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Enantiomerically pure (1*S*,5*R*) and racemic 3-(1-benzothiophen-2-yl)-8-azoniabicyclo[3.2.1]oct-2-ene acetate

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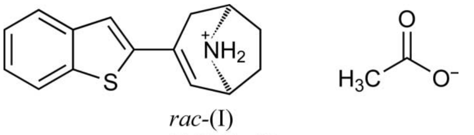
The title compound, $C_{15}H_{16}NS^+\cdot C_2H_3O_2^-$, has been crystallized as both a pure enantiomer (1*S*,5*R*) and a racemate. The racemate crystallizes in the space group *Cc*, with molecules of opposite handedness related to each other by the action of the *c*-glide. The enantiomer is essentially isostructural with the racemate, except that the glide symmetry is violated by interchange of CH and CH_2 groups within the seven-membered ring. The space-group symmetry is reduced to *P*1 with two molecules in the asymmetric unit. The enantiomer structure shows disorder of the thiophene ring for one of the molecules in the asymmetric unit. The major component of the disorder has the thiophene ring in the same position as in the racemate, but generates a higher-energy molecular conformation. The minor disorder component has different intermolecular interactions but retains a more stable molecular conformation.

Comment

The title compound shows a pharmacological profile as a triple monoamine re-uptake inhibitor, altering the level of activity of the monoamine neurotransmitters serotonin, noradrenaline and dopamine, for the treatment of neuropathic pain and other disorders of the central nervous system (Peters *et al.*, 2006). The chirality of the molecule depends on the position of the double bond relative to the NH_2^+ bridge in the bicyclic ring (see Scheme). For a given orientation of the seven-membered ring, the NH_2^+ bridge can lie either above or below the ring. In the solid state (with restricted rotation about the C—C bond between the thiophene and bicyclic rings), there is also the possibility for the S atom to lie either adjacent to the double bond (*cis*) or opposite it (*trans*).

The racemate, (I) (Fig. 1), and enantiomer, (II) (Fig. 2), are essentially isostructural. The primitive triclinic unit cell used to describe the structure of the enantiomer is transformed to the *C*-centred monoclinic cell of the racemate by the transformation matrix [011/0$\bar{1}$1/100]. Racemate (I) crystallizes in the space group *Cc*, with molecules of opposite handedness related to each other by the action of the *c*-glide. The thiophene ring adopts the *cis* orientation with respect to the double bond of the bicyclic ring, and there is no indication of any disorder. The molecules form hydrogen-bonded chains along the *c* axis, with the acetate anions linking between the NH_2^+ groups (Table 1 and Fig. 3).



rac-(I)
(1*S*,5*R*)-(II)

Initially, we also solved the structure of enantiomer (II) in the space group *Cc*, with the implication that racemization had occurred at some stage in the synthesis or crystallization process. However, chiral high-performance liquid chromatography (chiral HPLC) clearly showed that the sample was a single enantiomer, causing us to re-examine the diffraction data. Integration of the data for (II) in the reported primitive cell gave $R_{\rm int}$ = 0.019 for 5001 unique reflections. In the *C*-centred monoclinic setting used for the racemate, the $R_{\rm int}$ value increased to 0.104 for 1972 unique data, and 163 reflections violate the systematic absence conditions for the *c*-

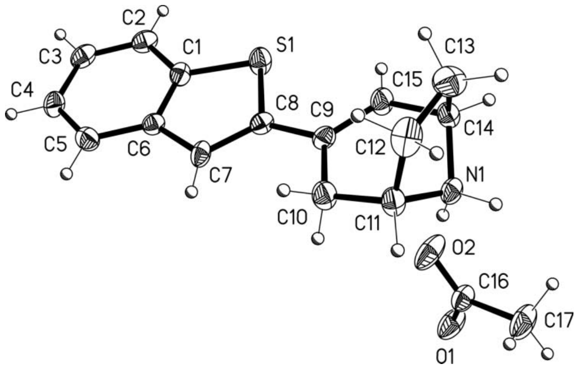


Figure 1
The molecular structure of racemate (I), with displacement ellipsoids drawn at the 50% probability level.

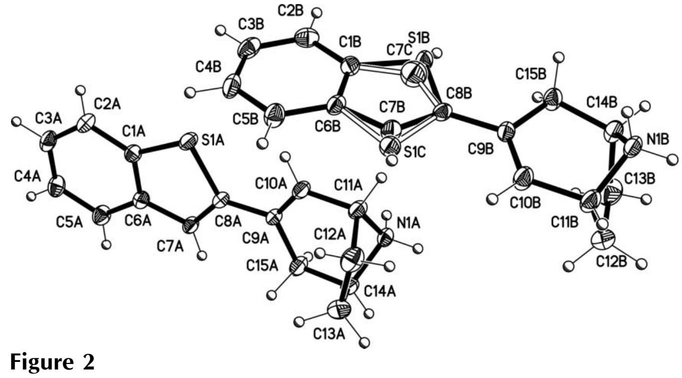


Figure 2
The two molecules in the asymmetric unit of enantiomer (II), with displacement ellipsoids drawn at the 50% probability level. Two orientations of the thiophene ring are present for one of the two molecules. For clarity, the acetate anions are not shown.

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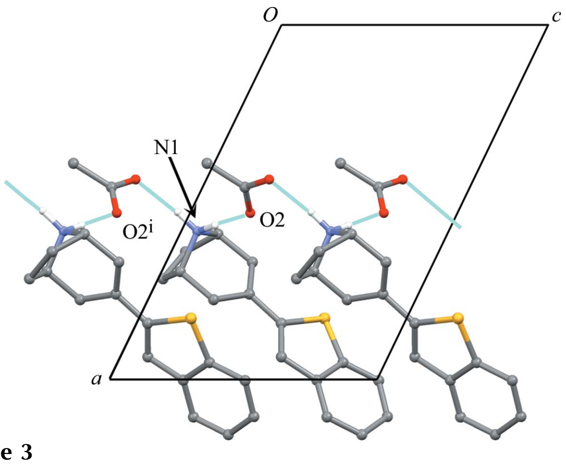
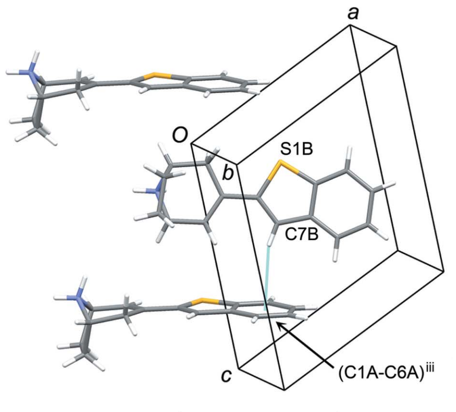


Figure 3
The hydrogen-bonded (pale solid lines) chain along the *c* axis in racemate (I). In enantiomer (II), these chains lie along the *a* axis. [Symmetry code: (i) $x, -y + 1, z - \frac{1}{2}$.]

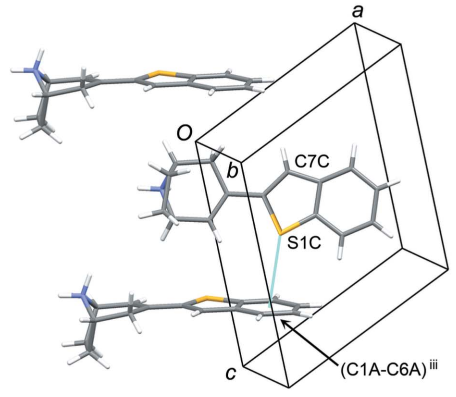
glide at the $3\sigma(I)$ level. Thus, application of the primitive setting for (II) is supported by the diffraction data.

