417, 4926	38240, 10174, 7285
R_{int}	0.037	0.043	0.075
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.618	0.687	0.685
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.124, 1.03	0.026, 0.058, 0.99	0.045, 0.093, 0.97
No. of reflections	3725	5417	10174
No. of parameters	264	320	527
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.01, -0.98	0.62, -0.25	0.92, -0.34
Absolute structure	–	Flack x determined using 1981 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	Flack x determined using 2575 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	-0.006 (3)	-0.002 (6)

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

with a Shimadzu FRC-10A fraction collector. One enantiomer (**4**) elutes from 11.6-12.8 minutes, and the other (**5**) elutes from 13.4–14.8 minutes using the method described above. Slow evaporation of the solutions of the pure enantiomers at room temperature afforded X-ray quality crystals over 1-5 days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. In **3** and **5**, H atoms attached to carbon were placed in calculated positions (C—H = 0.95–0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2–1.5 times those of the attached atoms. In **4**, the methyl group H atoms were placed in calculated positions as in **3** and **5** (due to poor geometry resulting from individual refinement) while the remainder were refined.

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supporting information

Synthesis, resolution and crystal structures of two enantiomeric rhodamine derivatives

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Computing details

For all compounds, data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(3) *rac*-6′-Bromo-3′-diethylamino-3*H*-spiro[2-benzofuran-1,9′-xanthen]-3-one

Crystal data

$C_{24}H_{20}BrNO_3$	$Z = 2$
$M_r = 450.32$	$F(000) = 460$
Triclinic, $P\bar{1}$	$D_x = 1.493$ Mg m^{-3}
$a = 8.3074$ (4) Å	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$b = 11.1871$ (5) Å	Cell parameters from 6586 reflections
$c = 11.7693$ (6) Å	$\theta = 3.9$–72.5°
$\alpha = 102.384$ (2)°	$\mu = 3.01$ mm^{-1}
$\beta = 91.106$ (2)°	$T = 150$ K
$\gamma = 109.581$ (2)°	Column, colourless
$V = 1001.60$ (8) Å^3	$0.11 \times 0.07 \times 0.06$ mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer	$T_{min} = 0.59$, $T_{max} = 0.84$
	7525 measured reflections
Radiation source: INCOATEC IμS micro-focus source	3725 independent reflections
	3415 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.037$
Detector resolution: 10.4167 pixels mm^{-1}	$\theta_{max} = 72.5°$, $\theta_{min} = 3.9°$
ω scans	$h = -10 \rightarrow 9$
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)	$k = -13 \rightarrow 13$
	$l = -12 \rightarrow 14$

Refinement

Refinement on F^2	264 parameters
Least-squares matrix: full	0 restraints
$R[F^2 > 2\sigma(F^2)] = 0.045$	Primary atom site location: structure-invariant direct methods
$wR(F^2) = 0.124$	
$S = 1.03$	Secondary atom site location: difference Fourier map
3725 reflections	

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2 + 0.6226P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\mathrm{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.19033 (4)	0.02441 (3)	0.64991 (3)	0.03278 (14)
O1	0.1667 (2)	0.41446 (18)	0.49152 (16)	0.0248 (4)
O2	0.2042 (2)	0.65283 (18)	0.77320 (15)	0.0217 (4)
O3	0.1991 (3)	0.7974 (2)	0.93699 (17)	0.0301 (4)
N1	0.2392 (3)	0.7234 (2)	0.25883 (19)	0.0265 (5)
C1	0.2155 (3)	0.3798 (3)	0.5878 (2)	0.0224 (5)
C2	0.1813 (3)	0.2475 (3)	0.5752 (2)	0.0257 (5)
H2	0.1266	0.1871	0.5040	0.031*
C3	0.2281 (3)	0.2048 (3)	0.6683 (2)	0.0263 (6)
C4	0.3066 (4)	0.2908 (3)	0.7742 (2)	0.0272 (6)
H4	0.3360	0.2601	0.8381	0.033*
C5	0.3404 (3)	0.4226 (3)	0.7836 (2)	0.0256 (5)
H5	0.3948	0.4826	0.8551	0.031*
C6	0.2970 (3)	0.4704 (3)	0.6915 (2)	0.0210 (5)
C7	0.3359 (3)	0.6138 (3)	0.7025 (2)	0.0205 (5)
C8	0.3204 (3)	0.6420 (3)	0.5850 (2)	0.0213 (5)
C9	0.3837 (3)	0.7690 (3)	0.5676 (2)	0.0256 (6)
H9	0.4463	0.8386	0.6313	0.031*
C10	0.3584 (4)	0.7966 (3)	0.4618 (2)	0.0268 (6)
H10	0.4044	0.8841	0.4540	0.032*
C11	0.2647 (3)	0.6962 (3)	0.3641 (2)	0.0228 (5)
C12	0.1999 (3)	0.5689 (3)	0.3810 (2)	0.0227 (5)
H12	0.1348	0.4990	0.3182	0.027*
C13	0.2302 (3)	0.5445 (2)	0.4882 (2)	0.0206 (5)
C14	0.1323 (3)	0.6234 (3)	0.1601 (2)	0.0265 (6)
H14A	0.0819	0.6652	0.1101	0.032*
H14B	0.0366	0.5614	0.1899	0.032*
C15	0.2312 (4)	0.5483 (3)	0.0865 (3)	0.0342 (7)
H15A	0.1533	0.4819	0.0223	0.051*

H15B	0.2806	0.5060	0.1354	0.051*
H15C	0.3236	0.6087	0.0545	0.051*
C16	0.3190 (3)	0.8529 (3)	0.2376 (2)	0.0271 (6)
H16A	0.3361	0.8444	0.1536	0.033*
H16B	0.4334	0.8949	0.2827	0.033*
C17	0.2128 (4)	0.9391 (3)	0.2713 (3)	0.0376 (7)
H17A	0.2746	1.0263	0.2594	0.056*
H17B	0.1924	0.9457	0.3538	0.056*
H17C	0.1027	0.9013	0.2227	0.056*
C18	0.5013 (3)	0.6985 (2)	0.7778 (2)	0.0205 (5)
C19	0.6676 (3)	0.7027 (3)	0.7611 (3)	0.0267 (6)
H19	0.6922	0.6516	0.6928	0.032*
C20	0.7980 (3)	0.7847 (3)	0.8483 (3)	0.0306 (6)
H20	0.9128	0.7881	0.8399	0.037*
C21	0.7623 (4)	0.8615 (3)	0.9472 (3)	0.0317 (6)
H21	0.8530	0.9160	1.0054	0.038*
C22	0.5968 (4)	0.8599 (3)	0.9619 (2)	0.0270 (6)
H22	0.5725	0.9142	1.0282	0.032*
C23	0.4670 (3)	0.7756 (3)	0.8758 (2)	0.0208 (5)
C24	0.2804 (3)	0.7489 (3)	0.8704 (2)	0.0220 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02583 (19)	0.02119 (19)	0.0485 (2)	0.00731 (13)	−0.00533 (13)	0.00453 (13)
O1	0.0247 (9)	0.0208 (10)	0.0236 (9)	0.0047 (7)	−0.0068 (7)	0.0006 (7)
O2	0.0143 (8)	0.0264 (10)	0.0211 (8)	0.0080 (7)	−0.0022 (7)	−0.0023 (7)
O3	0.0251 (10)	0.0369 (12)	0.0259 (9)	0.0147 (9)	0.0003 (8)	−0.0039 (8)
N1	0.0280 (12)	0.0273 (12)	0.0217 (11)	0.0089 (10)	−0.0037 (9)	0.0022 (9)
C1	0.0155 (11)	0.0237 (13)	0.0266 (13)	0.0072 (10)	−0.0008 (10)	0.0029 (10)
C2	0.0184 (12)	0.0216 (13)	0.0306 (13)	0.0041 (10)	−0.0037 (10)	−0.0023 (10)
C3	0.0172 (12)	0.0250 (14)	0.0341 (14)	0.0070 (10)	0.0015 (11)	0.0026 (11)
C4	0.0247 (13)	0.0263 (14)	0.0302 (14)	0.0082 (11)	−0.0018 (11)	0.0069 (11)
C5	0.0238 (13)	0.0256 (14)	0.0246 (12)	0.0077 (10)	−0.0021 (10)	0.0015 (10)
C6	0.0176 (11)	0.0195 (13)	0.0243 (12)	0.0066 (9)	0.0003 (10)	0.0017 (9)
C7	0.0155 (11)	0.0222 (13)	0.0220 (12)	0.0072 (9)	−0.0003 (9)	0.0004 (9)
C8	0.0201 (12)	0.0231 (13)	0.0197 (12)	0.0094 (10)	−0.0015 (9)	0.0002 (9)
C9	0.0269 (13)	0.0200 (13)	0.0251 (13)	0.0062 (10)	−0.0049 (10)	−0.0012 (10)
C10	0.0275 (13)	0.0217 (14)	0.0272 (13)	0.0066 (11)	−0.0049 (11)	0.0013 (10)
C11	0.0198 (12)	0.0262 (14)	0.0225 (12)	0.0106 (10)	−0.0022 (10)	0.0019 (10)
C12	0.0196 (12)	0.0249 (14)	0.0213 (12)	0.0094 (10)	−0.0029 (10)	−0.0018 (10)
C13	0.0151 (11)	0.0199 (13)	0.0248 (12)	0.0069 (9)	−0.0019 (9)	−0.0002 (9)
C14	0.0206 (12)	0.0318 (15)	0.0236 (13)	0.0072 (11)	−0.0063 (10)	0.0032 (11)
C15	0.0327 (15)	0.0360 (17)	0.0280 (14)	0.0104 (13)	−0.0036 (12)	−0.0021 (11)
C16	0.0211 (12)	0.0316 (15)	0.0258 (13)	0.0050 (11)	−0.0012 (10)	0.0078 (10)
C17	0.0331 (16)	0.0339 (17)	0.0481 (18)	0.0124 (13)	−0.0026 (13)	0.0138 (13)
C18	0.0162 (11)	0.0200 (12)	0.0239 (12)	0.0050 (9)	−0.0041 (9)	0.0044 (9)
C19	0.0203 (12)	0.0267 (14)	0.0337 (14)	0.0096 (11)	0.0009 (11)	0.0064 (11)

