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Crystal and molecular structures of three 2,2′-thio- and 2,2′-sulfonyl-bis(1,3-diarylprop-2-en-1-ones)

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The X-ray crystal structures of 2,2′-thio- and 2,2′-sulfonylbis(1,3-diarylprop-2-en-1-ones) are determined [**1**: 2,2′-thiobis(3-(*p*-chlorophenyl)-1-phenylprop-2-en-1-one), $C_{30}H_{20}Cl_2O_2S$, space group $C2/c$, $a = 14.275(3)$, $b = 6.280(1)$, $c = 26.533(5)$ Å, $\beta = 94.55(3)^\circ$, $Z' = 1/2$; **2**: 2,2′-sulfonylbis(1,3-diphenylprop-2-en-1-one), $C_{30}H_{22}O_4S$, space group $P\bar{1}$, $a = 9.652(1)$, $b = 12.044(1)$, $c = 12.182(1)$ Å, $\alpha = 61.985(6)$, $\beta = 77.511(5)$, $\gamma = 74.340(6)^\circ$, $Z' = 1$; **3**: 2,2′-sulfonylbis(3-(*p*-chlorophenyl)-1-phenylprop-2-en-1-one), $C_{30}H_{20}Cl_2O_4S$, space group $P\bar{1}$, $a = 8.294(1)$, $b = 13.175(2)$, $c = 13.470(1)$ Å, $\alpha = 62.870(9)$, $\beta = 83.796(7)$, $\gamma = 85.282(8)^\circ$, $Z' = 1$]. The C=C double bonds are all clearly defined. The sulfide **1** crystallizes on a crystallographic twofold axis, leading to a symmetric molecular conformation. The sulfones **2** and **3** crystallize on general positions, with different and irregular conformations.

KEY WORDS: Crystal structure; organosulfur compounds.

Introduction

2,2′-Thiobis(1,3-diarylprop-2-en-1-ones) are excellent synthons[1–5] for the synthesis of a variety of heterocyclic compounds containing two hetero atoms like thiazines, thianes, and dithianes whose applications as tranquilizers, sedatives, and other applications are reported in the literature.[6] An unequivocal stereochemical assignment of the double bond in these compounds by conventional methods is difficult because the alkene function is trisubstituted. In this context, we have determined the crystal structures of three compounds from this family, one sulfide, **1**, and two sulfones, **2** and **3**. The crystal structures shall not only define the molecular constitution unequivocally, but also give information on steric distortions of the prop-2-ene moieties.

Experimental

The thiobis compound **1** was obtained by condensation of bis(benzoylmethyl)sulfide with *p*-chlorobenzaldehyde. The sulfonylbis compounds **2** and **3** were obtained by oxidation of the corresponding thiobis compounds with

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Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
Formula	$C_{30}H_{20}Cl_2O_2S$	$C_{30}H_{22}O_4S$	$C_{30}H_{20}Cl_2O_4S$
CCDC deposite no.	CCDC-1003/6004	CCDC-1003/6005	CCDS-1003/6006
MW	515.42	478.54	547.42
Diffractometer	Kappa CCD	Turbo-CAD4	Turbo-CAD4
Temperature, K	125	RT	RT
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell dimensions			
a, Å	14.275(3)	9.652(1)	8.294(1)
b, Å	6.280(1)	12.044(1)	13.175(2)
c, Å	26.533(5)	12.182(1)	13.470(1)
α, deg	90	61.985(6)	62.870(9)
β, deg	94.55(3)	77.511(5)	83.796(7)
γ, deg	90	74.340(6)	85.282(8)
Volume, Å^3	2371.1(8)	1197.1(2)	1301.4(3)
Z	4	2	2
Z'	1/2	1	1
D_c, g/cm^{-3}	1.444	1.328	1.397
μ, mm^{-1}	0.390	0.171	0.365
Crystal size, mm	0.45 × 0.2 × 0.15	0.3 × 0.3 × 0.15	0.2 × 0.2 × 0.1
Measured reflections	4060	7307	9791
Unique reflections	2435	5491	5966
Unique with $I > 2\sigma(I)$	2259	2597	1772
$\triangle\rho_{\max}$, e Å^{-3}	0.33	0.22	0.23
R [for $I > 2\sigma(I)$]	0.039	0.068	0.093
R_w [for all data]	0.088	0.167	0.289

