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Patterns of soft C—H···O hydrogen bonding in diaryl sulfones

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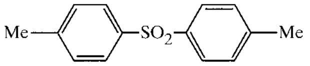
In bis(4-tolyl) sulfone, $C_{14}H_{14}O_2S$ (1), 2,5,4′-trimethyldiphenyl sulfone, $C_{15}H_{16}O_2S$ (2), and 4-chlorodiphenyl sulfone, $C_{12}H_9ClO_2S$ (3), the molecules are linked by soft C—H···O hydrogen bonds into three different types of one-dimensional aggregate: simple chains in (1), molecular ladders in (2) and chains of fused rings in (3). In each of 3,4-dimethyl-4′-chlorodiphenyl sulfone, $C_{14}H_{13}ClO_2S$ (4), and 2,5-dimethyldiphenyl sulfone, $C_{14}H_{14}O_2S$ (5), the C—H···O hydrogen bonds link the molecules into two different types of two-dimensional sheet, based on a (4,4) net in (4) and a (3,6) net in (5). The patterns of soft C—H···O hydrogen bonds in (1)—(5) are compared with those in other diaryl sulfones, mainly retrieved from the Cambridge Structural Database, whose substitution patterns preclude the formation of hard hydrogen bonds. Observed aggregation modes range from the formation of no C—H···O hydrogen bonds at all, *via* finite (zero-dimensional) arrays through one-, two- and three-dimensional systems.

1. Introduction

The SO_2 group in diaryl sulfones is a powerful acceptor of hydrogen bonds (Ferguson *et al.*, 1999). When hard (Braga *et al.*, 1995) hydrogen-bond donors, such as OH or NH_2 groups, are present the supramolecular aggregation is dominated between these donors and the SO_2 groups. Thus, for example, in $O_2S(C_6H_4OH)_2$ (Glidewell & Ferguson, 1996), the molecules are linked by O—H···O=S hydrogen bonds into pairwise-interwoven square nets built from $R_4^4(32)$ rings (Bernstein *et al.*, 1995); in $O_2S(C_6H_4NH_2)_2$, a combination of N—H···O and N—H···N hydrogen bonds generates a continuous three-dimensional framework (Bertolasi *et al.*, 1993). When hard hydrogen-bond donors are absent, it may be expected that C—H···O hydrogen bonds will occur instead, and in the bis-sulfone 2,5-bis-(4-chlorophenylsulfonyl)-1,4-dimethylbenzene, $(ClC_6H_4SO_2)_2C_6H_2(CH_3)_2$, the molecules are linked into molecular ladders by C—H···O hydrogen bonds (Wardell *et al.*, 2000).

In the present paper, we report the crystal structures, with particular emphasis on the supramolecular aggregation, of the diaryl sulfones (1)–(5), whose molecular structures are all designed to preclude the possibility of hard hydrogen bonding, and we compare these with other, related examples (6)–(18), mostly retrieved from the Cambridge Structural Database (CSD; Allen & Kennard, 1993). In all of these compounds the C—H bonds are the sole possible donors in any hydrogen bonds, but in several compounds there are potential hydrogen-bond acceptors other than the SO_2 group. Nonetheless, for very few of these compounds did the original reports make any mention of intermolecular aggregation by means of C—H···O hydrogen bonding.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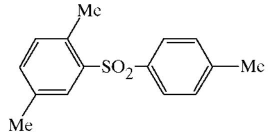
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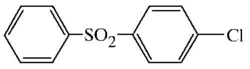
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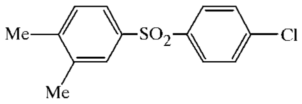
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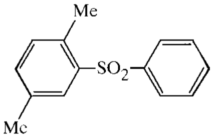

(5)

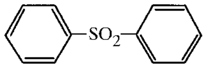
2. Experimental

2.1. Syntheses

Samples of (1) and (3) were obtained from Aldrich Chemical Company. Compound (2) was prepared by reaction of 4-toluenesulfonyl chloride with excess 1,4-dimethylbenzene in the presence of $AlCl_3$: the product was isolated by chromatography and recrystallized from ethanol, m.p. 383–385 K (literature m.p. 381–385 K; Burton & Praill, 1955); (5) was prepared by a similar method using benzenesulfonyl chloride with m.p. 383–385 K (literature m.p. 384 K; Novi *et al.*, 1982). Compound (4) was prepared by oxidation of the corresponding sulfide (Grant *et al.*, 1987) using 3-chloroperoxybenzoic acid: after crystallization from ethanol (4) had m.p. 343–344 K. Crystals of (1)–(5) suitable for single-crystal X-ray diffraction were grown from solutions in ethanol.

2.2. Data collection, structure solution and refinement

Details of cell data, data collection and refinement are summarized in Table 1 (Blessing, 1995, 1997; Bruker, 1997; Ferguson, 1999; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a*,*b*; Spek, 2000).[1] For (1)–(5) the space groups were uniquely assigned from the systematic absences: $P2_1/c$ for (1) and (3), $P2_1/n$ for (2), (4) and (5). The structures were all solved by direct methods using *SHELXS*97 (Sheldrick, 1997*a*) and refined with all data on F^2 using *SHELXL*97 (Sheldrick, 1997*b*). A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). All H atoms were located from difference maps and all were included in the refinements as riding atoms, with C—H 0.93–0.95 Å (aromatic), 0.96–0.98 Å (methyl). In (1), (4) and (5) the methyl groups were all modelled using six H sites with occupancy 0.5, offset from one another by 60° rotations: the two methyl groups in (2) could each be satisfactorily modelled with a single set of sites. Supramolecular analyses were made and the diagrams were prepared with the aid of *PLATON* (Spek, 2000).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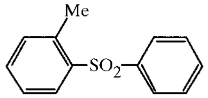
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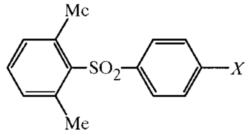
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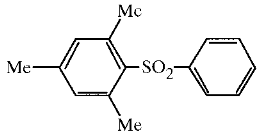
(9) X = Cl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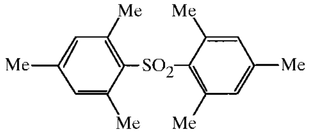
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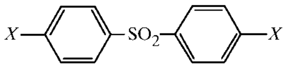
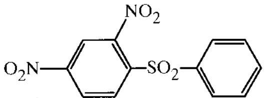

(12) X = F
(13) X = Cl
(14) X = Br
(15) X = I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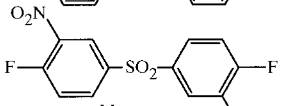
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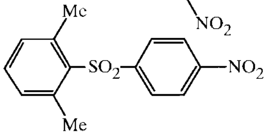
(18)

Figs. 1–5 show the molecular units in (1)–(5), and Figs. 6–19 show aspects of the crystal structures of (1)–(18): (6)–(18) are identified in Table 2. Table 3 gives details of the hydrogen bonding in (1)–(18) and Table 4 contains details of the short intermolecular halogen···halogen contacts in (14) and (15).