C20	0.0170 (12)	0.0315 (16)	0.0430 (16)	0.0067 (11)	−0.0027 (11)	0.0115 (12)
C21	0.0198 (13)	0.0340 (16)	0.0325 (14)	−0.0010 (11)	−0.0100 (11)	0.0075 (11)
C22	0.0263 (14)	0.0268 (14)	0.0208 (12)	0.0027 (11)	−0.0058 (10)	0.0019 (10)
C23	0.0186 (12)	0.0223 (13)	0.0198 (11)	0.0065 (10)	−0.0019 (9)	0.0029 (9)
C24	0.0197 (12)	0.0256 (14)	0.0186 (12)	0.0082 (10)	−0.0023 (10)	0.0007 (9)

Geometric parameters (Å, º)

Br1—C3	1.898 (3)	C11—C12	1.403 (4)
O1—C1	1.369 (3)	C12—C13	1.383 (4)
O1—C13	1.381 (3)	C12—H12	0.9500
O2—C24	1.362 (3)	C14—C15	1.520 (4)
O2—C7	1.510 (3)	C14—H14A	0.9900
O3—C24	1.203 (3)	C14—H14B	0.9900
N1—C11	1.366 (3)	C15—H15A	0.9800
N1—C16	1.455 (4)	C15—H15B	0.9800
N1—C14	1.458 (3)	C15—H15C	0.9800
C1—C2	1.384 (4)	C16—C17	1.512 (4)
C1—C6	1.397 (3)	C16—H16A	0.9900
C2—C3	1.383 (4)	C16—H16B	0.9900
C2—H2	0.9500	C17—H17A	0.9800
C3—C4	1.393 (4)	C17—H17B	0.9800
C4—C5	1.384 (4)	C17—H17C	0.9800
C4—H4	0.9500	C18—C23	1.380 (4)
C5—C6	1.398 (4)	C18—C19	1.386 (4)
C5—H5	0.9500	C19—C20	1.398 (4)
C6—C7	1.502 (4)	C19—H19	0.9500
C7—C8	1.496 (4)	C20—C21	1.390 (5)
C7—C18	1.514 (3)	C20—H20	0.9500
C8—C13	1.391 (3)	C21—C22	1.384 (4)
C8—C9	1.402 (4)	C21—H21	0.9500
C9—C10	1.373 (4)	C22—C23	1.395 (3)
C9—H9	0.9500	C22—H22	0.9500
C10—C11	1.420 (4)	C23—C24	1.475 (3)
C10—H10	0.9500		
C1—O1—C13	118.1 (2)	C12—C13—C8	123.2 (2)
C24—O2—C7	111.26 (18)	N1—C14—C15	112.8 (2)
C11—N1—C16	122.3 (2)	N1—C14—H14A	109.0
C11—N1—C14	121.8 (2)	C15—C14—H14A	109.0
C16—N1—C14	115.9 (2)	N1—C14—H14B	109.0
O1—C1—C2	115.3 (2)	C15—C14—H14B	109.0
O1—C1—C6	123.1 (2)	H14A—C14—H14B	107.8
C2—C1—C6	121.6 (2)	C14—C15—H15A	109.5
C3—C2—C1	118.8 (2)	C14—C15—H15B	109.5
C3—C2—H2	120.6	H15A—C15—H15B	109.5
C1—C2—H2	120.6	C14—C15—H15C	109.5
C2—C3—C4	121.9 (3)	H15A—C15—H15C	109.5

C2—C3—Br1	119.1 (2)	H15B—C15—H15C	109.5
C4—C3—Br1	119.0 (2)	N1—C16—C17	112.6 (2)
C5—C4—C3	117.9 (3)	N1—C16—H16A	109.1
C5—C4—H4	121.0	C17—C16—H16A	109.1
C3—C4—H4	121.0	N1—C16—H16B	109.1
C4—C5—C6	122.2 (3)	C17—C16—H16B	109.1
C4—C5—H5	118.9	H16A—C16—H16B	107.8
C6—C5—H5	118.9	C16—C17—H17A	109.5
C1—C6—C5	117.6 (2)	C16—C17—H17B	109.5
C1—C6—C7	120.7 (2)	H17A—C17—H17B	109.5
C5—C6—C7	121.7 (2)	C16—C17—H17C	109.5
C8—C7—C6	110.8 (2)	H17A—C17—H17C	109.5
C8—C7—O2	107.84 (19)	H17B—C17—H17C	109.5
C6—C7—O2	107.9 (2)	C23—C18—C19	120.9 (2)
C8—C7—C18	114.7 (2)	C23—C18—C7	110.1 (2)
C6—C7—C18	113.2 (2)	C19—C18—C7	129.0 (2)
O2—C7—C18	101.64 (19)	C18—C19—C20	117.7 (3)
C13—C8—C9	115.9 (2)	C18—C19—H19	121.2
C13—C8—C7	121.6 (2)	C20—C19—H19	121.2
C9—C8—C7	122.3 (2)	C21—C20—C19	121.1 (3)
C10—C9—C8	122.5 (2)	C21—C20—H20	119.4
C10—C9—H9	118.8	C19—C20—H20	119.4
C8—C9—H9	118.8	C22—C21—C20	121.0 (2)
C9—C10—C11	121.0 (3)	C22—C21—H21	119.5
C9—C10—H10	119.5	C20—C21—H21	119.5
C11—C10—H10	119.5	C21—C22—C23	117.5 (3)
N1—C11—C12	122.0 (2)	C21—C22—H22	121.3
N1—C11—C10	121.1 (2)	C23—C22—H22	121.3
C12—C11—C10	116.9 (2)	C18—C23—C22	121.8 (2)
C13—C12—C11	120.5 (2)	C18—C23—C24	108.6 (2)
C13—C12—H12	119.7	C22—C23—C24	129.6 (2)
C11—C12—H12	119.7	O3—C24—O2	122.2 (2)
O1—C13—C12	114.7 (2)	O3—C24—C23	129.5 (2)
O1—C13—C8	122.1 (2)	O2—C24—C23	108.3 (2)
C13—O1—C1—C2	−165.8 (2)	C9—C10—C11—C12	0.0 (4)
C13—O1—C1—C6	13.1 (4)	N1—C11—C12—C13	179.1 (2)
O1—C1—C2—C3	179.4 (2)	C10—C11—C12—C13	−1.0 (4)
C6—C1—C2—C3	0.5 (4)	C1—O1—C13—C12	169.3 (2)
C1—C2—C3—C4	0.8 (4)	C1—O1—C13—C8	−9.3 (3)
C1—C2—C3—Br1	−177.47 (19)	C11—C12—C13—O1	−176.9 (2)
C2—C3—C4—C5	−1.3 (4)	C11—C12—C13—C8	1.7 (4)
Br1—C3—C4—C5	176.9 (2)	C9—C8—C13—O1	177.3 (2)
C3—C4—C5—C6	0.6 (4)	C7—C8—C13—O1	−7.6 (4)
O1—C1—C6—C5	−180.0 (2)	C9—C8—C13—C12	−1.2 (4)
C2—C1—C6—C5	−1.2 (4)	C7—C8—C13—C12	173.9 (2)
O1—C1—C6—C7	0.1 (4)	C11—N1—C14—C15	−87.3 (3)
C2—C1—C6—C7	178.9 (2)	C16—N1—C14—C15	91.6 (3)

C4—C5—C6—C1	0.6 (4)	C11—N1—C16—C17	−87.7 (3)
C4—C5—C6—C7	−179.4 (2)	C14—N1—C16—C17	93.4 (3)
C1—C6—C7—C8	−15.1 (3)	C8—C7—C18—C23	115.2 (2)
C5—C6—C7—C8	164.9 (2)	C6—C7—C18—C23	−116.3 (2)
C1—C6—C7—O2	102.7 (3)	O2—C7—C18—C23	−0.9 (3)
C5—C6—C7—O2	−77.3 (3)	C8—C7—C18—C19	−66.8 (4)
C1—C6—C7—C18	−145.7 (2)	C6—C7—C18—C19	61.7 (4)
C5—C6—C7—C18	34.4 (3)	O2—C7—C18—C19	177.1 (3)
C24—O2—C7—C8	−118.3 (2)	C23—C18—C19—C20	1.8 (4)
C24—O2—C7—C6	122.0 (2)	C7—C18—C19—C20	−176.0 (3)
C24—O2—C7—C18	2.7 (3)	C18—C19—C20—C21	−1.4 (4)
C6—C7—C8—C13	18.8 (3)	C19—C20—C21—C22	−0.5 (5)
O2—C7—C8—C13	−99.0 (3)	C20—C21—C22—C23	1.9 (4)
C18—C7—C8—C13	148.5 (2)	C19—C18—C23—C22	−0.4 (4)
C6—C7—C8—C9	−166.4 (2)	C7—C18—C23—C22	177.8 (2)
O2—C7—C8—C9	75.8 (3)	C19—C18—C23—C24	−179.2 (2)
C18—C7—C8—C9	−36.7 (3)	C7—C18—C23—C24	−1.0 (3)
C13—C8—C9—C10	0.1 (4)	C21—C22—C23—C18	−1.5 (4)
C7—C8—C9—C10	−174.9 (3)	C21—C22—C23—C24	177.1 (3)
C8—C9—C10—C11	0.5 (4)	C7—O2—C24—O3	177.5 (2)
C16—N1—C11—C12	−174.2 (2)	C7—O2—C24—C23	−3.4 (3)
C14—N1—C11—C12	4.7 (4)	C18—C23—C24—O3	−178.2 (3)
C16—N1—C11—C10	5.9 (4)	C22—C23—C24—O3	3.1 (5)
C14—N1—C11—C10	−175.2 (2)	C18—C23—C24—O2	2.7 (3)
C9—C10—C11—N1	179.9 (3)	C22—C23—C24—O2	−175.9 (3)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C8–C13 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14B···O2[i]	0.99	2.68	3.649 (4)	165
C16—H16A···O3[ii]	0.99	2.64	3.522 (3)	148
C16—H16B···Br1[iii]	0.99	2.99	3.939 (3)	162
C17—H17A···Cg[iv]	0.98	2.75	3.666 (4)	156
C19—H19···O1[iii]	0.95	2.57	3.485 (4)	161
C20—H20···O3[v]	0.95	2.58	3.421 (3)	148