The structure of enantiomer (II) in the space group *P*1 contains two molecules in the asymmetric unit. The *c*-glide present in the structure of (I) is violated in (II) only by the interchange of the CH and CH_2 groups in one of the independent molecules. One of the two independent molecules is ordered, while the other displays disorder for the thiophene ring. The ordered molecule has the S atom in the *cis* orientation, while the disordered molecule has a *cis–trans* ratio of 0.161 (3):0.839 (3). This result was consistent in several crystals examined. The implication is that the orientation of the thiophene group is governed principally by the intermolecular interactions, rather than any intramolecular factor. The thiophene rings adopt (principally) the same orientation within the structures of (I) and (II), but the interchange of the CH and CH_2 groups in one of the two independent molecules of enantiomer (II) results in the *trans* conformation for the majority component. The principal intermolecular interaction influenced by the disorder involves a neighbouring benzene ring (C1*A*–C6*A*) of the thiophene group (Fig. 4). The majority *trans* component makes a C—H$\cdots\pi$ contact (H7B*A*$\cdots$*Cg*^{iii} = 2.77 Å; *Cg* is the centroid of the C1*A*–C6*A* ring), while the minority *cis* component makes an S$\cdots\pi$ contact [S1*C*$\cdots$*Cg*^{iii} = 3.159 (1) Å; symmetry code: (iii) $x - 1, y - 1, z$].

The fact that disorder is observed in (II) suggests that there must be some intramolecular preference for the *cis* conformation. Calculations for an isolated molecule using density functional theory (DFT) methods support this interpretation (see *Supplementary materials* for optimized molecular structures). Geometry optimization of an isolated molecule starting from the *trans* conformation causes the thiophene ring to rotate away from the plane containing the CH group by *ca* 31°. This alleviates a short H$\cdots$H contact (H7*BA*$\cdots$H10*B* = 2.29 Å) that exists in the coplanar arrangement observed in the crystal structure. By contrast, optimization of the *cis* conformation causes essentially no change from the conformation observed in the crystal structure. Thus, the coplanar *trans* conformation of the major disorder component in (II) is less favourable than the *cis* conformation in terms of the intramolecular energy, but this is outweighed by more favourable intermolecular interactions for the *trans* conformation in the crystal structure. In some molecules, the intermolecular preference for the *trans* conformation is overcome by the intramolecular preference for the *cis* arrangement.



trans (major component)



cis (minor component)

Figure 4
The intermolecular interactions for the two disorder components in enantiomer (II). For the *trans* component, a C—H$\cdots\pi$ contact is highlighted. For the *cis* component, an S$\cdots\pi$ contact is highlighted. [Symmetry code: (iii) $x - 1, y - 1, z$.]

Isostructural enantiomer/racemate pairs represent a special circumstance with regard to Wallach's rule (Brock *et al.*, 1991). In accordance with expectation, the calculated density of racemate (I) is found to be marginally higher than that of enantiomer (II) (1.304 *versus* 1.302 Mg m^{-3}), but the difference is barely significant and no firm conclusions can be drawn. Since the crystal structures of the enantiomer and racemate are essentially identical, their simulated powder X-ray diffraction (PXRD) patterns are also essentially identical, and any distinction between the pure enantiomer and the racemate cannot be expected to be made reliably by PXRD analysis. The enantiomer and racemate would also be expected to form solid solutions, which prevents optical resolution by crystallization. A similar case has been reported recently for citalopram oxalate (Lopez de Diego *et al.*, 2011). It is perhaps interesting that the closest comparable compound in the Cambridge Structural Database (Version 5.33; Allen, 2002) also exhibits pseudosymmetry, *viz.* (1*R*)-2-

(pyrimidin-5-yl)-8-azoniabicyclo[3.2.1]oct-2-ene oxalate propan-2-ol solvate (Gundisch *et al.*, 2001), which crystallizes in the space group $P2_1$, but clearly approximates $P2_1/c$.

Experimental

The title compound was synthesized in high enantiomeric purity (ee 98.9%) according to the method of Malmgren *et al.* (2011). The crystallization conditions are also described in Malmgren *et al.* (2011).

Racemate (I)

Crystal data

$C_{15}H_{16}NS^+ \cdot C_2H_3O_2^-$
$M_r = 301.39$
Monoclinic, *Cc*
$a = 13.316$ (3) Å
$b = 14.195$ (3) Å
$c = 9.020$ (2) Å
$\beta = 115.775$ (11)°
$V = 1535.3$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.22$ mm^{-1}
$T = 180$ K
0.20 × 0.10 × 0.07 mm

Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.830$, $T_{\max} = 0.985$
6763 measured reflections
2761 independent reflections
2318 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.084$
$S = 1.03$
2761 reflections
191 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), with 731 Friedel pairs
Flack parameter: 0.08 (6)

Enantiomer (II)

Crystal data

$C_{15}H_{16}NS^+ \cdot C_2H_3O_2^-$
$M_r = 301.39$
Triclinic, *P*1
$a = 9.0244$ (2) Å
$b = 9.7278$ (2) Å
$c = 9.7492$ (2) Å
$\alpha = 92.9699$ (10)°
$\beta = 107.4568$ (10)°
$\gamma = 107.5510$ (9)°
$V = 768.85$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.21$ mm^{-1}
$T = 180$ K
0.30 × 0.20 × 0.10 mm

Data collection

Bruker–Nonius X8 APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.686$, $T_{\max} = 0.978$
11591 measured reflections
5001 independent reflections
4845 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O2	0.92	1.74	2.659 (2)	175
N1—H1$B\cdots$O1$^{\rm i}$	0.92	1.84	2.748 (3)	168
N1—H1$B\cdots$O2$^{\rm i}$	0.92	2.50	3.125 (2)	125

Symmetry code: (i) $x, -y+1, z-\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °) for enantiomer (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1A—H1A2$\cdots$O2A	0.92	1.75	2.664 (2)	177
N1A—H1A1$\cdots$O1$B^{\rm ii}$	0.92	1.85	2.7550 (18)	168
N1B—H1B2$\cdots$O1$A^{\rm iii}$	0.92	1.83	2.7346 (19)	169
N1B—H1B1$\cdots$O2$B^{\rm iii}$	0.92	1.75	2.663 (2)	173

Symmetry codes: (ii) $x-1, y, z$; (iii) $x-1, y-1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.03$
5001 reflections
392 parameters
15 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Absolute structure: Flack (1983), with 1495 Friedel pairs
Flack parameter: −0.04 (4)

H atoms bound to C atoms were placed in idealized positions, with C—H = 1.00 (Csp^3—H), 0.99 (CH_2), 0.98 (CH_3) or 0.95 Å (Csp^2—H), and refined as riding, with $U_{\rm iso}$(H) = 1.2 or 1.5$U_{\rm eq}$(C). The H atoms of the NH_2^+ group were visible in difference Fourier maps in both structures, but were placed geometrically (N—H = 0.92 Å) and refined as riding [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N)] for the final refinements. In both cases, the absolute structure was established reliably by refinement of the Flack parameter. For enantiomer (II), the thiophene ring was modelled in *cis* and *trans* orientations with respect to the position of the C9*B*=C10*B* double bond by splitting atoms C7*B*/C7*C* and S1*B*/S1*C*. The C6*B*—S1*C*, C8*B*—S1*C*, C1*B*—S1*B* and C8*B*—S1*B* bonds were restrained to a common refined value with an s.u. of 0.02 Å, and the C6*B*—C7*B*, C7*B*—C8*B*, C1*B*—C7*C* and C7*C*—C8*B* bonds were restrained to a second common refined value with an s.u. of 0.02 Å. The five atoms of each thiophene ring were restrained to lie in a common plane, with an s.u. of 0.01 Å. The DFT calculations were carried out using the *DMol*^{3} module (Delley, 1990) in *Materials Studio* (Accelrys, 2011), employing the B3LYP function with the DNP 4.4 (double numerical plus *d*-functions plus polarization) basis set.

