

Crystal Structures of Dibenzo[ce]-1,2-dithiine and Its Related Oxides

Stephen M. Aucott, Heather L. Milton, Stuart D. Robertson,
Alexandra M. Z. Slawin, and J. Derek Woollins

School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16-9ST, UK

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ABSTRACT: *The X-ray structures of dibenzo[ce]-1,2-dithiine, dibenzo[ce]-1,2-dithiine-5,5-dioxide, dibenzo[ce]-1,2-dithiine-5,5,6-trioxide, and dibenzo[ce]-1,2-dithiine-5,5,6,6-tetraoxide are reported and compared with the related "constrained" naphthalene derivatives. The S-S distances vary upon oxidation of the S centers in the order S-S < SO-S > SO₂-S < SO₂-SO > SO₂-SO₂ i.e. the most oxidized sulfur atoms do not lead to the longest bond lengths. © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:346–351, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20101*

INTRODUCTION

Biphenyl-based systems are simple polycyclic aromatic hydrocarbons which allow substitution in the 2 and 2' position. The extent of strain in these compounds is dictated by the interaction between the substituents in these two positions, which can either be bonded to each other or not. We have previously studied the closely related naphthalene 1,8 disubstituted systems [1] which have many similarities and also many differences to the biphenyl systems. Unlike the naphthalene systems, if there is no bonding interaction between the two substituents then there will be no strain as the biphenyl backbone can rotate around the C(2)–C(7) bond, alleviating all the strain. This in turn reduces the effect of the size of

the substituents which is a major factor in the strain in nonbonded peri-substituted naphthalenes.

Also, when the substituents are bonded to each other, there is much less strain in the biphenyl systems than in their corresponding naphthalene derivatives. While there are slight twists possible in the five-membered (C₃S₂) ring of the naphthalene system, the ring is still relatively planar. However, there is much more movement possible in the six-membered (C₄S₂) ring of the biphenyl system. This flexibility allows the heterocyclic ring to deviate significantly from planarity. The flexible backbone also allows puckering of the heterocyclic ring, an effect seen in a variety of different biphenyl systems [2–7].

We have studied disulfide-substituted biphenyl systems and their related oxides in the solid state with the aim of investigating the molecular structures and steric strains in the heterocycles at the intramolecular level and also the effect of the oxygen atoms on the overall stacking of these compounds at the intermolecular level.

RESULTS AND DISCUSSION

Compounds **1–4** (see Fig. 1) were prepared by literature methods and have been studied by X-ray crystallography (vide infra).

The X-ray structures of **1**, **2**, **3**, and **4** are shown in Figs. 2–5, and selected bond lengths and angles are given in Table 1. The S–C bond lengths in each of the four structures (e.g. S(1)–C(1): **1** = 1.796(7) Å, **2** = 1.761(3) [1.761(3)] Å, **3** = 1.766(6) Å, **4** = 1.757(3) Å) are within the normal range expected.

Correspondence to: J. D. Woollins; e-mail: jdw3@st-and.ac.uk.
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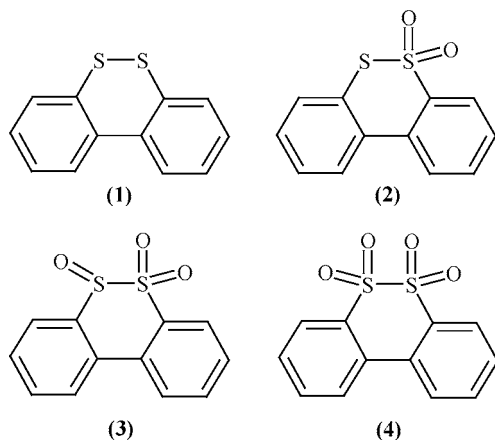


FIGURE 1 Structures of compounds 1–4.

The S(1)–S(8) bond lengths in **1**, **2**, and **4** (2.066(1) Å, 2.0649(13) [2.0606(13)] Å, and 2.1493(13) Å respectively) correspond well with the S–S bond lengths seen in the unconstrained compounds $C_6H_5-S-S-C_6H_5$ (2.03(05) Å) [8], $C_6H_5-S(O)_2-S-C_6H_5$ (2.080(3) [2.093] Å) [9], and $C_6H_5-S(O)_2-S(O)_2-C_6H_5$ (2.193(1) Å) [10]. A previous determination of the structure of **1** gave an S–S bond distance of 2.050(3) Å [11], which is also in good agreement with the structure obtained here. It is interesting to note that mono-oxidation at a sulfur atom appears to increase the bond length but further oxidation to an SO_2 group appears to shorten the S–S bond. The same pattern is seen as each sulfur is oxidized (Table 1).