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

(4) (1S)-6′-Bromo-3′-diethylamino-3H-spiro[2-benzofuran-1,9′-xanthen]-3-one

Crystal data

$C_{24}H_{20}BrNO_3$	$Z = 4$
$M_r = 450.32$	$F(000) = 920$
Orthorhombic, $P2_12_12_1$	$D_x = 1.488$ Mg m^{-3}
$a = 11.0772$ (6) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 13.0582$ (8) Å	Cell parameters from 9874 reflections
$c = 13.8966$ (8) Å	$\theta = 2.4–28.7°$
$V = 2010.1$ (2) Å^3	$\mu = 2.07$ mm^{-1}

T = 100 K

Column, colourless

0.31 × 0.12 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer	39006 measured reflections
Radiation source: fine-focus sealed tube	5417 independent reflections
Graphite monochromator	4926 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	R_{int} = 0.043
φ and ω scans	θ_{max} = 29.2°, θ_{min} = 2.1°
Absorption correction: multi-scan	$h = -15 \rightarrow 15$
(*SADABS*; Bruker, 2016)	$k = -17 \rightarrow 17$
T_{min} = 0.69, T_{max} = 0.82	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.026	
$wR(F^2)$ = 0.058	$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2]$
S = 0.99	where $P = (F_o^2 + 2F_c^2)/3$
5417 reflections	$(\Delta/\sigma)_{max}$ = 0.001
320 parameters	$\Delta\rho_{max}$ = 0.62 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack x determined using 1981 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Secondary atom site location: difference Fourier map	Absolute structure parameter: −0.006 (3)

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, colllected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at $\omega = -30.00$ and 210.00°. The scan time was 20 sec/frame.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Br1	0.23778 (2)	0.57329 (2)	0.58190 (2)	0.02156 (7)
O1	0.62242 (14)	0.63049 (13)	0.37859 (12)	0.0174 (4)
O2	0.83447 (14)	0.44945 (12)	0.52206 (11)	0.0149 (3)
O3	0.96324 (16)	0.34761 (13)	0.60162 (12)	0.0232 (4)
N1	0.93770 (19)	0.75727 (16)	0.17844 (14)	0.0191 (4)
C1	0.5808 (2)	0.59393 (17)	0.46462 (16)	0.0132 (5)
C2	0.4557 (2)	0.59644 (18)	0.47625 (18)	0.0166 (5)
H2	0.412 (3)	0.617 (2)	0.427 (2)	0.023 (7)*
C3	0.40723 (19)	0.56383 (17)	0.56230 (16)	0.0154 (5)

C4	0.4786 (2)	0.52661 (19)	0.63625 (18)	0.0178 (5)
H4	0.440 (2)	0.5053 (19)	0.693 (2)	0.017 (7)*
C5	0.6020 (2)	0.52317 (19)	0.62259 (18)	0.0163 (5)
H5	0.651 (3)	0.495 (2)	0.6671 (19)	0.020 (8)*
C6	0.6556 (2)	0.55733 (18)	0.53668 (17)	0.0138 (5)
C7	0.79072 (19)	0.55778 (16)	0.52627 (16)	0.0126 (4)
C8	0.8285 (2)	0.61105 (17)	0.43527 (16)	0.0132 (4)
C9	0.9502 (2)	0.63061 (18)	0.41480 (19)	0.0170 (5)
H9	1.007 (2)	0.6057 (19)	0.4633 (18)	0.012 (6)*
C10	0.9872 (2)	0.67728 (19)	0.33110 (18)	0.0178 (5)
H10	1.070 (3)	0.685 (2)	0.3211 (19)	0.020 (7)*
C11	0.9017 (2)	0.70912 (17)	0.26139 (16)	0.0148 (5)
C12	0.7793 (2)	0.68911 (17)	0.28086 (17)	0.0152 (5)
H12	0.722 (2)	0.7083 (19)	0.2415 (17)	0.013 (6)*
C13	0.7462 (2)	0.64179 (15)	0.36616 (15)	0.0129 (4)
C14	0.8504 (2)	0.7873 (2)	0.10481 (18)	0.0227 (5)
H14A	0.787 (3)	0.733 (2)	0.098 (2)	0.031 (8)*
H14B	0.891 (2)	0.789 (2)	0.0417 (18)	0.014 (6)*
C15	0.7924 (2)	0.8904 (2)	0.1260 (2)	0.0285 (6)
H15A	0.7563	0.8890	0.1903	0.043*
H15B	0.7296	0.9043	0.0781	0.043*
H15C	0.8539	0.9442	0.1231	0.043*
C16	1.0602 (2)	0.7975 (2)	0.16496 (19)	0.0198 (5)
H16A	1.047 (2)	0.866 (2)	0.1302 (18)	0.017 (7)*
H16B	1.089 (2)	0.820 (2)	0.230 (2)	0.021 (7)*
C17	1.1432 (2)	0.7252 (2)	0.1109 (2)	0.0253 (6)
H17A	1.1564	0.6633	0.1493	0.038*
H17B	1.2208	0.7591	0.0990	0.038*
H17C	1.1062	0.7066	0.0493	0.038*
C18	0.8524 (2)	0.59745 (18)	0.61583 (17)	0.0139 (5)
C19	0.8402 (2)	0.69192 (19)	0.65983 (18)	0.0179 (5)
H19	0.788 (2)	0.739 (2)	0.6336 (19)	0.019 (7)*
C20	0.9055 (2)	0.7091 (2)	0.74369 (19)	0.0228 (5)
H20	0.909 (3)	0.770 (3)	0.779 (2)	0.039 (9)*
C21	0.9793 (2)	0.6332 (2)	0.78279 (19)	0.0230 (6)
H21	1.024 (2)	0.649 (2)	0.8452 (19)	0.021 (7)*
C22	0.9906 (2)	0.5390 (2)	0.73893 (18)	0.0202 (5)
H22	1.040 (2)	0.4897 (19)	0.7606 (19)	0.013 (7)*
C23	0.9256 (2)	0.52284 (19)	0.65427 (18)	0.0158 (5)
C24	0.91472 (18)	0.42975 (18)	0.59411 (15)	0.0151 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01162 (10)	0.03082 (12)	0.02224 (12)	−0.00078 (9)	0.00204 (9)	−0.00572 (10)
O1	0.0111 (8)	0.0258 (9)	0.0152 (8)	−0.0016 (7)	−0.0013 (7)	0.0059 (7)
O2	0.0166 (8)	0.0134 (8)	0.0148 (8)	0.0025 (6)	−0.0012 (6)	0.0002 (6)
O3	0.0250 (9)	0.0233 (9)	0.0215 (10)	0.0091 (7)	−0.0017 (8)	0.0044 (7)

