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Intramolecular S···S and S···O close contacts in 1,8-bis(phenylsulfanyl)naphthalene derivatives of different sulfur valence state: an X-ray study

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Abstract

Four peri-substituted naphthalene derivatives, 1,8-bis(phenylsulfanyl)naphthalene (**1**), 1,8-bis[(2-methoxycarbonylphenyl)sulfanyl]naphthalene (**2**), bis[(2-methoxycarbonyl-phenyl)-sulfinyl]naphthalene (**3**) and bis[(2-methoxycarbonylphenyl)sulfonyl]naphthalene (**4**) with different valence states of sulfur were prepared and their molecular structures determined by X-ray diffraction. Data were collected on CAD-4 diffractometers with monochromated MoKα and CuKα radiations. Naphthalene ring torsions, aromatic ring orientations, S···S and S···O close contacts were analyzed and the controlling factors established. In both halves of the molecules, the naphthyl and phenyl rings assume axial–equatorial positions in bis-sulfides **1** and **2**, and twist-axial positions in bis-sulfoxide **3** and bis-sulfone **4**. The S···S distance was found to be 3.01, 3.18; 3.01 and 3.53 Å, for **1**, **2**, **3** and **4**, respectively. The equatorial S-phenyl rings in **2** and the steric crowd in **4** are unfavorable factors for S···S contacts. As expected, S(II)···O and S(IV)···O close contacts are formed in the equatorial and axial S-phenyl rings of **2** and **3**, respectively, with 2.72, 2.73 and 2.77, 2.83 Å distances. Steric repulsion in bis-sulfone **4** is moderated by two C(ar)–S(VI)···O(sulfonyl) type close contacts (2.89 and 3.02 Å), which join the two halves of the molecule. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; S···S and S···O nonbonded interaction; Conformation

1. Introduction

Since the pioneering work of Bezzi et al. [1], nearly thousand structures exhibiting intramolecular X–S···Y close contact appreciably shorter than the sum of the van der Waals radii of S and Y (Y = O, S, Se, N) were determined by X-ray diffraction. Among them a great number of structures with sulfur–oxygen close contacts can be found in which the S···O distances are longer than the usual S–O hypervalent bonds (1.66–2.05 Å) but shorter than the sum of the van der Waals radii (3.25 Å) [2]. Following our first experimental work published in 1977–1980 [3,4], we later systematically studied how S···O close contacts control the actual conformation of sulfides and disulfides [5], sulfoxides [6–8], sulfilimines [6–8,10]

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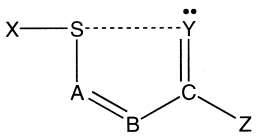
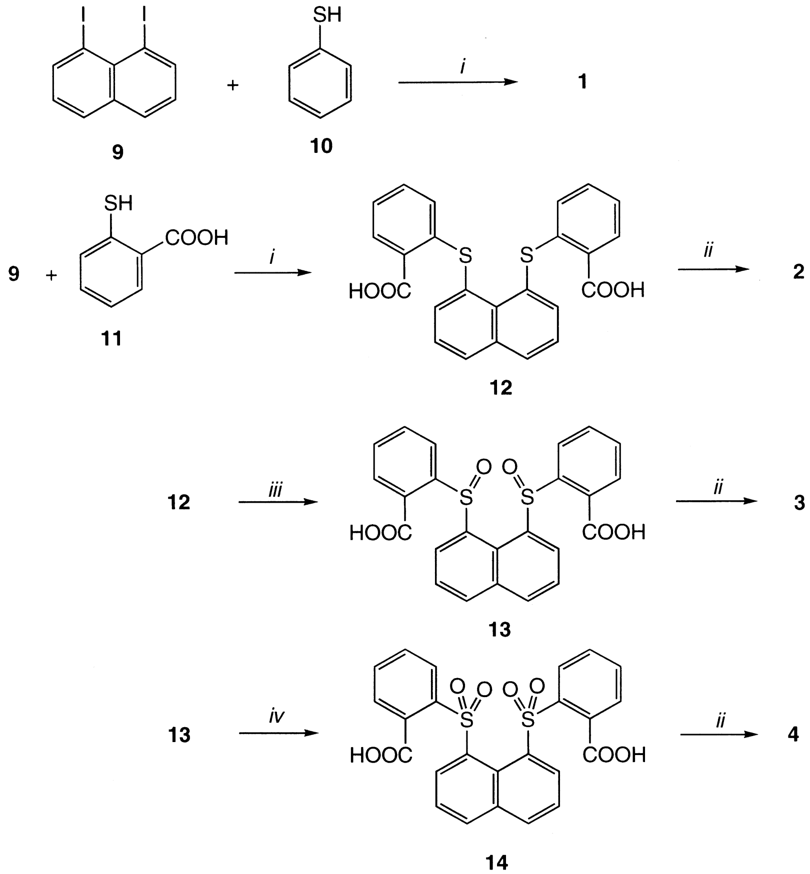


Scheme 1. General formula for compounds exhibiting effective intramolecular S···O nonbonded interaction (see text).

sulfenyl compounds, sulfinates and sulfonates [9], alkoxy- [11] and acylamino(diaryl) sulfonium salts [12,13] and spiro-λ^4-sulfanes [11,12,14]. We also experienced that reactivity in some cases is significantly affected by intramolecular S···O nonbonded interaction [15–18]. The quantum chemical interpretation of the nature of the S···O interaction was attempted first by semiempirical (e.g. extended Hückel in Ref. [19] calculations and later on by the ab initio SCF–MO method [20]. Systematic calculations showed that the attractive S···O interaction can be regarded as a weak hypervalent bond like that in unsymmetrical spiro-λ^4-sulfanes, and its extent may be well correlated with the shortening of the S···O distance. From experimental facts and calculations, we concluded that the S···O interaction is rather strong in compounds characterized by a general formula shown in Scheme 1 where (i) X is an electronegative or polarizable atom (e.g. O and S are more effective than C) and the X–S···O sequence is nearly linear (lone-pair delocalization to the σ^*_{X-S} antibonding orbital); (ii) in the conjugated sequence A = Csp^2, B, Y = Csp^2 or Nsp^2, Z = O(R), N(R$_2$), C(R$_3$), H or lone pair, and the five-membered conjugated ring closed by S···O contact is planar (quasi-aromatic



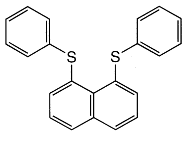
Scheme 2. Synthesis of compounds **1**–**4**. Reagents and conditions: (i) Cu_2O, pyridine; (ii) diazomethane, CH_2Cl_2–ether or dioxane–ether, (iii)TsNClNa, $KHCO_3$ aq, 100°C, 1 h; (iv) H_2O_2–AcOH, 100°C, 30 min.

system); (iii) in analogous compounds, the S···O interaction is weakened (i.e. the S···O distance increased) by increasing the oxidation number (2, 4 or 6) of the sulfur atom.

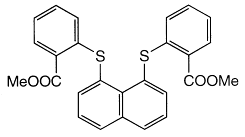
The importance of S···O interaction in controlling both the actual conformation and the reactivity of organosulfur compounds prompted us to investigate the naphthalene derivatives having S-aryl substituents in 1,8-positions. However, in this case a repulsive S···S interaction should also exist, from which stereochemistry becomes more complicated. As it has been shown by Glass et al. [21–23], the S···S nonbonded distances in peri-substituted naphthalene derivatives lie in the region of 2.93–3.63 Å, and therefore, they are shorter than the sum of the van der Waals radii (3.70 Å), but longer than the S–S covalent bond (2.01 Å) and the S···S distance (2.50–2.86 Å) found earlier in the case of attracting interaction [24,25]. Owing to the steric strain, the peri bond angles are increased and the sulfur atoms in 1,8-positions displace to the opposite sides of the least-squares plane of the naphthalene ring. The measure of the deviations was found to depend on the valence state of the sulfur atom.

