Self-assemblies of chiral *p*-haloaryl sulfoxides through C–H···O short contacts and halogen involving interactions

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Single crystal X-ray structure determination of four crystals of alkyl or aryl *p*-haloaryl sulfoxides is reported. Intramolecular short contacts between the *ortho*-hydrogen of the aryl ring and the oxygen of the sulfinyl group were found to determine the conformations of the sulfoxides. On the other hand, in the absence of classical hydrogen bond donors, crystal packing arrangements are the results of intermolecular aryl hydrogen–oxygen short contacts and of interactions involving halogen atoms. From a comparison of the structures of the investigated sulfoxides with other literature data, the crystal packings of these types of compound appear to derive from a complex balance among different interactions.

Introduction

Enantiopure sulfoxides are relevant compounds in organic chemistry, because they can be used as starting materials in the synthesis of several natural and biologically active compounds.[1] The first successful method of synthesis of chiral sulfoxides was reported by Andersen *et al.*[2a] and Mislow *et al.*[2b] The determination of the absolute configuration of a sulfur stereogenic centre by X-ray analysis was achieved firstly for menthyl *p*-iodophenylsulfinate[3a] and for a derivative of iberin, a naturally occurring sulfoxide.[3b] The stereochemical course of the Andersen–Mislow procedure was established after a long and complex work, based upon ORD and CD spectra,[2] and by a sequence of stereodefined reactions[3c] connecting sulfoxides of unknown configuration with menthyl *p*-iodophenylsulfinate or with iberin. Only later,[4] the absolute configuration of (+)-methyl *p*-tolyl sulfoxide, a chiral compound that was synthesised with the Andersen–Mislow procedure, was established by X-ray analysis.

Since then, several chiral non-racemic sulfoxides have been synthesised and many assignments of configuration by X-ray analysis have been performed, especially when other oxygen or nitrogen atoms were present, due to their aptitude to build stable crystal structures with the aid of strong hydrogen bonds. In the absence of these atoms, crystals suitable for an X-ray experiment were not easily obtained. Expedients were sometimes used to overcome this drawback.[5]

In our work on the synthesis of enantiopure sulfoxides,[6] we have reported recently the enantioselective synthesis of β-ketosulfoxides and β-hydroxysulfoxides.[7] The absolute configurations of (*R*)-*o*-bromophenyl phenacyl sulfoxide and of (*R*,*R*)-1-phenyl-2-(*p*-bromophenylsulfinyl)ethanol were determined by X-ray diffraction experiments.[7] In the former compound, the main interactions are due to the C–H···O hydrogen bonds between the methylene and the sulfinyl oxygen and between an aryl hydrogen and the carbonyl oxygen.[7] In the latter compound, the presence of the hydroxyl group built the three-dimensional framework with the aid of strong O–H···O hydrogen bonds, with a further contribution due to the C–H···O hydrogen bonds.[7]

In view of the interesting results mentioned above, we decided to extend our X-ray analysis to other sulfoxides not containing carbonyl or hydroxyl groups. In this paper we focus our attention on enantiopure alkyl or aryl *p*-halophenyl sulfoxides[6] and in their self-assemblies through C–H···O short contacts[8a–e] and halogen involving interactions.[8f]

Experimental

Materials

The crystals of *p*-bromophenyl methyl sulfoxide **1**, *p*-bromophenyl isopropyl sulfoxide **2**, *p*-bromophenyl phenyl sulfoxide **3** and chloromethyl *p*-chlorophenyl sulfoxide **4** were found to be suitable for the X-ray analysis.

(*R*)-*p*-Bromophenyl methyl sulfoxide **1**[9a] was synthesised by a cumene hydroperoxide oxidation in the presence of a complex prepared from titanium isopropoxide and diethyl (*R*,*R*)-tartrate. (*R*)-*p*-Bromophenyl isopropyl sulfoxide **2**[9b] and *p*-bromophenyl phenyl sulfoxide **3**[10] were prepared by reacting (1*R*,2*S*,5*R*)-menthyl (*S*)-*p*-bromobenzenesulfinate with isopropylmagnesium chloride and phenylmagnesium bromide, respectively, according to our procedure.[9b] *p*-Bromophenyl phenyl sulfoxide **3**, mp 93–94 °C (*n*-hexane), $[\alpha]_D^{25} = -3.3$ ($c = 1$, $CHCl_3$), was obtained in a 93% yield using this

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procedure. The enantiomeric purity was determined by chiral HPLC (Chiralcel OB-H column, eluent hexane–isopropanol 70 : 30) and the (*R*)-configuration of compound **3** could be deduced from the stereochemical course of the process.[9b] Chloromethyl *p*-chlorophenyl sulfoxide **4**[11] was obtained in a 69% yield by an enantioselective oxidation of the commercially available chloromethyl *p*-chlorophenyl sulfide with *tert*-butyl hydroperoxide in the presence of a catalytic amount of a complex prepared from titanium isopropoxide, (*R*)-1,1′-bi-2-naphthol and water, according to our previously reported procedure.[12] The enantiomeric purity was measured by chiral HPLC (Chiralcel OB-H column, eluent hexane–isopropanol 70 : 30) and was found to be 59%. The product was recrystallised three times to obtain the enantiomerically pure compound: chloromethyl *p*-chlorophenyl sulfoxide **4**, mp 102–104 °C (*n*-hexane), $[\alpha]_D^{25} = +162.5$ ($c = 1.7$, $CHCl_3$).

