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The X-Ray Structures of Sulfoxides

Amy L. Fuller · R. Alan Aitken · Bruce M. Ryan ·
Alexandra M. Z. Slawin · J. Derek Woollins

Abstract We have structurally characterized and investigated a range of sulfoxide compounds containing aryl and alkyl substituents. Compounds **1** and **3**–**6** all crystallize in an orthorhombic space group, where compounds **2** and **7** crystallize in a monoclinic space group. The unit cell parameters of the compounds are as follows: **1** (*Fdd2*), $a = 17.653(5)$ Å, $b = 53.153(14)$ Å, and $c = 10.071(3)$ Å; **2** (*P2$_1$/c*), $a = 7.894(13)$ Å, $b = 5.653(10)$ Å, and $c = 27.02(5)$ Å, $\beta = 97.347(15)°$; **3** (*P2$_1$2$_1$2$_1$*), $a = 5.7569(6)$ Å, $b = 12.2139(12)$ Å, and $c = 17.5974(18)$ Å; **4** (*Pca2$_1$*), $a = 8.256(4)$ Å, $b = 5.470(3)$ Å, and $c = 23.995(13)$ Å; **5** (*P2$_1$2$_1$2$_1$*), $a = 5.848(4)$ Å, $b = 7.568(5)$ Å, and $c = 27.650(17)$ Å; **6** (*Pbca*), $a = 10.0569(15)$ Å, $b = 9.9403(16)$ Å, and $c = 17.843(3)$ Å; and **7** (*Pc*), $a = 13.217(4)$ Å, $b = 5.3766(14)$ Å, and $c = 8.370(2)$ Å, $\beta = 90.673(6)°$. The S=O bond distances in these compounds range from 1.489(7) to 1.515(8) Å. In all seven structures, the O(1)–S–C bond angles vary from 105.1(4) to 111.7(30)° and the C(1)–S(1)–C(11) bond angles range from 94.1(4) to 100.56(12)°. The compounds contain unique intra- and intermolecular interactions depending on the groups attached to the sulfoxide moiety. The polarity of the sulfoxide bond in these compounds allows for intramolecular S···O interactions to occur. When the sulfur is bound to alkyl groups, there tends to be a shorter S···O intermolecular distance than when the sulfur is bound to aromatic substituents. Additionally, if the sulfur is flanked by an aryl group, the S–C bond distance is slightly shorter than if flanked by an alkyl group, suggesting a possible weak O···H$_{aryl}$ intramolecular interaction, weak conjugation of the aromatic ring with the S–O bond or both. Furthermore, if the sulfur is flanked by an alkyl group, a CH$_2$ proton of S–CH$_2$–R can be properly oriented to participate in an intermolecular hydrogen bond with the sulfoxide oxygen of another molecule.
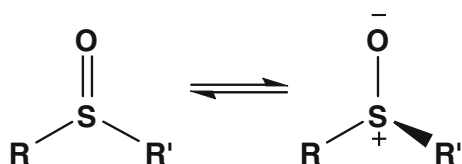
A. L. Fuller · R. A. Aitken · B. M. Ryan ·
A. M. Z. Slawin · J. D. Woollins (✉)
School of Chemistry, University of St Andrews, St Andrews,
Fife KY16 9ST, UK
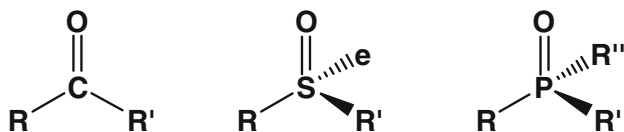e-mail: jdw3@st-and.ac.uk

Introduction

A sulfoxide is a molecule with the general formula R–S(=O)–R′, where R is an organic group. Structurally, these molecules display some interesting characteristics. There has been some debate over the nature of the S=O bond and a comparison with other well known molecules possessing the R(X=O)R′ motif (where X=C or P) illustrates why the S=O bond in sulfoxides is debated [1]. In the carbon analog R(C=O)R′, the carbon atom forms a typical p–p π bond with oxygen. In the sulfoxide or phosphine oxide (O=PR$_3$) molecules, however, it has been suggested that the oxygen contributes electrons from its unshared lone pairs from the 2p orbital to an empty 3d orbital of the central sulfur or phosphorus atom, i.e., d–p π bonding [1, 2]. However, there is some debate over the compatibility of the energy level overlap of the 3d orbital with the oxygen 2p orbital. The sulfoxide bond is probably best represented as being somewhere in between a double and a single bond, with significant ionic character [3]. This is represented by the two resonances structures in Fig. 1.