3. Results and discussion

3.1. Isomorphous and isomeric relationships

Compounds (6) and (7) are also isomorphous, as are (8) and (9); however, for neither of these pairs was the isomorphism noted in the latter of the two structure reports. As noted in the original report (Sime & Woodhouse, 1974*b*), (13)–(15) are isomorphous, with the molecules lying across twofold rotation axes. Of the compounds newly studied here, (3) is isomorphous with (6) and (7). However, despite the isomorphous nature of (8) and (9), (1) and (13) are not isomorphous. These

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0036). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$C_{14}H_{14}O_2S$	$C_{15}H_{16}O_2S$	$C_{12}H_9ClO_2S$	$C_{14}H_{13}ClO_2S$	$C_{14}H_{14}O_2S$
Chemical formula weight	246.31	260.34	252.7	280.75	246.31
Cell setting, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c (Å)	14.1773 (7), 7.7437 (4), 24.0161 (12)	8.3374 (6), 14.9785 (8), 10.9064 (6)	13.239 (3), 7.4521 (15), 11.737 (2)	12.9682 (14), 7.5293 (12), 14.4627 (17)	7.8879 (3), 10.9788 (4), 15.2489 (4)
β (°)	101.205 (1)	98.241 (3)	93.17 (3)	110.625 (7)	103.525 (2)
V (Å^3)	2586.3 (2)	1347.95 (14)	1156.3 (4)	1321.6 (3)	1283.93 (8)
Z	8	4	4	4	4
D_x (Mg m^{-3})	1.265	1.283	1.452	1.411	1.274
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	15 872	12 210	3848	9255	14 179
θ range (°)	1.46–25.03	2.32–27.39	1.54–25.0	1.81–25.85	2.30–27.32
μ (mm^{-1})	0.237	0.231	0.491	0.437	0.239
Temperature (K)	306 (2)	150 (2)	307 (2)	150 (2)	150 (2)
Crystal form, colour	Needle, colourless	Plate, colourless	Block, yellow	Block, colourless	Plate, colourless
Crystal size (mm)	0.56 × 0.18 × 0.13	0.2 × 0.2 × 0.025	0.40 × 0.28 × 0.24	0.10 × 0.08 × 0.05	0.20 × 0.15 × 0.05
Data collection					
Diffractometer	Bruker SMART 1000CCD	Kappa-CCD	Bruker SMART 1000CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
$T_{\min}$	0.879	0.929	0.828	0.958	0.954
$T_{\max}$	0.970	0.969	0.891	0.979	0.988
No. of measured, independent and observed parameters	15 872, 4554, 2746	12 210, 3060, 2172	7000, 2030, 1527	9255, 2545, 1332	14 179, 2895, 1990
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.023	0.037	0.020	0.053	0.038
$\theta_{\max}$ (°)	25.03	27.39	25.00	25.85	27.32
Range of h, k, l	$-16 \rightarrow h \rightarrow 16$ $-9 \rightarrow k \rightarrow 9$ $-28 \rightarrow l \rightarrow 22$	$-10 \rightarrow h \rightarrow 10$ $-18 \rightarrow k \rightarrow 19$ $-14 \rightarrow l \rightarrow 14$	$-15 \rightarrow h \rightarrow 15$ $-8 \rightarrow k \rightarrow 8$ $-8 \rightarrow l \rightarrow 13$	$-15 \rightarrow h \rightarrow 15$ $-9 \rightarrow k \rightarrow 9$ $-17 \rightarrow l \rightarrow 17$	$-10 \rightarrow h \rightarrow 10$ $-14 \rightarrow k \rightarrow 14$ $-19 \rightarrow l \rightarrow 19$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0399, 0.1009, 0.928	0.0466, 0.1173, 1.044	0.0386, 0.1076, 1.041	0.0591, 0.1575, 0.93	0.047, 0.1224, 1.044
No. of reflections and parameters used in refinement	4554, 311	3060, 166	2030, 145	2545, 165	2895, 156
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.1788P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0550P)^2 + 0.2889P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0760P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 0.0204P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	0.005	0.001	0.003	0.004
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.142, −0.23	0.24, −0.438	0.239, −0.396	0.342, −0.283	0.258, −0.422

Computer programs used: *SMART* (Bruker, 1997), *SAINT* (Bruker, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997*b*), *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999), *Kappa-CCD* server software (Nonius, 1997), *DENZO* (Otwinowski & Minor, 1997).

latter two compounds crystallize in different space groups, (1) in $P2_1/c$ with $Z' = 2$ and (13) in the $I2/a$ setting of $C2/c$ with $Z' = 0.5$.

Even in compounds which are isomorphous, subtle differences in interatomic distances can mean that one compound of an isomorphous pair may exhibit significant soft C—H···O hydrogen bonds, while the other does not. Thus, for example (see §§3.2.1 and 3.2.3), the structure of (15) contains C—H···O hydrogen bonds, while the structures of (13) and (14) do not. Likewise (see §3.2.3) the hydrogen-bonding behaviour of (3) differs from that of (6) and (7). Similar comments also apply to other types of intermolecular interaction (see §3.2.7).

More substantial differences in hydrogen-bonding behaviour will be noted amongst pairs of isomeric, but not isomorphous compounds. Thus, (1) and (5) are isomeric, as are compounds (2), (8) and (10), and (4) and (9). No two compounds within any of these isomeric series behave in the same manner (see §3.2).

3.2. Supramolecular structures

In (1)–(5) and (6)–(18) (Table 2), the C—H···O hydrogen bonding exhibits a variety of patterns: in some compounds, there are no C—H···O hydrogen bonds at all, while in others these interactions lead to aggregates which can be zero-dimensional (*i.e.* finite aggregates) or one-, two- or three-dimensional, and it is convenient to treat each of these variants in turn. Of the compounds (6)–(18) retrieved from the CSD, (6) is the unsubstituted parent diphenyl sulfone; (7)–(11) all contain methyl substituents, together with chloro in the case of (9); (12)–(15) contain only halogen substituents, symmetrically disposed; and (16)–(18) all contain nitro groups, which are themselves potentially good hydrogen-bond acceptors.

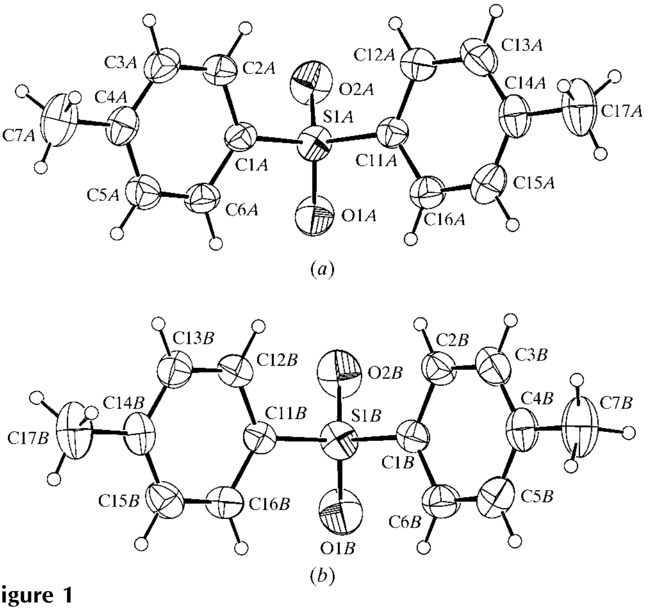

Figure 1
The two independent molecules in (1), showing the atom-labelling schemes: (*a*) molecule 1; (*b*) molecule 2. Displacement ellipsoids are drawn at the 30% probability level and only one set of H atom sites is depicted for each methyl group.

