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PREPARATION AND SPECTRAL PROPERTIES OF SYMMETRICAL S-ARYL ARENESULFONO- THIOATES (THIOSULFONATES)

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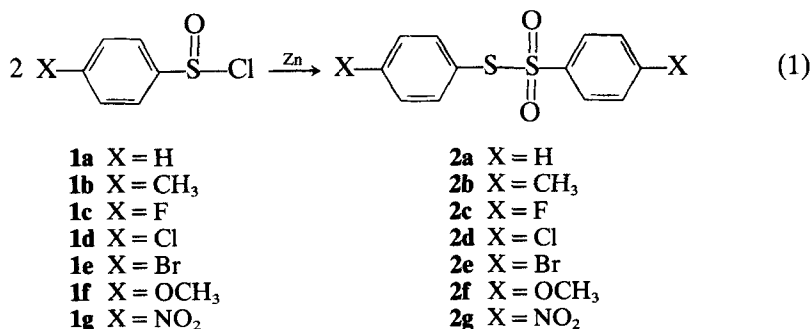
(Received July 7, 1987; in final form August 20, 1987)

Arenesulfinyl chlorides ($4\text{-X-C}_6\text{H}_4\text{S(O)Cl}$); $\text{X} = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$ react with activated zerovalent zinc in benzene at 6 to 8°C to give symmetrical S-aryl arenesulfonylthioates (thiosulfonates) in good to excellent yields. 2- and 3-Substituted arenesulfinyl chlorides ($\text{X} = \text{Cl}, \text{CH}_3$) give a mixture of products (disulfide, thiosulfinate, and/or thiosulfonate). 2,4,6-Triisopropylbenzenesulfinyl chloride reacts with zinc in 1,2-dimethoxyethane to give S-(2,4,6-triisopropylphenyl) 2,4,6-triisopropylbenzenesulfonylthioate and bis(2,4,6-triisopropylphenyl) disulfide. Possible mechanisms for the reactions, the ^1H and ^{13}C NMR spectra, and the chemical ionization and electron impact mass spectra of the thiosulfonates are discussed. The para carbon substituent chemical shifts ($\text{C}_p\text{-SCS}$) for the thiosulfonates and for symmetrical diaryl disulfides have been subjected to several dual substituent parameter (DSP) correlations.

Key Words: S-aryl arenesulfonylthioates (thiosulfonates); arenesulfinyl chlorides; ^1H and ^{13}C NMR; mass spectrometry; substituent shifts parameters.

INTRODUCTION

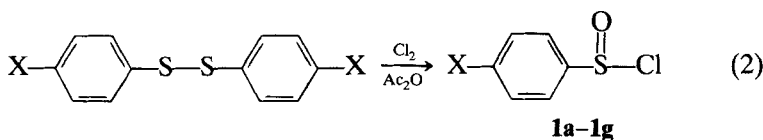
It has been observed²⁻⁶ that linear alkanesulfinyl chlorides react with activated zerovalent zinc⁶ to give symmetrical S-alkyl alkanesulfonylthioates (thiosulfonates) in good to excellent yields. The distribution and functionality of the products of these reactions are very sensitive to solvent effects and to structural effects in the alkanesulfinyl chlorides.²⁻⁵ It appears that the reaction of arenesulfinyl chlorides (**1**) with activated zerovalent zinc to give symmetrical S-aryl arenesulfonylthioates (**2**; Equation (1)) has not been systematically studied.⁷



S-Aryl arenesulfonylthioate esters (**2**), which are powerful sulfonylating⁸ or sulfidation agents,⁹ are useful for temporary blocking of mercapto groups in

protein chemistry.¹⁰ Symmetrical S-aryl arenesulfonothioates (**2**) have been generally prepared by the oxidation of disulfides,^{11,12} by the reaction of sulfinic acids with sulfonyl chlorides,¹³ by the oxidation of thiols with dinitrogen tetroxide,¹⁴ and by the reaction of sulfonyl chlorides with potassium iodide¹⁵ or with iron pentacarbonyl and boron trifluoride etherate.¹⁶ Some of these methods proceed in low to moderate yields, involve two or more steps, and afford side products such as sulfonic acids. Only isolated examples of the preparation of a limited number of symmetrical S-aryl arenesulfonothioates (**2**) involving zero-valent metals (iron,⁵ zinc,⁷ copper,^{17,18} silver,^{19,20}) have been reported.