N1	0.0158 (10)	0.0272 (11)	0.0142 (10)	−0.0032 (9)	0.0012 (8)	0.0036 (9)
C1	0.0139 (11)	0.0135 (11)	0.0123 (11)	−0.0014 (8)	0.0008 (9)	−0.0005 (8)
C2	0.0135 (11)	0.0208 (12)	0.0155 (12)	0.0006 (9)	−0.0034 (9)	0.0008 (9)
C3	0.0106 (9)	0.0156 (10)	0.0199 (12)	−0.0024 (9)	0.0005 (8)	−0.0047 (10)
C4	0.0176 (12)	0.0199 (12)	0.0161 (12)	−0.0039 (9)	0.0022 (10)	0.0019 (10)
C5	0.0159 (12)	0.0192 (11)	0.0138 (12)	−0.0002 (9)	−0.0023 (9)	0.0025 (10)
C6	0.0121 (10)	0.0130 (11)	0.0162 (11)	0.0002 (9)	0.0005 (9)	0.0008 (9)
C7	0.0127 (10)	0.0124 (10)	0.0127 (10)	0.0014 (8)	−0.0002 (8)	0.0001 (8)
C8	0.0125 (10)	0.0159 (10)	0.0111 (11)	0.0020 (8)	0.0004 (8)	0.0009 (9)
C9	0.0132 (10)	0.0221 (11)	0.0157 (11)	0.0019 (9)	−0.0022 (11)	0.0012 (11)
C10	0.0119 (11)	0.0243 (13)	0.0173 (12)	−0.0011 (10)	0.0021 (9)	0.0009 (10)
C11	0.0176 (11)	0.0146 (10)	0.0123 (11)	0.0002 (9)	0.0021 (9)	−0.0019 (9)
C12	0.0148 (11)	0.0179 (11)	0.0130 (11)	0.0005 (9)	−0.0024 (9)	0.0006 (8)
C13	0.0099 (10)	0.0143 (9)	0.0146 (10)	0.0000 (9)	−0.0001 (9)	−0.0019 (8)
C14	0.0230 (13)	0.0319 (14)	0.0133 (12)	−0.0058 (11)	−0.0017 (10)	0.0062 (10)
C15	0.0240 (14)	0.0340 (14)	0.0275 (14)	−0.0012 (11)	−0.0029 (11)	0.0130 (12)
C16	0.0191 (12)	0.0241 (13)	0.0162 (12)	−0.0046 (10)	0.0026 (10)	0.0020 (10)
C17	0.0207 (12)	0.0305 (14)	0.0248 (14)	−0.0004 (11)	0.0038 (10)	−0.0014 (11)
C18	0.0092 (10)	0.0201 (11)	0.0124 (10)	−0.0034 (8)	0.0010 (8)	0.0010 (9)
C19	0.0150 (12)	0.0175 (12)	0.0210 (13)	−0.0009 (9)	0.0006 (10)	−0.0012 (10)
C20	0.0182 (12)	0.0271 (14)	0.0231 (14)	−0.0071 (11)	0.0028 (10)	−0.0078 (11)
C21	0.0164 (12)	0.0373 (15)	0.0152 (12)	−0.0080 (11)	−0.0015 (10)	−0.0020 (11)
C22	0.0128 (11)	0.0318 (14)	0.0159 (12)	−0.0015 (10)	−0.0009 (10)	0.0062 (10)
C23	0.0116 (11)	0.0210 (12)	0.0149 (12)	−0.0004 (9)	0.0017 (9)	0.0033 (10)
C24	0.0120 (9)	0.0199 (10)	0.0133 (11)	0.0011 (9)	0.0024 (8)	0.0033 (10)

Geometric parameters (Å, º)

Br1—C3	1.901 (2)	C11—C12	1.408 (3)
O1—C1	1.367 (3)	C12—C13	1.386 (3)
O1—C13	1.389 (3)	C12—H12	0.87 (2)
O2—C24	1.363 (3)	C14—C15	1.520 (4)
O2—C7	1.496 (3)	C14—H14A	1.01 (3)
O3—C24	1.204 (3)	C14—H14B	0.98 (3)
N1—C11	1.372 (3)	C15—H15A	0.9800
N1—C14	1.461 (3)	C15—H15B	0.9800
N1—C16	1.467 (3)	C15—H15C	0.9800
C1—C6	1.385 (3)	C16—C17	1.517 (4)
C1—C2	1.395 (3)	C16—H16A	1.02 (3)
C2—C3	1.378 (3)	C16—H16B	0.99 (3)
C2—H2	0.88 (3)	C17—H17A	0.9800
C3—C4	1.385 (3)	C17—H17B	0.9800
C4—C5	1.381 (4)	C17—H17C	0.9800
C4—H4	0.93 (3)	C18—C23	1.375 (3)
C5—C6	1.406 (3)	C18—C19	1.384 (3)
C5—H5	0.90 (3)	C19—C20	1.390 (3)
C6—C7	1.504 (3)	C19—H19	0.92 (3)
C7—C8	1.503 (3)	C20—C21	1.395 (4)

C7—C18	1.512 (3)	C20—H20	0.93 (3)
C8—C13	1.384 (3)	C21—C22	1.378 (4)
C8—C9	1.401 (3)	C21—H21	1.02 (3)
C9—C10	1.376 (3)	C22—C23	1.396 (3)
C9—H9	0.98 (3)	C22—H22	0.90 (3)
C10—C11	1.417 (3)	C23—C24	1.480 (3)
C10—H10	0.93 (3)		
C1—O1—C13	118.57 (17)	C12—C13—O1	114.49 (19)
C24—O2—C7	111.15 (17)	N1—C14—C15	112.5 (2)
C11—N1—C14	121.3 (2)	N1—C14—H14A	109.6 (17)
C11—N1—C16	122.7 (2)	C15—C14—H14A	110.3 (16)
C14—N1—C16	115.2 (2)	N1—C14—H14B	109.3 (15)
O1—C1—C6	123.4 (2)	C15—C14—H14B	110.3 (15)
O1—C1—C2	115.3 (2)	H14A—C14—H14B	105 (2)
C6—C1—C2	121.2 (2)	C14—C15—H15A	109.5
C3—C2—C1	118.7 (2)	C14—C15—H15B	109.5
C3—C2—H2	123.4 (18)	H15A—C15—H15B	109.5
C1—C2—H2	117.9 (18)	C14—C15—H15C	109.5
C2—C3—C4	122.0 (2)	H15A—C15—H15C	109.5
C2—C3—Br1	119.29 (17)	H15B—C15—H15C	109.5
C4—C3—Br1	118.69 (17)	N1—C16—C17	113.6 (2)
C5—C4—C3	118.3 (2)	N1—C16—H16A	104.1 (15)
C5—C4—H4	123.7 (17)	C17—C16—H16A	113.0 (15)
C3—C4—H4	118.0 (17)	N1—C16—H16B	106.5 (16)
C4—C5—C6	121.6 (2)	C17—C16—H16B	115.7 (16)
C4—C5—H5	120.9 (19)	H16A—C16—H16B	103 (2)
C6—C5—H5	117.3 (19)	C16—C17—H17A	109.5
C1—C6—C5	118.1 (2)	C16—C17—H17B	109.5
C1—C6—C7	121.6 (2)	H17A—C17—H17B	109.5
C5—C6—C7	120.2 (2)	C16—C17—H17C	109.5
O2—C7—C8	108.32 (17)	H17A—C17—H17C	109.5
O2—C7—C6	108.81 (18)	H17B—C17—H17C	109.5
C8—C7—C6	111.12 (19)	C23—C18—C19	121.2 (2)
O2—C7—C18	102.10 (17)	C23—C18—C7	110.1 (2)
C8—C7—C18	114.09 (18)	C19—C18—C7	128.7 (2)
C6—C7—C18	111.86 (19)	C18—C19—C20	117.6 (2)
C13—C8—C9	116.1 (2)	C18—C19—H19	119.1 (17)
C13—C8—C7	122.29 (19)	C20—C19—H19	123.2 (17)
C9—C8—C7	121.6 (2)	C19—C20—C21	121.1 (3)
C10—C9—C8	122.6 (2)	C19—C20—H20	127 (2)
C10—C9—H9	122.6 (15)	C21—C20—H20	112 (2)
C8—C9—H9	114.8 (15)	C22—C21—C20	121.0 (2)
C9—C10—C11	120.6 (2)	C22—C21—H21	120.7 (16)
C9—C10—H10	118.0 (17)	C20—C21—H21	118.3 (16)
C11—C10—H10	121.4 (17)	C21—C22—C23	117.5 (2)
N1—C11—C12	121.8 (2)	C21—C22—H22	123.2 (16)
N1—C11—C10	121.0 (2)	C23—C22—H22	119.3 (16)

C12—C11—C10	117.3 (2)	C18—C23—C22	121.6 (2)
C13—C12—C11	120.1 (2)	C18—C23—C24	108.3 (2)
C13—C12—H12	118.2 (16)	C22—C23—C24	130.0 (2)
C11—C12—H12	121.6 (16)	O3—C24—O2	121.5 (2)
C8—C13—C12	123.2 (2)	O3—C24—C23	130.2 (2)
C8—C13—O1	122.23 (18)	O2—C24—C23	108.23 (19)
C13—O1—C1—C6	−7.0 (3)	C9—C10—C11—C12	−1.2 (3)
C13—O1—C1—C2	172.46 (19)	N1—C11—C12—C13	−178.9 (2)
O1—C1—C2—C3	−178.0 (2)	C10—C11—C12—C13	1.2 (3)
C6—C1—C2—C3	1.5 (3)	C9—C8—C13—C12	0.2 (3)
C1—C2—C3—C4	−1.5 (3)	C7—C8—C13—C12	−178.6 (2)
C1—C2—C3—Br1	176.79 (17)	C9—C8—C13—O1	−177.6 (2)
C2—C3—C4—C5	0.5 (4)	C7—C8—C13—O1	3.6 (3)
Br1—C3—C4—C5	−177.88 (18)	C11—C12—C13—C8	−0.7 (3)
C3—C4—C5—C6	0.7 (4)	C11—C12—C13—O1	177.3 (2)
O1—C1—C6—C5	179.1 (2)	C1—O1—C13—C8	4.4 (3)
C2—C1—C6—C5	−0.4 (3)	C1—O1—C13—C12	−173.62 (18)
O1—C1—C6—C7	1.7 (3)	C11—N1—C14—C15	84.3 (3)
C2—C1—C6—C7	−177.8 (2)	C16—N1—C14—C15	−85.6 (3)
C4—C5—C6—C1	−0.7 (4)	C11—N1—C16—C17	96.7 (3)
C4—C5—C6—C7	176.7 (2)	C14—N1—C16—C17	−93.5 (3)
C24—O2—C7—C8	117.59 (19)	O2—C7—C18—C23	2.5 (2)
C24—O2—C7—C6	−121.50 (19)	C8—C7—C18—C23	−114.1 (2)
C24—O2—C7—C18	−3.1 (2)	C6—C7—C18—C23	118.7 (2)
C1—C6—C7—O2	−113.6 (2)	O2—C7—C18—C19	−175.5 (2)
C5—C6—C7—O2	69.1 (3)	C8—C7—C18—C19	67.9 (3)
C1—C6—C7—C8	5.6 (3)	C6—C7—C18—C19	−59.3 (3)
C5—C6—C7—C8	−171.8 (2)	C23—C18—C19—C20	0.7 (3)
C1—C6—C7—C18	134.4 (2)	C7—C18—C19—C20	178.5 (2)
C5—C6—C7—C18	−43.0 (3)	C18—C19—C20—C21	−1.0 (4)
O2—C7—C8—C13	111.4 (2)	C19—C20—C21—C22	0.6 (4)
C6—C7—C8—C13	−8.1 (3)	C20—C21—C22—C23	0.0 (4)
C18—C7—C8—C13	−135.7 (2)	C19—C18—C23—C22	−0.1 (4)
O2—C7—C8—C9	−67.3 (3)	C7—C18—C23—C22	−178.3 (2)
C6—C7—C8—C9	173.2 (2)	C19—C18—C23—C24	177.1 (2)
C18—C7—C8—C9	45.6 (3)	C7—C18—C23—C24	−1.1 (3)
C13—C8—C9—C10	−0.2 (3)	C21—C22—C23—C18	−0.3 (4)
C7—C8—C9—C10	178.6 (2)	C21—C22—C23—C24	−176.8 (2)
C8—C9—C10—C11	0.8 (4)	C7—O2—C24—O3	−177.8 (2)
C14—N1—C11—C12	−1.9 (3)	C7—O2—C24—C23	2.6 (2)
C16—N1—C11—C12	167.3 (2)	C18—C23—C24—O3	179.5 (2)
C14—N1—C11—C10	178.0 (2)	C22—C23—C24—O3	−3.6 (4)
C16—N1—C11—C10	−12.9 (4)	C18—C23—C24—O2	−0.9 (3)
C9—C10—C11—N1	178.9 (2)	C22—C23—C24—O2	176.0 (2)