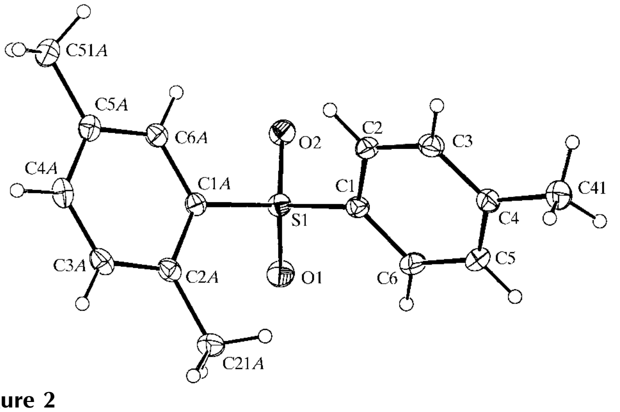

Figure 2
The asymmetric unit in (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

As Cotton *et al.* (1997) have noted, the criteria for the acceptance of non-covalently bonded contacts as hydrogen bonds have been undergoing a continuous relaxation in recent years. It is therefore appropriate to define the acceptance criteria adopted here for the C—H···O hydrogen bonds which are considered to be structurally significant. The C—H distances in (1)–(5), determined here, are all derived from X-ray diffraction data using the well established *SHELXL*97 values for riding C—H atoms (Sheldrick, 1997*b*). Consequently, since the structures of compounds (6)–(18) were all also derived from X-ray diffraction data, the C—H···O parameters in these compounds have all been derived from the atomic coordinates deposited in the CSD: no attempt has been made to convert the C—H distances into the so-called neutron-normalized distances. It is worthwhile to point out here that neither X-ray nor neutron diffraction can provide correct coordinates for an 'H atom': the two types of diffraction data provide coordinates for different components of atoms, which in the case of H are far from coincident with neither set of coordinates being more, or less, 'correct' than the other (Cotton & Luck, 1989). The acceptance criteria for C—H···O hydrogen bonds adopted here refer specifically to structural parameters derived from X-ray diffraction data. The C—H···O interactions in Table 3 all involve aromatic C—H bonds as donors and all are subject to the reasonably, but not excessively conservative criteria of an upper limit (within

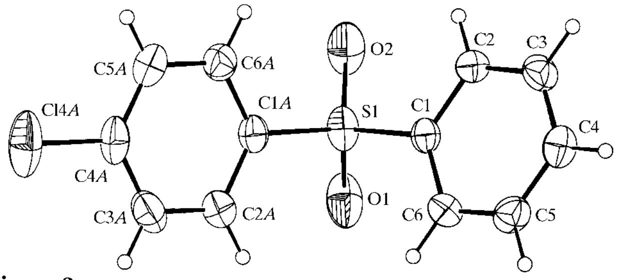

Figure 3
The asymmetric unit in (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

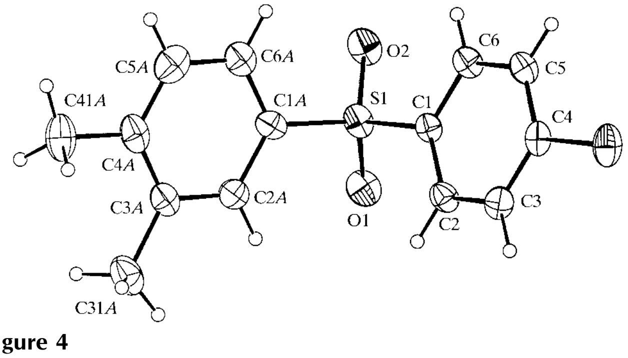

Figure 4
The asymmetric unit in (4), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and only one set of H atom sites is depicted for each methyl group.

experimental uncertainty) of 3.50 Å on the C· · ·O distance, combined with a lower limit on the C—H· · ·O angle of 130° and an upper limit on the H· · ·O distance of 2.60 Å. No account has been taken of interactions involving methyl C—H bonds which fall within these geometric criteria, firstly because methyl C—H bonds are less acidic than aromatic C—H bonds and, more importantly, because methyl groups are likely to be undergoing extensive libration, if not nearly free rotation about their proximal C—C bonds (Riddell & Rogerson, 1996, 1997). Any short contacts involving such groups are thus unlikely to have real structural significance.

3.2.1. Structures with no intermolecular hydrogen bonds within the acceptance criteria. Compounds (8) and (9) are isomorphous, and the molecular volume in (8) exceeds that in (9) by only *ca* 1.4%, reflecting the isosteric nature of the methyl and chloro substituents. In neither compound are there any C—H· · ·O hydrogen bonds or any $\pi \cdots \pi$ stacking interactions. The structure of (11) has been reported only from photographic data and no H atoms were either located or included in the refinements; however, since there are no intermolecular C· · ·O distances less than 3.50 Å, it may reasonably be inferred that there are no intermolecular C—H· · ·O hydrogen bonds. In (8), (9) and (11), therefore, the crystal structures contain isolated molecules. There are no C—H· · ·O hydrogen bonds in the isomorphous pair of (13) and (14), although in (14) there are short Br· · ·Br contacts (see §3.2.7).

3.2.2. Finite (zero-dimensional) hydrogen bonding. There is a single type of C—H· · ·O hydrogen bond in (12): only a single C—H bond, in one ring only, acts as a hydrogen-bond donor and only one of the O atoms acts as a hydrogen-bond acceptor. The C—H· · ·O hydrogen bonding in (12) generates a finite motif, a dimer containing a centrosymmetric $R_2^2(12)$

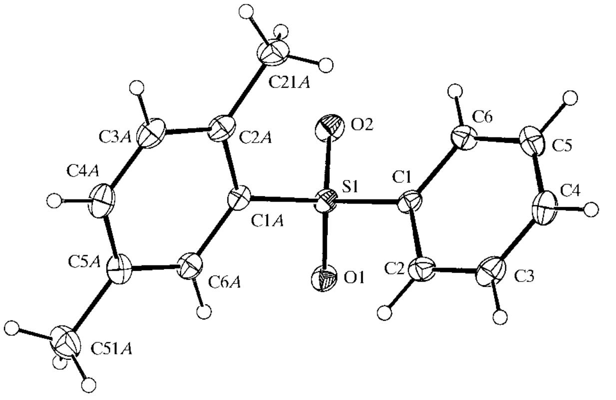

Figure 5
The asymmetric unit in (5), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and only one set of H atom sites is depicted for each methyl group.

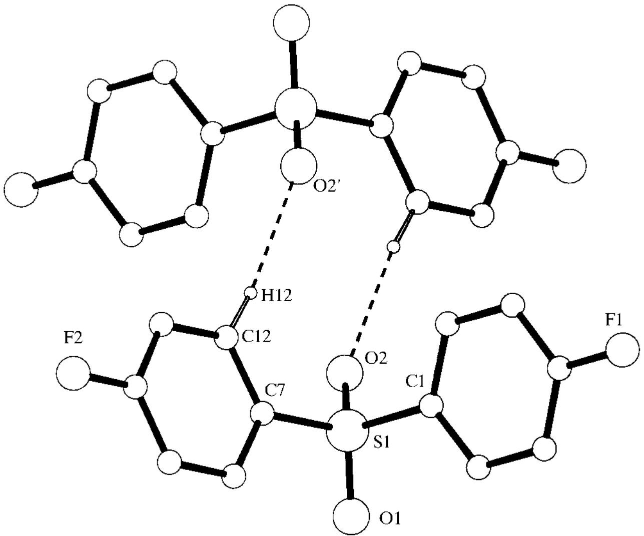

Figure 6
Part of the crystal structure of (12), showing the formation of a centrosymmetric $R_2^2(10)$ ring. For the sake of clarity H atoms not involved in the hydrogen bonding motif shown are omitted. The atom marked with a prime (′) is at the symmetry position $(-1 - x, 1 - y, -z)$.