Another important characteristic of sulfoxide molecules is their ability to be chiral. Chiral centers are mainly associated with tetrahedral carbon centered compounds, however, the carbon analog of sulfoxide, R(C=O)R′, is

Fig. 1 Two resonance structures of the sulfoxide bond

Fig. 2 Geometric comparison of a carbonyl carbon, a sulfoxide and a tertiary phosphine oxide

planar. When sulfur is bound to three substituents, such as in a sulfoxide, the lone pair of electrons on the sulfur atom forces the substituents into a pyramidal geometry. Since the sulfur now has four unique arms, it is most similar to chiral tertiary phosphine oxides (O=PRR′R″) (Fig. 2). The Cahn-Ingold-Prelog priority rules are used when deciding the stereochemistry of chiral sulfoxide compounds, and the unpaired electrons are assigned as the lowest priority group [3]. Many reaction pathways have been investigated in attempts to synthesize a sulfoxide with specific chirality, including the use of inorganic, organic, and enzymatic catalysts [4–6]. Specific chirality enables sulfoxides to be used as catalysts to transfer their chirality to carbon compounds [5]. Sulfoxide chirality is also becoming increasingly important in pharmaceutical synthesis [3].

Three classes of sulfoxide compounds have been previously described as having very specific hydrogen bonding interactions that enforce particular conformations in the molecule and influence crystal packing [7]. Here, we have investigated the structural properties of three types of sulfoxides where the R groups are alkyl–alkyl, alkyl–aryl, and aryl–aryl arms using X-ray crystallography. We discuss both intra- and intermolecular interactions that influence the packing of these compounds.

Experimental

General

Crystals of dibenzyl sulfoxide **1**, benzyl 4-chlorophenyl sulfoxide **2**, benzyl 4-methylphenyl sulfoxide **3**, benzyl phenyl sulfoxide **4**, di(p-tolyl) sulfoxide **5**, benzyl ethyl sulfoxide **6**, and 4-nitrobenzyl phenyl sulfoxide **7** were analyzed by X-ray crystallography. Crystallographic data for diphenyl sulfoxide (SOPh$_2$) was already determined [8]. Compounds **1** and **5** were purchased from Aldrich.

Compounds **2**–**4**, **6**, and **7** were prepared by oxidation of the relevant sulfides with NaIO$_4$ in aq. MeOH [9–13]. All compounds were recrystallized from a CH$_2$Cl$_2$/pentane solution.
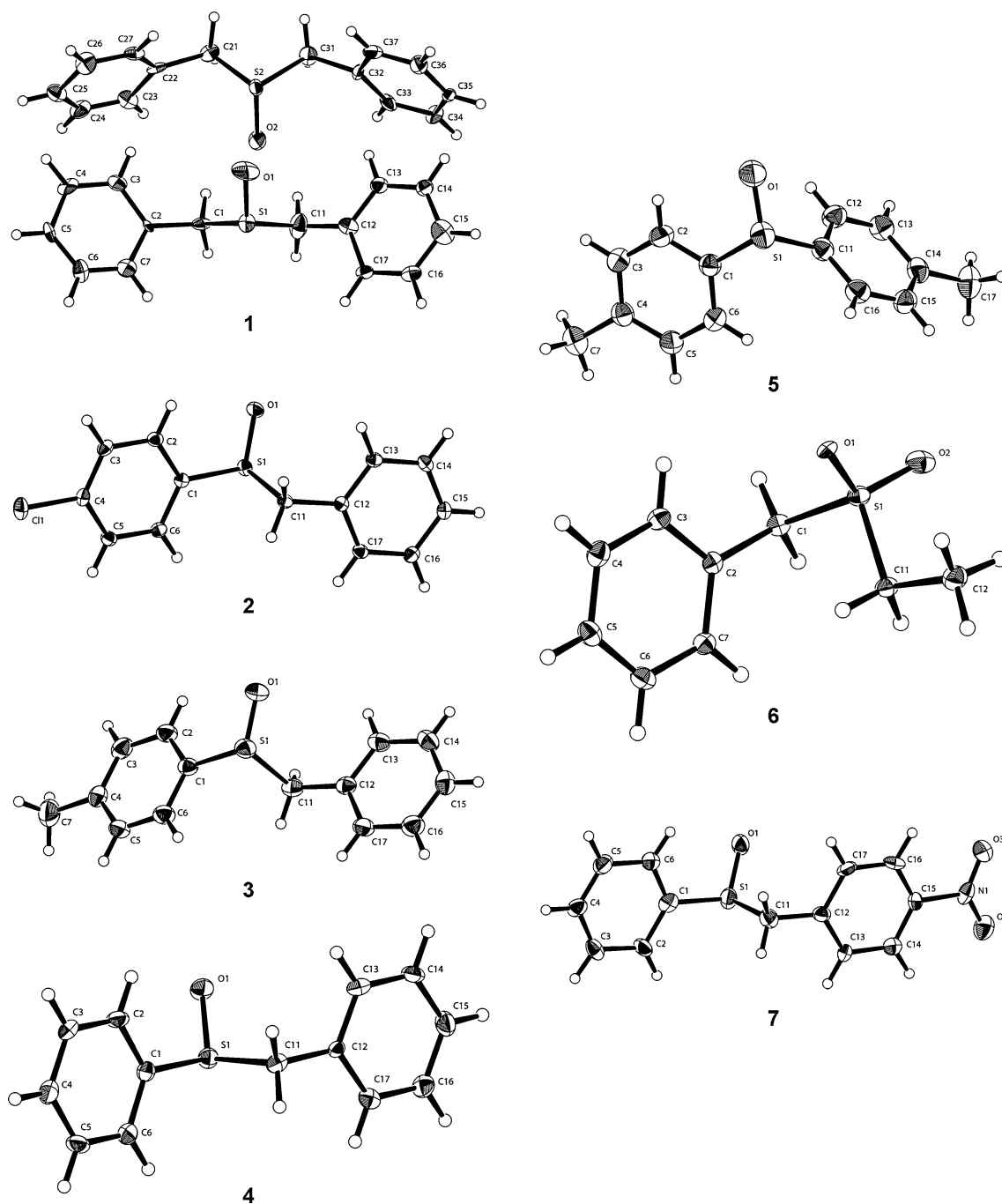
X-ray Crystallography