X-Ray crystallography

X-Ray data were collected at 293 K using a Nonius Kappa CCD area detector diffractometer, with Mo-Kα radiation ($\lambda = 0.71073$ Å), in ω and ϕ scan modes. Unit cell parameters are reported in Table 1. Data were corrected for Lorentz, polarisation and absorption effects.[13] The structures were solved by the direct method procedure of SIR97,[14] and refined by a full-matrix-least-square (FMLS) technique based on F^2 (SHELXL-97).[15] In all the refinements, the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were localised through difference Fourier maps and refined isotropically, with the exception of *p*-bromophenyl isopropyl sulfoxide **2**, where hydrogen atoms were placed in idealised positions riding on their attached atoms ($C–H_{Ar}$ 0.93 Å, $C–H_{Me}$ 0.96 Å, $U_{iso}(H) = 1.2U_{iso}(C)$). Geometrical calculations were performed using PARST.[16]

CCDC reference numbers 261489 (**1**), 261491 (**2**), 261492 (**3**) and 261493 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607545b. Data collection and refinement are reported in Table 1. The asymmetric units of sulfoxides **1–4** are depicted in Fig. 1.

Results and discussion

The X-ray analysis confirmed the configurations of compounds **1–3** that we had reported previously.[9] In particular, *p*-bromophenyl methyl sulfoxide **1** has the (*R*)-configuration (Flack parameter[17] 0.004(10)). *p*-Bromophenyl isopropyl sulfoxide **2** has the (*R*)-configuration (Flack parameter 0.01(2)). *p*-Bromophenyl phenyl sulfoxide **3** has the (*R*)-configuration (Flack parameter 0.02(1)), as discussed above. Chloromethyl *p*-chlorophenyl sulfoxide **4** has the (*S*)-configuration (Flack parameter −0.06(9)). Selected bond distances and angles are reported in Table 2. In all the structures, the S=O, C_{Ar}–S and C_{Me}–S bond distances were found to be similar to the reference values of 1.497, 1.790 and 1.809 Å, respectively.[18]

Intramolecular interactions

The conformations of the structures are determined by intramolecular short contacts between an *ortho*-hydrogen of the phenyl ring and the oxygen of the sulfinyl group. These attractive interactions have distances less than the sum of O···H van der Waals radii of 2.72 Å and maintain the sulfinyl and the phenyl groups roughly in the same plane. In Table 3, torsion angles around $S–C_{Ar}$ bonds and O···H intramolecular interaction distances are reported.

Table 1 Crystal data and structure refinement for **1**, **2**, **3** and **4**

	1	**2**	**3**	**4**
Empirical formula	C_7H_7BrOS	$C_9H_{11}BrOS$	$C_{12}H_9BrOS$	$C_7H_6Cl_2OS$
Formula weight	219.10	247.15	281.16	209.08
Temperature, wavelength	293(2) K, 0.71073 Å	293(2) K, 0.71073 Å	293(2) K, 0.71073 Å	293(2) K, 0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	$a = 8.9398(3)$ Å	$a = 9.4483(4)$ Å	$a = 6.1391(2)$ Å	$a = 4.6262(1)$ Å
	$b = 9.4924(3)$ Å	$b = 10.3257(5)$ Å	$b = 7.7239(2)$ Å	$b = 9.2833(3)$ Å
	$c = 10.0886(3)$ Å	$c = 10.9739(6)$ Å	$c = 24.0213(8)$ Å	$c = 20.7170(8)$ Å
Volume	856.12(5) Å^3	1070.62(9) Å^3	1139.04(6) Å^3	889.72(5) Å^3
Z, Calculated density	4, 1.700 Mg m^{-3}	4, 1.533 Mg m^{-3}	4, 1.640 Mg m^{-3}	4, 1.561 Mg m^{-3}
Absorption coefficient	4.976 mm^{-1}	3.988 mm^{-1}	3.760 mm^{-1}	0.901 mm^{-1}
$F(000)$	432	496	560	424
Crystal size (mm)	0.24 × 0.23 × 0.20	0.45 × 0.12 × 0.10	0.48 × 0.24 × 0.24	0.48 × 0.43 × 0.19
θ range for data collection	4.58° to 29.95°	3.95° to 27.54°	3.67° to 30.08°	3.93° to 30.07°
Limiting indices	$-12 \leq h \leq 12$	$-10 \leq h \leq 12$	$-8 \leq h \leq 8$	$-6 \leq h \leq 6$
	$-11 \leq k \leq 13$	$-13 \leq k \leq 13$	$-10 \leq k \leq 10$	$-12 \leq k \leq 13$
	$-13 \leq l \leq 14$	$-14 \leq l \leq 14$	$-33 \leq l \leq 33$	$-28 \leq l \leq 29$
Refl. collected/unique	10 420/2449 [$R_{int} = 0.036$]	12 038/2446 [$R_{int} = 0.046$]	6909/2994 [$R_{int} = 0.055$]	9817/2597 [$R_{int} = 0.031$]
Max. and min. transmission	0.4361 and 0.3814	0.6912 and 0.2670	0.4656 and 0.2655	0.8474 and 0.6715
Refinement method	FMLS on F^2	FMLS on F^2	FMLS on F^2	FMLS on F^2
Data/restraints/parameters	2088/0/119	1572/0/108	2391/0/172	2083/0/124
Goodness-of-fit on F^2	1.062	1.056	1.058	1.038
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0319$, $wR_2 = 0.0777$	$R_1 = 0.0561$, $wR_2 = 0.1546$	$R_1 = 0.0411$, $wR_2 = 0.0964$	$R_1 = 0.0343$, $wR_2 = 0.0761$
R indices (all data)	$R_1 = 0.0400$, $wR_2 = 0.0810$	$R_1 = 0.0866$, $wR_2 = 0.1720$	$R_1 = 0.0562$, $wR_2 = 0.1025$	$R_1 = 0.0510$, $wR_2 = 0.0836$
Flack parameter	0.004(10)	0.01(2)	0.02(1)	−0.06(9)
Largest diff. peak/hole	0.339/−0.657 e Å^{-3}	0.574/−0.424 e Å^{-3}	0.321/−0.564 e Å^{-3}	0.252/−0.259 e Å^{-3}