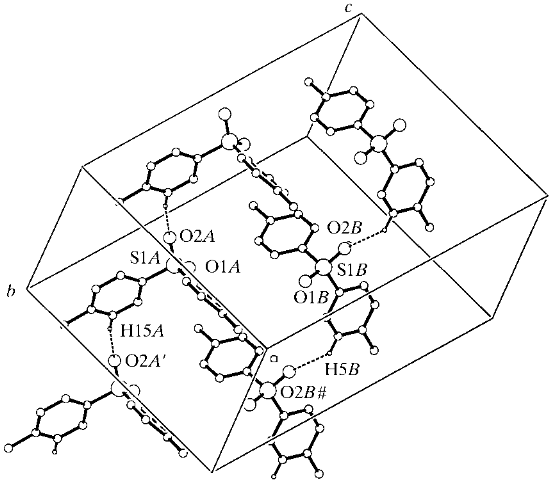

Figure 7
Part of the crystal structure of (1), showing the formation of two independent chains running parallel to [010]. Atoms are depicted as in Fig. 6. The atoms marked with a prime (′) or a hash (#) are both at the symmetry position $(x, 1 + y, z)$.

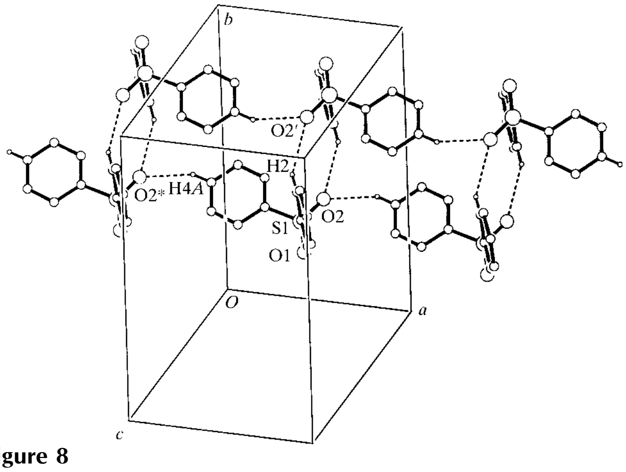

Figure 8
Part of the crystal structure of (2), showing the formation of a molecular ladder running parallel to [100]. Atoms are depicted as in Fig. 6. The atoms marked with a prime (′) or a star (*) are at the symmetry positions $(1 - x, 1 - y, -z)$ and $(-1 + x, y, z)$, respectively.

Table 2
Sulfones retrieved from the CSD.

Compound No.	CSD code	Space group	Z'	Reference
(6)	DPSULO	$P2_1/c$	1	Sime & Woodhouse (1974*a*)
(7)	NOFWEK	$P2_1/c$	1	Jeyakanthan *et al.* (1998)
(8)	NOFWAG	$C2/c$	1	Jeyakanthan *et al.* (1998)
(9)	RIWRUK	$C2/c$	1	Jeyakanthan & Velmurugan (1997)
(10)	TMPSUL10	$Pn2_1a$†	2	Chawdhury (1976)
(11)	HMPSUL	$Pbca$	1	Chawdhury & Hargreaves (1971)
(12)	DFPSLO	$P2_1/c$	1	Sime & Woodhouse (1974*a*)
(13)	CLPSUL10	$I2/a$	0.5	Sime & Woodhouse (1974*b*)
(14)	BPHSUL01	$I2/a$	0.5	Sime & Woodhouse (1974*b*)
(15)	IPSULO	$I2/a$	0.5	Sime & Woodhouse (1974*b*)
(16)	TEMCET	$P2_1$	1	Ellena *et al.* (1996)
(17)	NFPHSO	$P2_1/c$	1	Sime & Woodhouse (1974*a*)
(18)	NOFVUZ	$P2_1/n$	1	Jeyakanthan *et al.* (1998)

† Non-standard setting of $Pna2_1$.

ring (Fig. 6), but there are no C—H···F hydrogen bonds. Hence, the hydrogen-bonded aggregation is strictly finite and zero-dimensional.

3.2.3. One-dimensional hydrogen bonding. The crystal structures of (1)–(3) all contain C—H···O hydrogen bonds and in all three compounds the hydrogen bonds lead to the development of one-dimensional aggregation. However, all three compounds exhibit different one-dimensional motifs, simple chains in (1), molecular ladders in (2) and chains of fused rings in (3). In (1) there are two molecules in the asymmetric unit (Fig. 1): each type of molecule forms a single type of C—H···O hydrogen bond and the molecules are linked into *C*(6) chains, generated by translation and running parallel to the [010] direction (Fig. 7, Table 3). There are thus eight chains running through each unit cell, four of each type, but there are neither hydrogen bonds nor aromatic $\pi\cdots\pi$ stacking interactions between adjacent chains.

In (2) the molecules (Fig. 2) are linked by two types of C—H···O hydrogen bond (Table 3) into molecular ladders. Atom C4*A* in the molecule at (x, y, z) acts as a donor to O2 in the molecule at $(-1 + x, y, z)$, thus generating by translation a *C*(7) chain running parallel to the [100] direction. Four such chains run through each unit cell and these are linked in pairs by a further type of hydrogen bond. Atom C2 at (x, y, z) acts as a donor to O2 at $(1 - x, 1 - y, -z)$, thus giving rise to a centrosymmetric $R_2^2(10)$ ring motif. The combination of these rings with the translational chains generates a molecular ladder parallel to [100] in which an antiparallel pair of *C*(7) chains play the role of the uprights and the $R_2^2(10)$ rings act as

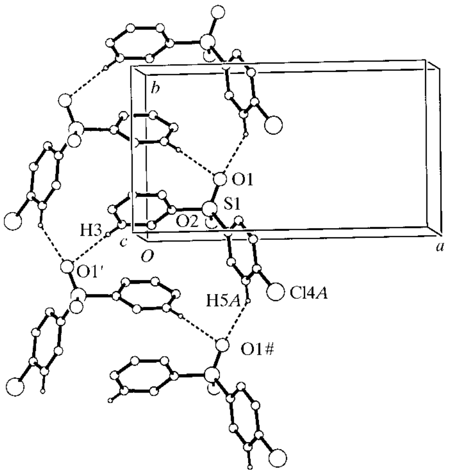

Figure 9
Part of the crystal structure of (3), showing the formation of a chain of fused $R_3^2(16)$ rings running parallel to [010]. Atoms are depicted as in Fig. 6. The atoms marked with a prime (′) or a hash (#) are at the symmetry positions $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(x, -1 + y, z)$, respectively.