Table 1 lists details of data collections and refinements for **1**–**7**. Data for **1**, **2**, **3**, **5**, and **7** were collected using a Rigaku SCX-Mini diffractometer (Mercury2 CCD) and **4** was collected using the St Andrews Robotic diffractometer (Saturn724 CCD) at either 125 or 293 K with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) whilst **6** was collected using a Rigaku MM007 RA/confocal optics and Mercury CCD at 93 K [14–16]. Intensity data were collected using ω (and ϕ for **7**) steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXL) [17]. Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. Details are available from the Cambridge Crystallographic Data Centre CCDC 689268–689274.

Results and Discussion

Structural Analysis Around Sulfur

Structures from the single X-ray analysis of the sulfoxides **1**–**7** are shown in Fig. 3. Compounds **1** and **6** have two alkyl arms attached to the sulfoxide moiety, **5** has two aryl groups attached, and **2**, **3**, **4**, and **7** have one alkyl (benzyl) and one aryl arm.

The bond lengths around the sulfur atom in **1**–**7** are shown in Table 2. These compounds have similar S–O bond distances ranging from 1.489(7) to 1.515(8) Å and are consistent with the reported average sulfoxide distance of 1.497(13) Å [18]. However, the S–C bond distances seem more sensitive to the substituents and range from 1.746(12) to 1.865(10) Å. There is a very slight difference in bond length depending on the organic group attached to the sulfur, though the range is larger for the alkyl case. If the group is aromatic, the S–C distances have a tendency to be slightly shorter (ranging from 1.798(2) to 1.811(2) Å) than if the group is alkyl (ranging from 1.746(12) to 1.839(2) Å). This could be due to a very weak conjugation of the π-system in the aromatic ring with the S=O double

Fig. 3 Thermal ellipsoid plots (30% probability ellipsoids) of **1–7**

bond. The average reported S–C bond distance is 1.818(1) Å [18].

Selected bond angles around the sulfur atom are shown in Table 2. Due to the lone pair of electrons on the sulfur, it adopts a pyramidal structure. The O(1)–S–C bond angle for all seven structures vary from 105.1(4) to 108.5(4)°, with the two extremes being present in **7**. The C(1)–S(1)–C(11) bond angles are smaller, ranging from 94.1(4) to 100.56(12)°. This difference reflects the stereochemical

impact of the lone pair of electrons on the sulfur atom. In **6**, the disorder in the oxygen atoms may be responsible for the larger O(2)–S–C bond angles of 109.2(3) and 111.7(3)°. The O(1)–S(1)–O(2) bond angle in **6** is 119.1(3)°.

O···H_aryl Intramolecular Interactions

When an aryl group is attached to the sulfur, not only is there the possibility of a weak conjugation of the double
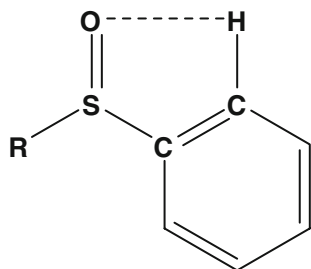
Table 1 Relevant crystal data and refinement parameters for **1**–**7**

