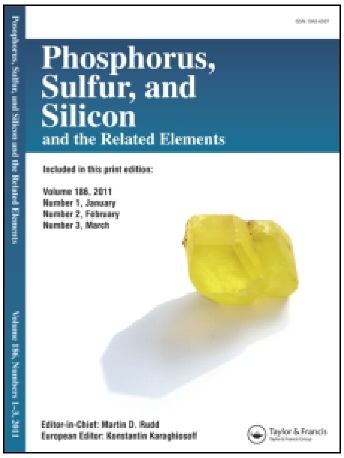

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SYNTHESIS AND CRYSTAL STRUCTURE DETERMINATION OF 2,2′-SULFINYL-BIS(4-METHYL PHENOL) AND 2,2′-THIO-BIS(4-METHYL PHENOL)

Abbas Shockravi,[a] *Robabeh Alizadeh,*[a] *Hossein Aghabozorg,*[a] *Abolghasem Moghimi,*[b] *Esmael Rostami,*[a] *and Samad Bavili*[a]
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2,2′-Sulfinyl-bis(4-methyl phenol) ***3*** *and it's thio derivative have been synthesized in this work. The reduction process of sulfoxide* ***3*** *to its thio derivative* ***5*** *was accomplished in the presence of* $Zn/AcOH/SiO_2$*, under microwave irradiation. The structures have been confirmed by spectroscopic (IR,* ^{1}*HNMR,* ^{13}*CNMR) and single crystal x-ray diffraction methods. 2,2′-Sulfinyl-bis(4-methyl phenol)* ***3*** *crystallizes in the space group Cc of the monoclinic system with four molecules in the unit cell of dimensions* $a = 11.425(2)$ Å, $b = 13.530(2)$ Å, $c = 9.5215(17)$ Å, $\beta = 117.289(4)$ Å, *and 2,2′-thio-bis(4-methyl phenol)* ***5*** *crystallizes in the space group* $P\ 2_12_12_1$ *of the orthorhombic system with four molecules in the unit cell of dimensions* $a = 9.021(1)$ Å, $b = 10.523(2)$ Å, $c = 13.607(2)$ Å, $\alpha = 90$. *The structures have been refined to final values for the crystallographic R factor of 0.0189(3) and 0.0248(5) based on 2999 and 3720 observed independent reflections respectively.*

Keywords: Friedel-Crafts; microwave; sulfide; sulfinyl; sulfoxide

The symmetric diaryl sulfides and their sulfoxide derivatives have been synthesized by many groups using different conditions.[1] Friedel-Crafts method is generally used for the synthesis of these compounds. Treatment of *p*-cresol **1** with thionyl chloride **2** and anhydrous aluminium chloride in dichloromethane afforded sulfoxide **3**. Recently, catalytic oxygenation of organosulfur compounds have found increased applications in asymmetric synthesis.[2] Also, metal catalyzed reactions of organosulfur compounds are of biological and industrial

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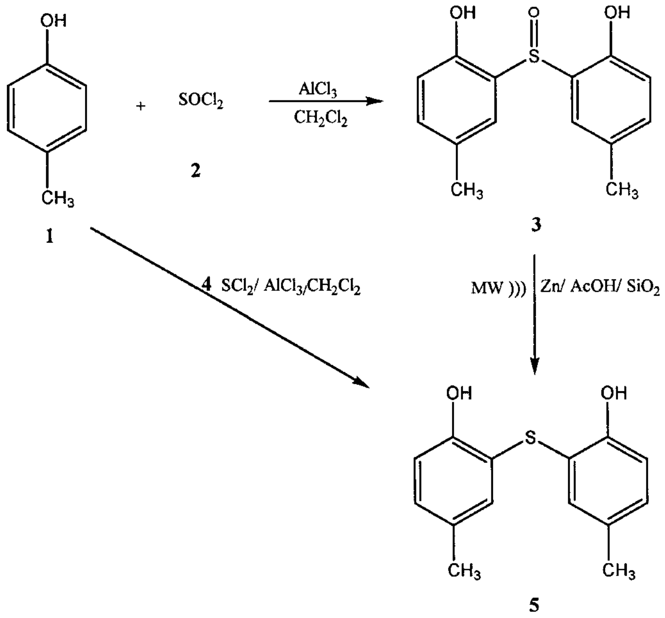
importance.[3] Rehder and coworkers have examined the vanadium-catalyzed oxygenation of sulfides to sulfoxides and sulfones.[4] Because of the importance of these compounds we were interested in the synthesis and crystal structure determination of them. We synthesized the sulfoxide **3** by using the same strategy in very good yield with some modifications in temperature and time interval of the reaction. In the ^{1}HNMR spectrum, the hydroxyl groups have appeared at 9.3 ppm and the aromatic hydrogens absorbed at 6.3–7.0 ppm (Scheme 1).



