organic compounds

π-Facial selectivities of diastereotopic ketones: p-bromobenzoates of 4-hetero-1-decalinols

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The crystal structures of the p-bromobenzoates of cis-4-oxa-1-decalinyl ($C_{16}H_{19}BrO_3$), trans-4-oxa-1-decalinyl ($C_{16}H_{19}BrO_3$), N-benzyl-cis-4-aza-1-decalinyl ($C_{23}H_{26}BrNO_2$), N-benzyl-trans-4-aza-1-decalinyl ($C_{23}H_{26}BrNO_2$) and trans-4-thia-1-decalinyl ($C_{16}H_{19}BrO_2S$) (decalin is perhydronaphthalene) have been determined as part of a study directed at predicting and interpreting the π-facial selectivities of diastereotopic ketones in reactions with nucleophiles. All five structures are composed of molecules that are separated by normal van der Waals distances. In all five structures, the heterocyclic and cyclohexyl rings adopt chair conformations, and the p-bromobenzoate groups are planar.

Comment

In studies directed at the evaluation of the cation complexation model (Jeyaraj *et al.*, 1997; Jeyaraj & Yadav, 1997; Yadav & Jeyaraj, 1998; Yadav *et al.*, 1999, 2000) in order to predict and interpret the π-facial selectivities of diastereotopic ketones in reactions with nucleophiles, we have determined the experimental selectivities of cis-4-oxa-1-decalone, (I), trans-4-oxa-1-decalone, (II), cis-N-benzyl-4-aza-1-decalone, (III), trans-N-benzyl-4-aza-1-decalone, (IV), and trans-4-thia-1-decalone, (V), from reductions with LiAlH₄ in Et₂O at 267–273 K, NaBH₄ in MeOH at 267–273 K, and NaCNBH₃ in aqueous MeOH at 297 K and pH 3–4. In each case, a mixture of two isomers was produced; the results of the study dealing with the ratios of the products formed will be reported elsewhere (Yadav *et al.*, 2001). The isomers were separated by careful chromatography over silica gel and the relative stereostructure of the major isomer was determined by single-crystal X-ray diffraction. The alcohols cis-4-oxa-1-decalinol, (VI), trans-4-oxa-1-decalinol, (VIII), N-benzyl-cis-4-aza-1-decalinol, (X), and N-benzyl-trans-4-aza-1-decalone, (XII), are liquids at room temperature. trans-4-Thia-1-decalinol,