Experimental details	1	2	3	4	5	6	7
Empirical formula	$C_{14}H_{14}OS$	$C_{13}H_{11}ClOS$	$C_{14}H_{14}OS$	$C_{13}H_{12}OS$	$C_{14}H_{14}OS$	$C_{9}H_{12}OS$	$C_{13}H_{11}O_3NS$
Formula weight	230.32	250.74	230.32	216.30	230.32	168.25	261.29
Temperature (°C)	−148(1)	−148(1)	20(1)	−148(1)	20(1)	−180(1)	−148(1)
Crystal color, habit	Colorless, platelet	Colorless, prism	Colorless, prism	Colorless, platelet	Colorless, prism	Colorless, prism	Colorless, block
Crystal dimensions (mm³)	0.25 × 0.20 × 0.05	0.35 × 0.21 × 0.18	0.33 × 0.21 × 0.21	0.15 × 0.15 × 0.03	0.22 × 0.20 × 0.15	0.20 × 0.15 × 0.15	0.24 × 0.16 × 0.15
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Lattice parameters	a = 17.653(5) Å b = 53.153(14) Å c = 10.071(3) Å	a = 7.894(13) Å b = 5.653(10) Å c = 27.02(5) Å β = 97.347(15)°	a = 5.7569(6) Å b = 12.2139(12) Å c = 17.5974(18) Å	a = 8.256(4) Å b = 5.470(3) Å c = 23.995(13) Å	a = 5.848(4) Å b = 7.568(5) Å c = 27.650(17) Å	a = 10.0569(15) Å b = 9.9403(16) Å c = 17.843(3) Å	a = 13.217(4) Å b = 5.3766(14) Å c = 8.370(2) Å β = 90.673(6)°
Volume (Å³)	V = 9449.2(41)	V = 1196.3(3)	V = 1237.3(2)	V = 1083.6(10)	V = 1223.7(14)	V = 1783.8(5)	V = 594.8(3)
Space group	Fdd2	P21/c	P212121	Pca21	P212121	Pbca	Pc
Z value	32	4	4	4	4	8	2
Dcalc (g/cm³)	1.295	1.392	1.236	1.326	1.250	1.253	1.459
$F_{(000)}$	3904	520	488	456	488	720	272
μ(MoKα) (cm⁻¹)	2.485	4.673	2.372	2.662	2.398	3.028	2.707
Diffractometer	Rigaku Mercury2	Rigaku Mercury2	Rigaku Mercury2	Rigaku Saturn	Rigaku Mercury2	Rigaku Mercury	Rigaku Mercury2
No. of reflections measured	Total: 16183	Total: 6986	Total: 10501	Total: 3884	Total: 10334	Total: 10735	Total: 4652
Unique	4143	2122	2171	1396	2142	1577	2053
R_{int}	0.128	0.053	0.031	0.073	0.042	0.051	0.131
Friedel pairs	1940	–	884	443	857	–	1008
Min. and max. transmissions	0.939, 0.988	0.847, 0.919	0.923, 0.951	0.960, 0.992	0.884, 0.958	0.940, 0.956	0.936, 0.960
No. of observations (all reflections)	4143	2122	2171	1396	2142	1577	2053
No. of variables	290	147	146	137	146	110	164
Reflection/parameter ratio	14.29	14.44	14.87	10.19	14.67	14.34	12.52
Residuals: R_1 (I > 2.00σ(I))	0.1122	0.0469	0.0364	0.068	0.0405	0.0602	0.1102
Residuals: R (all reflections)	0.1883	0.0547	0.043	0.0724	0.0490	0.0671	0.1816
Residuals: wR_2 (all reflections)	0.3320	0.1158	0.0852	0.1404	0.1077	0.1789	0.2638
Goodness of fit indicator	1.045	1.056	1.069	1.161	1.084	1.134	1.020
Flack parameter	0.1(2)	–	0.07(9)	0.4(2)	−0.01(10)	–	−0.1(2)
Maximum peak in final diff. map	1.24 e/Å3	0.29 e/Å3	0.21 e/Å3	0.36 e/Å3	0.14 e/Å3	0.82 e/Å3	0.60 e/Å3
Minimum peak in final diff. map	−0.49 e/Å3	−0.29 e/Å3	−0.12 e/Å3	−0.28 e/Å3	−0.15 e/Å3	−0.70 e/Å3	−0.33 e/Å3

bonds, but it has been suggested that an intramolecular interaction can exist between the sulfoxide oxygen and the ortho-hydrogen (H_{aryl}) on a neighboring aromatic ring [7]. The strength of the $O{\cdots}H_{aryl}$ interaction influences how the aromatic ring is oriented in the molecule and will ultimately influence crystal packing. Three measures can be used to determine the strength of the $O{\cdots}H_{aryl}$ intramolecular interaction; (1) the distance between the oxygen and hydrogen atom, (2) the O–S–C–C torsion angle, and (3) the O atom deviation from the S-aryl ring plane. For example, a stronger interaction will result in a shorter $O{\cdots}H_{aryl}$ distance, a smaller torsion angle, and a smaller deviation of the oxygen atom from the S-aryl plane. These three values can be found in Table 2. Figure 4 illustrates the possible $O{\cdots}H_{aryl}$ interaction and the O–S–C–C torsion angle being measured.