The known compound $C_{12}H_8S_2O$ (shown in Fig. 6) has an S–S distance of 2.097(1) Å [11], which is also consistent with the S–S bond lengths seen in **1–4**. The S–S bond length of the naphthalene analogue of **1** is 2.0879(8) [2.096(3)] Å, which is similar to that of **1**. However, the S–S bond lengths of **2–4** are slightly shorter than those

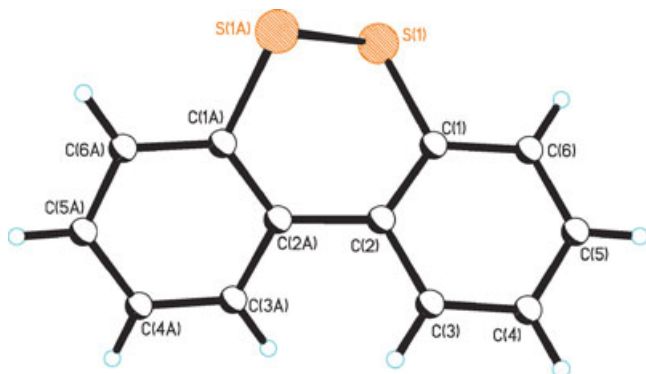


FIGURE 2 Crystal structures of $C_{12}H_8S_2$ **1**.

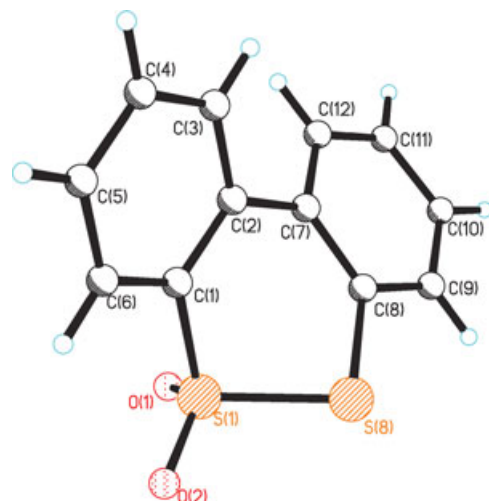


FIGURE 3 Crystal structure of one independent molecule of $C_{12}H_8S_2O_2$ **2**.

of the corresponding sulfur-bridged naphthalenes [**1**] (2.1143(14), 2.2520(13), 2.2204(19) [2.251(2)] Å). This is due to the lack of strain present in the C_4S_2 ring compared with the five-membered ring in the naphthalene ligands. Not only is the larger ring less strained, but the more flexible biphenyl backbone allows any strain that is left to be alleviated by puckering of the C_4S_2 ring. This can be seen quite clearly in Fig. 7. The flexibility of the biphenyl backbone is also demonstrated by the C(5)–C(6)–C(7)–C(12) torsion angles (Table 1). The largest deviation from planarity is seen in **2**, where C(5)–C(6)–C(7)–C(12) = 142.7(3)°. The smallest deviation (C(5)–C(6)–C(7)–C(12) = 151.8(3)°) is seen in **4**. This smaller deviation is a result of the steric influences of the four oxygen atoms which are present.