We wish to describe a facile method for the preparation of symmetrical S-aryl arenesulfonothioates (**2**) from readily available arenesulfinyl chlorides (**1**)^{2-5,22} and activated zerovalent zinc in benzene (Equations (1,2)). The infrared, ¹H NMR, and ¹³C NMR spectroscopy, and the electron impact mass spectroscopy (EIMS) and chemical ionization mass spectroscopy (CIMS) of S-aryl arenesulfonothioates (**2**) are also described.²³⁻²⁵



- 3a** X = H
3b X = CH₃
3c X = F
3d X = Cl
3e X = Br
3f X = OCH₃
3g X = NO₂

RESULTS AND DISCUSSION

Table I shows the yields, physical properties, and mass spectral data of thiosulfonates **2a-2e**, from the reaction of activated zerovalent zinc and the corresponding arenesulfinyl chlorides. The side product is the corresponding disulfide which is easily separated and may be subsequently used to prepare sulfinyl chlorides (**1**).^{21,26} Although the yields of thiosulfonates from this method, in benzene solvent, are good to excellent for some 4-substituted-arenesulfinyl chlorides, a mixture of products was obtained from 4-methoxybenzenesulfinyl chloride and the reaction with 4-nitrobenzenesulfinyl chloride was not complete after five days. In 1,2-dimethoxyethane (DME, 48 hours) ¹³C NMR and TLC analyses showed that 2-chloro-, 3-chloro-, and 3-methylbenzenesulfinyl chloride gave product mixtures which included disulfide and thiosulfonate, respectively. 2-Methylbenzenesulfinyl chloride gave bis (2-methylphenyl) disulfide (35% isolated) and a mixture of S-(2-methylphenyl) benzenesulfonothioate, and S-(2-methylphenyl) benzenesulfinothioate.

2,4,6-Triisopropylbenzenesulfinyl chloride, in 1,2-dimethoxyethane (DME), gave S-(2,4,6-triisopropylphenyl) benzenesulfinothioate (55%) and bis(2,4,6-triisopropylphenyl) disulfide (17%).^{26,27}

TABLE I

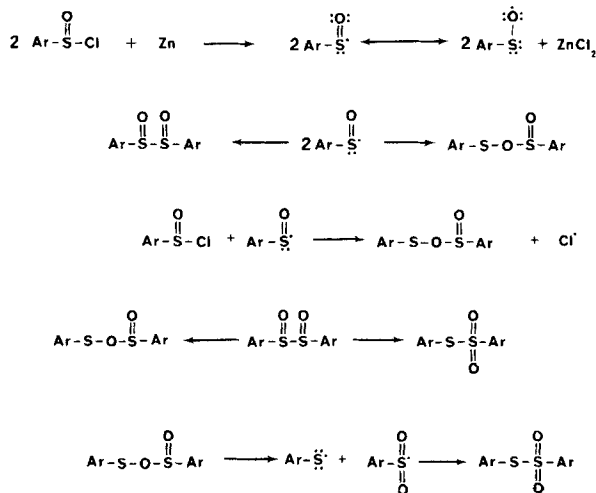
Yields, physical properties, and mass spectra of symmetrical S-aryl arenesulfonothioates

cmpd	X	Reaction time, h ^a	Yield, ^{b,c} %	m.p., °C	lit. m.p., °C	Mass spectra			
						Chemical ionization ^d [MH] ⁺ m/z	% of base peak	Electron impact [M] ⁺ m/z	% of base peak
2a	CH ₃	16	88 (6)	77–78	76–78 ^e	279	100	278	27
2b	H	5	91	38–39	44–45 ^e	251	100	250	23
2c	F	16	62 (18)	69–70	70–71 ^f	287	100	286	33
2d	Cl	16	75 (24)	135–136	134–136 ^e	319	100	318	6
2e	Br	16	80 (19)	158–159	159–160 ^g	409	100	408	6
2f	OCH ₃		^h						
2g	NO ₂	ⁱ							