Compounds 2–4 and 7 have one aryl group adjacent to the sulfoxide moiety enabling an intramolecular interaction to exist between the O and the H_{aryl}. The $O{\cdots}H_{aryl}$ distance in these compounds range from 2.50(1) to 2.61(1) Å. For the most part, as the $O{\cdots}H_{aryl}$ distance increases, the torsion angle also increases, reflecting the displacement of the O atom from the plane of the aromatic group. 2 has the shortest O⋯H interaction (2.50(1) Å), the smallest torsion angle (3.27(1)°), and the smallest oxygen deviation from the plane (0.142(3) Å). The $O{\cdots}H_{aryl}$ distance increases $2 < 4 < 3 \sim 7$ whilst the O–S–C–C torsion angle and the mean deviation of the oxygen atom increases $2 < 3 < 4 < 7$. Compound 3 displays some interesting behavior, as it has the second longest $O{\cdots}H_{aryl}$ distance of the series (2.61(1) Å), but a very tight torsion angle (8.16(1)°).
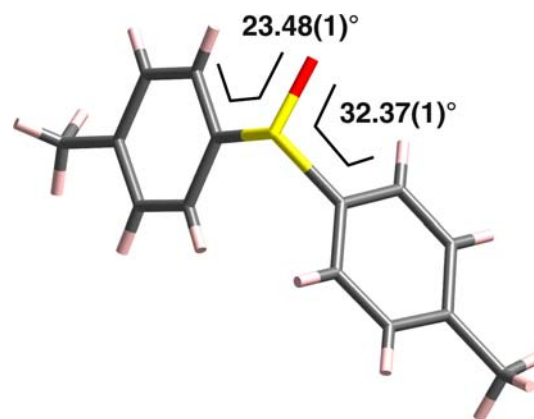
Compound 5 does not fit into the previous structural group because it has two aryl arms attached to the sulfoxide. However, this compound can be compared to the well known compound diphenyl sulfoxide ($SOPh_2$). Both phenyl arms in $SOPh_2$ have similar $O{\cdots}H_{aryl}$ bond distances of 2.51(1) and 2.57(1) Å and similar O–S–C–C torsion angles of 11.38(1) and 11.70(1)° [8]. Compound 5 has two p-tolyl substituents. While these arms are structurally

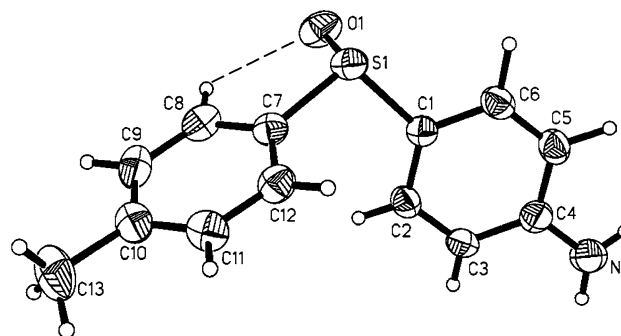similar to the phenyl arms in $SOPh_2$, they display different structural characteristics. Only one $O{\cdots}H_{aryl}$ distance (2.53(1) Å) is similar to $SOPh_2$, while the other one is significantly longer (2.75(1) Å). The O–S–C–C torsion angles for the two arms are also much larger in 5 than in $SOPh_2$, twisting to 23.48(1) and 32.37(1)° (Fig. 5).

Across the entire series, as the $O{\cdots}H_{aryl}$ distance increases, so does the torsion angle; 2 has the smallest $O{\cdots}H_{aryl}$ distance and the smallest torsion angle and 5 has the largest $O{\cdots}H_{aryl}$ distance and the largest torsion angle. There are only two exceptions to this trend: one arm of compound 5 and one arm of compound 3. Interestingly enough, in both exceptions, it seems to be a p-tolyl substituent causing the deviations. However, a crystallographic example of (−)-(S)-4-aminophenyl p-tolyl sulfoxide is known [19] (Fig. 6). The $O{\cdots}H_{aryl}$ distance of the p-tolyl group in this compound is 2.31(1) Å, which is much closer than the equivalent distance in 3 or 5. The p-tolyl group also has a O–S–C–C torsion angle of −10.8(3)°, which is less than that of 5 and only slightly larger than that of 3.