1.1. Model compounds

In this paper, we report the X-ray structure determinations of four 1,8-disubstituted naphthalene derivatives, 1,8-bis(phenylsulfanyl)naphthalene (**1**), 1,8-bis[(2-methoxycarbonylphenyl)sulfanyl]naphthalene (**2**), 1,8-bis[(2-methoxycarbonylphenyl)sulfinyl]-naphthalene (**3**) and 1,8-bis[(2-methoxycarbonyl-phenyl)sulfonyl]naphthalene (**4**). These compounds have sulfur atoms of different valence states in the peri positions giving rise to different S···S close contacts. Compounds **2**–**4** carry methoxycarbonyl groups in the *ortho* positions of the S-phenyl substituents, which may take part as donor groups in an S···O=C< close contact of 1,5 type. In order to elucidate how the structure is governed by both S···S and S···O nonbonded interactions and the rigidity of the molecular skeleton, the structures of compounds **1**–**4** are analyzed and compared with those of 1,8-bis(methylsulfanyl)naphthalene (**5**), and naphtho-(1,8-bc)-1,5-dithiocin derivatives of bis-sulfide (**6**), bis-sulfoxide (**7**) and bis-sulfone (**8**) type which were investigated earlier by Glass et al. [21–23].



1



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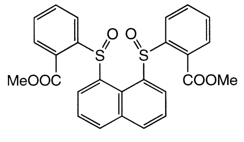

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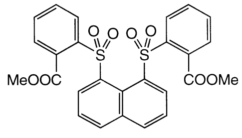

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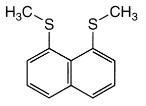

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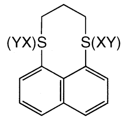

6 X, Y= lone pair
7 X=O, Y=lone pair
8 X, Y=O

1.2. Synthesis (Scheme 2)

Bis-sulfide **1** was prepared from 1,8-diiodonaphthalene (**9**) [26] and benzenethiol (**10**) in pyridine containing copper(I) oxide. To obtain bis-sulfide **2**, 1,8-diiodonaphthalene (**9**) was first coupled with 2-sulfanylbenzoic acid (**11**) then dicarboxylic acid **12** was converted with diazomethane into the corresponding dimethyl ester (bis-sulfide **2**). The oxidation of **12** with chloramine-T resulted in sulfoxide-dicarboxylic acid **13** which was treated with diazomethane to yield bis-sulfoxide **3**. The synthesis of bis-sulfone **4** started from **13** which was oxidized first with hydrogen peroxide to sulfone-dicarboxylic acid **14**, then the latter was methylated with diazomethane to yield **4**.

2. Experimental

2.1. Materials

Melting points (mp) were determined on a Boëtius micro melting point apparatus. Infrared (IR) spectra were taken on a Specord IR 75 (Zeiss, Jena) spectrophotometer. Microanalyses were carried out in the microanalytical laboratory of the Department of

Table 1
Crystal and relevant X-ray data for compounds **1**–**4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{22}H_{16}S_2$	$C_{26}H_{20}O_4S_2$	$C_{26}H_{20}O_6S_2$	$C_{26}H_{20}O_8S_2$
Molecular mass	344.47	460.54	492.54	524.54
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	P-1	Pn	$P2_12_12_1$
a (Å)	8.336(1)	7.771(1)	9.318(2)	8.453(1)
b (Å)	19.593(3)	9.275(1)	8.271(1)	12.279(1)
c (Å)	10.690(1)	16.620(1)	14.607(1)	22.290(1)
α (deg)	90	94.74(1)	90	90
β (deg)	91.57(1)	99.11(1)	95.23(1)	90
γ (deg)	90	106.72(1)	90	90
Cell volume (Å^3)	1745.3(4)	1122.3(2)	1121.1(3)	2313.6(3)
Z	4	2	2	4
$F(000)$	720	480	512	1088
D_c (g cm^{-3})	1.311	1.363	1.459	1.506
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan rate (deg min^{-1})	1–20	1–20	1–20	1–20
Scan width	$0.50 + 0.14 \tan\theta$	$0.50 + 0.14 \tan\theta$	$0.50 + 0.14 \tan\theta$	$0.50 + 0.14 \tan\theta$
X-ray radiation	MoKα	MoKα	MoKα	CuKα
λ (Å)	0.71073	0.71073	0.71073	1.54178
μ (mm^{-1})	0.304	0.268	0.280	2.545
Crystal size (mm)	0.60 × 0.30 × 0.20	0.30 × 0.30 × 0.15	0.60 × 0.45 × 0.35	0.25 × 0.12 × 0.10
θ range (deg)	2.44–31.96	2.31–34.96	2.46–32.63	3.97–74.45
Total reflections	6456	10463	4297	5325
Non-zero reflections	3206	4466	3565	4066
Number of reflections used in refinement	6040	9870	4296	4687
Parameters refined	217	291	309	327
Refinement on	F^2	F^2	F^2	F^2
σ level	2.0	2.0	2.0	2.0
Weighting scheme	$1/[\sigma^2(F_0^2) + (0.0530P)^2 + 0.1805P]$ $P = (F_0^2 + 2F_c^2)/3$	$1/[\sigma^2(F_0^2) + (0.0740P)^2 + 0.0480P]$ $P = (F_0^2 + 2F_c^2)/3$	$1/[\sigma^2(F_0^2) + (0.0617P)^2 + 0.3610P]$ $P = (F_0^2 + 2F_c^2)/3$	$1/[\sigma^2(F_0^2) + (0.0456P)^2 + 0.2689P]$ $P = (F_0^2 + 2F_c^2)/3$
$R = \Sigma\Delta F/\Sigma F_0$	0.0399	0.0498	0.0332	0.0328
$R = \Sigma w(\Delta F^2)/\Sigma\lvert F_0^2\rvert$	0.0998	0.1306	0.0839	0.0800
$S = \Sigma(w\lvert\lvert F_0\rvert - \lvert F_c\rvert\rvert)^2\ (N_0{-}P)^{1/2}$	0.999	0.991	1.041	1.041
Max LS shift to error ratio (Δ/σ)	0.001	0.000	0.000	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.304	0.318	0.418	0.149
$\Delta\rho_{min}$ (e Å^{-3})	− 0.311	− 0.250	− 0.417	− 0.254

Organic Chemistry by Dr H. Medzihradszky-Schweiger and co-workers.

Solvents were purified and dried by the usual methods. Evaporations were carried out under reduced pressure. Products obtained were dried in vacuo over P_2O_5 or KOH pellets, depending on the solvent used.

*2.2. 1,8-Bis(phenylsulfanyl)naphthalene (**1**)*

A mixture of 1,8-diiodonaphthalene (**9**) (7.54 g, 20 mmol), benzenethiol (**10**) (4.41 g, 10 mmol) and Cu_2O (2.86 g, 20 mmol) in dry pyridine (60 ml) was refluxed under N_2 (2 h) and, after cooling to room temperature, was poured into a mixture of ice (100 g) and cc HCl (100 ml). The precipitate was filtered off, washed with water, dried and then extracted with ether (100 ml). After evaporation, the crude product was crystallized from MeOH; yield: 3.7 g (55%); mp 75–76°. Elemental analysis — found: C, 76.5; H, 4.5; S, 18.5. $C_{22}H_{16}S_2$ requires: C, 76.70; H, 4.68; S, 18.62%.