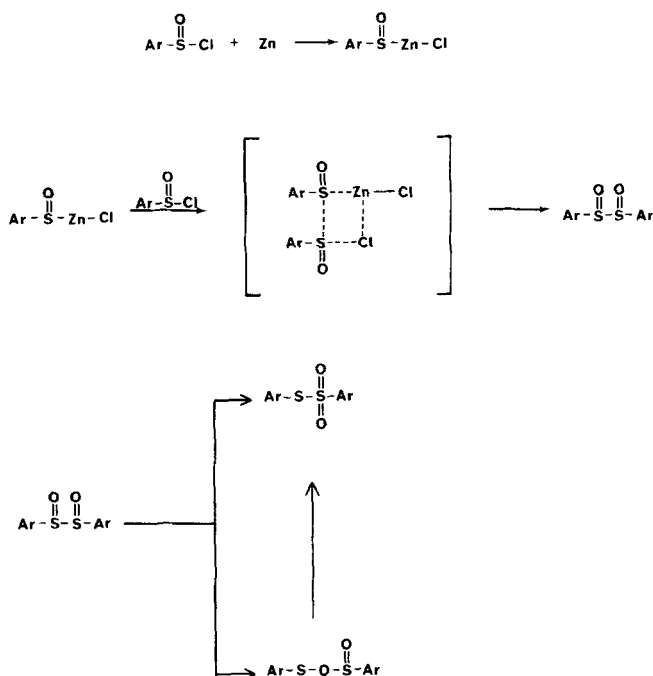
^a Reaction carried out in benzene at 6°C.^b Yield of pure isolated product.^c Isolated yield of corresponding diaryl disulfide in parentheses.^d 2-Methylpropane reactant gas.^e Reference 23.^f Reference 24.^g Reference 16a.^h Complex product mixture.ⁱ Reaction not complete after 5 days.

This procedure with 4-substituted arenesulfinyl chlorides has the advantages that symmetrical S-aryl arenesulfonothioates (**2a–2e**) are obtained in a facile one-step procedure starting with readily available sulfinyl chlorides²¹ in yields that are generally higher than those obtained with strong oxidizing agents.^{11,15}

Although the mechanism for the formation of thiosulfonates from the reaction of sulfinyl chlorides and zerovalent zinc is not known, it is highly probable that *vic*-disulfoxides (α -disulfoxides), O,S-sulfenyl sulfinates, and arenesulfinyl radicals are involved (Scheme I).^{2,3,28–34} The initially formed sulfinyl radicals may



SCHEME I



SCHEME II

dimerize to *vic*-disulfoxides and/or combine in a head-to-tail combination to give O,S-sulfinyl sulfinates. *vic*-Disulfoxides may rearrange to thiosulfonates or to O,S-sulfinyl sulfinates which may isomerize to thiosulfonates by radical (sulfonyl and thiyl) and/or nonradical pathways.

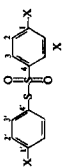
Scheme II shows another possible pathway for formation of *vic*-disulfoxides. Insertion of zerovalent zinc into the S-Cl bond followed by reaction with a second equivalent of sulfinyl chloride, possibly via a four-membered cyclic transition state, can lead to *vic*-disulfoxide. Thiyl radicals from the O,S-sulfinyl sulfinates (Scheme I) may combine to give the observed disulfides. The absence of *vic*-disulfones is consistent with the reported reluctance of sulfonyl radicals to dimerize to form sulfur-sulfur bonds.¹⁷

In a blank experiment, S-phenyl benzenesulfonylthioate (**2a**) did not react with zerovalent zinc. Thus, deoxygenation of thiosulfonate to disulfide or thiosulfinate does not appear to occur under these mild experimental conditions.^{2-5,22} Steric factors may also play a role in the reactions of 2-substituted arenesulfinyl chlorides.

The infrared and ¹³C NMR spectral data of thiosulfonates **2a-2e** are shown in Table II. The thiosulfonates show the characteristic strong infrared sulfone bands at 1325–1333 and 1137–1145 cm⁻¹ and the sulfur-sulfone band appears in the 1075–1077 cm⁻¹ region.

The replacement of a hydrogen atom in benzene by a substituent brings about changes in ¹³C NMR chemical shifts at the various ring carbon atoms (C-1 *ipso*, C-2 *ortho*, C-3 *meta*, C-4 *para*).³⁵⁻⁴⁴ Although these substituent chemical shifts