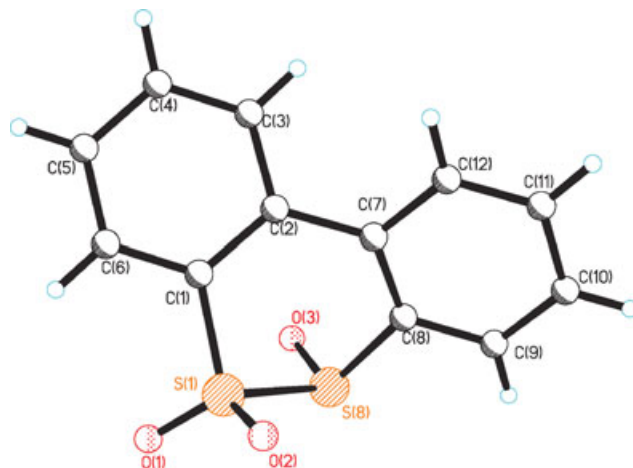
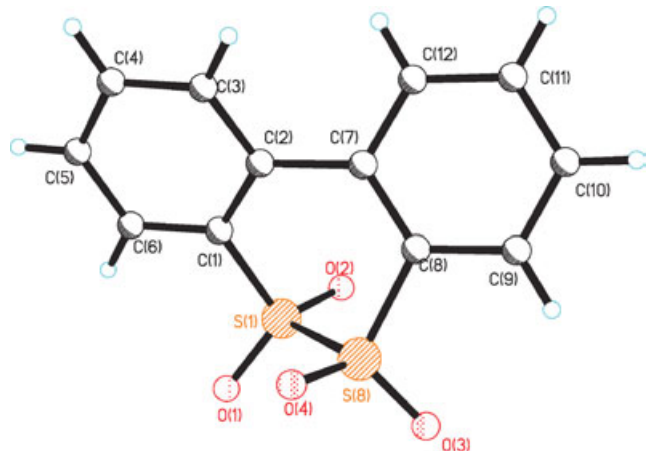


FIGURE 4 Crystal structure of $C_{12}H_8S_2O_3$ **3**.

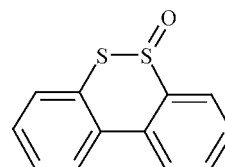
TABLE 1 Bond Lengths (Å) and Angles (°) for Compounds **1–4** and Also the Previously Studied Compound $C_{12}H_8S_2O$

Compound	1 ^a	2	3	4	
Formula	$C_{12}H_8S_2$	$C_{12}H_8S_2O_2$	$C_{12}H_8S_2O_3$	$C_{12}H_8S_2O_4$	$C_{12}H_8S_2O_1$
C(2)—C(7)	1.494(7)	1.492(5) [1.487(5)]	1.467(9)	1.504(5)	1.466(3)
S(1)—S(8)	2.066(1)	2.0649(13) [2.0606(13)]	2.171(3)	2.1494(13)	2.097(1)
S(1)—C(1)	1.796(7)	1.761(3) [1.761(3)]	1.766(6)	1.757(3)	1.782(2)
S(8)—C(8)	1.778(7)	1.783(3) [1.781(3)]	1.777(6)	1.757(3)	1.767(2)
S(1)—O(1)	—	1.438(2) [1.432(3)]	1.422(5)	1.425(2)	1.478(2)
S(1)—O(2)	—	1.435(3) [1.434(2)]	1.385(6)	1.426(2)	—
S(8)—O(3)	—	—	1.463(5)	1.436(3)	—
S(8)—O(4)	—	—	—	1.423(3)	—
C(1)—S(1)—S(8)	98.1(2)	99.45(11) [100.11(12)]	99.2(2)	97.48(12)	96.44(7)
C(8)—S(8)—S(1)	98.3(2)	95.88(12) [95.64(12)]	93.5(2)	97.68(12)	101.05(8)
S(1)—C(1)—C(2)	119.0(5)	118.6(3) [118.7(3)]	119.0(4)	120.6(3)	123.1(2)
S(8)—C(8)—C(7)	119.2(5)	122.3(3) [122.3(3)]	122.7(5)	120.3(3)	122.0(2)
O(2)—S(1)—O(1)	—	118.74(14) [118.60(15)]	120.1(3)	119.76(15)	—
O(2)—S(1)—C(1)	—	109.79(15) [109.88(16)]	113.1(3)	111.01(16)	—
O(1)—S(1)—C(1)	—	110.21(10) [109.19(15)]	109.0(3)	111.58(16)	107.67(9)
O(3)—S(8)—O(4)	—	—	—	120.21(17)	—
O(3)—S(8)—C(8)	—	—	110.4(3)	112.16(16)	—
O(4)—S(8)—C(8)	—	—	—	110.30(17)	—
C(3)—C(2)—C(7)—C(8)	144.1(7)	142.7(3) [144.0(3)]	−148.5(7)	151.8(3)	149.3
C(12)—C(7)—C(2)—C(1)	145.8(7)	147.9(3) [147.7(3)]	−148.7(6)	149.4(3)	154.6
S(1)—S(8)—C(8)—C(7)	42.4(5)	39.7(3) [40.8(3)]	−45.2(6)	45.2(3)	37.6
S(8)—S(1)—C(1)—C(2)	42.9(5)	48.0(3) [46.9(3)]	−44.8(5)	43.3(3)	43.4

^aThe metrical parameters for **1** are given according to the numbering scheme of **2–4**.