*2.3. 1,8-Bis[2-(methoxycarbonyl)phenylsulfanyl]-naphthalene (**2**)*

The solution of 1,8-diiodonaphthalene (**9**) (20 g, 53 mmol), 2-sulfanylbenzoic acid (**11**) (16.2 g, 106 mmol), Cu_2O (7.6 g, 53 mmol) in dry pyridine was refluxed under N_2 for 2 h. After cooling to room temperature, the mixture was poured into the mixture of ice (300 g) and cc HCl (300 ml). The precipitate was filtered off, washed with water and boiled in an aqueous solution of NaOH (10 g, 250 mmol in 500 ml of water) for 2 h and filtered. The filtrate was acidified with cc HCl (pH 1), the precipitate was filtered off, washed with water, dried and recrystallized from DMF–AcOH to afford pure 1,8-bis(2-carboxyphenylsulfanyl)naphthalene (**12**). Yield: 13.2 g (51%); mp 324–325°C; IR (KBr): 3680–2200br (O–H), 1705vs (C=O) cm^{-1}. Elemental analysis — found: C, 66.5; H, 3.6; O, 14.5; S, 14.5. $C_{24}H_{16}O_4S_2$ requires: C, 66.65; H, 3.73; O, 14.80; S, 14.83%.

Compound **2** was prepared from **12** with diazomethane in dichloromethane. M_p 170–172°C; IR (KBr): 1710vs (C=O) cm^{-1}. Elemental analysis — found: C, 67.9; H, 4.4; O, 13.7; S, 13.7. $C_{26}H_{20}O_4S_2$ requires: C, 67.80; H, 4.38; O, 13.90; S, 13.92%.

*2.4. 1,8-Bis[2-(methoxycarbonyl)phenylsulfinyl]-naphthalene (**3**)*

Sulfide dicarboxylic acid **12** (2 g, 4 mmol) was dissolved in a solution of 1 M $KHCO_3$ (15 ml) by heating, and chloramine-T ($TsNClNa\cdot 3H_2O$, 2.54 g, 9 mmol) was added. After heating at 100°C (1 h), the mixture was cooled to room temperature, the precipitate ($TsNH_2$) was filtered off, the filtrate extracted with EtOAc (3 × 10 ml) and then acidified with cc HCl (pH 1). The precipitate was filtered off, washed with water and dried to give 1,8-bis(2-carboxyphenylsulfinyl)naphthalene **13**. Yield: 1.77 g (94%); mp 202–205°C; IR (KBr): 3600–2200br (O–H), 1686s (C=O), 1003vs (S=O) cm^{-1}. Elemental analysis — found: C, 61.8; H, 3.3; O, 20.5; S, 13.8. $C_{24}H_{16}O_6S_2$ requires: C, 62.05; H, 3.47; O, 20.67; S, 13.80%.

Compound **3** was prepared from **13** with diazomethane in dioxane. M_p 257–260°C; IR (KBr): 1713vs (C=O), 1022vs (S=O) cm^{-1}. Elemental analysis — found: C, 63.1; H, 4.0; O, 19.2; S, 12.9. $C_{26}H_{20}O_6S_2$ requires: C, 63.40; H, 4.09; O, 19.49; S, 13.02%. X-ray data reveal that crystalline bis-sulfoxide **3** (with a symmetric constitution and with two asymmetric sulfur atom) is present in the racemic form (Fig. 3 shows the stereoscopic view of the *R*, *R*-enantiomer). The relative stability of the racemic bis-sulfoxide **3** may be attributed to the favorable position of the sulfinyl-oxygens (see Fig. 3 and Table 10).

*2.5. 1,8-Bis[2-(methoxycarbonyl)phenylsulfonyl]-naphthalene (**4**)*

Sulfoxide dicarboxylic acid **13** (0.99 g, 2 mmol) was dissolved in AcOH and H_2O_2 (30%, 7 ml) was added to the solution. The mixture was refluxed for 30 min, additional H_2O_2 (2 ml) was added and heating was continued for 1 h. After cooling to room temperature, the crystals precipitated were filtered off and dried to yield 1,8-bis(2-carboxyphenylsulfonyl)-naphthalene (**14**, 0.86 g, 89%), IR (KBr): 3650–2200br (O–H), 1700vs (C=O), 1315s (SO_2) cm^{-1}. Elemental analysis — found: C, 58.0; H, 3.3; O, 25.5; S, 12.7. $C_{24}H_{16}O_8S_2$ requires: C, 58.05; H, 3.25; O, 25.78; S, 12.92%.

Compound **4** was prepared from sulfone dicarboxylic acid **14** with diazomethane in dichloromethane. M_p

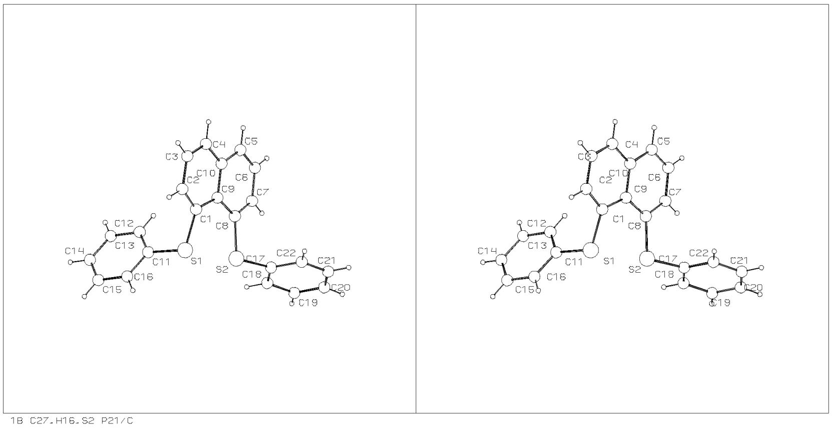

Fig. 1. Stereoscopic view of bis-sulfide **1** with numbering scheme for the nonhydrogen atoms.

297–300°C; IR (KBr): 1722vs (C=O), 1329vs (SO_2) cm^{-1}. Elemental analysis — found: C, 59.3; H, 3.7; O, 24.2; S, 12.0. $C_{26}H_{20}O_8S_2$ requires: C, 59.53; H, 3.84; O, 24.40; S, 12.22%.

2.6. Crystal structure determinations

Single crystals of X-ray quality were grown from a hot solution of **1** in methanol, a hot solution of **2** in DMF, while **3** and **4** were recrystallized from a 2:1 mixture of dioxane and water, and a mixture of DMF and water, respectively. Table 1 summarizes the relevant data concerning the crystal structure analyses.

Each data set was collected on a CAD-4 diffractometer equipped with graphite monochromator. Lattice parameters were refined by least squares fit for 25 reflections. Standard reflections (three for each data collection) indicated no decay of the crystals. All reflections were corrected for Lorenz and polarization effects. The crystallographic phase problems were solved by a direct method using program SHELXS [27]. The atomic positions for each structure were refined with anisotropic displacement parameters in F^2 mode using the program SHELXL93 [28]. The hydrogen positions were generated from assumed geometry and were refined isotropically in riding mode. Since the molecules of **4** exhibit molecular chirality in space group $P2_12_12_1$, Flack parameter [29] was refined on data collected with CuKα radiation. Furthermore, the visible C_2 symmetry of the molecules in **2** and **3** prompted us to check the possibility of establishing space groups

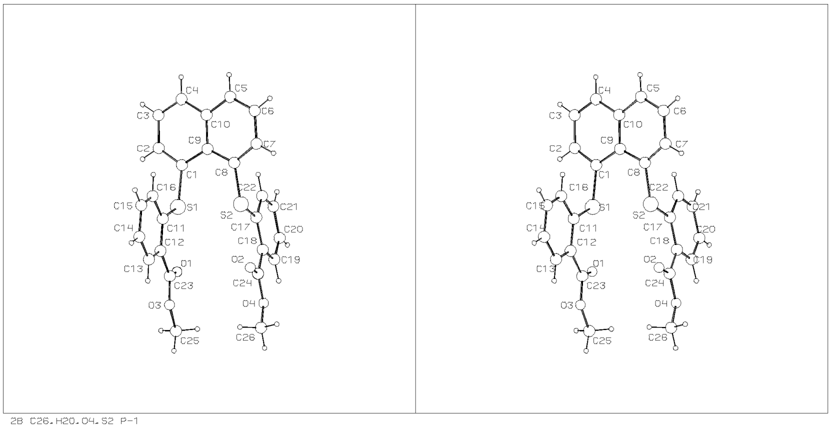

Fig. 2. Stereoscopic view of bis-sulfide **2** with numbering scheme for the nonhydrogen atoms.