hydrogen peroxide (30%) in glacial acetic acid.[7] [**1**; 2,2′-thiobis(3-(p-chlorophenyl)-1-phenylprop-2-en-1-one), **2**: 2,2′-sulfonylbis(1,3-diphenylprop-2-en-1-one), **3**: 2,2′-sulfonylbis (3-(p-chlorophenyl)-1-phenylprop-2-en-1-one)]. Crystals were grown from solutions in $CHCl_3$–MeOH [2:1 (v/v)]. X-ray diffraction data were collected at 125 K on a Nonius Kappa CCD diffractometer for **1**, and at RT on a Nonius Turbo-CAD4 diffractometer for **2** and **3** (Mo Kα radiation with $\lambda = 0.71073$ Å). Diffraction power of **2** and **3** was only moderate, leading to a relatively large number of weak reflections. The structures were solved[8] and refined[9] with standard methods (anisotropic refinement for non-H atoms, H atoms treated in the riding model, no absorption correction). Relevant crystallographic data are given in Table 1, and fractional atomic coordinates are given in Tables 2–4.

Table 2. Fractional Atomic Coordinates of **1** and Equivalent Isotropic Displacement Parameters

	x/a	y/b	z/c	U_{eq}^{a}
S	0.5000	0.19979(8)	0.7500	0.01413(13)
Cl	0.66735(3)	0.56905(7)	0.528274(14)	0.02792(13)
O1	0.62200(8)	−0.33552(17)	0.77711(4)	0.0214(2)
C1	0.60439(10)	−0.1519(2)	0.78791(5)	0.0150(3)
C2	0.59372(10)	0.0157(2)	0.74705(5)	0.0144(3)
C3	0.65634(11)	0.0165(2)	0.71166(5)	0.0166(3)
C11	0.59442(10)	−0.0876(2)	0.84150(5)	0.0151(3)
C21	0.61222(11)	0.1199(3)	0.85879(5)	0.0191(3)
C31	0.60443(12)	0.1692(3)	0.90940(6)	0.0232(3)
C41	0.57761(12)	0.0135(3)	0.94249(6)	0.0245(4)
C51	0.55994(12)	−0.1923(3)	0.92563(6)	0.0244(3)
C61	0.56940(11)	−0.2436(3)	0.87523(6)	0.0199(3)
C13	0.66108(10)	0.1594(2)	0.66812(5)	0.0159(3)
C23	0.69364(11)	0.0774(2)	0.62368(6)	0.0192(3)
C33	0.69472(11)	0.1995(3)	0.58023(5)	0.0206(3)
C43	0.66557(11)	0.4095(3)	0.58210(5)	0.0194(3)
C53	0.63697(11)	0.4986(2)	0.62607(6)	0.0199(3)
C63	0.63451(11)	0.3740(2)	0.66904(6)	0.0186(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Fractional Atomic Coordinates of **2** and Equivalent Isotropic Displacement Parameters