TABLE II
Infrared and ^{13}C NMR spectral data of symmetrical S-aryl arenesulfonothioates^{a,b,c}

	cmpd	X	IR (CDCl ₃) [cm ⁻¹]		¹³ C NMR (CDCl ₃ /TMS _{int}) δ [ppm]								
			asym	sym	S-SO ₂	C-1	C-2	C-3	C-4	C-1'	C-2'	C-3'	C-4'
	2a	H ^d	1330	1144	1076	133.9 (5.6)	129.6 (1.3)	127.6 (-0.7)	143.1 (14.8)	131.6 (3.3)	129.0 (0.7)	136.6 (8.3)	127.9 (-0.4)
	2b	CH ₃ ^e	1333	1143	1075	144.8 (16.5) (143.4)	130.4 (2.1) (130.3)	127.8 (-0.5) (127.5)	140.8 (12.5) (140.1)	142.3 (14.0) (141.1)	129.6 (1.3) (129.7)	136.7 (8.4) (136.5)	124.9 (-3.4) (124.9)
	2c	F	1333	1143	1075	165.9 (37.6) (168.4)	117.2 (-11.1) (116.6)	130.7 (2.4) (128.7)	139.2 (10.9) (138.7)	165.2 (36.9) (166.1)	116.5 (-11.8) (116.0)	139.1 (10.8) (137.7)	123.6 (-4.70) (123.5)
	2d	Cl	1333	1145	1077	140.8 (12.5) (139.8)	130.1 (1.8) (129.9)	129.5 (1.20) (129.0)	141.7 (13.4) (141.2)	138.8 (10.5) (137.5)	129.2 (0.9) (129.3)	137.9 (9.6) (138.0)	126.4 (-1.90) (126.0)
	2e	Br	1333	1145	1077	129.4 (1.1) (128.0)	133.2 (4.9) (132.8)	129.2 (0.9) (129.3)	142.3 (14.0) (141.6)	127.0 (-1.3) (125.7)	132.5 (4.2) (132.2)	138.1 (9.8) (138.3)	127.3 (-1.0) (126.4)
	2f	OCH ₃ ^f	1325	1137	1076	163.9 (35.6) (165.1)	115.2 (-13.1) (115.2)	130.2 (1.9) (128.5)	135.4 (7.1) (135.4)	162.6 (34.3) (162.8)	114.1 (-14.2) (114.6)	138.6 (10.3) (137.5)	119.4 (-8.9) (120.2)

^a Central solvent (CDCl_3) resonance at δ 77.273 ppm at 22.63 MHz.

^b Values in *first* row of parentheses are the substituent chemical shifts (SCS) as referred to benzene ($\delta_{\text{C}} = 128.31$ ppm). SCS = δ_{C} (observed - δ_{C} benzene); positive values imply deshielding [shift of a resonance to lower magnetic field (higher frequency)].

^c Values in *second* row of parentheses are calculated ^{13}C NMR resonances = δ_{C} unsubstituted thiosulfonate + SCS values of $\text{C}_6\text{H}_5\text{X}$.

^d 4-CH₃ $\delta_{\text{C}} = 21.8$ ppm; 4'-CH₃ $\delta_{\text{C}} = 21.6$ ppm.

^e 4-OCH₃ $\delta_{\text{C}} = 55.9$ ppm; 4'-OCH₃ $\delta_{\text{C}} = 55.7$ ppm.

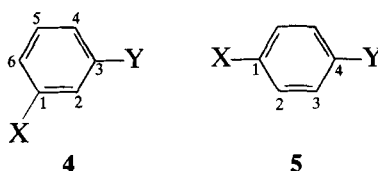
TABLE III
 ^{13}C substituent chemical shifts (ppm) for monosubstituent benzenes
 in deuteriochloroform^a

X	C ₁	C ₂	C ₃	C ₄
N(CH ₃) ₂	22.28	-15.66	0.74	-11.69
NH ₂	17.91	-13.25	0.88	-9.80
OCH ₃	31.21	-14.45	0.88	-7.68
F	34.51	-13.00	1.13	-4.39
Cl	5.93	0.31	1.40	-1.90
Br	-5.87	3.16	1.71	-1.50
CH ₃	9.52	0.68	-0.09	-3.05
H ^b	0.00	0.00	0.00	0.00
CF ₃	2.31	-3.13	0.40	3.41
CN	-15.96	3.72	0.70	4.35
CO ₂ C ₂ H ₅	2.14	1.17	-0.09	4.42
COCH ₃	8.69	0.15	-0.09	4.67
NO ₂	19.95	-4.85	0.93	6.22
CHO	8.06	1.36	0.63	6.07

^a Reference 37. Positive shifts are to high frequency. Digital resolution 0.05 ppm.