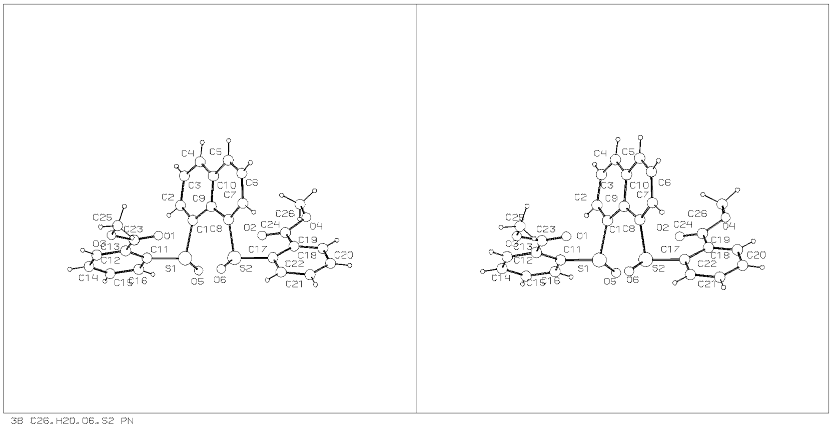

Fig. 3. Stereoscopic view of bis-sulfide **3** with numbering scheme for the nonhydrogen atoms.

with crystallographic twofold axes. These efforts were fruitless, however.

Crystal data (excluding structure factors) for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre and are also available from the authors.

3. Results and discussion

The stereoscopic views of compounds **1**–**4** are shown in Figs. 1–4. Relevant geometric parameters with estimated standard deviations in the last significant digits are listed in Tables 2–5. The last digits of the geometric data were omitted when discussed in the text. The structures **2**–**4** with *ortho*-COOMe substituents exhibit more or less distorted C_2 molecular (not crystallographic) symmetry, while that of **1** is free from any molecular symmetry.

3.1. Orientation of aromatic rings

The mutual positions of the naphthalene and phenyl rings in compounds **1**–**4** are presumably in a close correlation with S···S and S···O close contacts formed in an intramolecular manner. From a structural point of view, compounds **1**–**4** may be regarded as ‘Siamese twins’ composed from two diaryl sulfide, -sulfoxide or -sulfone parts which are fused through one of their benzene rings. In these twin-molecules, the orientation of S-naphthyl rings with regard to the C(ar)–S(1)–C(ar) and C(ar)–S(2)–C(ar) planes can

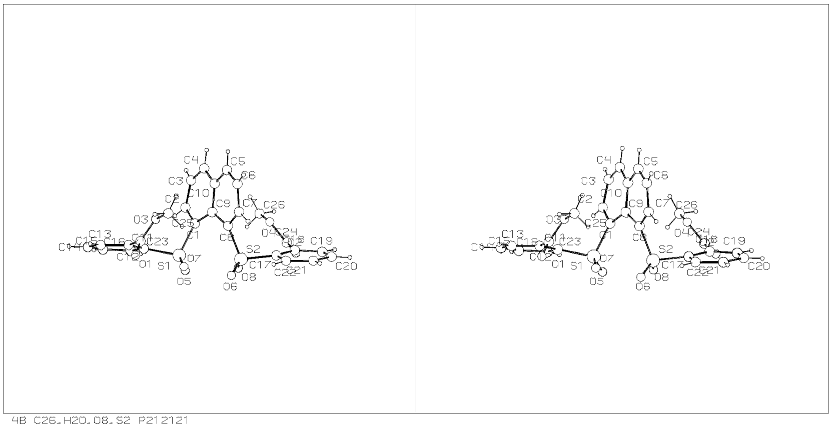

Fig. 4. Stereoscopic view of bis-sulfone **4** with numbering scheme for the nonhydrogen atoms.

Table 2
Relevant geometric parameters for bis-sulfide **1** with ESDs in parentheses

Interatomic distances (Å)			
S1···S2	3.005(1)	C9–C10	1.439(2)
C1–C9	1.432(2)	C8–C9	1.436(2)
C4–C10	1.412(3)	C5–C10	1.407(3)
S1–C1	1.780(2)	S2–C8	1.782(2)
S1–C11	1.773(2)	S2–C17	1.783(2)
Angles (deg)			
C1–C9–C8	127.2(1)	C4–C10–C5	119.5(2)
C9–C1–S1	124.0(1)	C9–C8–S2	121.9(1)
C1–S1–C11	102.7(1)	C8–S2–C17	102.5(1)
C1–S1···S2	82.0(1)	C8–S2···S1	83.5(1)
C11–S1···S2	105.1(1)	C17–S2···S1	168.5(1)
Torsion angles (deg)			
C10–C9–C1–S1	175.1(1)	C10–C9–C8–S2	172.1(1)
C9–C1–S1–C11	−95.2(1)	C9–C8–S2–C17	− 160.0(1)
C1–S1–C11–C12	26.1(2)	C8–S2–C17–C18	− 112.8(1)
S1–C1···C8–S2	− 10.9(1)	C11–S1···S2–C17	− 146.2(3)

be described by the torsion angles $\varphi_1 = $ C(9)–C(1)–S(1)–C(11) and $\varphi_2 = $ C(9)–C(8)–S(2)–C(17), while that of S-phenyl rings by the $\psi_1 = \mathrm{C(1)} - \mathrm{S(1)} - \mathrm{C(11)} - \mathrm{C(12)}$ and $\psi_2 = \mathrm{C(8)} - \mathrm{S(2)} - \mathrm{C(17)} - \mathrm{C(18)}$ torsion angles, respectively (Table 8). If φ or ψ are about 90°, the conformation is axial, if they are about 180°, the conformation is equatorial; the intermediate cases are designated as twist (cf. Refs. [5,6]).

The mutual *axial–equatorial* orientation of the naphthyl and phenyl rings in both halves of bis-sulfides **1** and **2** corresponds to the general trend observed in case of diaryl sulfides [5]. However, the 'aircraft-like' shape of molecule **1** turns into a 'medusa-like' one in molecule **2** (cf. Figs. 1 and 2) because in **2**, both phenyl rings are equatorial, i.e. coplanar with the C(ar)–S–C(ar) planes (and the naphthalene ring is axial in both S1 and S2 parts of the molecule). Similar to other diaryl sulfoxides, the two halves of the bis-sulfoxide **3** do not assume an ideal butterfly (axial–axial) conformation (cf. Ref. [6]) but a less crowded twist-axial conformation appears in both parts of the molecule (Table 6). Both phenyl rings here are axial, i.e. perpendicular to the C(ar)–S–C(ar) planes. The twist-axial conformations found for the two halves of bis-sulfone **4** are nearer to a butterfly (axial–axial) conformation than those in bis-sulfoxide **3**, i.e. the φ and ψ torsion angles in **4** are nearer to the ideal 90° than in **3** (Table 6).