**FIGURE 5** Crystal structure of $C_{12}H_8S_2O_4$ **4**.

The S=O bond lengths of **2** (1.438(2) [1.432(3)] and 1.435(3) [1.434(2)] Å) are comparable with those in **3** and **4** with the exception of the S(3)—O(8) bond of **3**. [1.463(5) Å], which is the longest S=O bond of all the structures discussed here. The O(1)—S(1)—C(1) angle of **2** is 110.21(10) [109.19(15)]°, and the O(2)—S(1)—C(1) angle is

**FIGURE 6** Structure of $C_{12}H_8S_2O$.

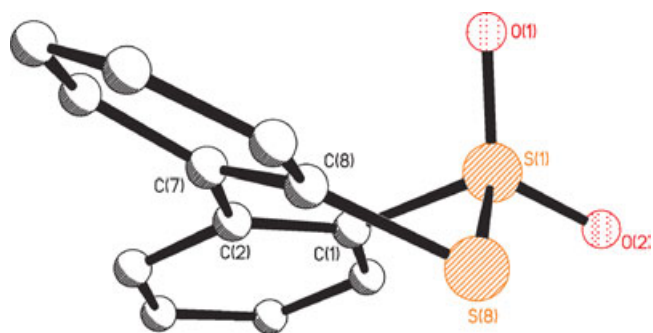


FIGURE 7 The puckered C_4S_2 ring in compound **2**.

$109.79(15)$ [$109.88(16)$] $^\circ$. These are very near to the ideal tetrahedral angle of 109.5° . The corresponding angles of **3** and **4** are also close to the ideal, ranging between $109.3(3)^\circ$ and $113.1(3)^\circ$. The largest deviations from ideal tetrahedral geometry are seen in the O–S–O angles of all three structures. It can be seen from Table 1 that this angle is much nearer to 120° . In **2–4**, there is one oxygen atom in the plane of the C(1) phenyl ring, and one oxygen atom pointing away from the plane. This geometry can clearly be seen in Fig. 3. In the structure of **3**, the third oxygen atom is at right angles to the C(12) phenyl ring, but the fourth