	x/a	y/b	z/c	$U_{\mathrm{eq}}{}^{a}$
S	0.27083(10)	0.43036(9)	0.42178(8)	0.0453(3)
O1	0.3852(3)	0.6718(2)	0.1846(2)	0.0622(7)
O1′	0.3077(3)	0.3854(3)	0.1880(3)	0.0826(9)
O2	0.3144(2)	0.4612(2)	0.50802(19)	0.0564(7)
O3	0.1795(2)	0.3380(2)	0.4682(2)	0.0598(7)
C1	0.2764(3)	0.6788(3)	0.2547(3)	0.0418(8)
C2	0.1867(3)	0.5765(3)	0.3063(3)	0.0381(8)
C3	0.0607(3)	0.5814(3)	0.2748(3)	0.0430(8)
C11	0.2348(3)	0.7811(3)	0.2982(3)	0.0394(8)
C21	0.0943(4)	0.8213(3)	0.3383(3)	0.0490(9)
C31	0.0609(5)	0.9224(4)	0.3694(3)	0.0611(10)
C41	0.1679(5)	0.9782(4)	0.3670(3)	0.0684(12)
C51	0.3080(5)	0.9358(4)	0.3323(3)	0.0655(11)
C61	0.3422(4)	0.8387(3)	0.2964(3)	0.0539(10)
C13	−0.0276(4)	0.6849(3)	0.1787(3)	0.0423(8)
C23	0.0261(5)	0.7868(3)	0.0781(3)	0.0571(10)
C33	−0.0621(5)	0.8766(4)	−0.0123(4)	0.0670(11)
C43	−0.2015(5)	0.8671(4)	−0.0062(4)	0.0681(12)
C53	−0.2556(4)	0.7677(4)	0.0925(4)	0.0605(10)
C63	−0.1702(4)	0.6770(3)	0.1841(3)	0.0507(9)
C1′	0.4070(4)	0.3309(3)	0.2526(3)	0.0476(9)
C2′	0.4290(3)	0.3796(3)	0.3389(3)	0.0389(8)
C3′	0.5532(4)	0.3981(3)	0.3516(3)	0.0422(8)
C11′	0.5064(3)	0.2137(3)	0.2490(3)	0.0404(8)
C21′	0.5258(4)	0.1986(4)	0.1399(3)	0.0546(10)
C31′	0.6139(4)	0.0910(4)	0.1349(4)	0.0697(12)
C41′	0.6815(4)	−0.0040(4)	0.2370(5)	0.0740(12)
C51′	0.6606(4)	0.0099(4)	0.3458(4)	0.0635(11)
C61′	0.5747(3)	0.1191(3)	0.3511(3)	0.0491(9)
C13′	0.6929(3)	0.3817(3)	0.2803(3)	0.0398(8)
C23′	0.8184(4)	0.3340(3)	0.3387(3)	0.0488(9)
C33′	0.9505(4)	0.3182(3)	0.2728(4)	0.0618(11)
C43′	0.9609(5)	0.3529(4)	0.1468(4)	0.0708(12)
C53′	0.8375(5)	0.4048(4)	0.0868(4)	0.0653(11)
C63′	0.7050(4)	0.4184(3)	0.1524(3)	0.0528(9)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

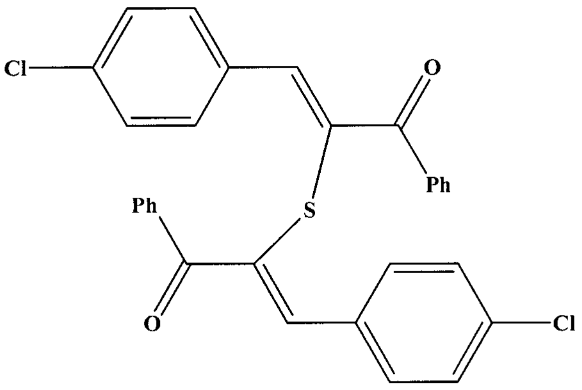
Table 4. Fractional Atomic Coordinates of **3** and Equivalent Isotropic Displacement Parameters