3.2. S···S interactions

The four naphthalene derivatives **1**–**4** bear the two sulfur atoms in the peri position, and therefore, they are unavoidably nearer to each other (3.00, 3.18, 3.01 and 3.53 Å, respectively) than the sum of their van der Waals radii. The repulsive S···S interaction between sulfur atoms should result in the stretching of C–C bonds and C–C–C bond angles in the naphthalene part, together with a twisting of the planar naphthalene ring. Indeed, the bond lengths around C9 is significantly longer than those around C10 (average 1.43 and 1.41 Å, respectively). The most affected C1–C9–C8 bond angles open to a mean value of 128°, whereas the analogous C4–C10–C5 bond angles remain near to the ideal 120°. However, all these deviations would promote the separation of the sulfur atoms only from a distance of 2.44–2.58 Å. An additional separation is provided by both the widening of the S1–C1–C9 and S2–C8–C9 bond angles, and a twisting of the naphthalene ring as shown by the nonbonded torsion angles S1–C1···C8–S2 (Table 7). The distortion of the 1,8-disubstituted naphthalene ring (cf. Refs. [21–23]) may also be described by the displacement of the sulfur atoms above and below the average plane of the naphthalene ring (ΔS1 and ΔS2 data in Table 7).

In bis-sulfides, the S(II)···S(II) nonbonded distances are obviously controlled by the repulsion

Table 3
Relevant geometric parameters for bis-sulfide **2** with ESDs in parentheses

Interatomic distances (Å)			
S1···S2	3.182(1)	C9–C10	1.429(2)
S1···O1	2.723(2)	S2···O2	2.727(1)
C1–C9	1.432(2)	C8–C9	1.440(2)
C4–C10	1.424(3)	C5–C10	1.407(3)
S1–C1	1.777(2)	S2–C8	1.778(2)
S1–C11	1.767(2)	S2–C17	1.766(2)
C12–C23	1.485(3)	C18–C24	1.476(3)
C23–O1	1.189(3)	C24–O2	1.193(2)
C23–O3	1.321(2)	C24–O4	1.330(2)
O1···O2	3.900(2)		
Angles (deg)			
C1–S1···O1	175.3(1)	C8–S2···O2	179.6(1)
C1–C9–C8	127.5(1)	C4–C10–C5	119.7(2)
C9–C1–S1	126.0(1)	C9–C8–S2	126.0(1)
C1–S1–C11	102.8(1)	C8–S2–C17	103.2(1)
C12–C23–O1	125.0(2)	C18–C24–O2	125.5(2)
C12–C23–O3	112.7(2)	C18–C24–O4	112.3(2)
O1–C23–O3	122.3(2)	O2–C24–O4	122.2(2)
C1–S1···S2	80.3(1)	C8–S2···S1	80.0(1)
C11–S1···S2	78.5(1)	C17–S2···S1	78.0(1)
Torsion angles (deg)			
C10–C9–C1–S1	177.6(1)	C10–C9–C8–S2	176.6(1)
C9–C1–S1–C11	79.5(2)	C9–C8–S2–C17	79.2(2)
C1–S1–C11–C12	−171.0(2)	C8–S2–C17–C18	−176.1(1)
S1–C11–C12–C23	−1.6(3)	S2–C17–C18–C24	−2.1(2)
C11–C12–C23–O1	−7.5(3)	C17–C18–C24–O2	−4.6(3)
C12–C23–O1···S1	8.6(3)	C18–C24–O2···S2	5.9(2)
C23–O1···S1–C11	−7.2(2)	C24–O2···S2–C17	−5.3(1)
O1···S1–C11–C12	4.2(2)	O2···S2–C17–C18	3.6(1)
C11–C12–C23–O1	−7.5(3)	C17–C18–C24–O2	−4.6(3)
C11–C12–C23–O3	173.2(2)	C17–C18–C24–O4	176.6(2)
C12–C23–O3–C25	175.5(2)	C18–C24–O4–C26	176.9(2)
S1–C1···C8–S2	−4.8(1)	C11–S1···S2–C17	144.8(1)
O1···S1···S2···O2	−5.4(1)		

between the p-type lone pairs of the sulfur atoms. Repulsion is thought to be relatively high (cf. Ref. [21]) when the axis of the sulfur p-orbitals are collinear and lie in the plane of the aromatic bonding system. This is the situation if the two corresponding torsion angles φ_1(C9–C1–S1–C11) and φ_2(C9–C8–S2–C17) are near 90°. The lone pair–lone pair repulsion is less effective when the axis of the sulfur p-orbitals are parallel and vertical to the plane of the aromatic (naphthalene) ring. In this case, the φ torsion angles are approximately 180°. On the other hand, an attractive part of the interaction may also operate if there is a nearly linear X–S(II)···S(II) sequence in the molecule, which may promote the delocalization of the sulfur lone pair to the antibonding σ^* (S–X) orbital (cf. Ref. [20]). In bis-sulfoxides and bis-sulfones, the repulsion between nonbonded oxygen atoms should also be taken into account. Geometric parameters related to S(II)···S(II) nonbonded interaction are shown in Table 8.

Bis-sulfide **1** is an *S*,*S*-diphenyl analogue of the *S*,*S*-dimethyl derivative **5** investigated earlier by Glass et al. [21]. The methyl–phenyl change in *S*-substituents does not cause any dramatic change in the molecular geometry. Table 7 shows that the torsion and the twisting of the naphthalene ring is similar in both compounds. However, the S(II)···S(II) nonbonded distance is somewhat longer in compound **1**

Table 4
Relevant geometric parameters for bis-sulfoxide **3** with ESDs in parentheses

Interatomic distances (Å)			
S1···S2	3.005(1)	C9–C10	1.437(3)
S1···O1	2.769(3)	S2···O2	2.831(3)
C1–C9	1.426(4)	C8–C9	1.434(4)
C4–C10	1.419(5)	C5–C10	1.410(4)
S1–C1	1.813(2)	S2–C8	1.814(3)
S1–C11	1.815(3)	S2–C17	1.820(3)
S1–O5	1.506(2)	S2–O6	1.483(3)
C12–C23	1.487(4)	C18–C24	1.489(4)
C23–O1	1.198(4)	C24–O2	1.198(4)
C23–O3	1.327(4)	C24–O4	1.326(4)
O1···O2	5.469(4)	O5···O6	4.553(3)
Angles (deg)			
O5–S1···O1	177.9(1)	O6–S2···O2	177.0(1)
C1–C9–C8	128.1(2)	C4–C10–C5	119.7(3)
C9–C1–S1	122.4(2)	C9–C8–S2	121.4(2)
C1–S1–C11	100.7(1)	C8–S2–C17	98.7(1)
C1–S1–O5	105.4(1)	C8–S2–O6	107.9(2)
C11–S1–O5	104.2(1)	C17–S2–O6	104.4(1)
C12–C23–O1	123.4(3)	C18–C24–O2	123.9(3)
C12–C23–O3	112.0(3)	C18–C24–O4	112.5(3)
O1–C23–O3	124.6(3)	O2–C24–O4	123.6(3)
C1–S1···S2	82.3(1)	C8–S2···S1	82.9(1)
C11–S1···S2	151.1(1)	C17–S2···S1	150.6(1)
Torsion angles (deg)			
C10–C9–C1–S1	−174.5(2)	C10–C9–C8–S2	−167.0(2)
C9–C1–S1–C11	138.1(2)	C9–C8–S2–C17	136.1(2)
C9–C1–S1–O5	−113.8(2)	C9–C8–S2–O6	−115.6(2)
O5–S1–C11–C12	173.4(2)	O6–S2–C17–C18	−173.7(3)
C1–S1–C11–C12	−77.6(3)	C8–S2–C17–C18	−62.5(3)
S1–C11–C12–C23	6.5(4)	S2–C17–C18–C24	0.6(4)
C11–C12–C23–O1	2.6(5)	C17–C18–C24–O2	−14.9(5)
C12–C23–O1···S1	−6.2(3)	C18–C24–O2···S2	14.8(3)
C23–O1···S1–C11	7.2(2)	C24–O2···S2···C17	−11.0(2)
O1···S1–C11–C12	−6.7(2)	O2···S2···C17–C18	4.9(2)
C11–C12–C23–O3	−177.3(3)	C17–C18–C24–O4	165.5(3)
C12–C23–O3–C25	177.0(4)	C18–C24–O4–C26	177.4(4)
S1–C1···C8–S2	−15.8(1)	C11–S1···S2–C17	−179.5(3)
O1···S1···S2···O2	−135.0(1)	O5–S1···S2–O6	−135.5(2)