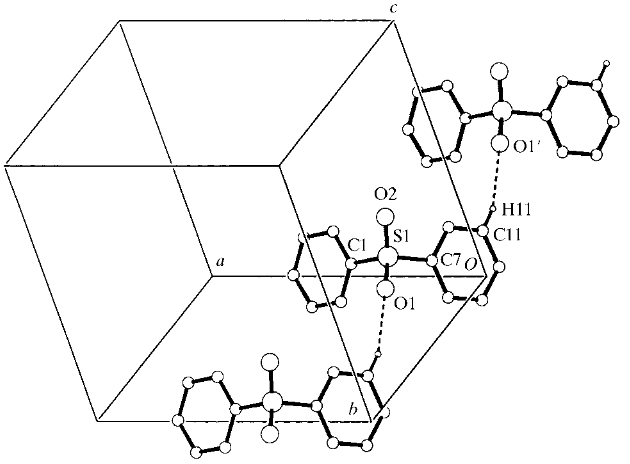

Figure 10
Part of the crystal structure of (6), showing a *C*(6) chain running parallel to [010]. Atoms are depicted as in Fig. 6. The atom marked with a prime (′) is at the symmetry position $(x, -1 + y, z)$.

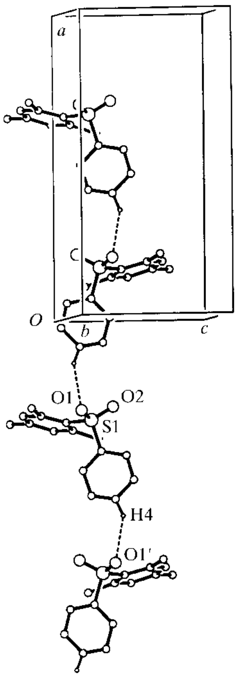

Figure 11
Part of the crystal structure of (10), showing one of the zigzag *C*(7) chains running parallel to [100]. Atoms are depicted as in Fig. 6. The atom marked with a prime (′) is at the symmetry position $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$.

Table 3
Hydrogen-bond geometry for (1)–(18) (Å, °).

The atom-numbering for (6)–(18) follows the original papers (Table 2).

	H···O	C···O	C—H···O	Motif	Direction
(1)					
C15*A*—H15*A*···O2*A*$^{\rm i}$	2.44	3.354 (3)	166	*C*(6) translation	[010]
C5*B*—H5*B*···O2*B*$^{\rm i}$	2.58	3.317 (3)	137	*C*(6) translation	[010]
(2)					
C2—H2···O2$^{\rm ii}$	2.59	3.306 (2)	134	$R_2^2(20)$	
C4*A*—H4*A*···O2$^{\rm iii}$	2.43	3.292 (2)	154	*C*(7) translation	[100]
(3)					
C3—H3···O1$^{\rm iv}$	2.58	3.500 (3)	169	*C*(6) spiral (2_1 axis)	[010]
C5*A*—H5*A*···O1$^{\rm v}$	2.53	3.326 (4)	143	*C*(6) translation	[010]
(4)					
C3—H3···O2$^{\rm vi}$	2.52	3.416 (5)	158	*C*(6) zigzag (*n* glide)	[101]
C5*A*—H5*A*···O1$^{\rm v}$	2.45	3.319 (6)	151	*C*(6) translation	[010]
(5)					
C3—H3···O2$^{\rm iii}$	2.41	3.317 (3)	161	*C*(6) translation	[100]
C4—H4···O1$^{\rm vii}$	2.55	3.392 (3)	147	*C*(7) spiral (2_1 axis)	[010]
C6—H6···O1$^{\rm viii}$	2.46	3.309 (3)	149	*C*(5) spiral (2_1 axis)	[010]
(6)					
C11—H11···O1$^{\rm v}$	2.51	3.398 (4)	163	*C*(6) translation	[010]
(7)					
C5—H5···O1$^{\rm v}$	2.48	3.376 (4)	159	*C*(6) translation	[010]
(10)					
C4—H4···O1$^{\rm ix}$	2.52	3.354 (4)	135	*C*(7) zigzag (*a* glide)	[100]
C4′—H4′···O1′$^{\rm x}$	2.43	3.330 (4)	148	*C*(7) zigzag (*a* glide)	[100]
(12)					
C12—H12···O2$^{\rm xi}$	2.37	3.364 (5)	163	$R_2^2(12)$	
(15)					
C5—H5···O1$^{\rm xii}$	2.51	3.441 (9)	144	$R_2^2(12)$ chain of rings	[001]
(16)					
C6—H6···O1$^{\rm xiii}$	2.48	3.251 (5)	141	*C*(5) spiral (2_1 axis)	[010]
(17)					
C6—H6···O4$^{\rm xiv}$	2.36	3.250 (6)	158	*C*(7) zigzag (*c* glide)	[001]
C11—H11···O1$^{\rm v}$	2.53	3.255 (6)	135	*C*(6) translation	[010]
C12—H12···O2$^{\rm iv}$	2.57	3.246 (6)	132	*C*(5) spiral (2_1 axis)	[010]
(18)					
C3′—H3′···O3$^{\rm xv}$	2.51	3.361 (3)	135	$R_2^2(12)$	
C5—H5···O3$^{\rm xvi}$	2.48	3.423 (4)	151	C(11) zigzag (*n* glide)	$[10\bar{1}]$
C5′—H5′···O3$^{\rm viii}$	2.52	3.341 (3)	138	*C*(5) spiral (2_1 axis)	[010]

Symmetry codes: (i) $x, 1+y, z$; (ii) $1-x, 1-y, -z$; (iii) $-1+x, y, z$; (iv) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $x, -1+y, z$; (vi) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (vii) $-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ix) $-\frac{1}{2}+x, y, \frac{1}{2}-z$; (x) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (xi) $-1-x, 1-y, -z$; (xii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (xiii) $-x, \frac{1}{2}+y, 1-z$; (xiv) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (xv) $-x, 1-y, -z$; (xvi) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

the rungs. These $R_2^2(10)$ rings are centred at $(n+\frac{1}{2}, \frac{1}{2}, 0)$ (n = zero or integer), while between the rungs there are $R_4^4(20)$ rings centred at $(n, \frac{1}{2}, 0)$ (n = zero or integer; Fig. 8). There are two such ladders running through each unit cell, related to one another by the glide planes: one lies largely in the domain $\frac{1}{4} < y < \frac{3}{4}$, and the other in the domain $-\frac{1}{4} < y < \frac{1}{4}$, so that there are no close interactions between neighbouring ladders.

There are two types of C—H···O hydrogen bond in (3) (Table 3), which link the molecules (Fig. 3) into a chain of fused rings. Atom C5*A* in the molecule at (x, y, z) acts as a donor to O1 at $(x, -1+y, z)$, thus generating by translation a *C*(6) chain parallel to [010]. Atom C3 in the molecule at (x, y, z) also acts as a donor to an O1 atom, this time in the molecule at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$: C3 in this molecule in turn acts as a donor to O1 at $(x, -1+y, z)$, thus generating a *C*(6) spiral parallel to [010]. The combination of these two *C*(6) motifs produces a chain of fused $R_3^2(16)$ rings running parallel to [010] (Fig. 9). Two of these chains run through each unit cell and there are aromatic $\pi\cdots\pi$ stacking interactions between adjacent chains. The ring C1–C6 at (x, y, z) is a component of a chain in the domain $-0.14 < z < 0.64$; this ring forms a $\pi\cdots\pi$ stacking interaction with the corresponding ring at $(-x, -y, 1-z)$, which lies in the chain in the domain $0.36 < z < 1.14$. The symmetry-related ring at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ in the original chain forms a $\pi\cdots\pi$ stacking interaction with the corresponding ring at $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$, which is a component of a chain in the domain $-0.64 < z < 0.14$. Hence, each chain is linked by aromatic $\pi\cdots\pi$ stacking interactions to its two immediate neighbours in the [001] direction.