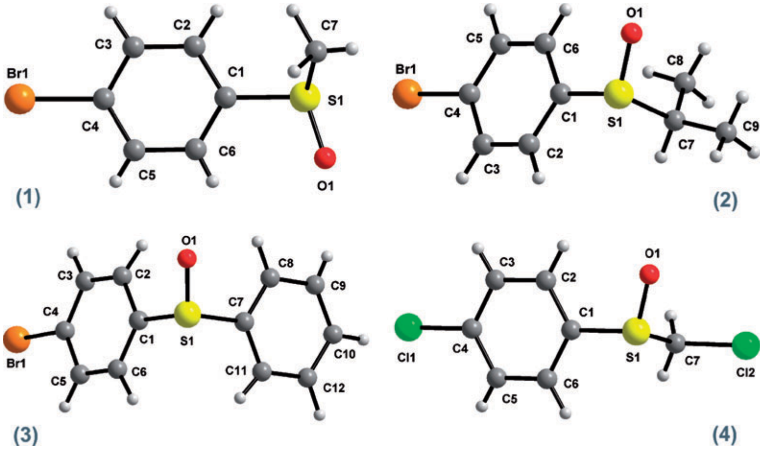


Fig. 1 View of the asymmetric units and atomic numbering schemes of (*R*)-*p*-bromophenyl methyl sulfoxide **1**, (*R*)-*p*-bromophenyl isopropyl sulfoxide **2**, (*R*)-*p*-bromophenyl phenyl sulfoxide **3** and (*S*)-chloromethyl *p*-chlorophenyl sulfoxide **4**.

The small deviations from planarity can be attributed to intramolecular steric repulsions between the isopropyl and phenyl substituents in compound **2** and between the two phenyl groups in compound **3**. In order to show if these conformations are typical for aryl sulfoxides, a search was performed on CSD structural files.[19] The selected retrieved compounds were divided into three classes: **I**, alkyl aryl sulfoxides and an aryl sulfinate;[4,20] **II**, aryl vinyl sulfoxides;[21] **III**, diaryl sulfoxides.[22]

Table 4 reports the structural data of selected simple aryl sulfoxides of class **I**. In these compounds, bulky substituents, which could affect the molecular conformations for steric reasons, are absent and sulfoxides involved in short intra- or intermolecular interactions, such as hydrogen bonds, were not considered. The data of Table 4 are in agreement with the present structural determinations showing short O···H (aromatic) interactions and coplanarity between the S=O group and the aromatic ring.

Different conformational features are present in aryl vinyl sulfoxides (Class **II**, Table 5), whose conformations are mainly determined by the tendency of the S=O bond to lie in the plane containing the $C1'{=}C2'$ double bond and its substituents rather than on the phenyl ring plane.

Diaryl sulfoxides are collected in Class **III** (Table 6).

When large substituents are not present in the *ortho*-positions of the phenyl rings, both rotations around the S–C(aryl) bonds can assume values only up to *ca.* 20°. Accordingly, the sulfinyl group is almost coplanar with both rings, which, however, undergo small rotations due to intramolecular repulsive van der Waals interactions between the aryl hydrogens. On the other hand, the presence of *ortho*-substituents[22c] gives rise to a rotation of a phenyl ring of up to *ca.* 50°, while the other aryl ring lies in the plane of the sulfinyl group. Similar effects were also found in 2-naphthyl phenyl sulfoxide and in peculiar diaryl sulfoxides containing *para*-substituted phenyls. For instance, in the 4-aminophenyl *p*-tolyl sulfoxide,[22d] the amino group is able to interact with the sulfinyl oxygen by rotating the *p*-aminophenyl group by an angle of *ca.* 80° to reach the best orientation, while the other aryl group rotates by only 10.8°.