Fig. 5 The X-ray structure of 5 showing the large O–S–C–C torsion angles

Fig. 4 Possible intramolecular interactions between the $O{\cdots}H_{aryl}$ can be described by the $O{\cdots}H_{aryl}$ distance, the O–S–C–C torsion angle, and the oxygen deviation from the S-aryl plane

Fig. 6 ORTEP drawing of (−)-(S)−4-aminophenyl p-tolyl sulfoxide: O1⋯H_{aryl} interaction is 2.31 Å and O1–S1–C7–C8 torsion angle is −10.8(3)°[19]

Table 2 Selected bond distances (Å) and bond angles (°) for SOPh$_2$[a] and **1–7**

	SOPh$_2$	1a	1b	2	3	4	5	6	7
S(1)–O(1)	1.4953(12)	1.505(9)		1.5050(19)	1.5032(16)	1.501(4)	1.495(2)	1.489(2)	1.489(7)
S(1)–C(1)	1.781(1)	1.805(9)		1.801(2)	1.808(2)	1.803(6)	1.798(2)	1.811(2)	1.809(10)
S(1)–C(11)	1.779(1)	1.746(12)		1.831(2)	1.839(2)	1.822(6)	1.794(2)	1.792(3)	1.865(10)
S(1)–O(2)								1.488(7)	
S(2)–O(2)			1.515(8)						
S(2)–C(21)			1.809(10)						
S(2)–O(31)			1.815(10)						
O(1)–S(1)–C(1)	106.77(6)	105.8(4)		106.69(10)	107.42(10)	106.0(2)	106.17(12)	108.14(12)	108.5(4)
O(1)–S(1)–C(11)	106.39(5)	106.7(5)		106.52(10)	106.66(10)	107.3(2)	108.21(12)	106.51(13)	105.1(4)
C(1)–S(1)–C(11)	98.5(1)	95.1(5)		97.52(10)	96.98(10)	97.9(2)	99.00(10)	100.56(12)	98.4(4)
O(1)–S(1)–O(2)								119.1(3)	
O(2)–S(1)–C(1)								109.2(3)	
O(2)–S(1)–C(11)								111.7(3)	
O(2)–S(2)–C(21)			108.2(4)						
O(2)–S(2)–C(31)			105.7(4)						
C(31)–S(2)–C(21)			94.1(4)						
Intramolecular interactions (Å) angles (°)									
O···H$_{aryl}$	2.51	2.57		2.50	2.61	2.54	2.75	2.53	2.61
O–S–C–C	11.38(1)	11.70(1)		3.27(1)	8.16(1)	17.64(1)	32.37(1)	23.48(1)	19.57(1)
O-phenyl (distance out of plane)				0.142(3)	0.230(3)	0.464(6)	0.803(3)	0.462(3)	0.506(11)
Intermolecular interactions (Å) angles (°)									
S···O	4.20(1)	3.58(1)	3.57(1)	4.31(1)	4.35(1)	4.02(1)	4.37(1)	3.99(1)	3.95(1)
								Ethyl / Benzyl	Benzyl
O···H$_{alkyl}$		2.80[b]	2.77[b]	2.29	2.50	2.46		2.48 / 2.53	2.49
O···C		3.54(1)[b]	3.51(1)[b]	3.27(1)	3.44(1)	3.38(1)		3.37(1) / 3.40(1)	3.37(1)
O···H–C angle		132.24[b]	132.72[b]	170.84	163.7	153.91		149.04 / 145.91	147.90

H$_{aryl}$ refers to the ortho-proton on the aromatic ring, where H$_{alkyl}$ refers to the benzyl proton
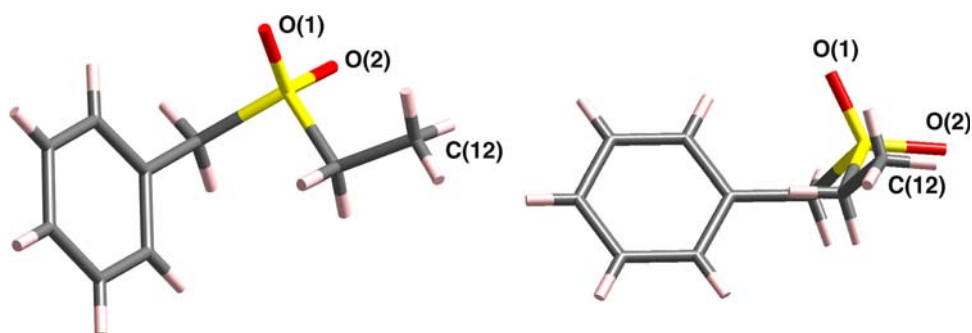
1a and **1b** refer to two independent molecules in the asymmetric unit

[a] Ref. [8]

[b] Average interaction from the two benzyl arms in each independent molecule

Fig. 7 Left, X-ray structure of **6** showing the disorder in the oxygen atom (O(1), 80% and O(2), 20% occupancy). Right, **6** is rotated bringing the ethyl group forward to show the alignment of O(2) and H_{methyl}

O···H_{methyl} Intramolecular Interactions

Compound **6** has two alkyl groups attached to the sulfoxide moiety, and it appears that an O···H_{methyl} intramolecular interaction could be present. In **6** there is a disordered oxygen atom, with 80% O(1) and 20% O(2) occupancy. Structurally there is a close contact between O(2) and C(12) (Fig. 7). In addition, O(2) and one H_{methyl} are perfectly eclipsed with a distance of 2.93(1) Å. This orientation does not exist when looking at O(1). Even though the O(1)···H_{methyl} distance is slightly shorter (2.80(1) Å), the atoms are ∼12° degrees out of alignment.