For both compounds, data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the Danish Natural Sciences Research Council and the Carlsberg Foundation for provision of the X-ray equipment, and to the Lundbeck Foundation for provision of the *Materials Studio* software.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3093). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2012). C**68**, o298–o301 [doi:10.1107/S0108270112030569]

Enantiomerically pure (1*S*,5*R*) and racemic 3-(1-benzothiophen-2-yl)-8-azoniabicyclo[3.2.1]oct-2-ene acetate

Brian Frøstrup, Dan Peters and Andrew D. Bond

(I) racemic 3-(1-benzothiophen-2-yl)-8-azoniabicyclo[3.2.1]oct-2-ene acetate

Crystal data

$C_{15}H_{16}NS^{+}\cdot C_2H_3O_2^{-}$
M_r = 301.39
Monoclinic, *Cc*
Hall symbol: C -2yc
a = 13.316 (3) Å
b = 14.195 (3) Å
c = 9.020 (2) Å
β = 115.775 (11)°
V = 1535.3 (6) Å^3
Z = 4
F(000) = 640
D_x = 1.304 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2096 reflections
θ = 2.2–24.1°
μ = 0.22 mm^{-1}
T = 180 K
Block, colourless
0.20 × 0.10 × 0.07 mm

Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
thin–slice *ω* and *φ* scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.830, T_{max} = 0.985
6763 measured reflections
2761 independent reflections
2318 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 28.3°, θ_{min} = 3.8°
$h = -16\rightarrow17$
$k = -18\rightarrow17$
$l = -12\rightarrow6$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.084
S = 1.03
2761 reflections
191 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), with 731 Friedel pairs
Flack parameter: 0.08 (6)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
S1	0.82597 (4)	0.69612 (4)	0.69210 (6)	0.02854 (16)
N1	0.58047 (15)	0.61525 (13)	0.0583 (2)	0.0226 (4)
H1A	0.5646	0.5674	0.1136	0.027*
H1B	0.5269	0.6164	−0.0491	0.027*
C1	0.95027 (18)	0.65266 (16)	0.8414 (3)	0.0221 (5)
C2	1.0011 (2)	0.67765 (16)	1.0075 (3)	0.0258 (6)
H2A	0.9662	0.7204	1.0515	0.031*
C3	1.1026 (2)	0.63897 (16)	1.1052 (3)	0.0269 (6)
H3A	1.1392	0.6562	1.2181	0.032*
C4	1.1535 (2)	0.57451 (16)	1.0422 (3)	0.0277 (5)
H4A	1.2234	0.5478	1.1131	0.033*
C5	1.1038 (2)	0.54946 (17)	0.8798 (3)	0.0275 (6)
H5A	1.1391	0.5058	0.8380	0.033*
C6	0.99990 (18)	0.58867 (15)	0.7750 (3)	0.0206 (5)
C7	0.93440 (18)	0.57468 (16)	0.6004 (3)	0.0230 (5)
H7A	0.9545	0.5327	0.5357	0.028*
C8	0.83954 (18)	0.62922 (15)	0.5387 (3)	0.0208 (5)
C9	0.75738 (18)	0.63749 (15)	0.3669 (3)	0.0213 (5)
C10	0.7731 (2)	0.58023 (17)	0.2430 (3)	0.0292 (6)
H10A	0.7631	0.5130	0.2628	0.035*
H10B	0.8506	0.5884	0.2573	0.035*
C11	0.69385 (19)	0.60461 (17)	0.0673 (3)	0.0261 (5)
H11A	0.6951	0.5554	−0.0112	0.031*
C12	0.7142 (2)	0.70305 (18)	0.0157 (4)	0.0374 (6)
H12A	0.7931	0.7217	0.0795	0.045*
H12B	0.6963	0.7041	−0.1029	0.045*
C13	0.6380 (2)	0.76940 (18)	0.0511 (3)	0.0363 (6)
H13A	0.5790	0.7949	−0.0522	0.044*
H13B	0.6807	0.8224	0.1217	0.044*
C14	0.5883 (2)	0.70743 (15)	0.1404 (3)	0.0234 (5)
H14A	0.5134	0.7307	0.1247	0.028*
C15	0.6673 (2)	0.69675 (16)	0.3202 (3)	0.0271 (6)
H15A	0.6546	0.7310	0.4011	0.033*
O1	0.43447 (16)	0.35790 (13)	0.2336 (2)	0.0392 (5)
O2	0.52871 (15)	0.48369 (13)	0.2234 (2)	0.0444 (5)
C16	0.4560 (2)	0.42187 (18)	0.1567 (3)	0.0282 (5)
C17	0.3890 (2)	0.4266 (2)	−0.0281 (3)	0.0421 (7)

H17A	0.3290	0.3798	−0.0632	0.063*
H17B	0.4378	0.4134	−0.0814	0.063*
H17C	0.3568	0.4897	−0.0595	0.063*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0257 (3)	0.0390 (3)	0.0187 (3)	0.0054 (3)	0.0076 (2)	−0.0028 (3)
N1	0.0225 (10)	0.0269 (12)	0.0143 (11)	−0.0023 (8)	0.0041 (9)	0.0016 (9)
C1	0.0209 (12)	0.0235 (12)	0.0198 (12)	−0.0016 (10)	0.0069 (11)	0.0051 (11)
C2	0.0321 (15)	0.0270 (14)	0.0193 (13)	−0.0041 (11)	0.0123 (12)	−0.0042 (11)
C3	0.0317 (14)	0.0297 (14)	0.0156 (13)	−0.0079 (11)	0.0068 (11)	−0.0013 (11)
C4	0.0237 (12)	0.0308 (13)	0.0184 (13)	0.0020 (11)	−0.0004 (11)	0.0032 (11)
C5	0.0270 (13)	0.0270 (14)	0.0273 (14)	0.0041 (11)	0.0107 (12)	−0.0023 (11)
C6	0.0229 (12)	0.0212 (12)	0.0171 (12)	−0.0017 (10)	0.0080 (10)	−0.0005 (10)
C7	0.0188 (12)	0.0275 (12)	0.0163 (13)	−0.0021 (10)	0.0017 (10)	0.0044 (10)
C8	0.0238 (12)	0.0221 (13)	0.0170 (12)	−0.0030 (10)	0.0092 (11)	−0.0008 (10)
C9	0.0219 (12)	0.0244 (12)	0.0169 (13)	−0.0016 (10)	0.0076 (10)	−0.0030 (10)
C10	0.0273 (13)	0.0369 (14)	0.0206 (14)	0.0070 (11)	0.0078 (12)	−0.0032 (11)
C11	0.0241 (13)	0.0356 (14)	0.0176 (12)	0.0075 (10)	0.0081 (11)	−0.0029 (10)
C12	0.0310 (13)	0.0535 (17)	0.0302 (14)	−0.0016 (13)	0.0158 (12)	0.0042 (13)
C13	0.0465 (16)	0.0311 (14)	0.0310 (16)	−0.0024 (13)	0.0167 (14)	0.0052 (12)
C14	0.0241 (12)	0.0272 (13)	0.0177 (12)	0.0065 (10)	0.0079 (10)	−0.0004 (10)
C15	0.0266 (13)	0.0339 (14)	0.0167 (13)	0.0050 (11)	0.0055 (11)	−0.0028 (11)
O1	0.0457 (11)	0.0416 (10)	0.0199 (10)	−0.0160 (9)	0.0046 (9)	0.0039 (8)
O2	0.0494 (12)	0.0506 (12)	0.0192 (10)	−0.0246 (10)	0.0018 (9)	0.0047 (9)
C16	0.0274 (13)	0.0330 (14)	0.0198 (13)	−0.0033 (12)	0.0061 (11)	−0.0003 (11)
C17	0.0444 (17)	0.0483 (16)	0.0192 (14)	−0.0113 (14)	0.0002 (13)	0.0057 (13)