	x/a	y/b	z/c	$U_{\mathrm{eq}}{}^{a}$
S	0.0152(2)	0.43149(15)	0.30718(16)	0.0744(6)
Cl	−0.8130(3)	0.72666(18)	−0.07281(18)	0.1140(8)
Cl′	−0.3833(3)	−0.08246(17)	0.92397(18)	0.1190(8)
O1	−0.3091(6)	0.5172(4)	0.4085(4)	0.1013(17)
O1′	−0.0112(5)	0.1594(4)	0.3649(4)	0.0978(16)
O2	0.0950(5)	0.4918(4)	0.3519(4)	0.0877(14)
O3	0.0984(5)	0.4022(4)	0.2234(4)	0.1004(16)
C1	−0.2412(8)	0.5741(6)	0.3162(6)	0.0704(19)
C2	−0.1638(7)	0.5130(5)	0.2517(6)	0.0633(17)
C3	−0.2109(8)	0.5155(5)	0.1608(6)	0.0674(18)
C11	−0.2249(8)	0.6959(6)	0.2690(7)	0.073(2)
C21	−0.1340(11)	0.7578(7)	0.1724(8)	0.105(3)
C31	−0.1224(13)	0.8734(9)	0.1329(9)	0.142(4)
C41	−0.2036(17)	0.9298(9)	0.1906(13)	0.164(7)
C51	−0.2932(14)	0.8664(10)	0.2839(13)	0.165(6)
C61	−0.3077(9)	0.7520(8)	0.3269(8)	0.123(3)
C13	−0.3559(8)	0.5721(5)	0.1031(6)	0.0692(19)
C23	−0.3599(10)	0.6059(6)	−0.0109(7)	0.084(2)
C33	−0.4986(11)	0.6575(5)	−0.0665(6)	0.083(2)
C43	−0.6379(9)	0.6688(5)	−0.0036(7)	0.0759(19)
C53	−0.6399(9)	0.6352(6)	0.1066(6)	0.076(2)
C63	−0.5019(8)	0.5849(5)	0.1627(5)	0.0696(18)
C1′	−0.1113(7)	0.2184(5)	0.3877(5)	0.0633(17)
C2′	−0.0613(6)	0.3068(5)	0.4174(6)	0.0625(17)
C3′	−0.0725(6)	0.2988(5)	0.5199(7)	0.0691(19)
C11′	−0.2871(7)	0.2039(5)	0.3878(5)	0.0531(15)
C21′	−0.3339(7)	0.1187(5)	0.3670(5)	0.0697(18)
C31′	−0.4939(9)	0.1047(6)	0.3631(6)	0.089(2)
C41′	−0.6102(8)	0.1776(7)	0.3783(6)	0.085(2)
C51′	−0.5649(7)	0.2611(6)	0.3995(6)	0.078(2)
C61′	−0.4047(7)	0.2773(5)	0.4053(5)	0.0672(18)
C13′	−0.1391(7)	0.2025(6)	0.6212(6)	0.0619(17)
C23′	−0.1141(8)	0.0878(6)	0.6444(6)	0.0686(18)
C33′	−0.1853(8)	0.0031(6)	0.7364(7)	0.074(2)
C43′	−0.2853(8)	0.0265(6)	0.8116(6)	0.079(2)
C53′	−0.3110(9)	0.1375(6)	0.7942(6)	0.087(2)
C63′	−0.2352(8)	0.2231(6)	0.7018(6)	0.0752(19)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

The molecular structures of **1**, **2**, and **3** as observed in the crystal structures are shown in Fig. 1. Relevant geometrical parameters are given in Table 5. The sulfide **1** crystallizes on a twofold crystallographic axis, forcing the conformation to be symmetrical (Fig. 1(a)). The bond angle at the S atom is normal [98.7(1)°]. In the propene groups, the bond lengths of C3=C2 = 1.347(2) and C2–C1 = 1.519(2) Å point at well-defined single and double bonds, respectively, confirming the expected molecular constitution.[7] The *p*-chlorophenyl groups are bonded to C3 in cis position with respect to S (Scheme 1). The resulting steric conflict S···C11 leads to appreciable widening of the S–C2=C3 angle to 124.9(1)°, whereas the angle C3=C2–C1 is narrowed to 117.9(1)°. The torsion angle S–C2=C3–C13 is only slightly twisted from the ideal value to −1.6(2)°. The two prop-2-ene groups at S are mutually arranged in



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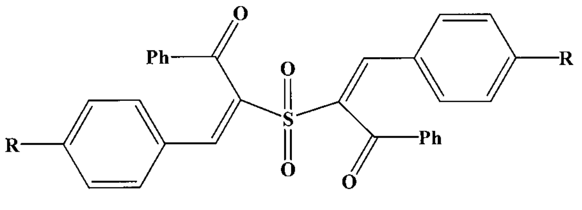
Scheme 1.