S, O Intermolecular Interactions

The sulfoxide bond has been described as a single bond with ionic character, with the sulfur bearing a formal positive charge and the oxygen bearing a formal negative charge [1, 3]. The large dipole moments in these bonds allow unique intermolecular interactions in the packing of these molecules. The intermolecular S···O distances range from 3.57(1) to 4.37(1) Å. The shortest distance is in **1** and the longest is in **5** (Table 2). In **1**–**7** sulfur bound to alkyl groups tends to have a shorter intermolecular S···O distance than when sulfur is bound to aromatic substituents. This could be due to one or a combination of several reasons. When aryl substituents are present, conjugation of the entire pi system in the molecule could reduce the positive dipole on the sulfur atom, lengthening the intermolecular S···O distance. Alternatively, alkyl groups could simply give more space for close approach of the oxygen atom. Thirdly, when alkyl substituents are present, any intermolecular O···H_{alkyl} interactions could help pull the S and O closer together.

O···H_{alkyl} Intermolecular Interactions

Sulfoxide compounds display some unique intermolecular interactions in their crystal packing. It has been suggested that a type of intermolecular O···H_{alkyl} interaction can occur in sulfoxi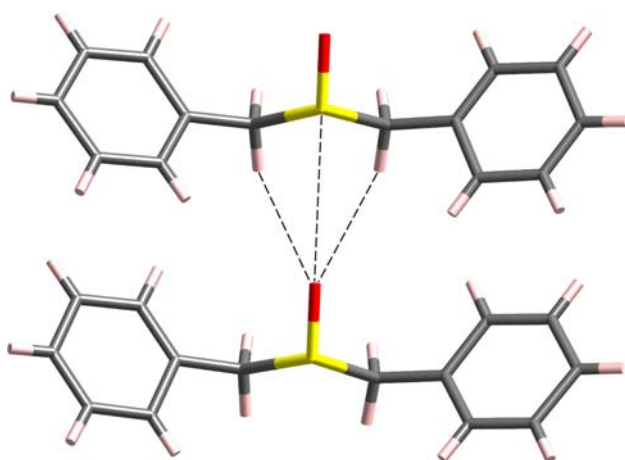des when the sulfur atom is flanked by a –CH_2–R group [7]. An interaction between the oxygen atom of one sulfoxide molecule and the hydrogen from the –CH_2–R group can be difficult to demonstrate because it is so weak. The O···H_{alkyl} distance, the O···C_{alkyl} distance, and the O···H–C angle can be used as evidence to help support or contradict this theory.

Significant intermolecular hydrogen bonding interactions are considered in these compounds if the O···H distances are <2.70 Å and the O···H–C angle is >120° [7]. Table 2 shows the O···H_{alkyl} distance, the O···C distance, and the O···H–C angle for compounds **1**–**7**. The weaker O···H–C interactions are longer than classical O···H–O hydrogen bond distances (∼2.30 Å), and they are less sensitive to deviations from ideal geometries than stronger H-bonds [20]. Therefore, a larger O···H–C angle can deviation from linearity, but that doesn't necessarily mean the hydrogen bond is weaker [7].
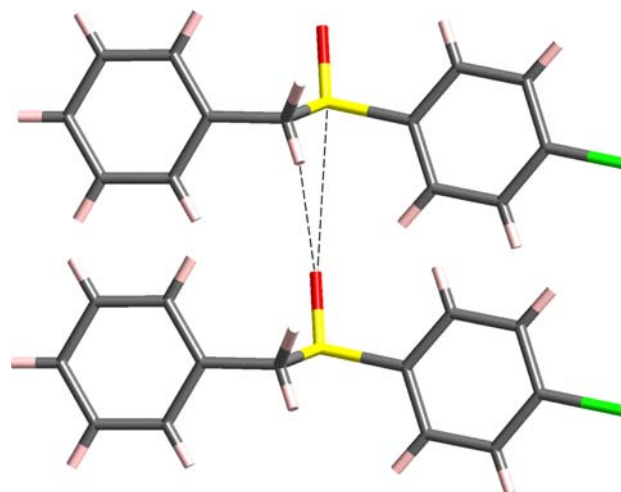
In this study, **1** and **6** have two alkyl arms adjacent to the sulfur. **1** has two benzyl groups (crystallizing with two independent molecules in the asymmetric unit cell, **1a** and **1b**). The values in Table 2 show the average interaction distances associated with each molecule. The average values for **1a** and **1b** are very close and are in most cases within experimental error of each other. Of all of the reported compounds, **1b** has the shortest S···O distance (3.57(1) Å), but the longest O···H_{alkyl} distance (2.77(1) Å), and the O···H–C atoms form a 132.72(1)° angle (Fig. 8).