(XIV), produced crystals of very poor quality. All of the alcohols were therefore converted to their p-bromobenzoate esters, *i.e.* cis-4-oxa-1-decalinyl p-bromobenzoate, (XVI), trans-4-oxa-1-decalinyl p-bromobenzoate, (XVII), N-benzyl-cis-4-aza-1-decalinyl p-bromobenzoate, (XVIII), N-benzyl-trans-4-aza-1-decalinyl p-bromobenzoate, (XIX), and trans-4-thia-1-decalinyl p-bromobenzoate, (XX), and the structures of these five compounds are presented in this paper.
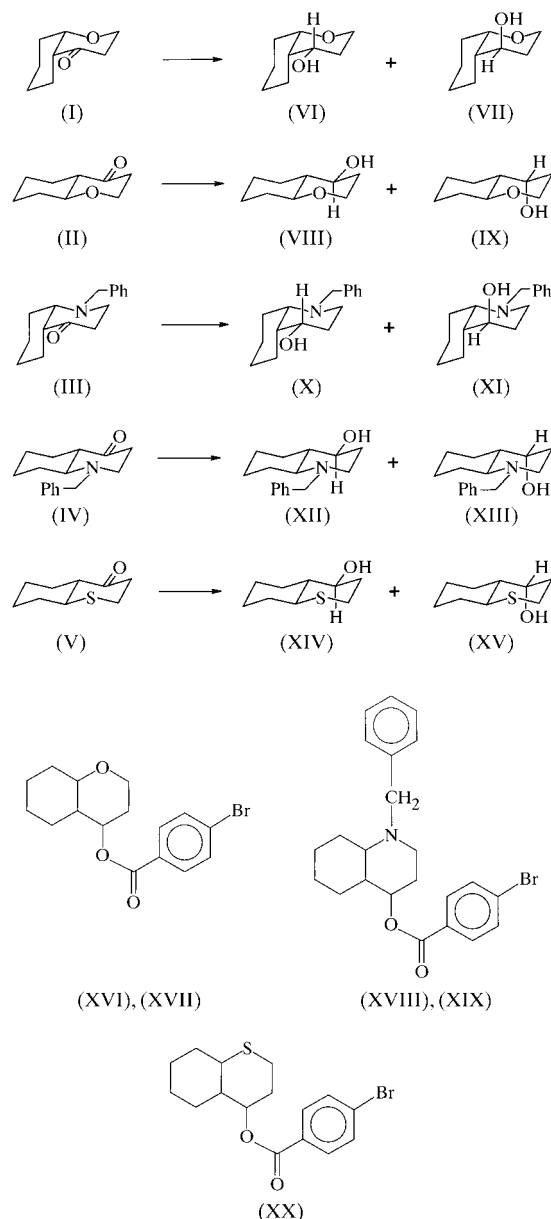
The structures of compounds (XVI)–(XX) (Figs. 1–5) are composed of independent molecules which are separated by normal van der Waals distances. The heterocyclic rings in all of the structures exhibit chair conformations, with torsion angles in the ranges ±53.3 (10)–63.5 (9), ±54.6 (6)–60.5 (6), ±53.1 (6)–64.8 (5), ±50.7 (3)–61.9 (3) and ±56.2 (4)–64.7 (5)° for (XVI)–(XX), respectively. The heterocyclic ring in (XIX) exhibits the highest degree of flattening amongst all the structures, having three torsion angles of −50.7 (3), 52.5 (4)

and 52.7 (3)°. The cyclohexyl rings in all five of the structures also exhibit chair conformations, with torsion angles in the ranges ±52.4 (11)–57.4 (11), ±54.5 (8)–55.4 (8), ±55.6 (7)–58.3 (6), ±53.0 (5)–58.1 (3) and ±54.7 (5)–58.0 (6)° for (XVI)–(XX), respectively.

The *p*-bromobenzoate groups in (XVI) and (XX) are essentially planar, with maximum deviations of 0.074 (7) and 0.066 (8) Å, respectively, from the least-squares planes of the phenyl ring C atoms. The O atoms of the corresponding groups in (XVII) and (XVIII) lie on opposite sides of the least-squares planes of the phenyl rings at distances of 0.179 (9) and 0.205 (9) Å in the former, and 0.229 (9) and 0.203 (9) Å in the latter. On the other hand, in (XIX), the carbonyl O atom lies 0.117 (7) Å out of the least-squares plane of the phenyl ring; the rest of the atoms of the *p*-bromo-benzoate group lie in this plane, with a maximum deviation of 0.043 (6) Å. These small but significant differences are also supported by a comparison of the angles between the mean planes of the phenyl rings and the carboxylate atoms, *e.g.* the

mean planes between phenyl ring C11–C16 and atoms O2, O3, C10 and C11 in (XVI) are inclined at 3.34 (14)°. The corresponding angles in (XVII)–(XX) are 9.9 (3), 11.2 (4), 2.8 (3) and 2.1 (4)°, respectively.

The conformational differences in the five structures are evident from a comparison of torsion angles. For example, the angle C2—C3—O2—C10 in (XVI) is −154.8 (9)°. The corresponding angles in the structures of (XVII)–(XX) are 113.6 (5), 149.8 (5), 97.8 (3) and −82.3 (5)°, respectively. The bond distances and angles in the five structures are normal and agree well with expected values (Orpen *et al.*, 1994).