SCHEME 1

The reduction of sulfoxide group to sulfide has been reported in different conditions; e.g., Zn/AcOH,[5] pph$_3$/I$_2$,[6] LAH/THI,[7] LAH/Et$_2$C,[8] and recently hv(300 nm)/NaOCH$_3$/CH3OH.[9] We found that in this case the reduction process can be carried out in the presence of Zn/AcOH/SiO$_2$ and microwave irradiation. This reaction took only five minutes with 100% yield. Absence of absorption band at 950–1050 cm^{-1} in the IR spectrum proved that the reduction of sulfoxide to sulfide group had taken place. In the ^{1}HNMR spectrum, the hydroxyl group absorbs at 8.5 ppm and the aromatic hydrogens appeared at 7–8 ppm. Crystal data for **5** ($C_{14}H_{14}O_2S$): space group $P2_12_12_1$, $a = 9.021(1)$ Å, $b = 10.523(2)$ Å, $c = 13.607(2)$ Å, $\alpha = 90°$.

TABLE I Selected Bond Distances (Å) and Bond Angles (°) for **3** and **5**

3				**5**			
S1—O1	1.536(2)	C1—C6	1.394(3)	S1—C1	1.779(2)	C5—C7	1.511(3)
S1—C8	1.778(2)	C8—C13	1.381(4)	S1—C8	1.780(2)	C12—C14	1.506(4)
S1—C1	1.778(2)	C1—C2	1.401(3)	C1—C6	1.391(3)	O1—C2	1.371(3)
O2—C2	1.352(3)	C8—C9	1.397(3)	C8—C13	1.395(3)	O2—C9	1.375(3)
O3—C9	1.353(3)			C1—C2	1.394(3)	O1—H(10)	0.81(4)
				C8—C9	1.399(3)	O2—H(20)	0.84(3)
O1—S1—C8	104.95(11)	C2—C1—S1	115.17(16)	C1—S1—C8	101.53(9)	O1—C2—C1	118.95(19)
O1—S1—C1	105.41(10)	C13—C8—S1	121.14(18)	C6—C1—S1	119.79(16)	O2—C9—C8	122.3(2)
C8—S1—C1	101.03(10)	O2—C2—C3	123.9(2)	C13—C8—S1	121.07(17)	O1—C2—C3	122.0(2)
C6—C1—C2	121.0(2)	O3—C9—C10	124.3(2)	C2—C1—S1	120.44(16)	O2—C9—C10	118.3(2)
C13—C8—C9	121.2(2)	O2—C2—C1	117.7(2)	C9—C8—S1	119.59(16)	C2—O1—H(10)	110(3)
C6—C1—S1	123.74(17)	O3—C9—C8	117.1(2)	C6—C1—C2	119.73(19)	C9—O2—H(20)	111(2)
C9—C8—S1	117.53(19)			C13—C8—C9	119.2(2)		

TABLE II Selected Torsion Angles (°) for **3** and **5**

3		**5**	
O1—S1—C1—C6	−88.40	C8—S1—C1—C6	92.66
O1—S1—C8—C9	−172.27	C8—S1—C1—C2	−89.66
O1—S1—C1—C2	88.58	S1—C1—C2—O1	2.00
O1—S1—C8—C13	3.10	S1—C1—C2—C3	−178.60
C8—S1—C1—C6	20.60	S1—C1—C6—C5	178.39
C1—S1—C8—C9	78.33	C1—S1—C8—C13	−89.03
C8—S1—C1—C2	−162.38	C1—S1—C8—C9	95.01
C1—S1—C8—C13	−106.30	S1—C8—C9—O2	−4.45
S1—C1—C2—O2	0.30	S1—C8—C9—C10	175.40
S1—C8—C9—O3	−8.00	O2—C9—C10—C11	−179.92
S1—C1—C2—C3	−178.84	S1—C8—C13—C12	−175.67
S1—C8—C9—C10	174.18		
S1—C1—C6—C5	177.99		
S1—C8—C13—C12	−175.02		
C6—C1—C2—O2	177.40		
C13—C8—C9—O3	176.60		