Intermolecular interactions

The lack of classical hydrogen bond donors and the presence of sulfinyl oxygens and halogens determine crystal packing arrangements characterised by short C–H···O contacts and by intermolecular interactions involving halogens, called "halogen bonding".[23] X-Ray crystal structural data showed that these D···X–C interactions (D = electron pair donor, X = electron pair halogen acceptor) are Lewis base–Lewis acid interactions, being approximately linear and having comparable strengths with hydrogen bonds.[23] *Ab initio* calculations showed that the electronic density is anisotropically distributed around the halogen nucleus and the effective atomic radius along the C–X bond axis is smaller than that in the direction perpendicular to this axis. The linear interaction maximises the two main directional attractive contributions to the interaction

Table 2 Selected bond lengths and angles (Å, °) for **1**, **2**, **3** and **4**

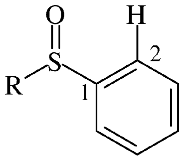
	1	**2**	**3**	**4**
C4–Br1	1.893(3)	1.885(6)	1.898(3)	—
S1=O1	1.494(3)	1.478(5)	1.483(3)	1.487(2)
C7–S1	1.786(4)	1.822(7)	1.796(3)	1.808(2)
C1–S1	1.789(3)	1.770(7)	1.799(3)	1.796(2)
Cl1–C4	—	—	—	1.740(2)
Cl2–C7	—	—	—	1.774(2)
O1–S1–C7	106.8(2)	107.6(3)	106.7(2)	105.9(1)
O1–S1–C1	106.8(1)	108.7(4)	106.9(2)	107.7(1)
C1–S1–C7	97.3(2)	98.0(4)	97.1(1)	94.6(1)

Table 3 Intramolecular H···O short interactions and torsion angles around S–C_{Ar} bonds

	$O{=}S{-}C_{Ar}{-}C_{Ar}$/°	H···O/Å
1	0.1	2.59
2	16.6	2.62
3	−13.1	2.53
	22.2[a]	2.51[a]
4	5.5	2.58

[a] Refers to $O{=}S{-}C'{-}C'$ angle and H′···O interaction.

Table 4 Structural parameters for selected aryl sulfoxides **I** retrieved from CSD files



I

REFCODE	Compound name	T1^a/°	O···H2/Å	Ref.
METOLS10	(+)-Methyl *p*-tolyl sulfoxide	5.0	2.53	4
CAPMSU	(−)-*o*-Carboxyphenyl methyl sulfoxide	−8.6	2.38	20*a*
CXPMSO	*o*-Carboxyphenyl methyl sulfoxide	11.9	2.36	20*b*
KONJIG	Methyl 2,3-difluorophenyl sulfoxide	−1.0	2.49	20*c*
KONJOM	Methyl 3,4-difluorophenyl sulfoxide	13.4	2.60	20*c*
KONJUS	Methyl 2,5-difluorophenyl sulfoxide	4.1	2.50	22*c*
KONKAZ	Methyl 3,5-difluorophenyl sulfoxide	14.8	2.57	20*c*
KONKON	Methyl 2-nitrophenyl sulfoxide	9.5	2.35	20*c*
OMOSUE	Methyl 4-nitrophenyl sulfoxide	6.6	2.49	20*d*
BPESOX	(+)-1,2-Dibromo-2-phenylethyl *p*-tolyl sulfoxide	−3.5	2.58	20*e*
QEXREQ	(*R*,*R*)-*p*-Chlorophenyl 1-chloro-2-phenylethyl sulfoxide	−16.4	2.53	20*f*
GADSUA	*meso*-Bis(phenylsulfinyl)methane	0.1	2.54	20*g*
		−6.4	2.44	
PSACAM	Phenylsulfinylacetamide	13.8	2.42	20*h*
QOQSEU	(*R*,*R*)-1,3-Bis(phenylsulfinyl)propane	−2.4	2.51	20*i*
		0.4	2.55	
SSESOX10	(*S*,*S*)-1,2-Bis(phenylsulfinyl)ethane	−17.3	2.55	20*j*
		−0.1	2.49	
ZEKBOG	(1*R*,2*S*,5*R*)-(−)-Menthyl (*S*)-4-bromobenzenesulfinate	3.6	2.48	20*k*

[a] T1 = O═S–C1–C2 torsion angle.