The crystal of (XX) chosen for analysis in this study belongs to a non-centrosymmetric space group, although the starting
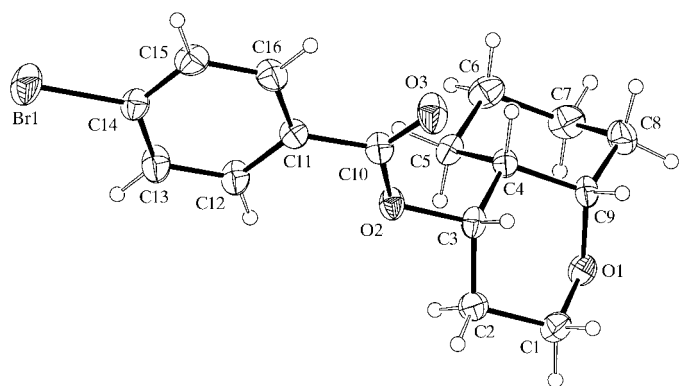

Figure 1
The molecular structure of (XVI) with the atom-numbering scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.
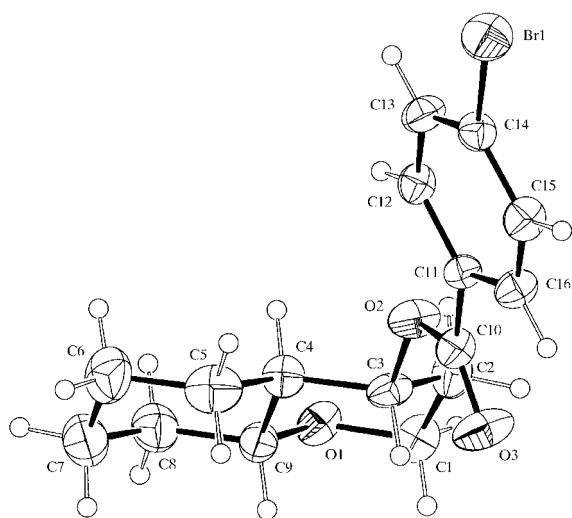

Figure 3
The molecular structure of (XVIII) with the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Figure 2
The molecular structure of (XVII) with the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Figure 4
The molecular structure of (XIX) with the atom-numbering scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.
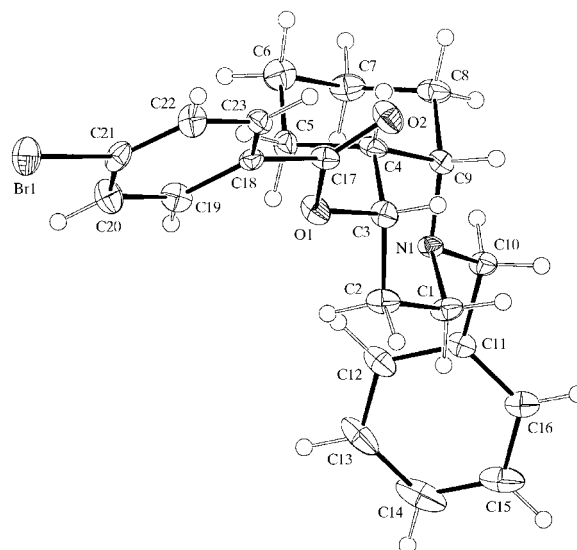
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Figure 5
The molecular structure of (XX) with the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.
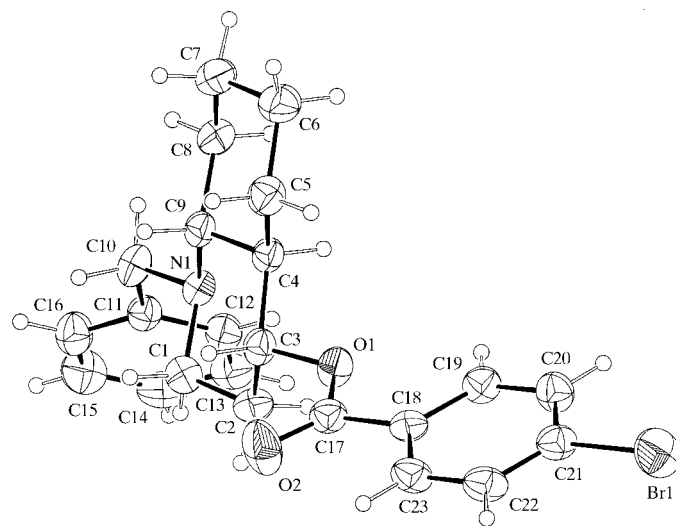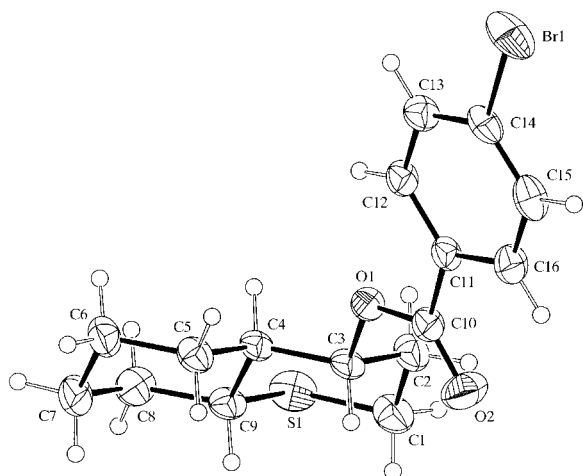
material was a racemic mixture. An absolute structure was established by the Flack (1983) method; the Flack parameter for the inverted structure was 1.04 (4).