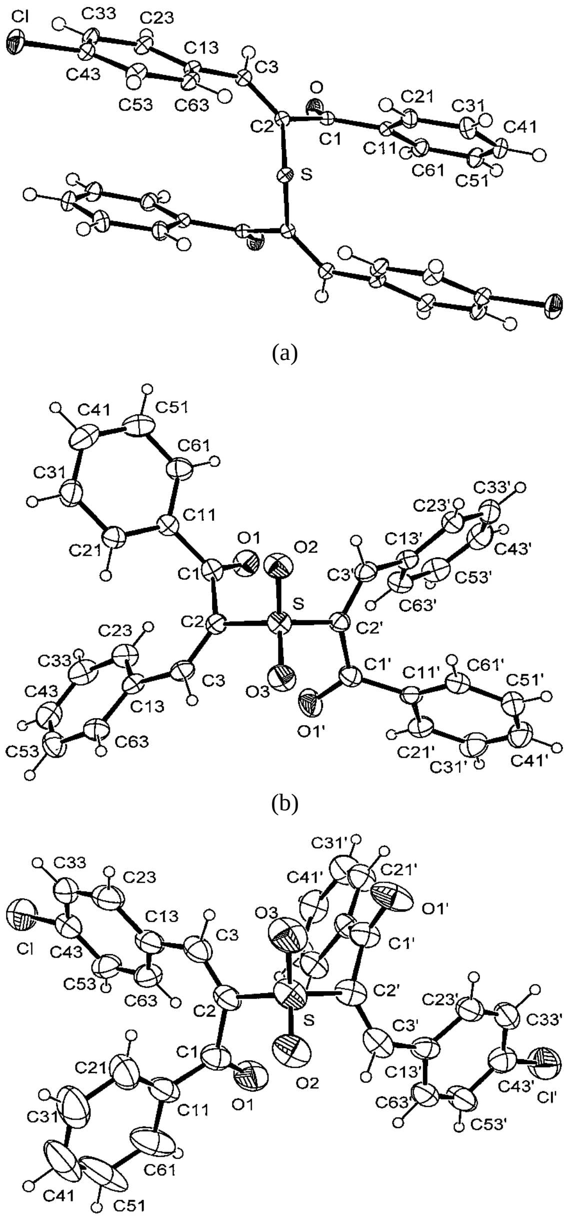
an antiparallel fashion, so that the *p*-chlorophenyl groups point in opposite directions, and the same is true for the two unsubstituted phenyl rings. The C=O groups point in almost the same directions, with an intramolecular O1· · ·O1′ separation of only 3.662(3) Å. Because of the roughly parallel alignment of the C=O dipoles, this is an unfavourable arrangement. A further interesting feature of **1** are intramolecular stacking interactions of the phenyl and *p*-chlorophenyl rings (Fig. 2). In this interaction, the midpoint of the phenyl ring has a normal distance of 3.92 Å from the *p*-chlorophenyl least squares plane.

The stereochemistry of the sulfones **2** and **3** differs from **1** in that the aromatic groups at the C3=C2 bonds are attached trans with respect to S (Scheme 2). Now, the steric conflict is not with S but with C1 and the phenyl ring attached to it, so that the angles C3=C2–C1 and C3′=C2′–C1′ are widened to values above 125°



2 : R = H
3 : R= Cl

Scheme 2.



(a)

(b)

(c)

Fig. 1. Molecular structure and atomic numbering scheme of **1**, **2**, and **3** shown in views roughly along the bisector of the C—S—C angle. Thermal ellipsoids are drawn at the 50% probability level for **1** and the 30% probability level for **2** and **3**.