Hydrogen-bond geometry (Å, º)

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
C14—H14$B\cdots$O3^{i}	0.99 (2)	2.68 (2)	3.621 (3)	160.7 (19)
C20—H20$\cdots$O3^{ii}	0.94 (2)	2.41 (3)	3.163 (3)	138 (3)

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

(5) (1R)-6′-Bromo-3′-diethylamino-3H-spiro[2-benzofuran-1,9′-xanthen]-3-one

Crystal data

C$_{24}$H$_{20}$BrNO$_3$	D_x = 1.502 Mg m$^{−3}$
M_r = 450.32	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 7498 reflections
a = 8.1529 (13) Å	θ = 2.2–25.3°
b = 18.185 (3) Å	μ = 2.09 mm$^{−1}$
c = 26.860 (4) Å	T = 100 K
V = 3982.3 (11) Å^3	Column, colourless
Z = 8	0.26 × 0.06 × 0.04 mm
$F(000)$ = 1840	

Data collection

Bruker SMART APEX CCD diffractometer	38240 measured reflections
Radiation source: fine-focus sealed tube	10174 independent reflections
Graphite monochromator	7285 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	R_{int} = 0.075
φ and ω scans	θ_{max} = 29.1°, θ_{min} = 1.4°
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)	h = −10→10
	k = −23→24
T_{min} = 0.70, T_{max} = 0.92	l = −35→36

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.045	H-atom parameters constrained
$wR(F^2)$ = 0.093	$w = 1/[\sigma^2(F_o^2) + (0.0089P)^2]$
S = 0.97	where $P = (F_o^2 + 2F_c^2)/3$
10174 reflections	$(\Delta/\sigma)_{max}$ = 0.001
527 parameters	$\Delta\rho_{max}$ = 0.92 e Å$^{−3}$
0 restraints	$\Delta\rho_{min}$ = −0.34 e Å$^{−3}$
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack x determined using 2575 quotients [(I^+)-(I^-)]/[(I^+)+(I^-)] (Parsons *et al.*, 2013)
Secondary atom site location: difference Fourier map	Absolute structure parameter: −0.002 (6)

Special details

Experimental. The diffraction data were collected in three sets of 363 frames (0.5° width in ω) at φ = 0, 120 and 240°. A scan time of 60 sec/frame was used.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

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

	x	y	z	U_{iso}*/U_{eq}
Br1	0.52585 (6)	0.63496 (3)	0.28218 (2)	0.02849 (13)
O1	0.6662 (4)	0.57150 (16)	0.46407 (11)	0.0189 (7)
O2	0.4245 (3)	0.39341 (16)	0.46124 (11)	0.0153 (7)
O3	0.2630 (4)	0.29559 (18)	0.44638 (11)	0.0207 (7)
N1	0.8582 (5)	0.5506 (2)	0.63051 (13)	0.0178 (8)
C1	0.6260 (5)	0.5413 (2)	0.41884 (16)	0.0160 (10)
C2	0.6056 (5)	0.5918 (2)	0.38032 (16)	0.0181 (10)
H2	0.6212	0.6429	0.3860	0.022*
C3	0.5626 (5)	0.5663 (3)	0.33398 (16)	0.0191 (10)
C4	0.5443 (5)	0.4916 (3)	0.32441 (16)	0.0199 (10)
H4	0.5175	0.4747	0.2920	0.024*
C5	0.5659 (5)	0.4425 (2)	0.36318 (16)	0.0180 (10)
H5	0.5552	0.3913	0.3571	0.022*
C6	0.6035 (5)	0.4671 (2)	0.41148 (16)	0.0149 (9)
C7	0.6029 (5)	0.4136 (2)	0.45477 (15)	0.0136 (9)
C8	0.6652 (5)	0.4501 (2)	0.50108 (15)	0.0130 (9)
C9	0.6964 (5)	0.4098 (2)	0.54461 (16)	0.0157 (10)
H9	0.6778	0.3583	0.5443	0.019*
C10	0.7528 (5)	0.4418 (2)	0.58754 (16)	0.0137 (9)
H10	0.7699	0.4124	0.6163	0.016*
C11	0.7859 (5)	0.5186 (2)	0.58949 (16)	0.0152 (9)
C12	0.7507 (5)	0.5598 (2)	0.54662 (16)	0.0156 (10)
H12	0.7657	0.6116	0.5467	0.019*
C13	0.6939 (5)	0.5246 (2)	0.50400 (16)	0.0147 (9)
C14	0.8803 (6)	0.5091 (3)	0.67630 (16)	0.0214 (11)
H14A	0.9644	0.5337	0.6970	0.026*
H14B	0.9215	0.4594	0.6680	0.026*
C15	0.7228 (6)	0.5018 (3)	0.70632 (17)	0.0221 (11)
H15A	0.6887	0.5504	0.7182	0.033*
H15B	0.7420	0.4693	0.7349	0.033*
H15C	0.6365	0.4809	0.6852	0.033*
C16	0.8935 (5)	0.6297 (3)	0.63138 (17)	0.0219 (10)
H16A	0.9442	0.6437	0.5993	0.026*
H16B	0.9746	0.6396	0.6580	0.026*
C17	0.7432 (6)	0.6778 (3)	0.64011 (19)	0.0303 (13)
H17A	0.7756	0.7297	0.6393	0.045*
H17B	0.6955	0.6663	0.6727	0.045*
H17C	0.6620	0.6684	0.6140	0.045*

C18	0.6792 (5)	0.3401 (2)	0.44466 (15)	0.0131 (9)
C19	0.8454 (5)	0.3221 (2)	0.44054 (16)	0.0153 (10)
H19	0.9282	0.3586	0.4430	0.018*
C20	0.8845 (6)	0.2494 (2)	0.43276 (15)	0.0179 (10)
H20	0.9964	0.2357	0.4295	0.022*
C21	0.7630 (6)	0.1948 (2)	0.42956 (16)	0.0174 (10)
H21	0.7943	0.1451	0.4244	0.021*
C22	0.5991 (6)	0.2123 (2)	0.43380 (15)	0.0163 (10)
H22	0.5162	0.1757	0.4315	0.020*
C23	0.5604 (5)	0.2865 (2)	0.44160 (15)	0.0132 (9)
C24	0.3991 (6)	0.3206 (2)	0.44915 (15)	0.0146 (9)
Br2	0.41662 (7)	0.36508 (3)	0.88995 (2)	0.03217 (14)
O4	0.3369 (4)	0.51090 (15)	0.72672 (11)	0.0169 (7)
O5	0.2069 (3)	0.69908 (16)	0.79230 (11)	0.0160 (7)
O6	0.1534 (4)	0.80937 (16)	0.82613 (12)	0.0197 (7)
N2	0.2868 (5)	0.61160 (19)	0.56403 (13)	0.0177 (9)
C25	0.3579 (5)	0.5173 (2)	0.77747 (15)	0.0138 (9)
C26	0.3746 (5)	0.4512 (2)	0.80330 (16)	0.0181 (10)
H26	0.3753	0.4054	0.7863	0.022*
C27	0.3900 (6)	0.4545 (2)	0.85438 (17)	0.0216 (11)
C28	0.3868 (6)	0.5198 (2)	0.88052 (17)	0.0210 (11)
H28	0.3940	0.5202	0.9158	0.025*
C29	0.3727 (5)	0.5850 (3)	0.85389 (16)	0.0188 (10)
H29	0.3722	0.6305	0.8713	0.023*
C30	0.3594 (5)	0.5848 (2)	0.80207 (16)	0.0147 (9)
C31	0.3510 (5)	0.6566 (2)	0.77414 (16)	0.0149 (9)
C32	0.3316 (5)	0.6439 (2)	0.71915 (16)	0.0134 (9)
C33	0.3218 (5)	0.7029 (2)	0.68601 (17)	0.0167 (10)
H33	0.3261	0.7515	0.6988	0.020*
C34	0.3063 (5)	0.6929 (2)	0.63567 (17)	0.0157 (10)
H34	0.2980	0.7347	0.6146	0.019*
C35	0.3021 (5)	0.6217 (2)	0.61428 (16)	0.0140 (9)
C36	0.3144 (5)	0.5622 (2)	0.64719 (16)	0.0155 (10)
H36	0.3142	0.5134	0.6346	0.019*
C37	0.3271 (5)	0.5742 (2)	0.69832 (17)	0.0153 (10)
C38	0.2429 (6)	0.6721 (3)	0.53094 (16)	0.0206 (11)
H38A	0.1740	0.7075	0.5495	0.025*
H38B	0.1762	0.6524	0.5032	0.025*
C39	0.3903 (7)	0.7128 (3)	0.50945 (19)	0.0316 (13)
H39A	0.4631	0.6776	0.4928	0.047*
H39B	0.4499	0.7373	0.5364	0.047*
H39C	0.3525	0.7495	0.4853	0.047*
C40	0.3094 (5)	0.5399 (2)	0.54013 (16)	0.0157 (10)
H40A	0.3904	0.5113	0.5596	0.019*
H40B	0.3559	0.5477	0.5065	0.019*
C41	0.1539 (6)	0.4950 (3)	0.53531 (18)	0.0235 (11)
H41A	0.0719	0.5232	0.5167	0.035*
H41B	0.1113	0.4835	0.5685	0.035*