^b The parent derivative has a shift 51.30 ppm from the central peak of CDCl₃ (128.31 from TMS).

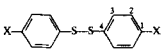
(SCS) are frequently additive and the ^{13}C NMR chemical shift in a disubstituted benzene may be calculated by adding appropriate SCS values of all substituents to the chemical shift of benzene, strict additivity does not always apply (Table III). Systematic nonadditivity appears to occur more in 1,3-disubstituted benzenes (**4**, Y fixed, X variable) than in 1,4-disubstituted benzenes (**5**, Y fixed, X variable).⁴⁰ In a given series, Y is regarded as the fixed substituent and X varies over a wide range of electron donating and withdrawing groups. Thus, there are four sites [relative to X: *ipso* (C-1), *ortho* (C-2), *meta* (C-3), and *para* (C-4)] at which the influence of the common substituent Y on SCS values of X can be measured.⁴⁴



Tables II and IV show the variation of para carbon substituent chemical shifts (C_p -SCS) for symmetrical S-aryl arenesulfonylthioates and symmetrical diaryl disulfides, respectively. A scan across the rows of Tables II and IV shows that the largest variation in SCS values of a given X substituent generally occurs at the sites *ipso* to X (C-1) and *para* to X (C-4). Tables II and IV show that for this series of compounds that para carbon substituent chemical shifts (C_p -SCS) are additive.

It is known that disulfides have strong lone pair interactions between the two sulfur atoms.⁴⁵⁻⁴⁷ The valence bond resonance structures (Equation (3)) involve the use of the 3d orbitals of the sulfur atoms which gives rise to *pd* π bonds and

TABLE IV
¹³C NMR spectral data of symmetrical diaryl disulfides^{a,b,c}

		¹³ C NMR (CDCl ₃ /TMS _{int}) δ [ppm]			
					
Cmpd	X	C-1	C-2	C-3	C-4
3a	H	127.4 (-0.9)	129.3 (1.0)	127.8 (-0.5)	137.3 (9.0)
3b	CH ₃ ^d	137.7 (9.4) (136.9)	130.0 (1.7) (130.0)	128.8 (0.5) (127.7)	134.2 (5.9) (134.3)
3c	F	162.9 (34.6) (161.9)	116.5 (-11.8) (116.3)	131.6 (3.3) (128.9)	132.5 (4.2) (132.9)
3d	Cl	134.0 (5.7) (133.3)	129.7 (1.4) (129.6)	129.6 (1.3) (129.2)	135.5 (7.2) (135.4)
3e	Br	120.7 (-7.6) (121.5)	131.7 (3.4) (132.5)	128.9 (0.6) (129.5)	135.2 (6.9) (135.8)
3f	OCH ₃ ^e	160.2 (31.9) (158.6)	114.8 (-13.5) (114.9)	132.8 (4.5) (128.9)	128.7 (0.4) (129.6)
3g	NO ₂	147.4 (19.1) (147.4)	124.7 (-3.6) (124.5)	126.8 (-1.5) (128.7)	144.4 (16.1) (143.5)

^a Central solvent (CDCl₃) resonance at δ77.273 ppm at 22.63 MHz.

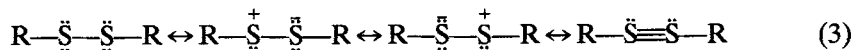
^b Values in *first* row of parentheses are the substituent chemical shifts (SCS) as referred to benzene (δ_C = 128.31 ppm). SCS = δ_C (observed) - δ_C (benzene); positive values imply deshielding [shift of a resonance to lower magnetic field (higher frequency)].

^c Values in *second* row of parentheses are calculated ¹³C NMR resonances = δ_C (calculated) = δ_C (diphenyl disulfide) + SCS value of C₆H₅X.

^d 4-CH₃ δ_C = 21.3 ppm.