Geometric parameters (Å, º)

S1—C1	1.731 (2)	C9—C10	1.469 (3)
S1—C8	1.751 (2)	C10—C11	1.514 (3)
N1—C11	1.484 (3)	C10—H10A	0.990
N1—C14	1.484 (3)	C10—H10B	0.990
N1—H1A	0.920	C11—C12	1.534 (3)
N1—H1B	0.920	C11—H11A	1.000
C1—C2	1.395 (3)	C12—C13	1.517 (4)
C1—C6	1.402 (3)	C12—H12A	0.990
C2—C3	1.367 (4)	C12—H12B	0.990
C2—H2A	0.950	C13—C14	1.524 (3)
C3—C4	1.398 (3)	C13—H13A	0.990
C3—H3A	0.950	C13—H13B	0.990
C4—C5	1.366 (3)	C14—C15	1.509 (3)
C4—H4A	0.950	C14—H14A	1.000
C5—C6	1.407 (3)	C15—H15A	0.950
C5—H5A	0.950	O1—C16	1.249 (3)
C6—C7	1.444 (3)	O2—C16	1.250 (3)
C7—C8	1.376 (3)	C16—C17	1.512 (4)
C7—H7A	0.950	C17—H17A	0.980

C8—C9	1.462 (3)	C17—H17B	0.980
C9—C15	1.373 (3)	C17—H17C	0.980

C1—S1—C8	91.68 (11)	C11—C10—H10B	108.8
C11—N1—C14	102.31 (17)	H10A—C10—H10B	107.7
C11—N1—H1A	111.3	N1—C11—C10	108.04 (18)
C14—N1—H1A	111.3	N1—C11—C12	101.56 (18)
C11—N1—H1B	111.3	C10—C11—C12	113.0 (2)
C14—N1—H1B	111.3	N1—C11—H11A	111.3
H1A—N1—H1B	109.2	C10—C11—H11A	111.3
C2—C1—C6	121.7 (2)	C12—C11—H11A	111.3
C2—C1—S1	126.77 (18)	C13—C12—C11	106.22 (19)
C6—C1—S1	111.54 (17)	C13—C12—H12A	110.5
C3—C2—C1	118.2 (2)	C11—C12—H12A	110.5
C3—C2—H2A	120.9	C13—C12—H12B	110.5
C1—C2—H2A	120.9	C11—C12—H12B	110.5
C2—C3—C4	121.3 (2)	H12A—C12—H12B	108.7
C2—C3—H3A	119.4	C12—C13—C14	103.70 (18)
C4—C3—H3A	119.4	C12—C13—H13A	111.0
C5—C4—C3	120.8 (2)	C14—C13—H13A	111.0
C5—C4—H4A	119.6	C12—C13—H13B	111.0
C3—C4—H4A	119.6	C14—C13—H13B	111.0
C4—C5—C6	119.6 (2)	H13A—C13—H13B	109.0
C4—C5—H5A	120.2	N1—C14—C15	108.21 (18)
C6—C5—H5A	120.2	N1—C14—C13	101.42 (18)
C1—C6—C5	118.5 (2)	C15—C14—C13	111.5 (2)
C1—C6—C7	112.4 (2)	N1—C14—H14A	111.7
C5—C6—C7	129.0 (2)	C15—C14—H14A	111.7
C8—C7—C6	112.1 (2)	C13—C14—H14A	111.7
C8—C7—H7A	123.9	C9—C15—C14	119.9 (2)
C6—C7—H7A	123.9	C9—C15—H15A	120.0
C7—C8—C9	127.3 (2)	C14—C15—H15A	120.0
C7—C8—S1	112.18 (17)	O1—C16—O2	124.1 (2)
C9—C8—S1	120.47 (16)	O1—C16—C17	118.5 (2)
C15—C9—C8	121.7 (2)	O2—C16—C17	117.5 (2)
C15—C9—C10	120.0 (2)	C16—C17—H17A	109.5
C8—C9—C10	118.26 (19)	C16—C17—H17B	109.5
C9—C10—C11	113.90 (19)	H17A—C17—H17B	109.5
C9—C10—H10A	108.8	C16—C17—H17C	109.5
C11—C10—H10A	108.8	H17A—C17—H17C	109.5
C9—C10—H10B	108.8	H17B—C17—H17C	109.5

C8—S1—C1—C2	177.6 (2)	S1—C8—C9—C15	−0.5 (3)
C8—S1—C1—C6	−0.21 (17)	C7—C8—C9—C10	2.0 (3)
C6—C1—C2—C3	0.9 (3)	S1—C8—C9—C10	179.61 (16)
S1—C1—C2—C3	−176.72 (17)	C15—C9—C10—C11	8.8 (3)
C1—C2—C3—C4	−1.3 (3)	C8—C9—C10—C11	−171.33 (19)
C2—C3—C4—C5	1.1 (4)	C14—N1—C11—C10	74.2 (2)
C3—C4—C5—C6	−0.3 (3)	C14—N1—C11—C12	−44.9 (2)

C2—C1—C6—C5	−0.2 (3)	C9—C10—C11—N1	−44.6 (3)
S1—C1—C6—C5	177.79 (17)	C9—C10—C11—C12	66.9 (3)
C2—C1—C6—C7	−178.6 (2)	N1—C11—C12—C13	23.1 (3)
S1—C1—C6—C7	−0.7 (2)	C10—C11—C12—C13	−92.4 (2)
C4—C5—C6—C1	−0.1 (3)	C11—C12—C13—C14	6.6 (3)
C4—C5—C6—C7	178.0 (2)	C11—N1—C14—C15	−67.7 (2)
C1—C6—C7—C8	1.5 (3)	C11—N1—C14—C13	49.7 (2)
C5—C6—C7—C8	−176.8 (2)	C12—C13—C14—N1	−33.9 (3)
C6—C7—C8—C9	176.19 (19)	C12—C13—C14—C15	81.1 (2)
C6—C7—C8—S1	−1.6 (2)	C8—C9—C15—C14	176.35 (19)
C1—S1—C8—C7	1.07 (17)	C10—C9—C15—C14	−3.8 (3)
C1—S1—C8—C9	−176.92 (18)	N1—C14—C15—C9	34.3 (3)
C7—C8—C9—C15	−178.1 (2)	C13—C14—C15—C9	−76.4 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2	0.92	1.74	2.659 (2)	175
N1—H1*B*···O1^{i}	0.92	1.84	2.748 (3)	168
N1—H1*B*···O2^{i}	0.92	2.50	3.125 (2)	125

Symmetry code: (i) *x*, −*y*+1, *z*−1/2.