H41C	0.1780	0.4491	0.5176	0.035*
C42	0.4921 (5)	0.7074 (2)	0.78662 (15)	0.0146 (9)
C43	0.6590 (5)	0.6963 (2)	0.78122 (17)	0.0173 (10)
H43	0.7009	0.6508	0.7692	0.021*
C44	0.7637 (6)	0.7538 (3)	0.79392 (16)	0.0202 (11)
H44	0.8789	0.7471	0.7912	0.024*
C45	0.7029 (6)	0.8208 (3)	0.81042 (16)	0.0188 (10)
H45	0.7765	0.8601	0.8171	0.023*
C46	0.5359 (6)	0.8311 (2)	0.81717 (15)	0.0171 (10)
H46	0.4936	0.8761	0.8296	0.021*
C47	0.4327 (5)	0.7732 (2)	0.80510 (15)	0.0140 (10)
C48	0.2526 (6)	0.7669 (2)	0.80989 (15)	0.0143 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0362 (3)	0.0288 (3)	0.0205 (2)	−0.0066 (2)	−0.0075 (2)	0.0118 (2)
O1	0.0273 (19)	0.0155 (17)	0.0138 (16)	−0.0017 (14)	−0.0018 (14)	0.0019 (13)
O2	0.0097 (16)	0.0177 (15)	0.0185 (16)	0.0001 (12)	0.0024 (13)	0.0030 (12)
O3	0.0149 (18)	0.028 (2)	0.0191 (18)	−0.0049 (15)	−0.0008 (14)	0.0029 (14)
N1	0.018 (2)	0.021 (2)	0.0152 (19)	0.0014 (17)	−0.0011 (16)	0.0002 (16)
C1	0.013 (2)	0.020 (2)	0.015 (2)	0.0021 (19)	−0.0005 (18)	−0.0004 (18)
C2	0.019 (3)	0.014 (2)	0.021 (2)	0.000 (2)	−0.002 (2)	0.0045 (18)
C3	0.016 (3)	0.024 (3)	0.017 (2)	−0.002 (2)	0.0003 (19)	0.0095 (19)
C4	0.019 (3)	0.027 (3)	0.014 (2)	−0.004 (2)	−0.0009 (19)	0.0027 (19)
C5	0.017 (3)	0.016 (2)	0.022 (2)	−0.0027 (19)	0.0017 (19)	0.0015 (19)
C6	0.010 (2)	0.015 (2)	0.019 (2)	0.0011 (19)	0.0011 (19)	0.0013 (18)
C7	0.010 (2)	0.014 (2)	0.017 (2)	−0.0022 (19)	0.0011 (18)	0.0006 (18)
C8	0.011 (2)	0.016 (2)	0.012 (2)	0.0033 (18)	0.0044 (18)	0.0017 (18)
C9	0.015 (2)	0.011 (2)	0.021 (2)	0.0030 (19)	0.0031 (19)	0.0022 (18)
C10	0.015 (2)	0.014 (2)	0.012 (2)	0.0042 (19)	0.0017 (18)	0.0010 (17)
C11	0.010 (2)	0.018 (2)	0.018 (2)	0.0016 (19)	0.0016 (19)	0.0004 (19)
C12	0.013 (2)	0.013 (2)	0.021 (2)	0.0006 (18)	0.0000 (19)	0.0001 (19)
C13	0.013 (2)	0.016 (2)	0.015 (2)	0.0046 (18)	0.0008 (18)	0.0054 (18)
C14	0.023 (3)	0.024 (3)	0.017 (2)	−0.001 (2)	−0.006 (2)	0.000 (2)
C15	0.025 (3)	0.025 (3)	0.016 (2)	−0.003 (2)	0.001 (2)	0.000 (2)
C16	0.022 (2)	0.021 (2)	0.023 (2)	0.000 (2)	0.0003 (19)	−0.001 (2)
C17	0.035 (3)	0.026 (3)	0.030 (3)	0.008 (2)	−0.001 (2)	−0.002 (2)
C18	0.016 (2)	0.015 (2)	0.009 (2)	0.0005 (18)	−0.0009 (17)	0.0006 (17)
C19	0.013 (2)	0.018 (2)	0.014 (2)	−0.0031 (19)	−0.0002 (18)	−0.0012 (18)
C20	0.016 (3)	0.023 (3)	0.015 (2)	0.002 (2)	0.0020 (19)	−0.0012 (19)
C21	0.025 (3)	0.010 (2)	0.018 (2)	0.006 (2)	0.002 (2)	−0.0019 (18)
C22	0.017 (2)	0.016 (2)	0.016 (2)	−0.007 (2)	−0.0005 (19)	−0.0013 (18)
C23	0.010 (2)	0.018 (2)	0.011 (2)	−0.0027 (18)	−0.0023 (17)	0.0008 (17)
C24	0.019 (2)	0.017 (2)	0.009 (2)	−0.002 (2)	−0.0042 (19)	0.0048 (17)
Br2	0.0550 (4)	0.0189 (2)	0.0226 (3)	−0.0016 (3)	−0.0038 (2)	0.0063 (2)
O4	0.0253 (18)	0.0118 (16)	0.0137 (16)	0.0004 (13)	−0.0002 (13)	−0.0007 (12)
O5	0.0130 (16)	0.0137 (16)	0.0214 (18)	0.0008 (13)	0.0012 (13)	−0.0047 (13)

O6	0.0212 (18)	0.0146 (17)	0.0234 (18)	0.0058 (14)	−0.0011 (14)	−0.0038 (13)
N2	0.025 (2)	0.0130 (19)	0.0146 (19)	0.0028 (16)	0.0010 (17)	0.0005 (15)
C25	0.011 (2)	0.019 (2)	0.011 (2)	−0.0026 (18)	0.0023 (18)	−0.0015 (18)
C26	0.023 (3)	0.013 (2)	0.018 (2)	−0.002 (2)	−0.001 (2)	0.0002 (18)
C27	0.024 (3)	0.016 (2)	0.025 (3)	−0.001 (2)	−0.005 (2)	0.002 (2)
C28	0.030 (3)	0.017 (2)	0.016 (2)	−0.001 (2)	−0.003 (2)	0.0015 (18)
C29	0.023 (3)	0.017 (2)	0.017 (2)	−0.003 (2)	−0.002 (2)	−0.0030 (19)
C30	0.012 (2)	0.016 (2)	0.017 (2)	−0.0029 (19)	−0.0013 (18)	−0.0002 (18)
C31	0.011 (2)	0.015 (2)	0.019 (2)	0.0036 (17)	0.0035 (18)	−0.0014 (18)
C32	0.013 (2)	0.012 (2)	0.016 (2)	−0.0023 (18)	−0.0001 (18)	0.0016 (19)
C33	0.014 (2)	0.014 (2)	0.022 (3)	0.0023 (19)	0.002 (2)	0.0011 (19)
C34	0.014 (2)	0.011 (2)	0.022 (2)	0.0005 (19)	−0.0011 (19)	0.0038 (19)
C35	0.011 (2)	0.016 (2)	0.015 (2)	0.0015 (17)	0.0013 (17)	−0.0025 (18)
C36	0.015 (2)	0.013 (2)	0.019 (2)	0.0032 (19)	0.0007 (19)	−0.0016 (19)
C37	0.011 (2)	0.015 (2)	0.020 (2)	−0.0014 (19)	0.0010 (18)	0.0013 (19)
C38	0.027 (3)	0.021 (3)	0.014 (2)	0.004 (2)	−0.003 (2)	0.0025 (19)
C39	0.040 (3)	0.023 (3)	0.032 (3)	0.001 (3)	0.011 (3)	0.006 (2)
C40	0.014 (2)	0.020 (2)	0.013 (2)	0.004 (2)	−0.0001 (18)	−0.0015 (18)
C41	0.019 (3)	0.024 (3)	0.027 (3)	0.001 (2)	0.001 (2)	−0.004 (2)
C42	0.018 (2)	0.012 (2)	0.014 (2)	−0.0009 (18)	−0.0014 (19)	−0.0008 (18)
C43	0.017 (2)	0.020 (2)	0.015 (2)	0.0016 (19)	0.000 (2)	−0.001 (2)
C44	0.017 (3)	0.025 (3)	0.019 (3)	−0.002 (2)	−0.0004 (19)	0.003 (2)
C45	0.020 (3)	0.021 (3)	0.016 (2)	−0.007 (2)	−0.0051 (19)	0.0021 (19)
C46	0.026 (3)	0.013 (2)	0.013 (2)	−0.001 (2)	−0.002 (2)	0.0020 (18)
C47	0.018 (3)	0.015 (2)	0.009 (2)	−0.0012 (19)	−0.0036 (18)	0.0028 (17)
C48	0.019 (2)	0.016 (2)	0.008 (2)	0.004 (2)	−0.0014 (18)	0.0019 (18)