RESULTS AND DISCUSSION

Molecular Structures

Crystallization of 2,2′-sulfinyl-bis(4-methyl phenol) **3** from ethanol at room temperature afforded colorless crystals whereas suitable crystals of 2,2′-thio-bis(4-methyl phenol) **5** have been obtained by slow evaporation of a toluene solution.

The perspective views of the molecular structure for **3** and **5** and the crystal packing diagrams are shown in Figures 1–4. The selected bond lengths and angles, selected torsion angles and intermolecular hydrogen bond distances are listed in Tables I–III.

The most important feature in the crystal structure of sulfinyl compound **3** is that the two phenyl rings possessing an OH group are anti to each other, while for the thio compound **5** these two groups are in

TABLE III Hydrogen Bond Distances (Å) and Angles (°) for **3** and **5**

D—H···A	d(D—H)	d(H···A)	<DHA	Symmetry transformation
		3		
O(2)—H(2O)···O(1)	0.93	1.82	148	[x, −y − 1, z − 1/2]
O(3)—H(3O)···O(1)	0.93	1.74	167	[x − 1/2, −y − 1/2, z− 1/2]
		5		
O(1)—H(1O)···O(2)	0.81	1.96	173	[x + 1/2, −y − 1/2, −z − 1]
O(2)—H(2O)···O(1)	0.84	2.04	162	Intermolecular

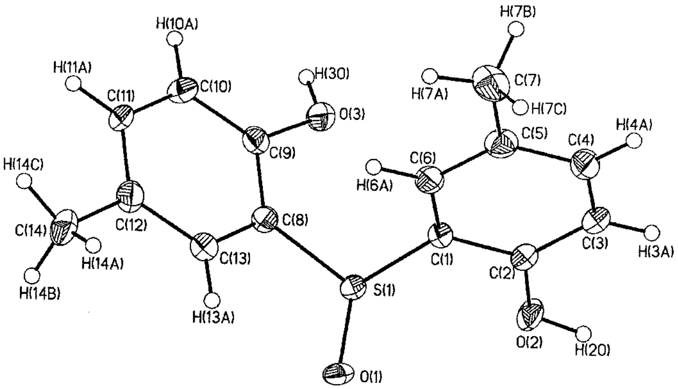


FIGURE 1 ORTEP drawing of the sulfoxide **3**.

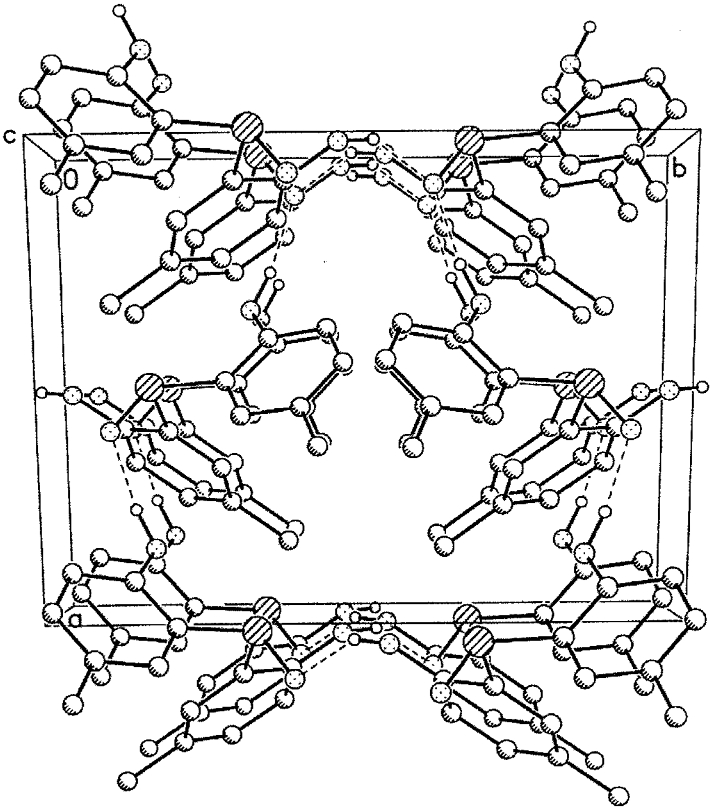


FIGURE 2 Unit cell packing diagram of the sulfoxide **3**.