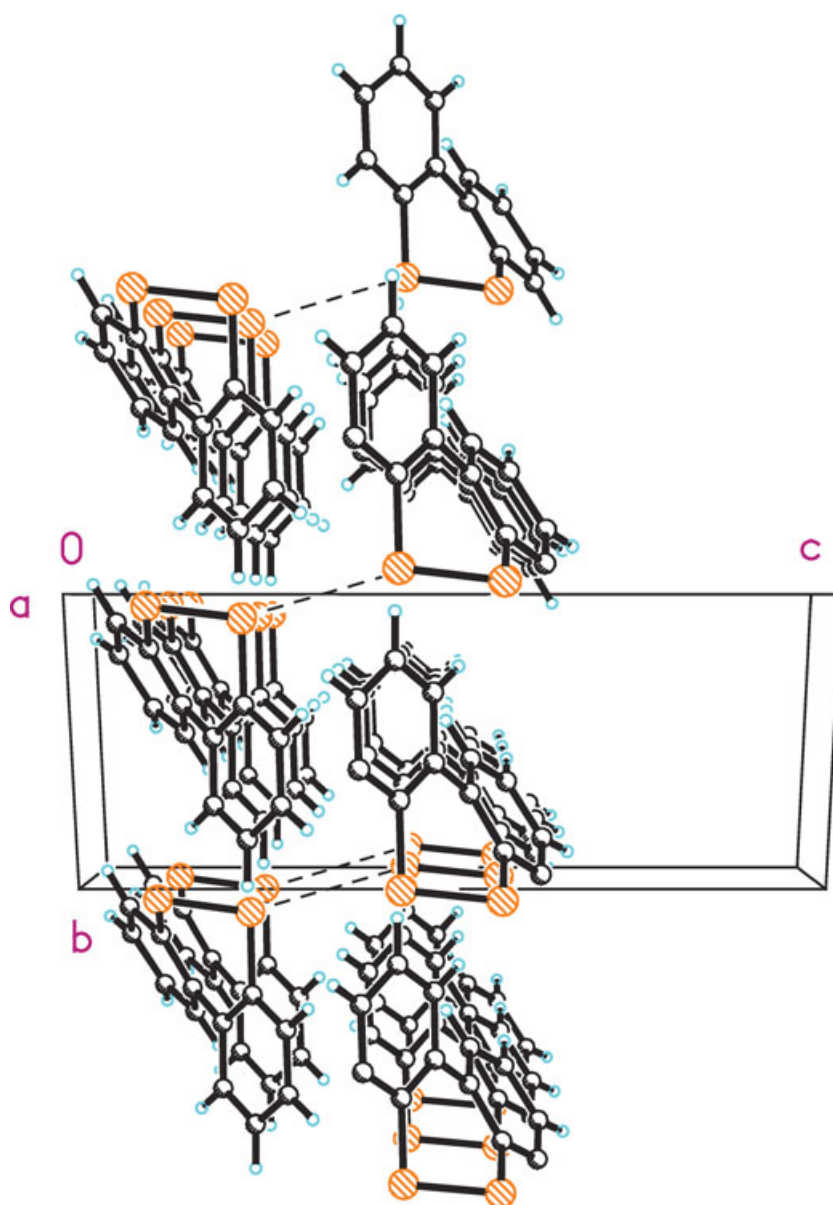


FIGURE 8 Packing diagram of **1**.

TABLE 2 Crystallographic Data for Compounds 1–4

Compound	1	2	3	4
Formula	C ₁₂ H ₈ S ₂	C ₁₂ H ₈ S ₂ O ₂	C ₁₂ H ₈ S ₂ O ₃	C ₁₂ H ₈ S ₂ O ₄
<i>M</i>	216.32	248.32	264.32	280.32
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 3 ₁ 21	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.317(4)	8.013(2)	9.604(5)	8.611(3)
<i>b</i> (Å)	7.317(4)	8.698(2)	7.200(4)	14.022(4)
<i>c</i> (Å)	16.084(8)	15.682(4)	16.327(8)	9.723(3)
α (°)	90	80.319(4)	90	90
β (°)	90	90.053(4)	105.268(8)	108.513(5)
γ (°)	120	83.357(4)	90	90
<i>U</i> (Å ³)	745.8(6)	1070.0(5)	1089.2(9)	1113.1(6)
<i>Z</i>	3	4	4	4
ρ_{calcd}	1.445	1.541	1.612	1.673
μ (mm ⁻¹)	0.485	0.476	0.479	0.480
Reflections measured	4289	5352	6295	6536
Independent reflections	871	3004	1999	2010
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0577, 0.1178	0.0555, 0.1501	0.0771, 0.1625	0.0493, 0.1053

oxygen atom in **4** is once again approximately in the plane of the phenyl ring.

The packing of **1** is strongly influenced by two S(1)⋯S(12) interactions at 3.49 Å and 3.50 Å (shown in Fig. 8). In all four structures discussed, the phenyl rings form two separate stacks. In the cases of **2** and **3**, one of these stacks is along the *a*-axis while the other set of phenyl rings stack along the *b*-axis. The distances between the phenyl rings are approximately 3.47 Å and 3.44 Å respectively. **4** is ordered along the *a*-axis, the distance between the phenyl rings is approximately 4.2 Å. **2** and **3** show a number of O⋯H interactions, the shortest of these being the O(21A)⋯H(23) interaction in **2** (2.515 Å) and the O(1B)⋯H(11A) interaction in **3** (2.514 Å). Although there are some O⋯H interactions in **4**, the steric bulk of the fourth oxygen atom prevents the extensive interactions seen in **2** and **3**.

EXPERIMENTAL

Dibenzo[*ce*]-1,2-dithiine [12], dibenzo[*ce*]-1,2-dithiine-5,5-dioxide [13], dibenzo[*ce*]-1,2-dithiine-5,5,6-trioxide [13], and dibenzo[*ce*]-1,2-dithiine-5,5,6,6-tetraoxide [14] were prepared according to literature procedures.

Details of the X-ray characterization experiments are given in Table 2. Data for **2**, **3** and **4** were collected at 125 K on a SMART diffractometer using Mo K α radiation while data for **1** was collected at 93 K on a Rigaku MM007/mercury diffractometer. In all structures, all non-H atoms were

refined anisotropically. All refinements were performed by using SHELXTL (version 6.12, Bruker AXS, 2001). CCCDC nos. 243652, 243647-9 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Single crystals suitable for X-ray diffraction studies of complexes **1**, **2**, **3**, and **4** were obtained by layering a solution of each complex in dichloromethane with hexane.

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