One-dimensional hydrogen-bonding motifs are also observed in (6), (7), (10), (15) and (16), but, with the exception of the isomorphous pair (6) and (7), all of these one-dimensional motifs are different. In (6) and (7), simple *C*(6) chains analogous to those in (1) are generated by translation (Fig. 10), although there is only a single type of chain in each structure. In (10), by contrast, each of the two independent types of molecule in the structure forms a *C*(7) chain generated by the action of a glide plane (Fig. 11): the chains formed by the two independent molecules do not interact. The chain in (16) (Fig. 12), is based on a *C*(5) motif and is generated by the action of a 2_1 screw axis. Thus, the aromatic rings in this group of compounds can be used for the formation of C—H···O hydrogen bonds, C—H bonds which can be *ortho*, as in (16), *meta*, as in (6) and (7), or *para*, as in (10), to the SO_2 unit, and the chain motifs can be generated by translation, or by the action of screw axes or glide planes.

The one-dimensional motif in (15) differs from the simple chains in (6), (7), (10) and (16), largely because the molecules in (15) have twofold rotational symmetry, so that the formation of a single type of C—H···O hydrogen bond means that each molecule acts as a double donor of hydrogen bonds and as a double acceptor. The resulting structure (Fig. 13) is a chain of centrosymmetric rings, each of $R_2^2(12)$ type and fused in spiro fashion at the S atoms.

3.2.4. Two-dimensional hydrogen bonding. Two-dimensional aggregation is observed in the methyl-substituted compounds (4) and (5), as well as in the nitro compound (17). In (4) there are two types of intermolecular C—H···O hydrogen bonds and each molecule is thus linked to four others by means of such bonds: the donors are two C—H bonds *meta* to SO_2 and each of the two sulfone O atoms acts as a single acceptor. Atom C5*A* at (x, y, z) acts as a donor to O1 at $(x, -1+y, z)$, thus forming by translation a $C(6)$ chain running parallel to [010] (Fig. 14): in this respect, the behaviour of (4) resembles that of (6) and (7) (see §3.2.3; Fig. 10). In addition, however, C3 in the other aryl ring of the molecule at (x, y, z) acts as a donor to O2 at $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, while C3 at $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ in turn acts as a donor to O2 at $(-1+x, y, -1+z)$: this hydrogen bond thus forms a second $C(6)$ chain motif, generated by the action of the glide plane at $y = 0.25$ and running parallel to [101]. The combination of these two $C(6)$ motifs leads to a square (4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(24)$ ring and lying parallel to $(10\bar{1})$ (Fig. 14). There are two such nets passing through each unit cell, but they are not interwoven.

The structure of (5) contains three types of intermolecular C—H···O hydrogen bond, but the supramolecular aggregation is still only two-dimensional, even though each molecule is linked to six others. All of the C—H donors are in the unsubstituted aryl ring and both O atoms acts as hydrogen-bond acceptors: O1 is a single acceptor and O2 is a double acceptor (Table 3). As in (4), (6) and (7), one motif is a $C(6)$ chain generated by translation: atom C3 at (x, y, z) acts as a donor to O2 at $(-1+x, y, z)$ (Fig. 15). In addition, C4 at (x, y, z) acts as a donor to O1 at $(-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, thus generating a $C(7)$ spiral around the 2_1 axis along $(-\frac{1}{4}, y, \frac{1}{4})$. Similarly, C6 at (x, y, z) acts as a donor to O1 at $(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, thus generating a $C(5)$ spiral around the 2_1 axis along $(\frac{1}{4}, y, \frac{1}{4})$: this latter motif mirrors the one-dimensional aggregation in (16) (see §3.2.3; Fig. 12). The combination of the two spiral motifs parallel to [010] and the translational motif along [100] generates a (3,6) net (Batten & Robson, 1998) lying parallel to (001) and containing a checkerboard pattern of $R_3^2(10)$ and $R_3^3(14)$ rings (Fig. 15).

Table 4
Geometry of C—*X*···*X*′ fragments in (14) and (15) (Å, °).

X	*X*′	*X*···*X*′	C—*X*···*X*′
(14)			
Br	Br^{i}	3.65	91
Br	Br^{ii}	3.65	162
(15)			
I	I^{i}	3.90	104
I	I^{ii}	3.90	172

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

By contrast with (16) (§3.2.3), where the nitro groups do not participate in the intermolecular hydrogen bonding, in (17) one of the four nitro O atoms acts as an acceptor in addition to the two sulfone O atoms. As in (5), molecules of (17) act as triple donors and triple acceptors: each molecule of (17) is thus linked to six others but, as in (5) the resulting supramo-

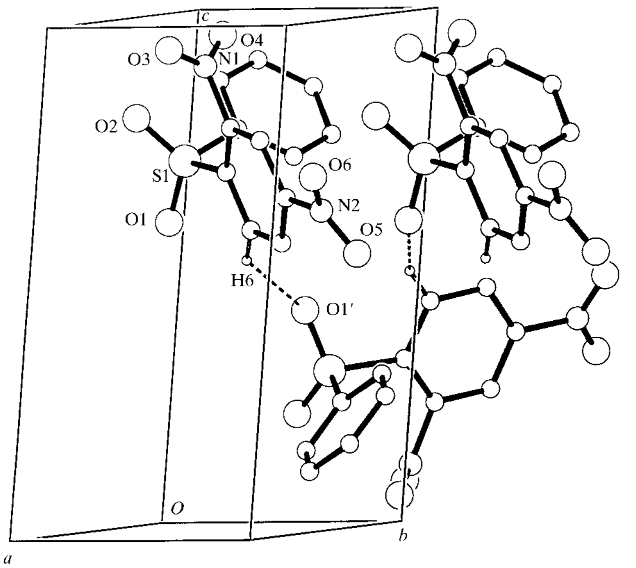

Figure 12
Part of the crystal structure of (16), showing one of the spiral $C(5)$ chains running parallel to [010]. Atoms are depicted as in Fig. 6. The atom marked with a prime (′) is at the symmetry position $(-x, \frac{1}{2}+y, 1-z)$.