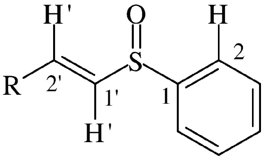
energy, electrostatics and charge transfer, and minimises the exchange repulsion along the C–X bond axis.^{24}

As far as the C–H···O intermolecular contacts are concerned, we have considered, in general, the interactions where the H···O distance is less than 2.70 Å and the C–H···O angle is greater than 120° to be significant. Although still longer than conventional hydrogen bonds, there is also a tendency for linearity in these contacts, a parameter that arises from the electrostatic components of the interaction energy. However, although the trend toward linearity is fundamental to the contact, the degree of directionality depends on the polarity of the donor. Accordingly, the weaker C–H···O bonds are less sensitive to deviations from ideal geometries than stronger H-bonds.$^{8b–d}$ In the present structures, in fact, some C–H···O interactions deviate significantly from linearity, acting, in most cases, as a mere support for halogen bonds.

Main intermolecular interactions for compounds **1–4** are collected in Table 7.

In (*R*)-*p*-bromophenyl methyl sulfoxide **1** (Fig. 2), the bromine atom forms a short contact with the oxygen atom of the adjacent molecule, Br1···O1 = 3.220(2) Å (the sum of van der Waals radii for O and Br is 3.37 Å^{18}), giving rise to infinite head-to-tail $\mathrm{Br_{Ar}}$···O chains. This halogen bonding, C4–Br1···O1, links the molecules in heterodromic chains held

Table 5 Structural parameters for selected vinyl aryl sulfoxides **II** retrieved from CSD files

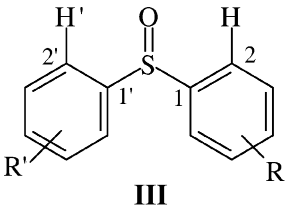


II

REFCODE	Compound name	T1^a/°	O···H2/Å	T2^a/°	O···H2′/Å	Ref.
FOPLEB	Benzyl (*E*)-3-(*p*-tolylsulfinyl)acrylate	14.2	2.64	8.2	2.31	21*a*
KUXDUC	Methyl (*E*,*S*)-3-phenyl-2-(phenylsulfinyl)prop-2-enoate	48.1	2.93	11.1	2.33	21*b*
NIMKEZ	(+)-1-*p*-Tolylsulfinyl-1-methylsulfenyl-2-phenylethene	36.1	2.82	−3.0	2.26	21*c*
PABXIZ	(*R*,*R*)-2-Phenylsulfinyl-3-hydroxy-3-phenylpropene	32.5	2.66	1.2	2.35	21*d*
RUGJEI	(*Z*)-1-Chloro-1-*p*-tolylsulfinyl-2-(*p*-bromophenyl)ethene	40.2	2.85	3.6	2.41	21*e*

[a] T1 = O═S–C1–C2 and T2 = O═S–C1′–C2′ torsion angles.

Table 6 Structural parameters for selected diaryl sulfoxides **III** retrieved from CSD files



III

REFCODE	Compound name	T1[a]/°	O···H2/Å	T2[a]/°	O···H2′/Å	Ref.
DPHSOX02	Diphenyl sulfoxide	11.4	2.50	−11.7	2.57	22*a*
YECBUB	(*S*)-4-(*N*,*N*-Dimethylamino)phenyl 4-(2-propenyl)phenyl sulfoxide	−0.2	2.45	−22.9	2.62	22*b*
		−2.6	2.50	21.1	2.61	
YECCEO	(*S*)-*p*-Tolyl 4-(*N*,*N*-dimethylamino)phenyl sulfoxide	−2.3	2.46	−24.6	2.59	22*b*
YECCAK	(*S*)-4-(2-Propyl)phenyl 4-(*N*,*N*-dimethylamino)phenyl sulfoxide	−2.1	2.46	−26.0	2.68	22*b*
DIFSAM	Dimethyl 2,2′-sulfinyldibenzoate	−5.2	2.37	45.3	2.71	22*c*
DIFSIU	2,2′-Dinitrophenyl sulfoxide	1.2	2.35	−51.9	2.80	22*c*
CULFEU	Methyl 2-(2-nitrophenylsulfinyl)benzoate	0.1	2.36	51.0	2.82	22*c*
CULFOE	Methyl 2-(2-nitrophenylsulfinyl)phenylacetate	6.6	2.32	−49.0	2.82	22*c*
MIFKIV	(−)-(*S*)-4-Aminophenyl *p*-tolyl sulfoxide	−10.8	2.31	−77.5	3.43	22*d*
AYIHEV	2-Naphthyl phenyl sulfoxide	1.2	2.51	−50.4	2.97	22*e*

[a] T1 = O=S–C1–C2 and T2 = O=S–C1′–C2′ torsion angles.

together by C–H···O hydrogen bonds. The C2–H2···O1 interaction makes up infinite folded layers down the *a* axis, while the C5–H5···O1 interaction joins the different layers, stabilising the three-dimensional framework.

In (*R*)-*p*-bromophenyl isopropyl sulfoxide **2**, the bromine atom is still involved in a short contact interaction with the sulfinyl oxygen of the adjacent molecule, Br1···O1 = 3.254(5) Å, giving rise to halogen bonding C4–Br1···O1 chains down the *b* axis (Fig. 3). The different chains are joined together by C–H···O hydrogen bonds (C2–H2···O1 = 2.467 Å and C5–H5···O1 = 2.675 Å) that stabilise the chains laterally (Fig. 4).