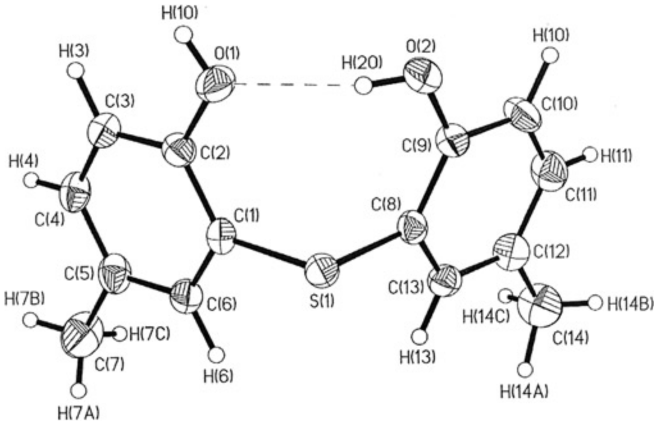


FIGURE 3 ORTEP drawing of the sulfide **5**.

one side and syn to each other (Figures 1 and 3). This can be related to the steric constraints within the compound **3** which is caused by the S=O group. Therefore the hydrogen-bonding pattern is completely different (Figures 2 and 4; Table III). There is an intramolecular hydrogen bonding between two hydroxyl groups for compound **5** (Figures 3 and 4). The <C–S–C angles are comparable in the two compounds. One important feature in the crystal structure of the thio compound **5** is the presence of three crystallographically independent molecules of 2,2′-thio bis(4-methyl phenol), (Figure 4), which are connected to each other with strong hydrogen bonding interaction (Table III) while for compound **3** there is hydrogen bonding between the O atom of the S=O group and the OH group, providing an extended organic network in both case.

EXPERIMENTAL

X-ray Structure Analysis

Analysis on single crystals of **3** and **5** were carried out on a Bruker SMART CCD area detector diffractometer (Mo K_α radiation, graphite monochromator, $\lambda = 0.71073$ Å) at −163°C (110K). Diffracted data were corrected for absorption using the SADABS program. Some softwares[10] including SMART (data collection), SAINT$^+$ (cell refinement and data reduction), SHELXTL (version 5.10, structure solution and refinement; molecular graphics and publication material) and SHELXL-97 were used. A crystal of dimensions $0.35 \times 0.20 \times 0.15$ mm^3 (**3**) and