In **6**, the sulfur is flanked by one benzyl group and one ethyl group. The S···O distance is 3.99(1) Å, which is longer than in **1**. Intermolecular O···H_{alkyl} interactions with the O···H–C of the benzyl arm are shorter and more linear than that of **1**. The O···H_{alkyl} distance in **6** is 2.53(1) Å and an O···C–H angle is 145.91(0)°. The ethyl arm shows an even shorter O···H_{alkyl} distance of 2.48(1) Å, with a more linear O···C–H angle of 149.04(1)°.
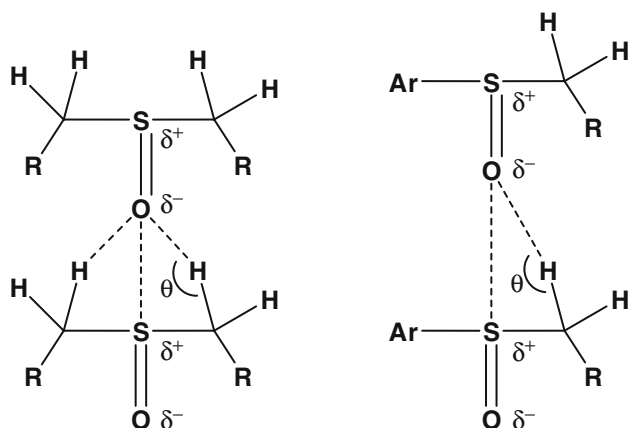
Given the benchmarks discussed earlier, if there is an O···H_{alkyl} interaction, it would have to be considered very weak. However, two weak O···H–C intermolecular interactions could pull the molecules closer together and decrease the O···S distance and decrease the O···H–C angle (Fig. 9).

Fig. 8 Possible intermolecular interactions in **1**

Fig. 10 Possible intermolecular interactions in **2**

Fig. 9 Simple depiction of intermolecular hydrogen bonding inter-actions in sulfoxide compounds with two alkyl arms (left) and an alkyl and aryl arms (right)

Compounds **2–4** and **7** have one alkyl and one aryl group. The S···O interactions in these molecules are slightly longer (range from 3.95(1) to 4.35(1) Å) than the compounds with two alkyl groups (**1**: 3.57(1) and 3.58(1) and **6**: 3.99(1) Å). **3** has the longest S···O distance of 4.35(1) Å. The O···H_{alkyl} distances range from 2.29(1) in **2** to 2.50(1) Å in **3**. The O···H_{alkyl}–C angles are more linear in these compounds than in the alkyl/alkyl compounds ranging from 1.47.90(1) in **7** to 170.84(1)° in **2**. Possible intermolecular interactions for **2** are shown in Fig. 10. This could be due to having only one –CH_2-R arm available for O···H_{alkyl} intramolecular interaction, which would allow the molecules to align in a more linear fashion. It could also be due to the lengthening of the S···O interaction, which would also increase the O···H_{alkyl}–C angle (Fig. 9).

5 is the only compound in this study containing two aryl groups and unsurprisingly has the longest S···O intramolecular interaction (4.37(1) Å).

Conclusions

We have structurally characterized and investigated sulf-oxide compounds **1–7**. The S=O bond distances in these compounds are all very similar ranging from 1.489(7) to 1.515(8) Å. In all seven structures, the O(1)–S–C bond angles vary from 105.1(4) to 108.5(4)° and the C(1)–S(1)–C(11) bond angles range from 94.1(4) to 100.56(12)°.

We find that compounds **1–7** contain unique intra- and intermolecular interactions depending on the groups attached to the sulfoxide moiety. The polarity of the sulf-oxide bond in these compounds allows for an intramolecular S···O interaction to occur. When the sulfur is bound to alkyl groups, there tends to be a shorter S···O intermolecular distance than when the sulfur is bound to aromatic substituents. Additionally, if the sulfur is flanked by an aryl group, the S–C bond distance is slightly shorter than if flanked by an alkyl group. These distances suggest a possible interaction, which could be weak conjugation, O···H_{aryl} intramolecular interaction, or both. The strength of these combined interactions would also determine the amount of twisting the aryl group can undergo and would also influence the molecular packing. Furthermore, if the sulfur is flanked by an alkyl group, a CH_2 proton of S–CH_2–R can be properly oriented to participate in an intermolecular hydrogen bond with the sulfoxide oxygen of another molecule.

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