^e 4-OCH₃ δ_C = 55.5 ppm.

partially positive (deshielding) sulfur atoms. Thus, C-4 (δ_C = 137.3 ppm) in diphenyl disulfide is more deshielded than the carbon atoms in benzene. None of the ¹³C NMR resonances in the diaryl disulfides in this study correlated with the single substituent constants shown in Table V. Several DSP analyses of the SCS data for disulfides (Table VI) show that resonance effects (Equation (4)) dominate the shifts at the *para* (C-4) position, confirming the importance of π electron density changes brought about by interactions between the two sulfur atoms such as shown in Equation (3). Table VI shows that only C-3 and C-4 of the disulfides correlate well with several DSP equations when the respective ¹³C NMR chemical shifts are compared with the substituent constants in Table V. The best correlations are with σ_I + σ_{R(BA)} and σ_I + σ_R⁺.



$$\text{C}_p\text{-SCS} = 0.34\sigma_{\text{I}} + 0.92\sigma_{\text{R}} \quad (4)$$

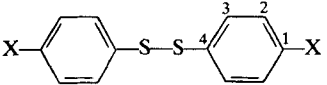
TABLE V
 Substituent constants^{a,b,c}

Substituent	σ	σ^+	σ^-	σ_R^0	$\sigma_{R(A)}^-$	σ_R^+	σ_I	$\sigma_{R(BA)}$	F	R
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-CH ₃	-0.17	-0.31	-0.17	-0.11	-0.11	-0.25	-0.04	-0.11	-0.01	-0.41
4-F	0.06	-0.07	0.06	-0.34	-0.45	-0.57	0.50	-0.45	0.74	-0.60
4-Cl	0.23	0.11	0.23	-0.23	-0.23	-0.36	0.46	-0.23	0.72	-0.24
4-Br	0.23	0.15	0.23	-0.19	-0.19	-0.30	0.44	-0.19	0.72	-0.18
4-OCH ₃	-0.27	-0.78	-0.27	-0.45	-0.45	-1.02	0.27	-0.61	0.54	-1.68
4-NO ₂	0.78	0.78	1.24	0.15	0.46	0.15	0.65	0.15	1.00	1.00

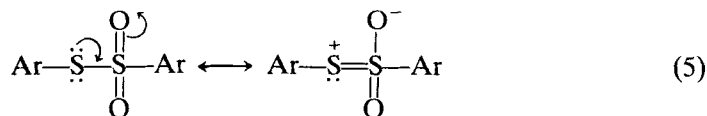
^a σ , σ^+ , and σ^- values taken from Reference 35.^b σ_R^0 , $\sigma_{R(A)}^-$, σ_R^+ , σ_I , and $\sigma_{R(BA)}$ taken from Reference 36.^c F and R values taken from Reference 39.

TABLE VI

Correlation coefficients (*r*) of substituent chemical shifts (SCS) of symmetrical diaryl disulfides with various dual substituent parameters (DSP)

					
Carbon atom	$\sigma_I + \sigma_{R(BA)}$	F + R	$\sigma_I + \sigma_R^0$	$\sigma_I + \sigma_{R(A)}^-$	$\sigma_I + \sigma_R^+$
C-1	0.629	0.590	0.630	0.599	0.719
C-2	0.737	0.710	0.679	0.660	0.794
C-3	0.995	0.973	0.973	0.936	0.962
C-4	0.989	0.978	0.992	0.965	0.992

Replacement of a hydrogen atom in benzene by C₆H₅SSO₂ gives an SCS of 14.8 ppm at C-4 while replacement with C₆H₅SO₂S gives an SCS of -0.4 ppm at C-4'. Attempts to correlate the ¹³C NMR resonances at C-4 or C-4' with a single substituent constant were unsuccessful (Table V). Table VII shows that Taft's parameters ($\sigma_I + \sigma_{R(BA)}$)³⁶ give better correlations for thiosulfonates than do Swain's field and resonance parameters (F and R).^{39, 48-51}



EXPERIMENTAL

High resolution mass spectra were obtained with a VG 7070E-HF mass spectrometer (70 eV). Medium resolution mass spectra were obtained with a Finnigan 9610 GC-EI-CI mass spectrometer with a Nova 3 data system operating at an ionization potential of 70 or 100 eV. Chemical ionization mass spectra were obtained by using 2-methylpropane as the reactant gas.