Experimental

cis-Ketone (I) was synthesized using the method of Kozikowski & Li (1985). However, copper(II) trifluoromethanesulfonate was used instead of zinc(II) trifluoromethanesulfonate for the closure of the heterocyclic ring, as the latter was found ineffective in this case. The product was isomerized to a mixture of *cis*-(I) and *trans*-(II) by reflux in EtOH–Et$_3$N. *trans*-Ketone (II) was separated from this mixture by chromatography over silica gel. *trans*-Ketone (IV) was prepared according to the literature protocol of Traverso (1955) for the formation of *trans*-(V) and isomerized to a mixture of *cis*-(III) (minor) and *trans*-(IV) (major) by treatment with 1,8-diazabi-cyclo[5.4.0]undec-6-ene (DBU) in CH$_2$Cl$_2$ at 297 K. The *cis*-(III) compound was isolated from this mixture by chromatographic methods. *trans*-Ketone (V) was fully resistant to isomerization (DBU–CH$_2$Cl$_2$, 297 K) to its *cis*-analogue. All the reductions were carried out following standard procedures. Alcohols (VI), (VIII), (X), (XII) and (XIV) were esterified with *p*-bromobenzoyl chloride (*p*-BrC$_6$H$_4$COCl) following standard methods, and the resulting benzoates, (XVI)–(XX), were recrystallized from benzene, EtOAc/petroleum ether, EtOAc, petroleum ether and C$_6$H$_5$Cl/petroleum ether, respectively.

Compound (XVI)

Crystal data

C$_{16}$H$_{19}$BrO$_3$	$D_x = 1.500$ Mg m^{-3}
$M_r = 339.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 12
$a = 10.906$ (2) Å	reflections
$b = 8.052$ (4) Å	$\theta = 10–20°$
$c = 17.195$ (3) Å	$\mu = 2.74$ mm^{-1}
$\beta = 95.98$ (2)°	$T = 170$ (2) K
$V = 1501.8$ (8) Å^3	Prismatic, colourless
$Z = 4$	$0.48 \times 0.42 \times 0.33$ mm

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.08$
$\omega/2\theta$ scans	$\theta_{max} = 25°$
Absorption correction: empirical	$h = 0 \rightarrow 12$
via ψ scan (3 reflections; North *et al.*, 1968)	$k = 0 \rightarrow 9$
	$l = -20 \rightarrow 20$
$T_{min} = 0.28$, $T_{max} = 0.41$	3 standard reflections
2646 measured reflections	every 200 reflections
2646 independent reflections	intensity decay: <1.1%
693 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2)]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.109$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
$S = 0.94$	$\Delta\rho_{min} = -0.77$ e Å^{-3}
2646 reflections	Extinction correction: *SHELXL*97
182 parameters	(Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.00061 (16)

Table 1
Selected geometric parameters (Å, °) for (XVI).