Geometric parameters (Å, º)

Br1—C3	1.893 (4)	Br2—C27	1.899 (4)
O1—C1	1.373 (5)	O4—C25	1.379 (5)
O1—C13	1.389 (5)	O4—C37	1.383 (5)
O2—C24	1.379 (5)	O5—C48	1.373 (5)
O2—C7	1.510 (5)	O5—C31	1.488 (5)
O3—C24	1.201 (5)	O6—C48	1.200 (5)
N1—C11	1.379 (5)	N2—C35	1.368 (5)
N1—C14	1.455 (5)	N2—C38	1.458 (5)
N1—C16	1.466 (6)	N2—C40	1.465 (5)
C1—C6	1.376 (6)	C25—C26	1.394 (6)
C1—C2	1.394 (6)	C25—C30	1.394 (6)
C2—C3	1.374 (6)	C26—C27	1.379 (6)
C2—H2	0.9500	C26—H26	0.9500
C3—C4	1.390 (6)	C27—C28	1.380 (6)
C4—C5	1.383 (6)	C28—C29	1.388 (6)
C4—H4	0.9500	C28—H28	0.9500
C5—C6	1.406 (6)	C29—C30	1.396 (6)
C5—H5	0.9500	C29—H29	0.9500
C6—C7	1.516 (6)	C30—C31	1.508 (6)

C7—C8	1.499 (6)	C31—C32	1.503 (6)
C7—C18	1.499 (6)	C31—C42	1.513 (6)
C8—C13	1.376 (6)	C32—C37	1.387 (6)
C8—C9	1.403 (6)	C32—C33	1.395 (6)
C9—C10	1.371 (6)	C33—C34	1.370 (6)
C9—H9	0.9500	C33—H33	0.9500
C10—C11	1.423 (6)	C34—C35	1.418 (6)
C10—H10	0.9500	C34—H34	0.9500
C11—C12	1.403 (6)	C35—C36	1.401 (6)
C12—C13	1.391 (6)	C36—C37	1.394 (6)
C12—H12	0.9500	C36—H36	0.9500
C14—C15	1.522 (6)	C38—C39	1.525 (7)
C14—H14A	0.9900	C38—H38A	0.9900
C14—H14B	0.9900	C38—H38B	0.9900
C15—H15A	0.9800	C39—H39A	0.9800
C15—H15B	0.9800	C39—H39B	0.9800
C15—H15C	0.9800	C39—H39C	0.9800
C16—C17	1.524 (6)	C40—C41	1.513 (6)
C16—H16A	0.9900	C40—H40A	0.9900
C16—H16B	0.9900	C40—H40B	0.9900
C17—H17A	0.9800	C41—H41A	0.9800
C17—H17B	0.9800	C41—H41B	0.9800
C17—H17C	0.9800	C41—H41C	0.9800
C18—C23	1.377 (6)	C42—C47	1.382 (6)
C18—C19	1.398 (6)	C42—C43	1.384 (6)
C19—C20	1.376 (6)	C43—C44	1.393 (6)
C19—H19	0.9500	C43—H43	0.9500
C20—C21	1.404 (6)	C44—C45	1.388 (6)
C20—H20	0.9500	C44—H44	0.9500
C21—C22	1.378 (6)	C45—C46	1.386 (6)
C21—H21	0.9500	C45—H45	0.9500
C22—C23	1.402 (6)	C46—C47	1.386 (6)
C22—H22	0.9500	C46—H46	0.9500
C23—C24	1.467 (6)	C47—C48	1.478 (6)
C1—O1—C13	118.4 (3)	C25—O4—C37	118.8 (3)
C24—O2—C7	110.6 (3)	C48—O5—C31	111.4 (3)
C11—N1—C14	120.6 (4)	C35—N2—C38	121.5 (4)
C11—N1—C16	120.7 (4)	C35—N2—C40	122.7 (3)
C14—N1—C16	118.1 (4)	C38—N2—C40	115.8 (4)
O1—C1—C6	123.5 (4)	O4—C25—C26	115.6 (4)
O1—C1—C2	114.9 (4)	O4—C25—C30	122.9 (4)
C6—C1—C2	121.6 (4)	C26—C25—C30	121.5 (4)
C3—C2—C1	118.7 (4)	C27—C26—C25	117.8 (4)
C3—C2—H2	120.7	C27—C26—H26	121.1
C1—C2—H2	120.7	C25—C26—H26	121.1
C2—C3—C4	121.7 (4)	C26—C27—C28	122.8 (4)
C2—C3—Br1	118.9 (3)	C26—C27—Br2	118.3 (3)

C4—C3—Br1	119.4 (3)	C28—C27—Br2	118.9 (3)
C5—C4—C3	118.6 (4)	C27—C28—C29	118.3 (4)
C5—C4—H4	120.7	C27—C28—H28	120.9
C3—C4—H4	120.7	C29—C28—H28	120.9
C4—C5—C6	121.1 (4)	C28—C29—C30	121.2 (4)
C4—C5—H5	119.4	C28—C29—H29	119.4
C6—C5—H5	119.4	C30—C29—H29	119.4
C1—C6—C5	118.2 (4)	C25—C30—C29	118.4 (4)
C1—C6—C7	121.3 (4)	C25—C30—C31	121.8 (4)
C5—C6—C7	120.2 (4)	C29—C30—C31	119.8 (4)
C8—C7—C18	113.9 (4)	O5—C31—C32	108.6 (3)
C8—C7—O2	109.8 (3)	O5—C31—C30	108.8 (3)
C18—C7—O2	101.8 (3)	C32—C31—C30	111.1 (3)
C8—C7—C6	110.6 (3)	O5—C31—C42	102.2 (3)
C18—C7—C6	115.5 (3)	C32—C31—C42	113.0 (3)
O2—C7—C6	104.3 (3)	C30—C31—C42	112.6 (3)
C13—C8—C9	115.8 (4)	C37—C32—C33	116.3 (4)
C13—C8—C7	122.7 (4)	C37—C32—C31	122.6 (4)
C9—C8—C7	121.4 (4)	C33—C32—C31	121.0 (4)
C10—C9—C8	122.7 (4)	C34—C33—C32	122.2 (4)
C10—C9—H9	118.7	C34—C33—H33	118.9
C8—C9—H9	118.7	C32—C33—H33	118.9
C9—C10—C11	120.7 (4)	C33—C34—C35	121.5 (4)
C9—C10—H10	119.6	C33—C34—H34	119.2
C11—C10—H10	119.6	C35—C34—H34	119.2
N1—C11—C12	121.1 (4)	N2—C35—C36	121.7 (4)
N1—C11—C10	121.7 (4)	N2—C35—C34	121.6 (4)
C12—C11—C10	117.1 (4)	C36—C35—C34	116.6 (4)
C13—C12—C11	119.8 (4)	C37—C36—C35	120.4 (4)
C13—C12—H12	120.1	C37—C36—H36	119.8
C11—C12—H12	120.1	C35—C36—H36	119.8
C8—C13—O1	122.2 (4)	O4—C37—C32	122.5 (4)
C8—C13—C12	123.8 (4)	O4—C37—C36	114.7 (4)
O1—C13—C12	114.0 (4)	C32—C37—C36	122.8 (4)
N1—C14—C15	112.9 (4)	N2—C38—C39	113.8 (4)
N1—C14—H14A	109.0	N2—C38—H38A	108.8
C15—C14—H14A	109.0	C39—C38—H38A	108.8
N1—C14—H14B	109.0	N2—C38—H38B	108.8
C15—C14—H14B	109.0	C39—C38—H38B	108.8
H14A—C14—H14B	107.8	H38A—C38—H38B	107.7
C14—C15—H15A	109.5	C38—C39—H39A	109.5
C14—C15—H15B	109.5	C38—C39—H39B	109.5
H15A—C15—H15B	109.5	H39A—C39—H39B	109.5
C14—C15—H15C	109.5	C38—C39—H39C	109.5
H15A—C15—H15C	109.5	H39A—C39—H39C	109.5
H15B—C15—H15C	109.5	H39B—C39—H39C	109.5
N1—C16—C17	114.1 (4)	N2—C40—C41	114.3 (4)
N1—C16—H16A	108.7	N2—C40—H40A	108.7