(II) (1*S*,5*R*)-3-(1-benzothiophen-2-yl)-8-azoniabicyclo[3.2.1]oct-2-ene acetate

Crystal data

$C_{15}H_{16}NS^{+}\cdot C_2H_3O_2^{-}$	$Z = 2$
$M_r = 301.39$	$F(000) = 320$
Triclinic, *P*1	$D_x = 1.302$ Mg m^{-3}
Hall symbol: P 1	Mo *Kα* radiation, $\lambda = 0.71073$ Å
$a = 9.0244$ (2) Å	Cell parameters from 9266 reflections
$b = 9.7278$ (2) Å	$\theta = 2.7$–28.3°
$c = 9.7492$ (2) Å	$\mu = 0.21$ mm^{-1}
$\alpha = 92.9699$ (10)°	$T = 180$ K
$\beta = 107.4568$ (10)°	Block, colourless
$\gamma = 107.5510$ (9)°	0.30 × 0.20 × 0.10 mm
$V = 768.85$ (3) Å^3	

Data collection

Bruker Nonius X8APEX-II CCD area-detector diffractometer	11591 measured reflections
Radiation source: fine-focus sealed tube	5001 independent reflections
Graphite monochromator	4845 reflections with $I > 2\sigma(I)$
thin–slice *ω* and *φ* scans	$R_{\mathrm{int}} = 0.019$
Absorption correction: multi-scan *SADABS* (Sheldrick, 2003)	$\theta_{\max} = 28.3°$, $\theta_{\min} = 3.8°$
	$h = -8 \rightarrow 12$
	$k = -12 \rightarrow 12$
$T_{\min} = 0.686$, $T_{\max} = 0.978$	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	$S = 1.03$
Least-squares matrix: full	5001 reflections
$R[F^2 > 2\sigma(F^2)] = 0.028$	392 parameters
$wR(F^2) = 0.074$	15 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.1048P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Absolute structure: Flack (1983), with 1495 Friedel pairs
Flack parameter: −0.04 (4)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1A	0.92758 (5)	0.78674 (4)	0.67832 (5)	0.02490 (10)	
N1A	0.29271 (17)	0.62201 (14)	0.35050 (14)	0.0202 (3)	
H1A1	0.1853	0.5669	0.2986	0.024*	
H1A2	0.3481	0.6539	0.2867	0.024*	
C1A	1.0775 (2)	0.95512 (17)	0.75951 (17)	0.0199 (3)	
C2A	1.2436 (2)	0.98124 (19)	0.83688 (18)	0.0230 (4)	
H2AA	1.2880	0.9039	0.8468	0.028*	
C3A	1.3410 (2)	1.12308 (19)	0.89839 (17)	0.0244 (4)	
H3AA	1.4540	1.1433	0.9524	0.029*	
C4A	1.2772 (2)	1.23727 (19)	0.88308 (19)	0.0260 (4)	
H4AA	1.3475	1.3341	0.9257	0.031*	
C5A	1.1127 (2)	1.21131 (18)	0.80647 (18)	0.0250 (4)	
H5AA	1.0698	1.2897	0.7968	0.030*	
C6A	1.0092 (2)	1.06753 (17)	0.74282 (16)	0.0195 (3)	
C7A	0.8359 (2)	1.01438 (16)	0.66399 (16)	0.0190 (3)	
H7AA	0.7707	1.0760	0.6420	0.023*	
C8A	0.7738 (2)	0.86641 (16)	0.62369 (16)	0.0186 (3)	
C9A	0.6018 (2)	0.77596 (16)	0.54911 (16)	0.0178 (3)	
C10A	0.5530 (2)	0.63007 (17)	0.52372 (18)	0.0211 (3)	
H10A	0.6332	0.5830	0.5517	0.025*	
C11A	0.3751 (2)	0.53857 (17)	0.45227 (18)	0.0214 (3)	
H11A	0.3628	0.4416	0.4019	0.026*	
C12A	0.2819 (2)	0.5227 (2)	0.5611 (2)	0.0300 (4)	
H12A	0.3484	0.5064	0.6560	0.036*	
H12B	0.1759	0.4411	0.5237	0.036*	
C13A	0.2538 (2)	0.6702 (2)	0.5748 (2)	0.0310 (4)	
H13A	0.3235	0.7292	0.6713	0.037*	
H13B	0.1370	0.6554	0.5632	0.037*	
C14A	0.3014 (2)	0.74739 (17)	0.45242 (19)	0.0225 (3)	

H14A	0.2210	0.7963	0.4041	0.027*	
C15A	0.4780 (2)	0.85361 (17)	0.50280 (19)	0.0244 (4)	
H15A	0.4970	0.9068	0.4224	0.029*	
H15B	0.4936	0.9261	0.5855	0.029*	
S1B	0.42432 (6)	0.17978 (5)	0.28834 (6)	0.02165 (17)	0.839 (3)
C7B	0.3395 (3)	0.1674 (2)	0.5171 (3)	0.0217 (5)	0.839 (3)
H7BA	0.2756	0.1459	0.5798	0.026*	0.839 (3)
S1C	0.3073 (4)	0.1548 (3)	0.5558 (3)	0.0212 (10)*	0.161 (3)
C7C	0.4172 (9)	0.1825 (5)	0.3422 (16)	0.035 (4)*	0.161 (3)
H7CA	0.4147	0.1703	0.2441	0.042*	0.161 (3)
N1B	−0.20674 (17)	−0.14930 (14)	0.11866 (14)	0.0212 (3)	
H1B1	−0.1515	−0.2135	0.1495	0.025*	
H1B2	−0.3139	−0.2010	0.0628	0.025*	
C1B	0.5733 (2)	0.26028 (16)	0.45439 (17)	0.0213 (3)	
C2B	0.7393 (2)	0.33661 (18)	0.4762 (2)	0.0255 (4)	
H2BA	0.7806	0.3444	0.3969	0.031*	
C3B	0.8408 (2)	0.39987 (18)	0.6156 (2)	0.0265 (4)	
H3BA	0.9533	0.4536	0.6323	0.032*	
C4B	0.7821 (2)	0.38696 (19)	0.73292 (19)	0.0264 (4)	
H4BA	0.8552	0.4309	0.8282	0.032*	
C5B	0.6190 (2)	0.31092 (19)	0.71210 (18)	0.0253 (4)	
H5BA	0.5795	0.3027	0.7924	0.030*	
C6B	0.5119 (2)	0.24589 (15)	0.57087 (17)	0.0202 (3)	
C8B	0.27246 (19)	0.12536 (15)	0.37092 (16)	0.0178 (3)	
C9B	0.0996 (2)	0.05028 (16)	0.28095 (16)	0.0185 (3)	
C10B	−0.0217 (2)	0.0225 (2)	0.33677 (18)	0.0273 (4)	
H10B	0.0045	0.0491	0.4385	0.033*	
C11B	−0.1993 (2)	−0.0497 (2)	0.24428 (18)	0.0273 (4)	
H11B	−0.2680	−0.1017	0.3015	0.033*	
C12B	−0.2687 (3)	0.0605 (2)	0.1638 (2)	0.0374 (5)	
H12C	−0.2314	0.1550	0.2283	0.045*	
H12D	−0.3907	0.0228	0.1267	0.045*	
C13B	−0.1981 (3)	0.0766 (2)	0.0377 (2)	0.0357 (5)	
H13C	−0.2864	0.0649	−0.0560	0.043*	
H13D	−0.1131	0.1737	0.0538	0.043*	
C14B	−0.1229 (2)	−0.04465 (18)	0.03746 (17)	0.0226 (3)	
H14B	−0.1482	−0.0917	−0.0643	0.027*	
C15B	0.0621 (2)	0.00580 (19)	0.11972 (17)	0.0231 (4)	
H15C	0.1051	−0.0743	0.1055	0.028*	
H15D	0.1186	0.0897	0.0796	0.028*	
O1A	0.47056 (17)	0.73005 (17)	−0.05354 (14)	0.0364 (3)	
O2A	0.45648 (17)	0.70628 (18)	0.16624 (14)	0.0437 (4)	
C16A	0.3919 (2)	0.68835 (19)	0.03088 (18)	0.0247 (4)	
C17A	0.2069 (2)	0.6116 (2)	−0.0333 (2)	0.0350 (5)	
H17A	0.1744	0.5926	−0.1396	0.052*	
H17B	0.1498	0.6737	−0.0052	0.052*	
H17C	0.1772	0.5189	0.0037	0.052*	
O1B	0.96725 (17)	0.44813 (13)	0.23143 (17)	0.0360 (3)	
O2B	0.96090 (17)	0.66694 (15)	0.18906 (18)	0.0408 (4)	