¹H NMR spectra were recorded at 250 MHz (Bruker WM-250) and at 300 MHz (GE 300) with the solvent(s) noted. Chemical shifts (δ) are reported downfield from internal Me₄Si (~0.5% for Fourier

TABLE VII

Correlation coefficients (r) of substituent chemical shifts (SCS) of symmetrical S-aryl arenesulfonothioates with various dual substituent parameters (DSP)

$X = H, CH_3, F, Cl, Br, OCH_3, NO_2$

Carbon atom	$\sigma_I + \sigma_{R(BA)}$	F + R	$\sigma_I - \sigma_R^0$	$\sigma_I + \sigma_{R(a)}$	$\sigma_I + \sigma_R^+$
C-1	0.887	0.784	0.855	0.957	0.808
C-2	0.920	0.834	0.865	0.943	0.840
C-3	0.991	0.954	0.982	0.997	0.975
C-4	0.997	0.988	0.998	0.969	0.993
C-1'	0.886	0.781	0.852	0.955	0.805
C-2'	0.927	0.843	0.874	0.947	0.850
C-3'	0.983	0.949	0.971	0.989	0.966
C-4'	0.994	0.981	0.998	0.974	0.988

transform) at $\delta = 0.00$ ppm. ^{13}C NMR data were obtained with a Bruker WM-250 or GE 300 MHz spectrometer.

Reagents and solvents were purified by standard procedures. Dinitrogen was dried by passing it through a column of Drierite and 5 Å molecular sieves.

Thin layer chromatography was performed on Merck precoated silica gel 60 F-254 (250 μ m thick) glass plates which were developed in a solvent mixture of hexanes (Mallinkrodt)/ethyl ethanoate (9:1 by volume). After the solvent had risen to the top, the plates were immersed in phosphomolybdic acid and charred.

Activation of zinc metal.⁶ To a 25 ml Erlenmeyer flask were added 2.0 g (0.03 mmol) of Mallinckrodt zinc metal dust (97.1%) and 20 ml of 2% (v/v) hydrochloric acid. The mixture was stirred (ca. 5 min) until the zinc became silver in color. After suction filtration, the zinc was washed successively with 50 ml of water, 20 ml of 95% ethanol, 20 ml of 2-propanone, and 20 ml of anhydrous ether. The zinc was transferred to a 25-ml round-bottomed flask which was heated in a water bath at 90°C while the excess solvent was removed under reduced pressure (ca. 20 min at 2 torr). The activated zerovalent zinc was used within 20 min after drying.

Preparation of disulfides. Disulfides **3a–3g** were prepared in excellent yields by the oxidation of the corresponding thiols with bromine/aqueous potassium hydrogen carbonate in a two-phase system.^{21d} The physical properties of the disulfides agreed with literature reports.

Preparation of arenesulfinyl chlorides. The method of Douglass and coworkers²¹ was used to prepare the arenesulfinyl chlorides used in this study. The bp and mp of the sulfinyl chlorides agreed with literature values.

S-(4-Methylphenyl) 4-methylbenzenesulfonothioate (2b). Typical procedure: To an oven-dried dinitrogen-purged 100 ml round-bottomed flask was added a solution of 4-methylbenzenesulfinyl chloride (**1b**, 0.87 g, 5.0 mmol) in dry benzene (20 ml). Activated zinc powder (0.55 g, 8.4 mmol),⁶ in a previously dried and nitrogen-purged powder addition funnel with a specially grooved Teflon auger, was added over a twenty min period to the vigorously stirred solution. It is important to add the zinc metal at a rate so that it remains granular and free flowing in the reaction mixture. The reaction mixture was maintained from 6 to 8°C during the first hour and then allowed to warm to 22 to 24°C. TLC analysis using 5:1 hexanes-ethyl ethanoate was used to follow the progress of the reaction.

After 16 h the reaction mixture was filtered and the zinc was washed with ca. 15 ml of dry benzene. The wash solution and filtrate were combined and the solvent evaporated on a rotatory evaporator. The product mixture of S-(4-methylphenyl) 4-methylbenzenesulfonothioate (**2b**) and bis(4-methylphenyl) disulfide (**3b**) were separated via column chromatography on 200 g of MCB 230–400 mesh silica gel in a 10 cm diameter column. The disulfide (**3b**) was eluted with 800–900 ml of hexanes. Recrystallization of **3b** from aqueous ethanol gave 40 mg (6%); mp 44–45°C (lit.⁵² mp 44–45°C; R_f