The pattern of the crystal packing is different for *p*-haloaryl sulfoxides **3** and **4**. (*R*)-*p*-Bromophenyl phenyl sulfoxide **3** adopts a butterfly conformation (C–S–C angle = 97.1(1)°), both aryl groups being almost coplanar with the S=O bond (Fig. 5). Halogen bonding Br···O was absent, probably due to steric reasons. Accordingly, the molecules are embedded into columnar arrays down the *a* axis by C–H···O interactions between the aryl hydrogen H6 and the oxygen atom O1, forming short C6–H6···O1 hydrogen bonds. Moreover, non-negligible C···H and Br···H interactions stabilise the framework.

In (*S*)-chloromethyl *p*-chlorophenyl sulfoxide **4**, the chlorine atoms of the chloromethyl and the *p*-chlorophenyl groups are involved in a short contact interaction, Cl1···Cl2 = 3.458(1) Å (sum of van der Waals radii = 3.50 Å), giving rise to $Cl_{Ar}\cdots Cl_{Me}$ infinite zig-zag chains (Fig. 6). This head-to-tail interaction can be classified into the reported second type class[25a,b] of Cl···Cl short contacts (one C–Cl···Cl angle of about 180° (Cl1···Cl2–C_{Me}) and the other of about 90° (C_{Ar}–Cl1···Cl2)). This seems to be consistent with a particular

Table 7 Intermolecular interactions

D–X···A	D–X/Å	D···A/Å	X···A/Å	D–X···A/°
1				
C2–H2···$O1^{I}$	0.97(4)	3.421(4)	2.47(5)	167(4)
C5–H5···$O1^{II}$	0.83(5)	3.362(4)	2.64(5)	147(4)
C4–Br1···$O1^{III}$	1.893(3)	5.082(4)	3.220(2)	167.0(4)
Symmetry: **I**: $-x, y + \frac{1}{2}, -z - \frac{1}{2}$; **II**: $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; **III**: $x, y, 1 - z$				
2				
C2–H2···$O1^{I}$	0.93	3.382(7)	2.68	133
C5–H5···$O1^{II}$	0.93	3.376(9)	2.47	165
C4–Br1···$O1^{III}$	1.889(3)	4.942(4)	3.325(5)	176.1(5)
Symmetry: **I**: $x + \frac{1}{2}, -y - \frac{1}{2}, -z + 1$; **II**: $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2} + 1$; **III**: $x, 1 + y, z$				
3				
C6–H6···$O1^{I}$	1.02(4)	3.036(4)	2.45(4)	116(3)
Symmetry: **I**: $x - 1, y, z$				
4				
C6–H6···$O1^{I}$	0.97(2)	3.391(3)	2.54(2)	148(2)
C7–H71···$O1^{I}$	0.91(3)	3.083(3)	2.46(3)	126(2)
C4–Cl1···$Cl2^{II}$	1.740(2)	4.170(2)	3.458(1)	101.5(2)
C7–Cl2···$Cl1^{III}$	1.774(2)	5.203(2)	3.458(1)	167.2(2)
Symmetry: **I**: $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2} + 1$; **II**: $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; **III**: $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$				

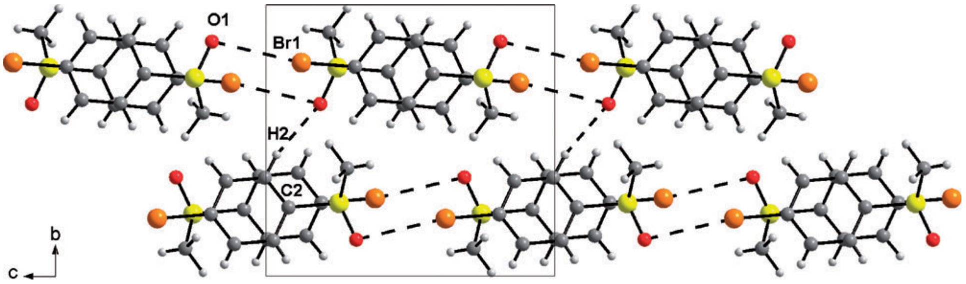


Fig. 2 (*R*)-*p*-Bromophenyl methyl sulfoxide **1**: chain of molecules linked by C4–Br1···O1 halogen bonds and C2–H2···O1 interactions.

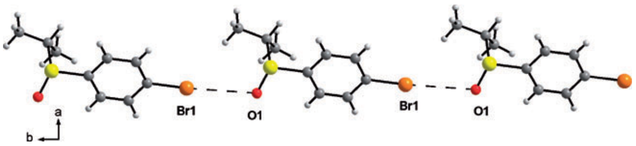


Fig. 3 (*R*)-*p*-Bromophenyl isopropyl sulfoxide **2**: chain of molecules linked by C4–Br1···O1 halogen bonds.