C16B	0.8922 (2)	0.53307 (18)	0.18487 (19)	0.0252 (4)
C17B	0.7061 (2)	0.4739 (2)	0.1185 (3)	0.0411 (5)
H17D	0.6684	0.3671	0.1072	0.062*
H17E	0.6723	0.5044	0.0229	0.062*
H17F	0.6572	0.5121	0.1823	0.062*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1A	0.0146 (2)	0.01952 (18)	0.0364 (2)	0.00667 (14)	0.00257 (16)	−0.00194 (15)
N1A	0.0134 (7)	0.0219 (6)	0.0218 (6)	0.0027 (5)	0.0044 (5)	0.0012 (5)
C1A	0.0153 (8)	0.0205 (7)	0.0219 (7)	0.0033 (6)	0.0064 (6)	0.0017 (6)
C2A	0.0155 (8)	0.0268 (8)	0.0268 (8)	0.0086 (7)	0.0050 (6)	0.0074 (6)
C3A	0.0145 (8)	0.0321 (8)	0.0227 (7)	0.0042 (7)	0.0042 (6)	0.0054 (6)
C4A	0.0187 (8)	0.0235 (8)	0.0279 (8)	0.0009 (6)	0.0032 (7)	0.0019 (6)
C5A	0.0209 (9)	0.0205 (8)	0.0298 (8)	0.0047 (7)	0.0054 (7)	0.0032 (6)
C6A	0.0168 (8)	0.0208 (7)	0.0195 (7)	0.0050 (6)	0.0052 (6)	0.0038 (5)
C7A	0.0154 (8)	0.0196 (7)	0.0208 (7)	0.0075 (6)	0.0029 (6)	0.0037 (6)
C8A	0.0140 (8)	0.0216 (7)	0.0204 (7)	0.0075 (6)	0.0044 (6)	0.0029 (6)
C9A	0.0130 (8)	0.0208 (7)	0.0191 (7)	0.0066 (6)	0.0040 (6)	0.0025 (5)
C10A	0.0141 (8)	0.0215 (8)	0.0261 (7)	0.0070 (6)	0.0035 (6)	0.0024 (6)
C11A	0.0146 (8)	0.0179 (7)	0.0299 (8)	0.0052 (6)	0.0052 (6)	0.0029 (6)
C12A	0.0235 (9)	0.0333 (9)	0.0323 (9)	0.0052 (7)	0.0112 (7)	0.0115 (7)
C13A	0.0251 (10)	0.0375 (10)	0.0329 (9)	0.0098 (8)	0.0147 (8)	0.0000 (7)
C14A	0.0150 (8)	0.0199 (7)	0.0314 (8)	0.0069 (6)	0.0052 (6)	0.0010 (6)
C15A	0.0157 (8)	0.0172 (7)	0.0356 (9)	0.0056 (6)	0.0022 (7)	0.0017 (6)
S1B	0.0145 (3)	0.0281 (3)	0.0185 (3)	0.00221 (18)	0.00562 (18)	−0.00133 (16)
C7B	0.0173 (11)	0.0280 (11)	0.0194 (10)	0.0037 (8)	0.0094 (9)	0.0036 (8)
N1B	0.0132 (7)	0.0224 (6)	0.0248 (7)	0.0043 (5)	0.0036 (5)	0.0029 (5)
C1B	0.0216 (9)	0.0206 (7)	0.0209 (7)	0.0102 (6)	0.0026 (6)	0.0023 (6)
C2B	0.0271 (10)	0.0244 (8)	0.0311 (8)	0.0106 (7)	0.0156 (7)	0.0075 (7)
C3B	0.0155 (8)	0.0213 (8)	0.0409 (9)	0.0043 (6)	0.0084 (7)	0.0071 (7)
C4B	0.0164 (8)	0.0275 (8)	0.0274 (8)	0.0043 (6)	−0.0008 (6)	0.0017 (6)
C5B	0.0194 (9)	0.0298 (8)	0.0235 (8)	0.0043 (7)	0.0065 (7)	0.0043 (6)
C6B	0.0144 (8)	0.0184 (7)	0.0260 (8)	0.0044 (6)	0.0048 (6)	0.0034 (6)
C8B	0.0144 (8)	0.0187 (7)	0.0214 (7)	0.0048 (6)	0.0083 (6)	0.0035 (5)
C9B	0.0150 (8)	0.0187 (7)	0.0191 (7)	0.0036 (6)	0.0040 (6)	0.0016 (5)
C10B	0.0170 (9)	0.0418 (10)	0.0193 (7)	0.0051 (7)	0.0063 (6)	−0.0006 (7)
C11B	0.0149 (8)	0.0428 (10)	0.0216 (7)	0.0056 (7)	0.0073 (6)	−0.0004 (7)
C12B	0.0243 (10)	0.0386 (10)	0.0465 (11)	0.0147 (8)	0.0063 (8)	−0.0088 (8)
C13B	0.0317 (11)	0.0317 (9)	0.0419 (11)	0.0144 (8)	0.0048 (9)	0.0112 (8)
C14B	0.0165 (8)	0.0287 (8)	0.0201 (7)	0.0049 (6)	0.0048 (6)	0.0038 (6)
C15B	0.0171 (8)	0.0300 (8)	0.0190 (7)	0.0027 (7)	0.0069 (6)	0.0014 (6)
O1A	0.0187 (7)	0.0580 (8)	0.0237 (6)	0.0017 (6)	0.0059 (5)	0.0057 (6)
O2A	0.0200 (7)	0.0712 (10)	0.0235 (6)	−0.0047 (7)	0.0041 (5)	0.0062 (6)
C16A	0.0150 (8)	0.0297 (8)	0.0249 (8)	0.0040 (6)	0.0041 (6)	0.0030 (6)
C17A	0.0172 (9)	0.0449 (11)	0.0316 (9)	−0.0007 (8)	0.0039 (7)	0.0017 (8)
O1B	0.0198 (7)	0.0231 (6)	0.0544 (8)	0.0055 (5)	−0.0015 (6)	0.0073 (6)
O2B	0.0186 (7)	0.0238 (6)	0.0695 (10)	0.0046 (5)	0.0016 (7)	0.0110 (6)
C16B	0.0162 (8)	0.0248 (8)	0.0284 (8)	0.0038 (7)	0.0018 (6)	0.0021 (6)

C17B	0.0175 (10)	0.0323 (10)	0.0581 (13)	0.0017 (8)	−0.0031 (9)	0.0095 (9)

Geometric parameters (Å, º)

S1A—C1A	1.7397 (15)	C7C—H7CA	0.950
S1A—C8A	1.7485 (17)	N1B—C14B	1.488 (2)
N1A—C11A	1.484 (2)	N1B—C11B	1.494 (2)
N1A—C14A	1.500 (2)	N1B—H1B1	0.920
N1A—H1A1	0.920	N1B—H1B2	0.920
N1A—H1A2	0.920	C1B—C2B	1.401 (3)
C1A—C2A	1.397 (2)	C1B—C6B	1.401 (2)
C1A—C6A	1.402 (2)	C2B—C3B	1.375 (3)
C2A—C3A	1.379 (2)	C2B—H2BA	0.950
C2A—H2AA	0.950	C3B—C4B	1.394 (3)
C3A—C4A	1.392 (3)	C3B—H3BA	0.950
C3A—H3AA	0.950	C4B—C5B	1.380 (2)
C4A—C5A	1.384 (3)	C4B—H4BA	0.950
C4A—H4AA	0.950	C5B—C6B	1.404 (2)
C5A—C6A	1.410 (2)	C5B—H5BA	0.950
C5A—H5AA	0.950	C8B—C9B	1.471 (2)
C6A—C7A	1.433 (2)	C9B—C10B	1.327 (2)
C7A—C8A	1.365 (2)	C9B—C15B	1.515 (2)
C7A—H7AA	0.950	C10B—C11B	1.504 (2)
C8A—C9A	1.465 (2)	C10B—H10B	0.950
C9A—C10A	1.338 (2)	C11B—C12B	1.535 (3)
C9A—C15A	1.505 (2)	C11B—H11B	1.000
C10A—C11A	1.502 (2)	C12B—C13B	1.540 (3)
C10A—H10A	0.950	C12B—H12C	0.990
C11A—C12A	1.528 (3)	C12B—H12D	0.990
C11A—H11A	1.000	C13B—C14B	1.529 (3)
C12A—C13A	1.536 (3)	C13B—H13C	0.990
C12A—H12A	0.990	C13B—H13D	0.990
C12A—H12B	0.990	C14B—C15B	1.528 (2)
C13A—C14A	1.542 (3)	C14B—H14B	1.000
C13A—H13A	0.990	C15B—H15C	0.990
C13A—H13B	0.990	C15B—H15D	0.990
C14A—C15A	1.528 (2)	O1A—C16A	1.248 (2)
C14A—H14A	1.000	O2A—C16A	1.251 (2)
C15A—H15A	0.990	C16A—C17A	1.520 (2)
C15A—H15B	0.990	C17A—H17A	0.980
S1B—C1B	1.7232 (16)	C17A—H17B	0.980
S1B—C8B	1.7536 (16)	C17A—H17C	0.980
C7B—C8B	1.356 (3)	O1B—C16B	1.240 (2)
C7B—C6B	1.425 (3)	O2B—C16B	1.255 (2)
C7B—H7BA	0.950	C16B—C17B	1.516 (3)
S1C—C8B	1.727 (4)	C17B—H17D	0.980
S1C—C6B	1.747 (4)	C17B—H17E	0.980
C7C—C8B	1.375 (10)	C17B—H17F	0.980
C7C—C1B	1.449 (10)		