Table 5. Selection of Geometric Parameters

	1	**2**	**3**
Bond lengths			
S─C2	1.775(2)	1.769(3)	1.778(6)
S─C2′		1.770(3)	1.746(6)
S═O2		1.435(2)	1.428(4)
S═O3		1.434(2)	1.444(4)
C2─C1	1.510(2)	1.509(4)	1.500(8)
C2′─C1′		1.496(4)	1.493(8)
C3═C2	1.347(2)	1.331(4)	1.311(8)
C3′═C2′		1.330(4)	1.329(8)
C1═O1	1.219(2)	1.213(3)	1.221(7)
C1′═O1′		1.213(3)	1.202(6)
Bond angles			
C2─S1─C2′	98.7(1)	103.9(1)	102.8(3)
S─C2═C3	124.9(1)	118.5(2)	118.4(5)
S─C2′═C3′		117.1(2)	117.8(5)
S─C2─C1	117.1(1)	112.1(2)	113.8(5)
S─C2′─C1′		116.2(2)	116.7(5)
C3═C2─C1	117.9(1)	129.4(3)	127.7(6)
C3′═C2′─C1′		126.5(3)	125.5(6)
C2═C3─C13	128.7(1)	130.0(3)	128.1(6)
C2′═C3′─C13′		127.2(3)	125.2(6)
C2─C1─C11	118.9(1)	119.0(3)	118.6(6)
C2′─C1′─C11′		119.3(3)	118.8(5)
Torsion angles			
C2′─S─C2─C1	−53.7(1)	−65.1(2)	80.5(5)
C2─S─C2′─C1′		−72.4(3)	81.7(5)
S─C2═C3─C13	−1.6(2)	−175.7(3)	177.3(5)
S─C2′═C3′─C13′		−170.6(3)	177.7(4)
S─C2─C1─C11	−43.4(2)	−102.5(3)	105.5(6)
S─C2′─C1′─C11′		−137.4(3)	−104.9(6)
S─C2─C1─O1	137.6(1)	73.3(3)	−71.4(7)
S─C2′─C1′─O1′		41.4(4)	75.7(7)
O1═C1─C2═C3	−43.4(2)	−104.8(4)	110.1(8)
O1′═C1′─C2′═C3′		−132.7(4)	−105.3(8)
C2═C3─C13─C23	−146.3(2)	18.9(5)	154.4(7)
C2′═C3′─C13′─C23′		−143.6(3)	39.2(9)
C2─C1─C11─C21	−25.7(2)	−28.2(4)	−4.5(10)
C2′─C1′─C11′─C21′		−154.1(3)	−176.3(6)
C1─C2═C3─C13	179.4(1)	2.2(6)	−4.2(11)
C1′─C2′═C3′─C13′		3.4(5)	−1.3(10)

Note. Distances are given in Å, and angles in deg.

whereas S─C2═C3 is slightly narrowed (Table 5). The overall conformations are very different as in **1**, lacking short intramolecular C═O· · ·O═C contacts and intramolecular face-to-face stacking interactions of the aromatic groups (Figs. 1(b) and 1(c)). Furthermore, both sulfones crystallize on general positions, and their conformations have no internal symmetries. Nevertheless, the bond lengths in the propene group clearly verify the structure assignment shown in Scheme 2.

Apart from the covalent geometry, the intermolecular interactions deserve a look too. The molecules carry no conventional hydrogen bond donors, so that the C═O acceptors must be expected to accept weak C─H· · ·O hydrogen bonds as a resort.[10,11] Indeed, numerous such interactions are formed. In **1**, for example, O1 is involved

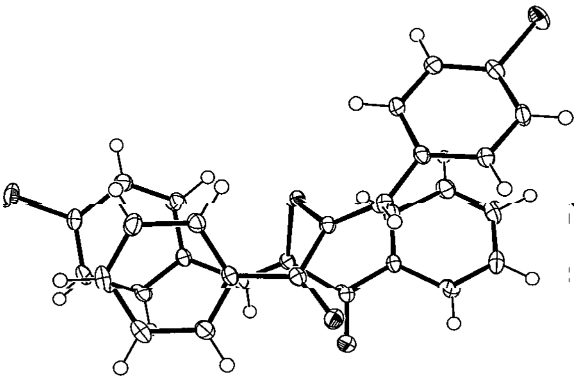


Fig. 2. Compound **1** drawn in a projection on the plane of the *p*-chlorophenyl group to show the intramolecular π-stacking interaction.

in an interaction C63–H···O1=C1 $(x, 1 + y, z)$ with H···O = 2.40, C···O = 3.42 Å, C–H···O = 157° (for C–H = 1.08 Å) which is a very good geometry for a hydrogen bond of this kind. In **2** and **3**, related interactions are formed too, but need not be discussed here in greater detail.

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