Br1—C14	1.895 (8)	O2—C10	1.324 (9)
O1—C1	1.421 (9)	O2—C3	1.458 (7)
O1—C9	1.439 (10)	O3—C10	1.228 (9)
C1—O1—C9	111.6 (7)	C10—O2—C3	117.9 (7)

Compound (XVII)

Crystal data

C$_{16}$H$_{19}$BrO$_3$	$Z = 2$
$M_r = 339.22$	$D_x = 1.485$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.643$ (2) Å	Cell parameters from 25
$b = 10.679$ (2) Å	reflections
$c = 8.772$ (2) Å	$\theta = 10–15°$
$\alpha = 96.32$ (2)°	$\mu = 2.71$ mm^{-1}
$\beta = 111.32$ (2)°	$T = 293$ (2) K
$\gamma = 110.49$ (2)°	Plate, colourless
$V = 758.5$ (3) Å^3	$0.60 \times 0.40 \times 0.15$ mm

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.03$
$\omega/2\theta$ scans	$\theta_{max} = 25°$
Absorption correction: empirical	$h = 0 \rightarrow 11$
via ψ scan (3 reflections; North *et al.*, 1968)	$k = -12 \rightarrow 11$
	$l = -10 \rightarrow 9$
$T_{min} = 0.28$, $T_{max} = 0.67$	3 standard reflections
2702 measured reflections	every 200 reflections
2702 independent reflections	intensity decay: <0.8%
1169 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{max} < 0.001$
2702 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
181 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (XVII).

Br1—C14	1.880 (5)	O2—C10	1.344 (6)
O1—C9	1.410 (6)	O2—C3	1.456 (6)
O1—C1	1.407 (6)	O3—C10	1.200 (6)
C9—O1—C1	111.9 (4)	C10—O2—C3	119.2 (4)

Compound (XVIII)

Crystal data

$C_{23}H_{26}BrNO_2$	$Z = 2$
$M_r = 428.36$	$D_x = 1.409$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.914$ (3) Å	Cell parameters from 12
$b = 13.144$ (3) Å	reflections
$c = 6.922$ (2) Å	$\theta = 10–15°$
$\alpha = 96.06$ (2)°	$\mu = 2.05$ mm^{-1}
$\beta = 106.22$ (2)°	$T = 170$ (2) K
$\gamma = 100.42$ (3)°	Prismatic, colourless
$V = 1009.6$ (5) Å^3	$0.60 \times 0.40 \times 0.32$ mm

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.09$
$\omega/2\theta$ scans	$\theta_{max} = 25°$
Absorption correction: empirical	$h = 0 \rightarrow 14$
via ψ scan (3 reflections; North *et al.*, 1968)	$k = -15 \rightarrow 15$
	$l = -8 \rightarrow 7$
$T_{min} = 0.39$, $T_{max} = 0.52$	3 standard reflections
3574 measured reflections	every 200 reflections
3574 independent reflections	intensity decay: <1.1%
1407 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.018P)^2]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{max} < 0.001$
3574 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
244 parameters	$\Delta\rho_{min} = -0.76$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (XVIII).