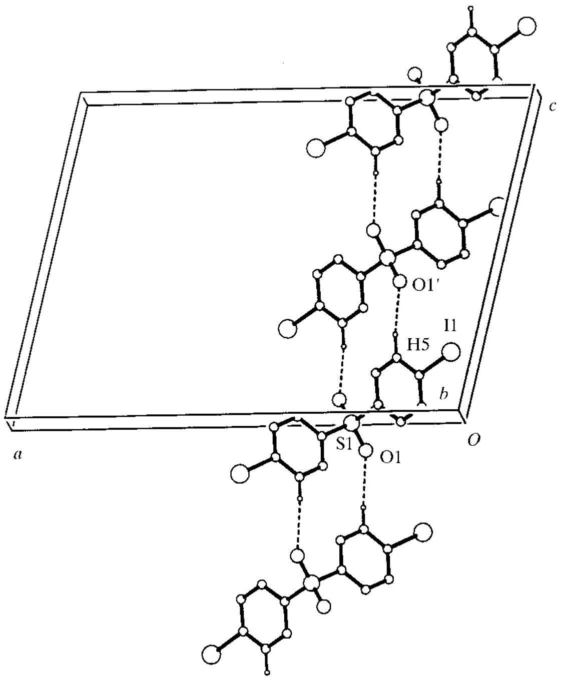

Figure 13
Part of the crystal structure of (15), showing a chain of centrosymmetric $R_2^2(12)$ rings running parallel to [001]. Atoms are depicted as in Fig. 6. The atom marked with a prime (′) is at the symmetry position $(x, \frac{1}{2}-y, \frac{1}{2}+z)$.

lecular structure is again only two-dimensional. There are two parallel motifs involving sulfone O atoms as acceptors; one is the now-familiar *C*(6) translational chain and the other is spiral lying around a 2_1 screw axis (Fig. 16). Orthogonal to these is the third motif, which involves a nitro O atom as an acceptor, and this is a *C*(7) zigzag chain generated by a glide plane (Fig. 17). The combination of these motifs generates a continuous two-dimensional sheet.

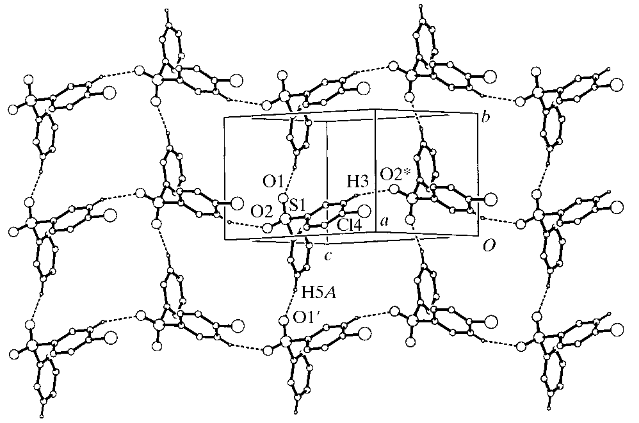

Figure 14
Part of the crystal structure of (4), showing the *C*(6) chains running parallel to [010] and [101], which generate a (4,4) net of $R_4^4(24)$ rings parallel to $(10\bar{1})$. Atoms are depicted as in Fig. 6. The atoms marked with a prime (′) or a star (*) are at the symmetry positions $(x, -1+y, z)$ and $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, respectively. Methyl groups are omitted for the sake of clarity.

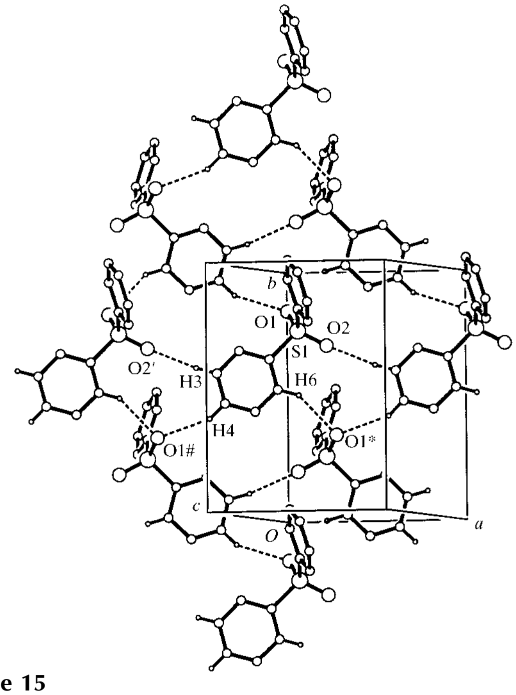

Figure 15
Part of the crystal structure of (5), showing the formation of a sheet parallel to (001) built from a *C*(6) translational chain running parallel to [100], and *C*(5) and *C*(7) spirals running parallel to [010]. Atoms are depicted as in Fig. 6. The atoms marked with a prime (′), a star (*) or a hash (#) are at the symmetry positions $(-1+x, y, z)$, $(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ and $(-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, respectively. Methyl groups are omitted for the sake of clarity.

3.2.5. Three-dimensional hydrogen bonding. Compound (18) differs from all of those previously discussed in that the intermolecular C—H···O hydrogen bonds do not involve the SO_2 group at all. There are three types of C—H···O hydrogen bond present, all involving the nitro O atoms as acceptors. Two of these serve to generate (4,4) nets built from $R_4^2(20)$ and $R_4^4(32)$ rings, arranged in a checker-board fashion (Fig. 18), while the third type joins adjacent sheets to form a continuous three-dimensional framework.

3.2.6. General comments on hydrogen bonding. When a crystal structure contains a single molecular species which acts as a single donor and as a single acceptor of hydrogen bonds, chain formation is the necessary consequence and no supramolecular aggregation of higher dimensionality is possible. The aggregation of simple diaryl sulfones, where the nature of the substituents precludes the formation of hard hydrogen bonds of O—H···O, O—H···N or N—H···O types, is dominated by chain-forming motifs (Table 3). Depending upon whether C—H bonds at the 2-, 3- or 4-positions are involved as hydrogen-bond donors to the sulfone O atoms as acceptors, the chain-forming motifs are of *C*(5), *C*(6) or *C*(7) types. For the compounds considered in this paper, the *C*(5) chains are all generated by the action of 2_1 screw axes, *C*(6) are mostly generated by translation and most of the small number of *C*(7) motifs are generated by glide planes. Against this, it must be noted that in diphenyl sulfoxide (DPHSOX01; Yatsenko *et al.*, 1986) there are *C*(5) chains generated by glide planes. Longer chain-forming motifs are possible in the presence of other acceptors, such as nitro groups, as observed in (18) where a *C*(11) motif can be identified.

If there are chain motifs in more than one direction, as in (4), (5), (17) and (18), the supramolecular aggregation of higher dimensionality results: a two-dimensional structure generated by hydrogen bonding involving a single molecular

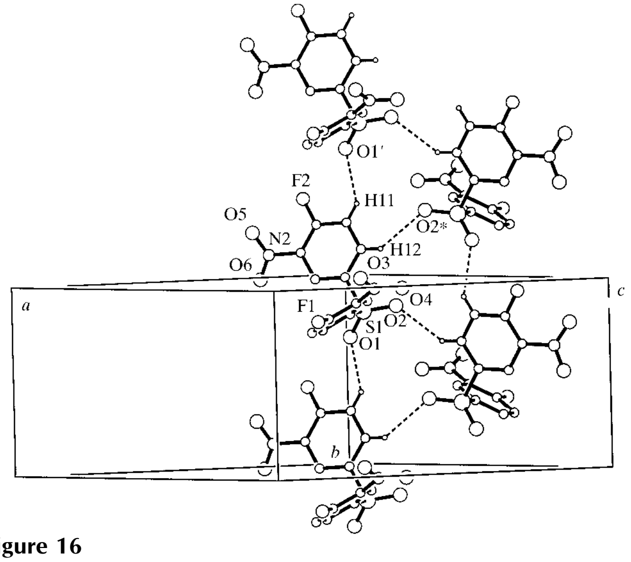

Figure 16
Part of the crystal structure of (17), showing the *C*(5) and *C*(6) chains running parallel to [010]. Atoms are depicted as in Fig. 6. The atoms marked with a prime (′) or a star (*) are at the symmetry positions $(x, -1+y, z)$ and $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, respectively.

species requires at least twofold donor and acceptor behaviour, while three-dimensional aggregation can be generated by either twofold or threefold donor/acceptor behaviour. Twofold donor/acceptor behaviour can lead to two-dimensional plane nets or to three-dimensional diamondoid structures.