(3.01 Å) than in the methyl-analogue **5** (2.93 Å), which may be ascribed to a stronger lone pair–lone pair repulsion in the former case. In bis-sulfide **1**, only one of the C9–C(ar)–S–C(ar) torsion angles is nearly 180° (see φ_1 and φ_2 in Table 6), whereas in compound **5**, both the torsion angles are 180°. The relatively short S(II)···S(II) distances in bis-sulfide **5** may also be correlated with two favorable quasi-linear C–S(II)···S(II) moieties which provide an attractive part for the S(II)···S(II) interaction. In bis-sulfide **1**, there is only one such sequence (see Table 8). Here, it should be mentioned that the S(II)···S(II) distance may become even shorter if the counter-atom is changed (e.g. 2.86 Å with an S–S···S sequence in Ref. [25]).

In bis-sulfide **2**, which is an o,o'-bis(methoxycarbonyl) derivative of compound **1**, the bond angles of the naphthalene ring are strongly distorted, while the disposition of sulfur atoms above and below the naphthalene ring is relatively small (Table 7). The S(II)···S(II) nonbonded distance is remarkably longer (3.18 Å) than in the unsubstituted compound **l**. The

Table 5
Relevant geometric parameters for bis-sulfone **4** with ESDs in parentheses

Interatomic distances (Å)			
S1···S2	3.531(1)	C9–C10	1.433(3)
S1···O3	3.304(2)	S2···O4	3.164(2)
S1···O6	3.022(2)	S2···O5	2.890(2)
C1–C9	1.436(3)	C8–C9	1.431(3)
C4–C10	1.413(3)	C5–C10	1.414(3)
S1–C1	1.783(2)	S2–C8	1.791(2)
S1–C11	1.788(2)	S2–C17	1.791(2)
C12–C23	1.501(3)	C18–C24	1.492(4)
C23–O3	1.333(3)	C24–O4	1.334(3)
O3···O4	6.345(2)	O5···O8	2.841(2)
O5···O6	2.847(2)	O7···O8	4.627(3)
O6···O7	3.072(2)		
Angles (deg)			
O7–S1···O3	170.7(1)	O8–S2···O4	171.7(1)
C11–S1···O6	174.7(1)	C17–S2···O5	178.6(1)
C1–C9–C8	129.0(2)	C4–C10–C5	119.5(2)
C9–C1–S1	124.5(2)	C9–C8–S2	125.2(2)
C1–S1–C11	105.3(1)	C8–S2–C17	103.8(1)
C1–S1–O5	109.6(1)	C8–S2–O6	109.4(1)
C1–S1–O7	109.2(1)	C8–S2–O8	110.2(1)
O5–S1–O7	120.6(1)	O6–S2–O8	120.5(1)
C11–S1–O5	105.6 (1)	C17–S2–O6	106.4 (1)
C11–S1–O7	105.5 (1)	C17–S2–O8	105.1 (1)
C12–C23–O1	124.4(2)	C18–C24–O2	124.2(2)
C12–C23–O3	110.8(2)	C18–C24–O4	111.1(2)
O1–C23–O3	124.7(2)	O2–C24–O4	124.5(3)
C1–S1···S2	72.3(1)	C8–S2···S1	71.3(1)
C11–S1···S2	151.8(1)	C17–S2···S1	157.9(1)
Torsion angles (deg)			
C10–C9–C1–S1	− 156.7(2)	C10–C9–C8–S2	− 152.0(2)
C9–C1–S1–C11	119.8(2)	C9–C8–S2–C17	125.2(2)
C9–C1–S1–O5	6.7(2)	C9–C8–S2–O6	12.0(2)
C9–C1–S1–O7	− 127.4(2)	C9–C8–S2–O8	− 122.6(2)
O5–S1–C11–C12	23.3(2)	O6–S2–C17–C18	25.3(2)
O7–S1–C11–C12	151.9(2)	O8–S2–C17–C18	154.1(2)
C1–S1–C11–C12	− 92.6(2)	C8–S2–C17–C18	− 90.1(2)
S1–C11–C12–C23	12.3(3)	S2–C17–C18–C24	12.0(3)
C11–C12–C23–O1	− 123.1(3)	C17–C18–C24–O2	− 132.8(3)
C11–C12–C23–O3	61.1(3)	C17–C18–C24–O4	52.1(3)
Torsion angles (deg)			
C12–C23–O3···S1	− 54.2(2)		
C23–O3···S1–C11	54.0(2)		
O3···S1–C11–C12	− 29.7(2)	C18–C24–O4···S2	− 49.9(2)
S1–C1–C9–C8	24.1(3)	C24–O4···S2–C17	48.9(2)
C1–C9–C8–S2	27.2(3)	O4··S2–C17–C18	− 28.5(2)
C9–C8–S2···O5	− 55.6(2)	C9–C8–S2–O6	12.0(2)
C8–S2···O5–S1	71.9(1)	C8–S2–O6···S1	− 51.5(1)
S2···O5–S1–C1	− 47.1(1)	S2–O6···S1–C1	76.5(1)
O5–S1–C1–C9	6.7(2)	O6···S1–C1–C9	− 55.1(2)
C12–C23–O3–C25	− 179.7(2)	C18–C24–O4–C26	− 176.4(2)
S1–C1···C8–S2	42.5(1)	C11–S1···S2–C17	− 138.2(2)
O3···S1···S2···O4	− 110.3(1)		
O5–S1···S2–O6	129.4(1)	O7–S1···S2–O8	− 112.3(1)
O5–S1···S2–O8	7.4(1)	O7–S1···S2–O6	9.7(1)

Table 6
Geometric parameters indicating the separation of the C_{ar}–S peri bonds (the last digits with estimated standard deviations are omitted)

Compound	Torsion angle (L')[a]	Conformation[b]	Torsion angle (L')[a]	Conformation[b]
1	φ_1 (−95)	N_1: axial	φ_2 (−160)	N_2: equatorial
	ψ_1 (26)	P_1: equatorial	ψ_2 (−113)	P_2: axial
2	φ_1 (80)	N_1: axial	φ_2 (79)	N_2: axial
	ψ_1 (−171)	P_1: equatorial	ψ_2 (−176)	P_2: equatorial
3	φ_1 (138)	N_1: twist	φ_2 (136)	N_2: twist
	ψ_1 (−78)	P_1: axial	ψ_2 (−63)	P_2: axial
	ω_1 (173)	–[c]	ω_2 (−174)	–[c]
4	φ_1 (120)	N_1: twist	φ_2 (125)	N_2: twist
	ψ_1 (−93)	P_1: axial	ψ_2 (−90)	P_2: axial
	ω_1 (23)	–[d]	ω_2 (25)	–[d]
	ω'_1 (152)	–[d]	ω'_2 (154)	–[d]

[a] φ_1 = C9–C1–S1–C11; φ_2 = C9–C8–S2–C17; ψ_1 = C1–S1–C11–C12; ψ_2 = C8–S2–C17–C18; ω_1 = O5–S1–C11–C12; ω_2 = O6–S2–C17–C18; ω'_1 = O7–S1–C11–C12; ω'_2 = O8–S2–C17–C18.