C1A—S1A—C8A	91.90 (8)	C6B—C1B—C7C	95.9 (6)
C11A—N1A—C14A	102.09 (12)	C2B—C1B—S1B	125.46 (13)
C11A—N1A—H1A1	111.4	C6B—C1B—S1B	113.12 (13)
C14A—N1A—H1A1	111.4	C3B—C2B—C1B	118.04 (16)
C11A—N1A—H1A2	111.4	C3B—C2B—H2BA	121.0
C14A—N1A—H1A2	111.4	C1B—C2B—H2BA	121.0
H1A1—N1A—H1A2	109.2	C2B—C3B—C4B	121.45 (16)
C2A—C1A—C6A	122.19 (14)	C2B—C3B—H3BA	119.3
C2A—C1A—S1A	126.93 (13)	C4B—C3B—H3BA	119.3
C6A—C1A—S1A	110.84 (12)	C5B—C4B—C3B	120.68 (16)
C3A—C2A—C1A	117.79 (17)	C5B—C4B—H4BA	119.7
C3A—C2A—H2AA	121.1	C3B—C4B—H4BA	119.7
C1A—C2A—H2AA	121.1	C4B—C5B—C6B	119.25 (17)
C2A—C3A—C4A	121.46 (16)	C4B—C5B—H5BA	120.4
C2A—C3A—H3AA	119.3	C6B—C5B—H5BA	120.4
C4A—C3A—H3AA	119.3	C1B—C6B—C5B	119.16 (15)
C5A—C4A—C3A	120.72 (15)	C1B—C6B—C7B	109.44 (17)
C5A—C4A—H4AA	119.6	C5B—C6B—C7B	131.34 (18)
C3A—C4A—H4AA	119.6	C1B—C6B—S1C	125.16 (17)
C4A—C5A—C6A	119.40 (18)	C5B—C6B—S1C	115.66 (17)
C4A—C5A—H5AA	120.3	C7B—C8B—C7C	95.8 (6)
C6A—C5A—H5AA	120.3	C7B—C8B—C9B	129.51 (17)
C1A—C6A—C5A	118.44 (16)	C7C—C8B—C9B	134.7 (6)
C1A—C6A—C7A	112.34 (13)	C7C—C8B—S1C	110.4 (6)
C5A—C6A—C7A	129.18 (17)	C9B—C8B—S1C	114.89 (16)
C8A—C7A—C6A	113.33 (15)	C7B—C8B—S1B	110.41 (15)
C8A—C7A—H7AA	123.3	C9B—C8B—S1B	120.03 (11)
C6A—C7A—H7AA	123.3	S1C—C8B—S1B	125.07 (15)
C7A—C8A—C9A	127.68 (15)	C10B—C9B—C8B	122.01 (14)
C7A—C8A—S1A	111.57 (12)	C10B—C9B—C15B	120.16 (14)
C9A—C8A—S1A	120.72 (11)	C8B—C9B—C15B	117.83 (14)
C10A—C9A—C8A	122.57 (16)	C9B—C10B—C11B	122.18 (15)
C10A—C9A—C15A	120.18 (15)	C9B—C10B—H10B	118.9
C8A—C9A—C15A	117.25 (13)	C11B—C10B—H10B	118.9
C9A—C10A—C11A	121.94 (16)	N1B—C11B—C10B	108.52 (15)
C9A—C10A—H10A	119.0	N1B—C11B—C12B	100.41 (14)
C11A—C10A—H10A	119.0	C10B—C11B—C12B	110.77 (16)
N1A—C11A—C10A	108.47 (13)	N1B—C11B—H11B	112.2
N1A—C11A—C12A	101.38 (14)	C10B—C11B—H11B	112.2
C10A—C11A—C12A	111.13 (14)	C12B—C11B—H11B	112.2
N1A—C11A—H11A	111.8	C11B—C12B—C13B	103.48 (16)
C10A—C11A—H11A	111.8	C11B—C12B—H12C	111.1
C12A—C11A—H11A	111.8	C13B—C12B—H12C	111.1
C11A—C12A—C13A	102.85 (13)	C11B—C12B—H12D	111.1
C11A—C12A—H12A	111.2	C13B—C12B—H12D	111.1
C13A—C12A—H12A	111.2	H12C—C12B—H12D	109.0
C11A—C12A—H12B	111.2	C14B—C13B—C12B	105.28 (15)
C13A—C12A—H12B	111.2	C14B—C13B—H13C	110.7
H12A—C12A—H12B	109.1	C12B—C13B—H13C	110.7

C12A—C13A—C14A	106.09 (15)
C12A—C13A—H13A	110.5
C14A—C13A—H13A	110.5
C12A—C13A—H13B	110.5
C14A—C13A—H13B	110.5
H13A—C13A—H13B	108.7
N1A—C14A—C15A	107.56 (14)
N1A—C14A—C13A	101.86 (13)
C15A—C14A—C13A	113.28 (15)
N1A—C14A—H14A	111.2
C15A—C14A—H14A	111.2
C13A—C14A—H14A	111.2
C9A—C15A—C14A	111.74 (13)
C9A—C15A—H15A	109.3
C14A—C15A—H15A	109.3
C9A—C15A—H15B	109.3
C14A—C15A—H15B	109.3
H15A—C15A—H15B	107.9
C1B—S1B—C8B	91.19 (8)
C8B—C7B—C6B	115.8 (2)
C8B—C7B—H7BA	122.1
C6B—C7B—H7BA	122.1
C8B—S1C—C6B	85.40 (18)
C8B—C7C—C1B	123.1 (11)
C8B—C7C—H7CA	118.4
C1B—C7C—H7CA	118.4
C14B—N1B—C11B	101.97 (13)
C14B—N1B—H1B1	111.4
C11B—N1B—H1B1	111.4
C14B—N1B—H1B2	111.4
C11B—N1B—H1B2	111.4
H1B1—N1B—H1B2	109.2
C2B—C1B—C6B	121.40 (14)
C2B—C1B—C7C	142.7 (6)
C14B—C13B—H13D	110.7
C12B—C13B—H13D	110.7
H13C—C13B—H13D	108.8
N1B—C14B—C15B	107.82 (13)
N1B—C14B—C13B	102.99 (15)
C15B—C14B—C13B	113.55 (15)
N1B—C14B—H14B	110.7
C15B—C14B—H14B	110.7
C13B—C14B—H14B	110.7
C9B—C15B—C14B	111.35 (15)
C9B—C15B—H15C	109.4
C14B—C15B—H15C	109.4
C9B—C15B—H15D	109.4
C14B—C15B—H15D	109.4
H15C—C15B—H15D	108.0
O1A—C16A—O2A	123.78 (16)
O1A—C16A—C17A	118.57 (15)
O2A—C16A—C17A	117.64 (16)
C16A—C17A—H17A	109.5
C16A—C17A—H17B	109.5
H17A—C17A—H17B	109.5
C16A—C17A—H17C	109.5
H17A—C17A—H17C	109.5
H17B—C17A—H17C	109.5
O1B—C16B—O2B	124.04 (17)
O1B—C16B—C17B	118.97 (15)
O2B—C16B—C17B	116.99 (17)
C16B—C17B—H17D	109.5
C16B—C17B—H17E	109.5
H17D—C17B—H17E	109.5
C16B—C17B—H17F	109.5
H17D—C17B—H17F	109.5
H17E—C17B—H17F	109.5