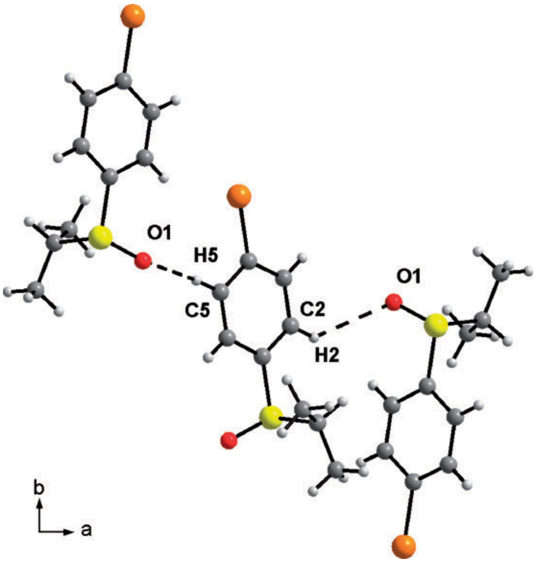


Fig. 4 (*R*)-*p*-Bromophenyl isopropyl sulfoxide **2**: C2–H2···O1 and C5–H5···O1 interactions.

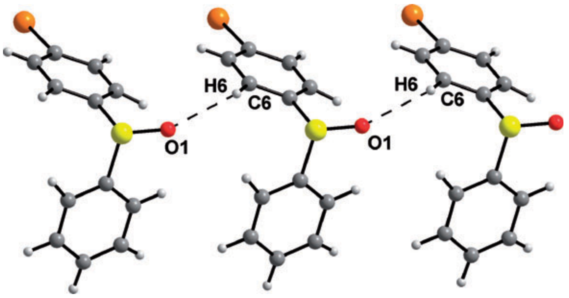


Fig. 5 (*R*)-*p*-Bromophenyl phenyl sulfoxide **3**: chain of molecules linked by C6–H6···O1 hydrogen bonds.

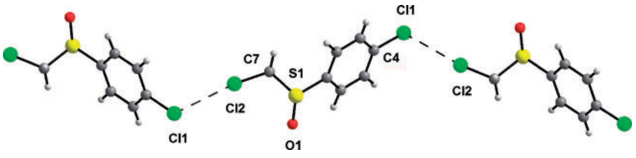


Fig. 6 (*S*)-Chloromethyl *p*-chlorophenyl sulfoxide **4**: chain of molecules linked by C7–Cl2···Cl1–C4 halogen bonds.

halogen bond, C–Cl···Cl′–C, where one Cl atom behaves as a Lewis base and the other as a Lewis acid. Nucleophiles and electrophiles interact perpendicularly or linearly according to an already reported model.[24b,25c] The zig-zag chains are embedded into the three-dimensional framework by C–H···O hydrogen bonds, the strongest ones involving the methylene hydrogen with the oxygen atom, C7–H71···O1 = 2.46(3) Å, and the aryl hydrogen with the oxygen atom, C6–H6···O1 = 2.54(3) Å (Fig. 7).

In summary, the interactions between the bromine and the sulfinyl oxygen indicate that the halogen bonding plays a crucial role in the crystal packing of molecules **1–2**. However, in spite of a large number of molecules that contain halogens as substituents on aromatic rings and belong to classes **I–III**, only two other structures form similar chains, as reported in the CSD files. In menthyl (*S*)-4-bromobenzenesulfinate[20k] the chains are built up by Br···O interactions (Br···O = 3.13 Å) (Fig. 8), while in (*R*,*R*)-*p*-chlorophenyl 1-chloro-2-phenylethyl sulfoxide[20f] the contacts involve chlorine and oxygen atoms (Cl···O = 3.18 Å) (Fig. 9).

In the crystal packings of class **III** diaryl sulfoxides, the C–H···O interactions are predominant over the halogen···O interactions, as in compound **3**. 2-Naphthyl phenyl sulfoxide[22e] and diphenyl sulfoxide[22a] are typical examples of these compounds. In 2-naphthyl phenyl sulfoxide, the chains involve interactions between an *ortho*-hydrogen of the phenyl ring and the oxygen of the sulfinyl group, while in diphenyl sulfoxide the sulfinyl oxygen interacts with a *para*-hydrogen (Fig. 10).

In other cases, the C–H···O═S interactions form chains that are interconnected by dipolar short contacts involving S═O groups, as in methyl 2,3-difluorophenyl sulfoxide (Fig. 11).[20c]

Conclusions

The analysis of the crystal patterns of the reported haloaryl sulfoxides has shown that different arrangements are present