[b] N_1: naphthalene ring S1 side; N_2: naphthalene ring S2 side; P_1: S_1 phenyl ring; P_2: S_2-phenyl ring; axial: perpendicular to the C(ar)–S–C(ar) plane; equatorial: coplanar with the C(ar)–S–C(ar) plane; twist: intermediate between axial and equatorial.

[c] S = O bond is coplanar with the phenyl ring.

[d] S = O bond is nearly coplanar with the phenyl ring.

observed value is near the transannular S(II)···S(II) distance (3.23 Å in Ref. [21]) found for the naphtho–dithiocin derivative **6** of rigid structure, in which the sulfide–sulfur atoms bound to naphthalene ring in 1,8-positions are connected with a trimethylene bridge. The elongation of the S(II)···S(II) contact may be explained in both cases by an increased lone pair–lone pair interaction. In compound **2**, the C(9)–C(ar)–S–C(ar) torsion angles in both halves of the molecule are near 90° (see φ_1 and φ_2 in Table 6), meaning that the axis of the sulfur p-orbitals are unfavorably collinear. In addition, quasi-linear C–S(II)···S(II) sequences as favorable structural factors are not present in **2** (see Table 8). However, it may be mentioned that in bis-sulfoxide **2**, the geometry appears well-suited for delocalization of the p-type lone pair on sulfur through the phenyl ring into the carbonyl π-system. This would decrease the electron-density on sulfur lowering the repulsion between collinear lone pair sulfur orbitals.

In bis-sulfoxide **3**, which is the *S*,*S*′-dioxide of compound **2**, the disposition of the sulfur atoms above and below the naphthalene ring is of a high degree (Table 7). However, owing to favorable

Table 7
Geometric parameters related to S···S nonbonded interactions in compounds **1**–**4** (the last digits with estimated standard deviations are omitted)

Compound	S1–C1–C9 (deg)	S2–C8–C9 (deg)	S1–C1···C8–S2 (deg)	ΔS1 (Å)	ΔS2 (Å)
1	124	122	− 11	0.19	− 0.27
	(122)[a]	(121)[a]	(−13)	(−0,29)[a]	(0.31)[a]
2	126	126	− 5	0.02	− 0,05
	(127)[b]	(126)[b]	(−9)	(0.34)[b]	(−0.07)[b]
3	122	121	− 16	0.28	− 0.46
	(124)[c]	(125)[c]	(2)[c]	(0.08)[c]	(0.20)[c]
4	125	125	43	0.79	− 0.91
	(123)[d]	(123)[d]	(−55)[d]	(−1.02)[d]	(1.02)[d]

[a] Taken from Ref. [21] for **5**.

[b] Taken from Ref. [21] for **6**.

[c] Taken from Ref. [23] for **7**.

[d] Taken from Ref. [23] for **8**.

Table 8
Torsion angles determining the aromatic ring positions in compounds **1**–**4** (the last digits with estimated standard deviations are omitted)

Compound	C–S1···S2 (deg)[a]	S1···S2 (Å)
1	θ_1 (105)	3.01
	θ_2 (169)	(2.93)[b]
2	θ_1 (79)	3.18
	θ_2 (78)	(3.23)[c]
3	θ_1 (151)	3.01
	θ_1 (151)	(3.05)[d]
4	θ_1 (152)	3.53
	θ_2 (158)	(3.63)[e]

[a] θ_1 = C11–S1···S$_2$; θ_2 = C17–S2···S1.
[b] Taken from Ref. [21] for **5**.
[c] Taken from Ref. [21] for **6**.
[d] Taken from Ref. [23] for **7**.
[e] Taken from Ref. [23] for **8**.

structural factors, the S(IV)···S(IV) distance is surprisingly short (3.01 Å). The C9–C1–S1–O5, C9–C8–S2–O6 and O5–S1···S2–O6 torsion angles of −114, −116 and −136°, respectively, suggest only a moderate repulsion between the sulfinyl-oxygens (and in the same way between the sulfur lone pairs). In addition, two quasi-linear C–S(IV)···S(IV) sequences assisting the formation of the S(IV)···S(IV) close contact also occur in bis-sulfoxide **3** (see Table 8).

It is remarkable that the transannular S···S distances are similarly short in bis-sulfoxide **7** (3.05 Å in Ref. [23]) and in two heterocyclic sulfide–sulfoxides both having a rigid eight- or seven-membered ring (3.01 and 3.06 Å in Refs. [22,30], respectively). Owing to a nearly linear (165–174°) O = S···S sequence found in all of these models, an attractive part for S···S interaction should exist, which causes the characteristic shortening of the S···S nonbonded distance in compounds of the sulfoxide type.

In bis-sulfone **4**, which is the *S*,*S*′-tetroxide of compound **2**, the torsion and the twisting of naphthalene ring as well as the disposition of sulfur atoms above and below the naphthalene ring are of maximum degree (Table 8), which may be attributed to a steric crowd around the sulfur atoms. At the same time, the nonbonded S(VI)···S(VI) distance in bis-sulfone **4** is extremely long (3.53 Å), as compared to those in **1**–**3**. However, the transannular S(VI)···S(VI) distance in the heterocyclic bis-sulfone **8** is even longer (3.65 Å in Ref. [23]) although the SO$_2$ groups disrotate and the oxygen atoms are placed rather far from each other. Thus, it may be assumed that bis-sulfone **4**, in which the SO$_2$ groups face each other, is somewhat stabilized by intramolecular nonbonded interactions (see Section 3.3). Other data in the literature also indicate that S···S nonbonded contacts involving an SO$_2$ group are rather loose. In models derived from compound **6** [23], the transannular S···S distances of 3.27 and 3.40 Å were found for a sulfide–sulfone and a sulfoxide–sulfone, respectively.

3.3. S···O interactions

As expected, in both halves of the bis-sulfide **2**, S(II)···O close contacts (2.72 and 2.73 Å) are formed between the sulfide–sulfur atoms and the carbonyl-oxygens of the *ortho*-methoxycarbonyl substituents on the equatorial phenyl rings (Table 9). The conformational analysis of bis(2-methoxycarbonylphenyl) sulfide [5] showed that a much closer S···O contact is formed in the equatorial S-phenyl ring than in the

Table 9
Geometric parameters related to S···O nonbonded interactions in compounds **2**–**4** (the last digits with estimated standard deviations are omitted)

Compound	C–S···O (deg)[a]	S···O (Å)	O=S···O (deg)[b]	S···O (Å)
2	θ_1 (175)	2.72		
	θ_2 (180)	2.73		
3			η_1 (178)	2.77
			η_2 (177)	2.83
4	θ_3 (175)	3.02	η_3 (171)	3.30
	θ_4 (179)	2.89	η_4 (172)	3.16

[a] θ_1 = C1–S1···O1; θ_2 = C8–S2···O2; θ_3 = C11–S1···O6; θ_4 = C17–S2···O5.
[b] η_1 = O5–S1···O1; η_2 = O6–S2···O2; η_3 = O7–S1···O3; η_1 = O8–S2···O4.