C8A—S1A—C1A—C2A	177.24 (16)
C8A—S1A—C1A—C6A	−0.48 (12)
C6A—C1A—C2A—C3A	0.3 (2)
S1A—C1A—C2A—C3A	−177.21 (13)
C1A—C2A—C3A—C4A	−0.7 (3)
C2A—C3A—C4A—C5A	0.7 (3)
C3A—C4A—C5A—C6A	−0.3 (3)
C2A—C1A—C6A—C5A	0.1 (2)
S1A—C1A—C6A—C5A	177.94 (13)
C2A—C1A—C6A—C7A	−177.92 (15)
S1A—C1A—C6A—C7A	−0.08 (17)
C4A—C5A—C6A—C1A	−0.1 (2)
C4A—C5A—C6A—C7A	177.57 (16)
C1A—C6A—C7A—C8A	0.81 (19)
C2B—C1B—C6B—C5B	0.7 (2)
C7C—C1B—C6B—C5B	−177.7 (2)
S1B—C1B—C6B—C5B	−177.79 (14)
C2B—C1B—C6B—C7B	178.27 (16)
C7C—C1B—C6B—C7B	−0.16 (14)
S1B—C1B—C6B—C7B	−0.25 (12)
C2B—C1B—C6B—S1C	179.34 (17)
C7C—C1B—C6B—S1C	0.91 (15)
C4B—C5B—C6B—C1B	−0.2 (2)
C4B—C5B—C6B—C7B	−177.14 (16)
C4B—C5B—C6B—S1C	−178.97 (17)
C8B—C7B—C6B—C1B	−0.44 (16)
C8B—C7B—C6B—C5B	176.69 (18)
C8B—S1C—C6B—C1B	−1.73 (18)

C5A—C6A—C7A—C8A	−176.95 (17)	C8B—S1C—C6B—C5B	176.90 (14)
C6A—C7A—C8A—C9A	176.59 (15)	C6B—C7B—C8B—C7C	0.79 (18)
C6A—C7A—C8A—S1A	−1.16 (17)	C6B—C7B—C8B—C9B	−176.65 (15)
C1A—S1A—C8A—C7A	0.94 (13)	C6B—C7B—C8B—S1B	0.91 (17)
C1A—S1A—C8A—C9A	−176.98 (13)	C1B—C7C—C8B—C7B	−1.0 (2)
C7A—C8A—C9A—C10A	−175.23 (17)	C1B—C7C—C8B—C9B	176.22 (19)
S1A—C8A—C9A—C10A	2.3 (2)	C1B—C7C—C8B—S1C	−2.0 (3)
C7A—C8A—C9A—C15A	3.8 (2)	C6B—S1C—C8B—C7C	1.8 (2)
S1A—C8A—C9A—C15A	−178.63 (12)	C6B—S1C—C8B—C9B	−176.81 (13)
C8A—C9A—C10A—C11A	177.58 (14)	C1B—S1B—C8B—C7B	−0.86 (13)
C15A—C9A—C10A—C11A	−1.4 (3)	C1B—S1B—C8B—C9B	176.96 (13)
C14A—N1A—C11A—C10A	−65.81 (16)	C7B—C8B—C9B—C10B	5.4 (3)
C14A—N1A—C11A—C12A	51.25 (14)	C7C—C8B—C9B—C10B	−171.0 (2)
C9A—C10A—C11A—N1A	30.9 (2)	S1C—C8B—C9B—C10B	7.2 (2)
C9A—C10A—C11A—C12A	−79.7 (2)	S1B—C8B—C9B—C10B	−171.93 (15)
N1A—C11A—C12A—C13A	−37.56 (16)	C7B—C8B—C9B—C15B	−175.16 (17)
C10A—C11A—C12A—C13A	77.53 (17)	C7C—C8B—C9B—C15B	8.4 (3)
C11A—C12A—C13A—C14A	10.82 (18)	S1C—C8B—C9B—C15B	−173.39 (15)
C11A—N1A—C14A—C15A	75.78 (15)	S1B—C8B—C9B—C15B	7.5 (2)
C11A—N1A—C14A—C13A	−43.57 (16)	C8B—C9B—C10B—C11B	177.90 (16)
C12A—C13A—C14A—N1A	19.48 (18)	C15B—C9B—C10B—C11B	−1.5 (3)
C12A—C13A—C14A—C15A	−95.74 (17)	C14B—N1B—C11B—C10B	−65.34 (17)
C10A—C9A—C15A—C14A	9.6 (2)	C14B—N1B—C11B—C12B	50.88 (16)
C8A—C9A—C15A—C14A	−169.49 (14)	C9B—C10B—C11B—N1B	30.4 (2)
N1A—C14A—C15A—C9A	−46.99 (18)	C9B—C10B—C11B—C12B	−79.0 (2)
C13A—C14A—C15A—C9A	64.8 (2)	N1B—C11B—C12B—C13B	−37.13 (17)
C8B—C7C—C1B—C2B	−177.0 (2)	C10B—C11B—C12B—C13B	77.39 (18)
C8B—C7C—C1B—C6B	0.8 (2)	C11B—C12B—C13B—C14B	10.55 (19)
C8B—C7C—C1B—S1B	−179.5 (7)	C11B—N1B—C14B—C15B	75.95 (17)
C8B—S1B—C1B—C2B	−177.82 (15)	C11B—N1B—C14B—C13B	−44.38 (16)
C8B—S1B—C1B—C6B	0.64 (11)	C12B—C13B—C14B—N1B	20.20 (18)
C6B—C1B—C2B—C3B	−1.2 (2)	C12B—C13B—C14B—C15B	−96.11 (17)
C7C—C1B—C2B—C3B	176.3 (2)	C10B—C9B—C15B—C14B	9.9 (2)
S1B—C1B—C2B—C3B	177.17 (13)	C8B—C9B—C15B—C14B	−169.50 (13)
C1B—C2B—C3B—C4B	1.1 (3)	N1B—C14B—C15B—C9B	−47.76 (19)
C2B—C3B—C4B—C5B	−0.6 (3)	C13B—C14B—C15B—C9B	65.68 (19)
C3B—C4B—C5B—C6B	0.2 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
X—X···X$^{\text{i}}$	0	0	0	0
N1*A*—H1*A*2···O2*A*	0.92	1.75	2.664 (2)	177
N1*A*—H1*A*1···O1*B*$^{\text{ii}}$	0.92	1.85	2.7550 (18)	168
N1*B*—H1*B*2···O1*A*$^{\text{iii}}$	0.92	1.83	2.7346 (19)	169
N1*B*—H1*B*1···O2*B*$^{\text{iii}}$	0.92	1.75	2.663 (2)	173

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