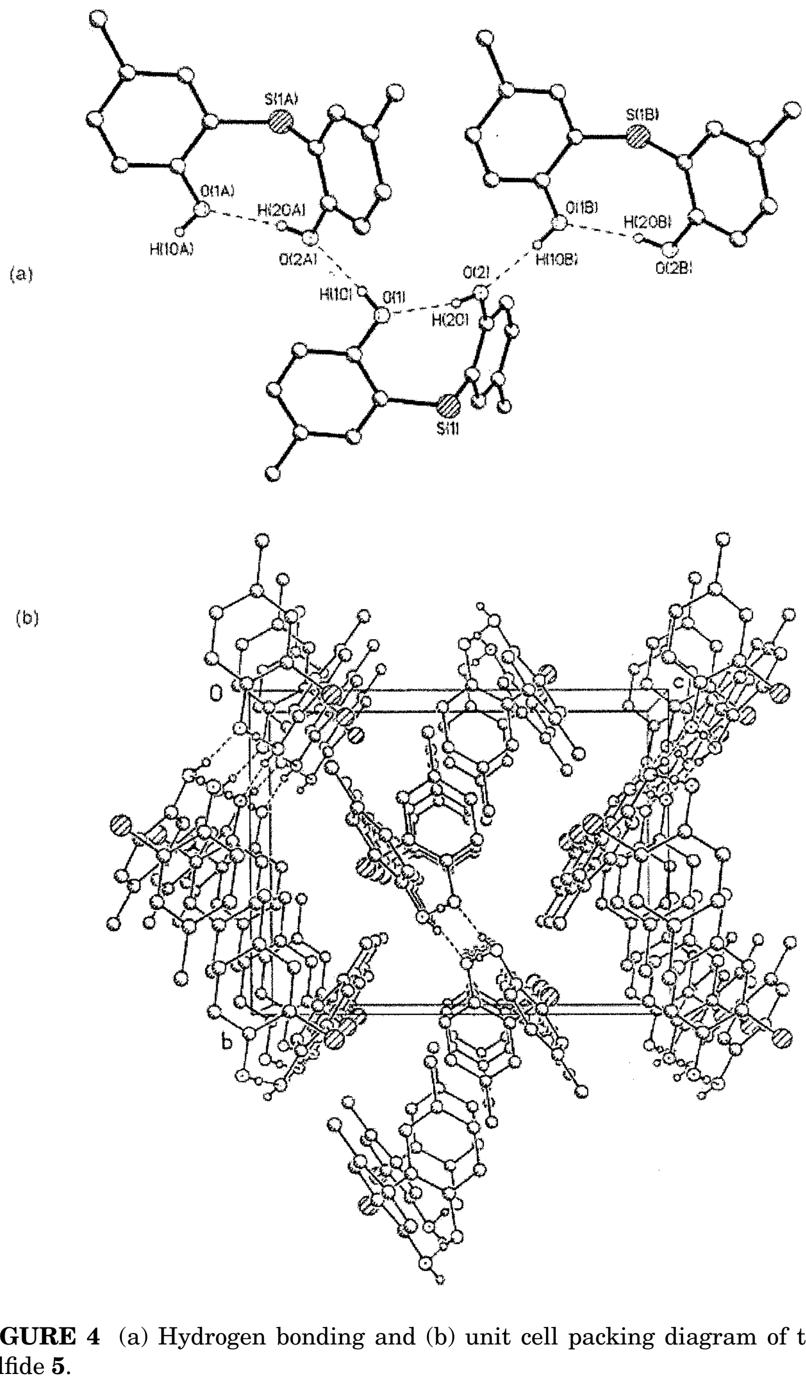


FIGURE 4 (a) Hydrogen bonding and (b) unit cell packing diagram of the sulfide **5**.

TABLE IV Crystallographic Data for **3** and **5**

	3	**5**
Empirical formula	$C_{14}H_{14}O_3S$	$C_{14}H_{14}O_2S$
fw	262.31	246.31
Space group	*Cc*	$P2_12_12_1$
T,k	110(2)	110(2)
λ(Mo k_α), Å	0.71073	0.71073
a, Å	11.425(2)	9.021(2)
b, Å	13.530(2)	10.523(2)
c, Å	9.522(2)	13.607(2)
α, deg	90°	90°
β, deg	117.29(4)	90°
γ, deg	90°	90°
V, Å^3	1308.0(4)	1291.7(2)
Z	4	4
D_{calcd}, g cm^{-3}	1.332	1.267
μ, mm^{-1}	0.244	1.237
Independent reflections	2999 [R(int) = 0.0189]	3720 [R(int) = 0.0248]
$R1/wR2$ (obs data)^a	0.0443/0.1149^b	0.0473/0.1065^c
$R1/wR2$ (all data)^a	0.0470/0.1178^b	0.0565/0.1112^c

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[b] $w = 1/[\sigma^2(F_o^2) + (0.0830P)^2 + 0.5854P]$; $P = (F_o^2 + 2F_c^2)/3$.
[c] $w = 1/[\sigma^2(F_o^2) + (0.0500P)^2 + 0.8000P]$.

$0.6 \times 0.5 \times 0.4$ mm^3 (**5**) were mounted in a glass capilary, and the data were collected in the range $2.51 \le \theta \le 28.99°$ (**3**) and $2.45 \le \theta \le 30.02°$ (**5**), with $-15 \le \mathrm{h} \le 15$, $-18 \le \mathrm{k} \le 6$, $-11 \le 1 \le 12$ (**3**) and $-12 \le \mathrm{h} \le 10$, $-14 \le \mathrm{k} \le 12$, $-18 \le \mathrm{l} \le 17$ (**5**). The structures were solved by direct method and refined by full-matrix least-squares based on F^2. The crystallographic data are listed in Table IV.

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