Table 10
Nonbonded O···O distances in compounds **2**–**4** (the last digits with estimated standard deviations are omitted)

Compound	O···S···S···O (deg)[a]	O···O (Å)	O=S···S=O (deg)[b]	O···O (Å)
2	ξ_1 (−5)	O1···O2 (3.90)		
3	ξ_1 (−135)	O1···O2 (5.47)	χ_1 (−136)	O5···O6 (4.55)
4	ξ_2 (−110)	O3···O4 (6.35)	χ_1 (129)	O5···O6 (2.85)
			χ_2 (7)	O5···O8 (2.84)
			χ_3 (10)	O6···O7 (3.07)
			χ_4 (−112)	O7···O8 (4.63)

[a] ξ_1 = O1···S1···S2···O2; ξ_2 = O3···S1···S2···O4.

[b] χ_1 = O5–S1···S2–O6; χ_2 = O5–S1···S2–O8; χ_3 = *O*7–S1···S2–O6; χ_4 = O7–S1···S2–O8.

axial one (2.72 and 3.08 Å). On this basis, we may explain why both methoxycarbonyl-substituted phenyl rings in **2** occupy equatorial positions, although the conformation is unfavorable for the S···S interaction.

The C(ar) counter-atoms in **2** which are joined linearly to the S(II)···O moieties assist the formation of effective S(II)···O close contacts. The torsional angles for the S–C(ar)–C(ar)–C(sp^2)–O(carbonyl) sequences in the S-phenyl rings (−2, −8° and −2, −5° for the S1- and S2-moieties, respectively) point to favorable planar five-membered 'rings' closed by S(II)···O close contacts. Although the nonbonded O···S···S···O moiety is practically synperiplanar, the carbonyl-oxygens lie far from each other (Table 10).

As it is known from the conformational analysis of bis(2-methoxycarbonylphenyl) sulfoxide [6], a much closer S(IV)···O contact is formed in the axial S-phenyl ring than in the twisted one (2.73 and 3.04 Å). In this case, a favorable linear O=S(IV)···O sequence is formed in the axial aryl ring, and the coplanarity of the S=O bond and the S-phenyl ring allows a conjugative interaction between them. These facts explain why the methoxycarbonyl-substituted S-phenyl rings in the two halves of bis-sufoxide **3** assume the axial conformations (leaving the twist positions for the naphthalene ring). The S(IV)···O nonbonded distances in **3** (2.77 and 2.83 Å) meet with the expectations (Table 9). Owing to the different positions of the S-phenyl rings, the 'aircraft-like' molecular shape of **3** differs significantly from the 'medusa-like' **2**.

The torsional angles for the four-atom parts of the S–C(ar)–C(ar)–C(sp^2)–O(carbonyl) sequences in the S-phenyl rings of bis-sulfoxide **3** (7, 3° and 1, −15° in the S1- and S2-moieties, respectively) here also indicate the favorable formation of planar five-membered rings closed by S(IV)···O close contact. In contrast with the case in **2**, the nonbonded O···S···S···O moiety in **3** is not synperiplanar but anticlinal, thus the carbonyl-oxygens lie even farther from each other (Table 10). The nearly axial positions of S-phenyl rings in both halves of the molecule allow the conjugation with the S(IV)=O bonds (see torsion angles ω in Table 8). At the same time, the sulfinyl-oxygens assume an anticlinal position in the O5–S1···S2–O6 moiety (see O5···O6 distance in Table 10) and as mentioned earlier they do not influence the S···S interaction.

The twist-axial conformations of the two halves of bis-sulfone **4** with axial S-phenyl groups are near to those of bis-sulfoxide **3**. This type of conformation promotes the conjugation between the sulfonyl and phenyl groups, as S=O bonds are nearly coplanar with the phenyl rings (see the torsion angles ω in Table 6; both sulfonyl-oxygens emerge only by about 25° over the phenyl plane).

As shown in Fig. 4, there is a steric crowd in the structure of **4**, which contains eight oxygen atoms not too far from each other. Consequently, the *ortho*-methoxycarbonyl groups no more remain coplanar with the S-phenyl ring. The torsion angles found for the four-atom parts of the S–C(ar)–C(ar)–C(sp_2)–O(carbonyl) sequences (12, −123° and 12, −133° in the S1- and S2-moieties, respectively) point to a drastic turning out of the *ortho*-substituents from the common plane. Thus, carbonyl-oxygens get too far from sulfur(VI) atoms to form effective close contacts. On the other hand, methoxy-oxygens come somewhat near the sulfur atoms and two weak S(VI)···O(methoxy) nonbonded contacts of 3.16 and 3.30 Å are formed both as a part of a linear O=S(VI)···O(methoxy) sequence (Table 9).

However, it is striking to note that the sulfone groups in **4** do not disrotate as in the heterocyclic bis-sulfone **8**. This phenomenon may be explained by the formation of two additional S(VI)···O(sulfonyl) close contacts which join the two halves of the molecule and are assisted by linear C(ar)–S(VI)···O(sulfonyl) bridges (Table 9). Here, the nonbonded distances are 2.89 and 3.02 Å. It should be noted that S(VI)···O close contacts of 1,5 type were registered only in few cases in the literature (2.91–3.22 Å, cf. Refs. [1,6–8]). The nonbonded distances observed earlier were not far from the sum of the van der Waals radii (3.25 Å), and thus they proved to be significantly longer than the S(II)···O and S(IV)···O distances.

The S(VI)···O(methoxy) contacts close in both parts of the molecule a five-membered ring. Owing to the turning out of the methoxycarbonyl groups from the plane of the phenyl groups, these rings are far from being favorably planar (cf. Ref. [1]). The torsion angles for the four-atom sections in the S–C(ar)–C(ar)–C(sp^2)–O(methoxy) sequences are 12/12, 61/52, −54/−50, 54/49, −30/−29°, starting from the S1/ S2 atoms. The five-membered rings with O(3) and O(4) atoms assume a twisted envelope form characterized by the puckering parameters [31] $Q_3 = 0.786(3)$ Å, $\Phi_3 = 332.2(2)°$ and $Q_4 = 0.712(3)$ Å, $\Phi_4 = 332.7(2)°$, respectively.

On the contrary, the S(VI)···O(sulfonyl) close contacts lead to the formation of a distorted six-membered ring, giving the first analyzed example of an S(VI)···O contact of 1,6 type. The four-atom sections of the rings with an S–C(ar)–C(ar)–C(ar)–S′–O′ sequence may be characterized by the torsional angles 24/27, 27/24, 12/7, −52/−47, 77/72 and −55/−56°, starting from the S1/S2 atoms. The puckering parameters for the stretched rings with O(5) and O(6) atoms are $Q_5 = 0.831(3)$ Å, $\theta_5 = 58.8(1)$ $\Phi_5 = 339.5(2)°$ and $Q_6 = 0.898.3(3)$ Å, $\theta_6 = 58.5(1)$ $\Phi_6 = 335.8(2)°$, respectively. Both parameter sets indicate a transitional state between the half-chair and screw-boat forms. The relative positions of oxygen atoms and O···O nonbonded distances in bis-sulfone **4** are shown in Table 10.

3.4. Intermolecular distances

The intermolecular distances observed for compounds **1–4** are significantly longer than the sum of the van der Waals radii showing that there no longer exists any intermolecular S···S and S···O close contacts, which might control the actual molecular conformations. The minimum intermolecular S···S distances for **1–4**: >6, >6, >6 and 5.397 Å, respectively; while the minimum intermolecular S···O distances for **2–4**: 4.774(1), 4.853(4) and 4.342(2) Å, respectively. The aromatic rings in two neighboring molecules are also too far from each other to contribute to the geometries observed.

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