C17—C16—H16A	108.7	C41—C40—H40A	108.7
N1—C16—H16B	108.7	N2—C40—H40B	108.7
C17—C16—H16B	108.7	C41—C40—H40B	108.7
H16A—C16—H16B	107.6	H40A—C40—H40B	107.6
C16—C17—H17A	109.5	C40—C41—H41A	109.5
C16—C17—H17B	109.5	C40—C41—H41B	109.5
H17A—C17—H17B	109.5	H41A—C41—H41B	109.5
C16—C17—H17C	109.5	C40—C41—H41C	109.5
H17A—C17—H17C	109.5	H41A—C41—H41C	109.5
H17B—C17—H17C	109.5	H41B—C41—H41C	109.5
C23—C18—C19	120.7 (4)	C47—C42—C43	120.6 (4)
C23—C18—C7	110.5 (4)	C47—C42—C31	110.0 (4)
C19—C18—C7	128.8 (4)	C43—C42—C31	129.4 (4)
C20—C19—C18	117.5 (4)	C42—C43—C44	117.8 (4)
C20—C19—H19	121.2	C42—C43—H43	121.1
C18—C19—H19	121.2	C44—C43—H43	121.1
C19—C20—C21	121.7 (4)	C45—C44—C43	121.3 (4)
C19—C20—H20	119.2	C45—C44—H44	119.4
C21—C20—H20	119.2	C43—C44—H44	119.4
C22—C21—C20	121.0 (4)	C46—C45—C44	120.7 (4)
C22—C21—H21	119.5	C46—C45—H45	119.7
C20—C21—H21	119.5	C44—C45—H45	119.7
C21—C22—C23	116.9 (4)	C47—C46—C45	117.6 (4)
C21—C22—H22	121.5	C47—C46—H46	121.2
C23—C22—H22	121.5	C45—C46—H46	121.2
C18—C23—C22	122.1 (4)	C42—C47—C46	121.9 (4)
C18—C23—C24	108.9 (4)	C42—C47—C48	108.2 (4)
C22—C23—C24	129.0 (4)	C46—C47—C48	129.9 (4)
O3—C24—O2	121.1 (4)	O6—C48—O5	121.3 (4)
O3—C24—C23	131.2 (4)	O6—C48—C47	130.7 (4)
O2—C24—C23	107.7 (4)	O5—C48—C47	108.0 (4)
C13—O1—C1—C6	3.3 (6)	C37—O4—C25—C26	−177.1 (4)
C13—O1—C1—C2	−177.9 (4)	C37—O4—C25—C30	4.2 (6)
O1—C1—C2—C3	−179.0 (4)	O4—C25—C26—C27	−177.7 (4)
C6—C1—C2—C3	−0.2 (7)	C30—C25—C26—C27	1.1 (6)
C1—C2—C3—C4	−2.1 (7)	C25—C26—C27—C28	1.1 (7)
C1—C2—C3—Br1	177.4 (3)	C25—C26—C27—Br2	−178.9 (3)
C2—C3—C4—C5	1.8 (7)	C26—C27—C28—C29	−2.1 (7)
Br1—C3—C4—C5	−177.7 (3)	Br2—C27—C28—C29	177.9 (3)
C3—C4—C5—C6	0.8 (7)	C27—C28—C29—C30	1.0 (7)
O1—C1—C6—C5	−178.7 (4)	O4—C25—C30—C29	176.6 (4)
C2—C1—C6—C5	2.7 (7)	C26—C25—C30—C29	−2.1 (6)
O1—C1—C6—C7	7.1 (7)	O4—C25—C30—C31	−4.8 (6)
C2—C1—C6—C7	−171.5 (4)	C26—C25—C30—C31	176.5 (4)
C4—C5—C6—C1	−3.0 (7)	C28—C29—C30—C25	1.0 (7)
C4—C5—C6—C7	171.3 (4)	C28—C29—C30—C31	−177.6 (4)
C24—O2—C7—C8	−128.9 (4)	C48—O5—C31—C32	−116.1 (4)

C24—O2—C7—C18	−7.9 (4)	C48—O5—C31—C30	122.8 (3)
C24—O2—C7—C6	112.6 (3)	C48—O5—C31—C42	3.5 (4)
C1—C6—C7—C8	−12.5 (6)	C25—C30—C31—O5	122.8 (4)
C5—C6—C7—C8	173.4 (4)	C29—C30—C31—O5	−58.7 (5)
C1—C6—C7—C18	−143.7 (4)	C25—C30—C31—C32	3.3 (5)
C5—C6—C7—C18	42.2 (5)	C29—C30—C31—C32	−178.2 (4)
C1—C6—C7—O2	105.5 (4)	C25—C30—C31—C42	−124.7 (4)
C5—C6—C7—O2	−68.6 (5)	C29—C30—C31—C42	53.8 (5)
C18—C7—C8—C13	141.0 (4)	O5—C31—C32—C37	−121.2 (4)
O2—C7—C8—C13	−105.6 (4)	C30—C31—C32—C37	−1.6 (5)
C6—C7—C8—C13	9.0 (6)	C42—C31—C32—C37	126.2 (4)
C18—C7—C8—C9	−39.6 (5)	O5—C31—C32—C33	60.6 (5)
O2—C7—C8—C9	73.7 (5)	C30—C31—C32—C33	−179.8 (4)
C6—C7—C8—C9	−171.7 (4)	C42—C31—C32—C33	−52.0 (5)
C13—C8—C9—C10	−0.3 (6)	C37—C32—C33—C34	0.9 (6)
C7—C8—C9—C10	−179.7 (4)	C31—C32—C33—C34	179.1 (4)
C8—C9—C10—C11	−1.4 (7)	C32—C33—C34—C35	−1.1 (7)
C14—N1—C11—C12	174.3 (4)	C38—N2—C35—C36	168.1 (4)
C16—N1—C11—C12	2.9 (6)	C40—N2—C35—C36	−10.5 (6)
C14—N1—C11—C10	−9.5 (6)	C38—N2—C35—C34	−11.8 (6)
C16—N1—C11—C10	179.0 (4)	C40—N2—C35—C34	169.5 (4)
C9—C10—C11—N1	−173.3 (4)	C33—C34—C35—N2	−179.9 (4)
C9—C10—C11—C12	3.0 (6)	C33—C34—C35—C36	0.1 (6)
N1—C11—C12—C13	173.2 (4)	N2—C35—C36—C37	−178.9 (4)
C10—C11—C12—C13	−3.1 (6)	C34—C35—C36—C37	1.1 (6)
C9—C8—C13—O1	−179.1 (4)	C25—O4—C37—C32	−2.4 (6)
C7—C8—C13—O1	0.3 (6)	C25—O4—C37—C36	176.8 (4)
C9—C8—C13—C12	0.2 (6)	C33—C32—C37—O4	179.5 (4)
C7—C8—C13—C12	179.6 (4)	C31—C32—C37—O4	1.3 (6)
C1—O1—C13—C8	−7.1 (6)	C33—C32—C37—C36	0.4 (6)
C1—O1—C13—C12	173.5 (4)	C31—C32—C37—C36	−177.9 (4)
C11—C12—C13—C8	1.6 (7)	C35—C36—C37—O4	179.4 (4)
C11—C12—C13—O1	−179.1 (4)	C35—C36—C37—C32	−1.4 (7)
C11—N1—C14—C15	−77.4 (5)	C35—N2—C38—C39	91.9 (5)
C16—N1—C14—C15	94.2 (5)	C40—N2—C38—C39	−89.4 (5)
C11—N1—C16—C17	76.2 (5)	C35—N2—C40—C41	90.8 (5)
C14—N1—C16—C17	−95.4 (5)	C38—N2—C40—C41	−87.9 (5)
C8—C7—C18—C23	122.5 (4)	O5—C31—C42—C47	−5.1 (4)
O2—C7—C18—C23	4.4 (4)	C32—C31—C42—C47	111.4 (4)
C6—C7—C18—C23	−107.9 (4)	C30—C31—C42—C47	−121.7 (4)
C8—C7—C18—C19	−54.7 (6)	O5—C31—C42—C43	175.9 (4)
O2—C7—C18—C19	−172.8 (4)	C32—C31—C42—C43	−67.6 (6)
C6—C7—C18—C19	74.9 (6)	C30—C31—C42—C43	59.3 (6)
C23—C18—C19—C20	0.8 (6)	C47—C42—C43—C44	−1.4 (7)
C7—C18—C19—C20	177.7 (4)	C31—C42—C43—C44	177.5 (4)
C18—C19—C20—C21	−0.7 (6)	C42—C43—C44—C45	−1.4 (7)
C19—C20—C21—C22	0.4 (7)	C43—C44—C45—C46	3.4 (7)
C20—C21—C22—C23	−0.2 (6)	C44—C45—C46—C47	−2.4 (6)

C19—C18—C23—C22	−0.7 (6)	C43—C42—C47—C46	2.4 (7)
C7—C18—C23—C22	−178.1 (4)	C31—C42—C47—C46	−176.7 (4)
C19—C18—C23—C24	177.7 (4)	C43—C42—C47—C48	−176.1 (4)
C7—C18—C23—C24	0.3 (5)	C31—C42—C47—C48	4.8 (5)
C21—C22—C23—C18	0.4 (6)	C45—C46—C47—C42	−0.4 (6)
C21—C22—C23—C24	−177.7 (4)	C45—C46—C47—C48	177.6 (4)
C7—O2—C24—O3	−171.6 (4)	C31—O5—C48—O6	179.9 (4)
C7—O2—C24—C23	8.4 (4)	C31—O5—C48—C47	−0.9 (4)
C18—C23—C24—O3	174.5 (4)	C42—C47—C48—O6	176.6 (4)
C22—C23—C24—O3	−7.2 (8)	C46—C47—C48—O6	−1.7 (8)
C18—C23—C24—O2	−5.4 (5)	C42—C47—C48—O5	−2.5 (5)
C22—C23—C24—O2	172.8 (4)	C46—C47—C48—O5	179.2 (4)

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the C8–C13 and O1,C1,C6,C7,C8,C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*B*···*Cg*[i]	0.99	2.81	3.583 (4)	136
C40—H40*A*···*Cg*1	0.99	2.79	3.534 (4)	132
C40—H40*B*···*Cg*2	0.99	2.83	3.580 (4)	133

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