Br1—C21	1.894 (5)	N1—C1	1.457 (6)
O1—C17	1.348 (6)	N1—C10	1.464 (6)
O1—C3	1.457 (6)	N1—C9	1.467 (6)
O2—C17	1.207 (6)		
C17—O1—C3	117.3 (4)	C1—N1—C9	110.1 (4)
C1—N1—C10	109.5 (4)	C10—N1—C9	113.9 (4)

Compound (XIX)

Crystal data

$C_{23}H_{26}BrNO_2$	$Z = 2$
$M_r = 428.36$	$D_x = 1.339$ Mg m^{-3}
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 9.561$ (2) Å	Cell parameters from 25
$b = 9.822$ (2) Å	reflections
$c = 13.202$ (3) Å	$\theta = 20–25°$
$\alpha = 78.34$ (2)°	$\mu = 2.76$ mm^{-1}
$\beta = 78.21$ (2)°	$T = 293$ (2) K
$\gamma = 61.92$ (3)°	Plate, colourless
$V = 1062.7$ (4) Å^3	$0.52 \times 0.40 \times 0.17$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	2585 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.02$
Absorption correction: empirical	$\theta_{max} = 68°$
via ψ scan (3 reflections; North *et al.*, 1968)	$h = 0 \rightarrow 11$
	$k = -9 \rightarrow 11$
$T_{min} = 0.31$, $T_{max} = 0.63$	$l = -15 \rightarrow 15$
3862 measured reflections	3 standard reflections
3862 independent reflections	every 200 reflections
	intensity decay: <2.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 0.43P]$
$wR(F^2) = 0.135$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3862 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
245 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	(Sheldrick, 1997)
	Extinction coefficient: 0.0052 (5)

Table 4
Selected geometric parameters (Å, °) for (XIX).

Br1—C21	1.891 (3)	N1—C1	1.456 (4)
O1—C17	1.320 (4)	N1—C9	1.467 (4)
O1—C3	1.459 (3)	N1—C10	1.473 (4)
O2—C17	1.200 (4)		
C17—O1—C3	119.5 (2)	C1—N1—C10	108.9 (3)
C1—N1—C9	110.5 (2)	C9—N1—C10	112.5 (2)

Compound (XX)

Crystal data

$C_{16}H_{19}BrO_2S$	$D_x = 1.491$ Mg m^{-3}
$M_r = 355.28$	Cu $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25
$a = 8.886$ (2) Å	reflections
$b = 5.3714$ (9) Å	$\theta = 15–25°$
$c = 16.599$ (3) Å	$\mu = 4.76$ mm^{-1}
$\beta = 92.70$ (2)°	$T = 293$ (2) K
$V = 791.4$ (3) Å^3	Prismatic, colourless
$Z = 2$	$0.40 \times 0.25 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	2563 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.014$
Absorption correction: empirical	$\theta_{max} = 68°$
via ψ scan (3 reflections; North *et al.*, 1968)	$h = 0 \rightarrow 10$
	$k = -6 \rightarrow 5$
$T_{min} = 0.28$, $T_{max} = 0.39$	$l = -19 \rightarrow 19$
2984 measured reflections	3 standard reflections
1617 independent reflections (plus 1180 Friedel-related reflections)	every 200 reflections
	intensity decay: <0.1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
$wR(F^2) = 0.133$	$\Delta\rho_{min} = -0.52$ e Å^{-3}
$S = 1.04$	Extinction correction: *SHELXL*97
2797 reflections	(Sheldrick, 1997)
182 parameters	Extinction coefficient: 0.0237 (16)
H-atom parameters constrained	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2$	Flack parameter = −0.05 (3)
$+ 0.65P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 5
Selected geometric parameters (Å, °) for (XX).

Br1—C14	1.897 (4)	O1—C10	1.324 (6)
S1—C1	1.790 (6)	O1—C3	1.462 (4)
S1—C9	1.816 (5)	O2—C10	1.193 (6)
C1—S1—C9	97.6 (2)	C10—O1—C3	118.3 (4)

organic compounds

In all five structures, most of the H atoms were located from difference maps. All H atoms were placed at geometrically idealized positions (C—H = 0.93–1.00 Å) and refined utilizing riding models.

For compounds (XVI), (XVII) and (XVIII), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*. For compounds (XIX) and (XX), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*. For all five compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1192). Services for accessing these data are described at the back of the journal.

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