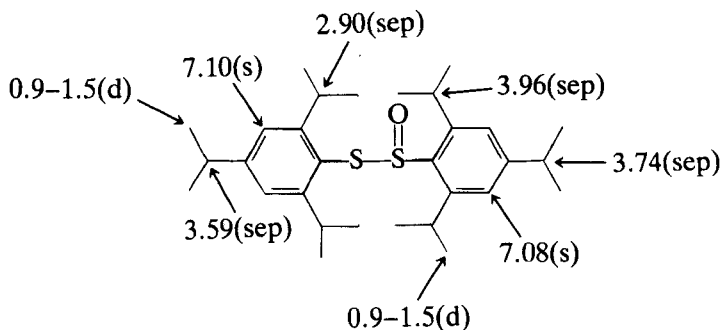
0.62 (5:1 hexanes-ethyl ethanoate)). The thiosulfonate (**2b**) was eluted immediately after the disulfide (**3b**) with 400–500 ml of ethyl ethanoate (1:9). Recrystallization from petroleum ether (30–60°C) gave 0.65 g (88%) of thiosulfonate **2b**, mp 75–76°C (lit.⁹ mp 73–75°C); $R_f = 0.38$ (5:1 hexanes-ethyl ethanoate).

2,4,6-Triisopropylbenzenesulfinic acid was prepared from 2,4,6-triisopropylbenzenesulfonyl chloride²⁷ as previously described (mp 87–88°C; lit.⁵³ mp 84.5–87°C).

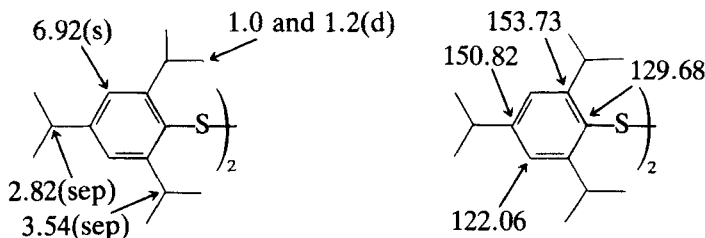
2,4,6-Triisopropylbenzenesulfinyl chloride was prepared by modifying previously published procedures.^{54–56} To a solution of freshly distilled thionyl chloride (0.40 g, 3.35 mmol) in 15 ml of dry diethyl ether in a 50 ml round-bottomed flask was added 2,4,6-triisopropylbenzenesulfinic acid (0.66 g, 2.5 mmol) in portions via a powder funnel. The reaction flask was purged with dry deoxygenated nitrogen and stirred at 30–35°C for five hours. The solvent was removed in vacuo and the residue, which was recrystallized from dry petroleum ether (45–60°C), gave 0.55 g (93%) of 2,4,6-triisopropylbenzenesulfinyl chloride, mp 73–74°C.

S-(2,4,6-triisopropylphenyl) 2,4,6-triisopropylbenzenesulfinothioate. The general procedure described above for the reaction of arenesulfinyl chloride and zerovalent zinc was used. In a 100-ml round-bottomed flask containing 2,4,6-triisopropylbenzenesulfinyl chloride (0.29 g, 1.0 mmol) in 10 ml of dry dimethoxyethane was added activated zinc (0.17 g, 1.65 mmol). The reaction mixture was stirred for 48 hours. A TLC analysis of the reaction mixture in 1:9 ethyl ethanoate/hexanes gave 3 spots of $R_f = 0.40$, 0.60, and 0.72. Flash chromatography on a 30 mm diameter column packed with 14 cm of 230–400 mesh silica gel using 400 ml of 1:9 ethyl ethanoate/hexanes gave separation of the bottom spot ($R_f = 0.40$, 7.3 mg), which was not identified. Flash chromatography of the remainder of the reaction mixture in the same manner using 100 ml of hexanes followed by 100 ml of ethyl ethanoate led to separation of the other two components. The middle spot ($R_f = 0.60$) afforded 135.6 mg (55%) of *S*-(2,4,6-triisopropylphenyl) 2,4,6-triisopropylbenzenesulfinothioate, mp 135–136°C (dec) [lit. mp 135–136°C] and the upper spot ($R_f = 0.72$) afforded 39.7 mg (17%) of bis-(2,4,6-triisopropylphenyl) disulfide, mp 80–81 °C [lit.^{26,27,53} mp 80–81°C].

S-(2,4,6-triisopropylphenyl) 2,4,6-triisopropylbenzenesulfinothioate. CIMS m/z 487 $[MH]^+$ 19.7% of base; m/z 237 100%; EIMS m/z 149 100%.



Bis-(2,4,6-triisopropylphenyl) disulfide. CIMS m/z 471 $[MH]^+$ 45.9% of base peak; m/z 237 100%, EIMS m/z 236 $[M]^+$ 36.5% of base peak; m/z 151 100%.



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