The formation of finite (zero-dimensional) cyclic aggregates requires the formation of paired C—H···O hydrogen bonds and such $R_2^2(n)$ motifs are usually generated around centres of inversion. It is striking that although all of the compounds considered in this paper, except for (10) and (16), crystallize in centrosymmetric space groups, such cyclic motifs are rather uncommon: only in (12) is a genuinely zero-dimensional aggregate formed.

The absence of any C—H···O hydrogen bonds in (8) and (9) is unexpected and somewhat puzzling, in comparison to the behaviour of (2) and (10), which are isomeric with (8), and that of (4), which is isomeric with (9). On the other hand, the differing behaviour of (1) and (5), in which the supramolecular aggregation is one- and two-dimensional, respectively, shows that isomeric pairs differing only marginally in the placing of the methyl substituents can behave quite differently.

3.2.7. Non-bonded halogen···halogen contacts. In the original report on the structures of (13)–(15) it was noted (Sime & Woodhouse, 1974*b*) that there were intermolecular $X\cdots X$ contacts significantly shorter than the sum of the van der Waals radii (Bondi, 1964) when X = Br or I. The C—$X\cdots X$ geometries for (14) and (15) (Table 4) are admirably consistent with the generalizations proposed (Ramasubbu *et al.*, 1986) from the results of database analysis, namely that in structures where the $X\cdots X$ distances are significantly less than the van der Waals sum, the observed C—$X\cdots X$ angles are clustered around 180° and around 90°. In systems of the type C—$X\cdots X$—C one of the C—$X\cdots X$ angles is generally close to 180° and the other to 90° (Table 4, Fig. 19). In (3), (4), (9) and (13) there are no intermolecular Cl···Cl contacts which are significantly shorter than the sum of the van der Waals radii.

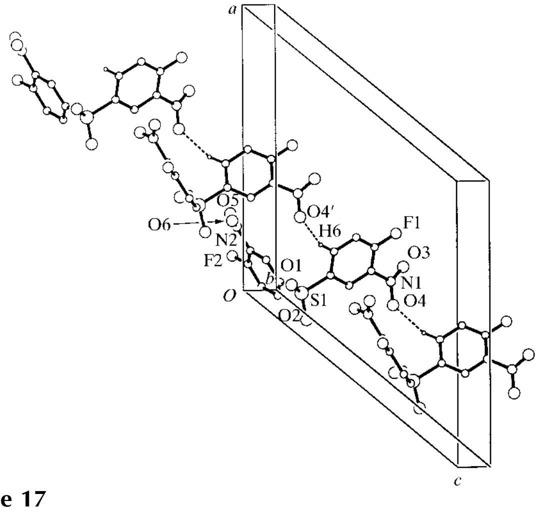

Figure 17
Part of the crystal structure of (17), showing the $C(7)$ chain running parallel to [001]. Atoms are depicted as in Fig. 6. The atom marked with a prime (′) is at the symmetry position $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$.

3.3. Molecular conformations and dimensions

For diaryl sulfones, the commonest conformation for the C_6–SO_2–C_6 skeleton is that of exact or approximate C_2 symmetry, with each aryl ring almost coplanar with a C—S—O fragment (Ferguson *et al.*, 1999). With the exception of (1) and (10), all of the compounds considered in this paper exhibit this conformation, while (13)–(15) exhibit exact C_2 symmetry. Although the simplest interpretation is in terms of the polarity of the aromatic C—H bonds *ortho* to the SO_2 unit, in which both O atoms are involved, one with each ring (Ferguson *et al.*, 1999), the C_2 conformation persists even in (11), although the rings are displaced from coplanarity with the C—S—O fragments. Both molecules in (1) have approximate C_s symmetry, with close contacts between C—H bonds from both rings and a single O atom. It is interesting to note that in diphenyl sulfoxide, C—H bonds from both rings form close contacts with the single O atom, giving a conformation close to C_s symmetry. In both molecules of (10), the unsubstituted ring is almost coplanar with an adjacent C—S—O plane, but the substituted ring is displaced by *ca* 25°, so that the overall

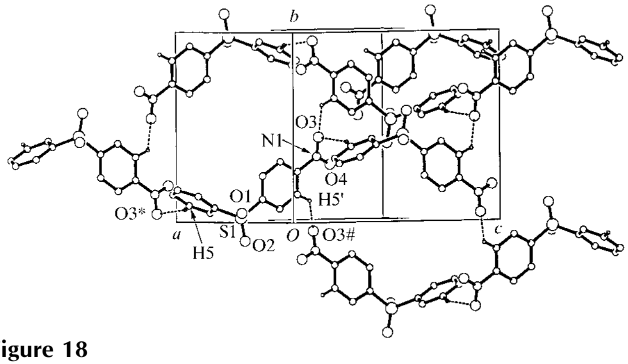

Figure 18
Part of the crystal structure of (18), showing a (4,4) net built from $R_4^2(20)$ and $R_4^4(32)$ rings. Atoms are depicted as in Fig. 6. The atoms marked with a star (*) or a hash (#) are at symmetry positions $(\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ and $(\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, respectively: the atom H5′ is designated as such in the original report. Methyl groups are omitted for the sake of clarity.

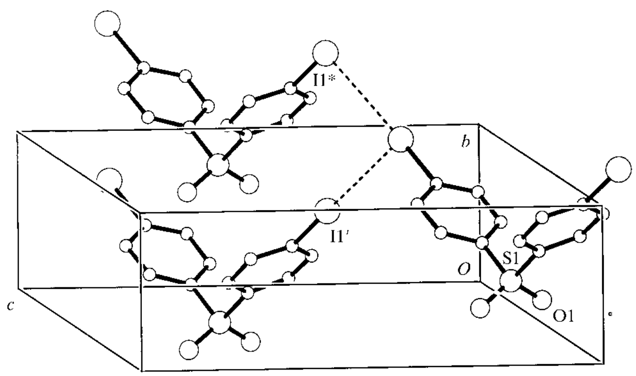

Figure 19
Part of the crystal structure of (15), showing the geometry of the C—I···I contacts. For the sake of clarity H atoms are omitted. The atoms marked with a prime (′) or a star (*) are at the symmetry positions $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ and $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, respectively.

skeletal symmetry is only C_1. The bond lengths and angles in (1)–(5) show no unusual features.

4. Concluding comments

In the diaryl sulfones (1)–(5), whose structures are reported here, the substituent types preclude the formation of hard hydrogen bonds. All of (1)–(5) exhibit soft C—H···O hydrogen bonds and the dominant mode of supramolecular aggregation is chain formation. For the related diaryl sulfones (6)–(18) retrieved from the CSD, chain formation is again the dominant mode of aggregation, with a variety of motifs observed. Where the molecules utilize more than one C—H bond, the resulting supramolecular aggregation may be zero-, one-, two- or three-dimensional, but the constituent one-dimensional substructures can exhibit a rich diversity of form.

Diffraction data for (2), (4) and (5) were collected *via* the EPSRC X-ray Crystallographic Service at the University of Southampton: we thank Professor M. B. Hursthouse and his staff for their assistance.

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