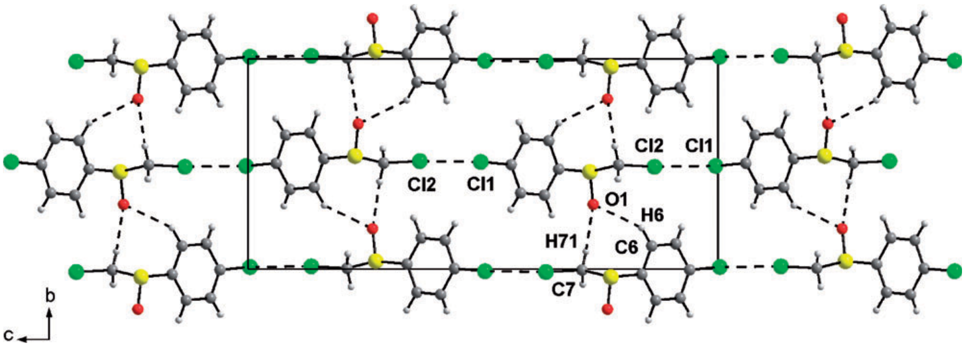


Fig. 7 Three-dimensional framework of (*S*)-chloromethyl *p*-chlorophenyl sulfoxide **4**: chain of molecules held by Cl1···Cl2 halogen bonds and C7–H71···O1 and C6–H6···O1 interactions.

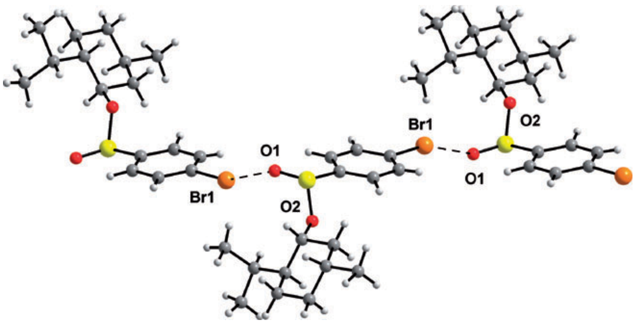


Fig. 8 Chain of molecules of menthyl (*S*)-4-bromobenzenesulfinate linked by Br1···O1 halogen bonds.

in the absence of strong hydrogen bond donors. These arrangements cannot be easily predicted. The conformations of the sulfoxides are determined by intramolecular short contacts between the *ortho*-hydrogen of the aryl ring and the oxygen of the sulfinyl group. On the other hand, the building of the three-dimensional frameworks is due to different types of interactions, largely within their respective van der Waals distances. In this respect, we have found that a short contact between the aryl hydrogens and the sulfinyl oxygens is always present, and a relevant role is played by halogen bonding. Columnar arrays of molecules are built by the interactions of the bromine atom with the sulfinyl oxygen atom, or by the head-to-tail interaction between two different chlorine atoms.

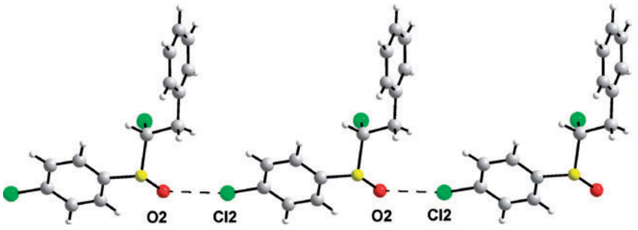


Fig. 9 Chain of molecules of (*R*,*R*)-*p*-chlorophenyl 1-chloro-2-phenylethyl sulfoxide linked by Cl2···O2 halogen bonds.

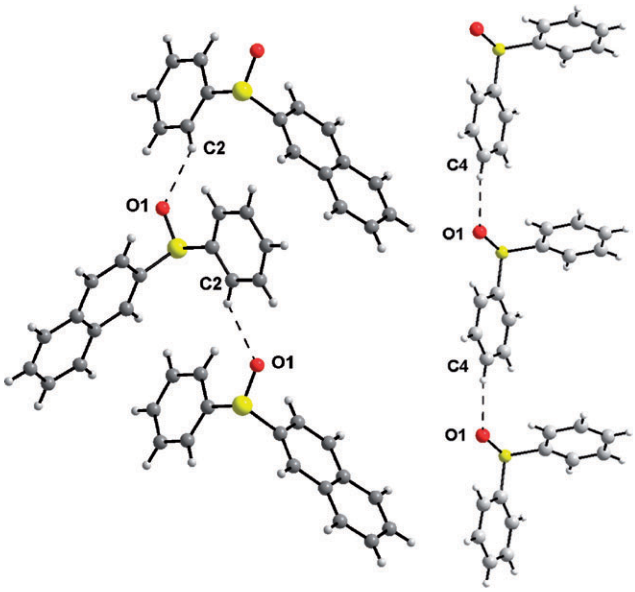


Fig. 10 Chains of molecules of 2-naphthyl phenyl sulfoxide (left) and diphenyl sulfoxide (right) linked by C–H···O hydrogen bonds.

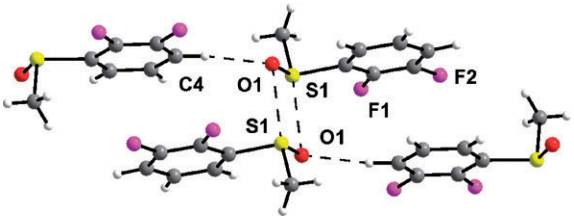


Fig. 11 Chains of molecules of methyl 2,3-difluorophenyl sulfoxide linked by C–H···O hydrogen bonds and interconnected by dipolar interactions involving S═O groups.

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