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SYNTHESIS, CRYSTAL, AND MOLECULAR STRUCTURES AND CONFORMATIONS OF NAPHTHO[1,8-b,c]-1,5-DITHIOCIN-1,1-DIOXIDE,-1,5-DIOXIDE,-1,1,5-TRIOXIDE AND -1,1,5,5-TETRAOXIDE

Richard S. Glass* and Jeffrey L. Broeker

Department of Chemistry, The University of Arizona, Tucson, AZ 85721

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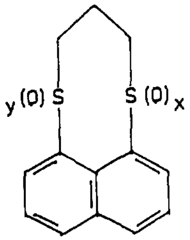
Abstract- Chemoselective oxidation of the known naphtho[1,8,-*b*,*c*]-1,5-dithiocin, dithioether 1, to the corresponding -1,1-dioxide: monosulfone 3, 1,5-dioxide: cis-disulfoxide 4, or -1,1,5,5-tetraoxide: disulfone 6 can be accomplished with potassium permanganate and a phase transfer catalyst in a two phase system in 66% yield, with sodium metaperiodate in aqueous methanol in 95% yield, or ruthenium tetraoxide in 70% yield, respectively. Oxidation of the known monosulfoxide 2 with potassium permanganate and a phase transfer catalyst in a two phase system also gave monosulfone 3 in 73% yield. The corresponding -1,1,5-trioxide: sulfoxide-sulfone 5 was selectively prepared in quantitative yield by oxidation of the monosulfone 3 with sodium metaperiodate in aqueous methanol. The crystal and molecular structures, and conformations of naphtho[1,8-*b*,*c*]-1,5-dithiocin-1,1-dioxide (3), -1,5-dioxide (4), -1,1,5-trioxide (5), and -1,1,5,5-tetraoxide (6) were determined by single crystal X-ray analysis. These compounds crystallize in the monoclinic space group $P2_{1/c}$ with a=13.184(4)Å, b=13.182(5)Å, c=7.106(1)Å, β=104.14(5)°, and Z=4, the orthorhombic space group P_{bca} with a=17.931(2)Å, b=13.108(3)Å, c=20.280(4)Å, and Z=16, the monoclinic space group $P2_{1/n}$ with a=9.298(1)Å, b=10.264 (2)Å, c=13.396(2)Å, β=110.06(1)°, and Z=4, and the orthorhombic space group P_{bca} with a=12.258(3)Å, b=9.997Å, c=20.168Å, and Z=8, respectively. The structures were solved by direct methods. Full-matrix least-squares refinement led to conventional R factors of 0.034, 0.046, 0.041, and 0.049, respectively. The conformations of the molecules in the solid state were distorted boat, boat with cis-diequatorial sulfoxide; boat with equatorial sulfoxide, and the unusual twist conformer, respectively.

This paper and the following one present results on the conformations of naphtho[1,8-*b*,*c*]-1,5-dithiocin and its S-oxides. The results are of relevance to conformational analysis of medium-sized heterocycles and transannular interaction of some sulfur functional groups (thioether, sulfoxide, and sulfone) with each other.

Conformational analysis of medium-sized heterocycles is of considerable current interest.[1] There are several reasons for this interest. Replacement of methylene groups in cycloalkanes by heteroatoms have important consequences in their conformational behavior. With more than one heteroatom in the ring the geometry of the ring may confer unusual chemistry due to transannular effects, e.g. the redox chemistry of 1,5-dithiocane.[2] Owing to our interest in transannular interactions in naphtho[1,8-*b*,*c*]-1,5-dithiocin, 1,[3-6] a series of its S-oxides have been prepared and studied. The conformation of naphtho[1,8,-*b*,*c*]-1,5-dithiocin in the solid state[3] and that of the corresponding 1-oxide 2 in the solid state and solution[4] were determined previously. The short S...S distance and geometry about the sulfoxide sulfur atom in 2 suggest S...S interaction. The nature of this interaction was investigated by vibronic analysis using SCF/STO-3G[5] and SCF/STO-3G*[6] *ab initio* calculations. This paper reports the solid state conformations of naphtho[1,8-*b*,*c*]-1,5-dithiocin-1,1-



1, x=y=0; 4, x=y=1

2, x=1, y=0; 5, x=2, y=1

3, x=2, y=0; 6, x=y=2

dioxide (3), -1,5-dioxide (4), 1,1,5-trioxide (5), and 1,1,5,5-tetraoxide (6) determined by X-ray crystallographic methods. These studies provide information on interaction between various sulfur moieties, i.e. sulfide, sulfoxide and sulfone, constrained to be very close to each other. In addition, the unique conformational aspects of this unusual ring system in which an eight-membered ring is constrained by the naphthalene ring annulated with it have been ascertained.

RESULTS AND DISCUSSION

Synthesis

Oxidation of naphtho[1,8-b,c]-1,5-dithiocin 1 with potassium permanganate in a two-phase system with phase transfer catalysis[7] yielded monosulfone 3 in 66% yield. This reaction probably proceeds via monosulfoxide 2 and indeed monosulfoxide 2 is oxidized under these conditions to monosulfone 3 in 73% yield. The selective oxidation of one of the sulfur atoms in dithioether 1 to the sulfone without oxidation of the other sulfur atom may be due to selective coordination of the sulfoxide oxygen in intermediate monosulfoxide 2 by permanganate.[8] Such a rationalization has been suggested before to account for the selective oxidation of 1,3-dithietane-1-oxide to 1,3-dithietane-1,1-dioxide.[9] Oxidation of dithioether 1 with three molar equivalents of sodium metaperiodate in aqueous methanol[10,11] provided disulfoxide 4 in 95% yield. Only one stereoisomeric disulfoxide is obtained and it is the cis isomer as unequivocally revealed by x-ray crystallographic analysis.

Unsuccessful attempts to isomerize the cis disulfoxide 4 to the trans-isomer were made. Disulfoxide 4 underwent no change over several days at room temperature in methanol saturated with hydrochloric acid[12-14] as monitored by TLC analysis. Dissolution of disulfoxide 4 in concentrated sulfuric acid followed by hydrolysis gave disproportionation products: sulfoxide 2 and sulfoxide-sulfone 5. Treatment of disulfoxide 4 with trimethyloxonium tetrafluoroborate[14,15] produced monosulfone 3.[16]

Monosulfone 3 on treatment with sodium metaperiodate in aqueous methanol[10,11] afforded sulfoxide-sulfone 5 in quantitative yield. Attempts to prepare disulfone 6 by oxidation of dithioether 1 with six molar equivalents of potassium hydrogen persulfate (oxone) in aqueous methanol[17] gave a mixture of disulfoxide 4, sulfoxide-sulfone 5, and disulfone 6. Oxidation of disulfoxide 4 with potassium permanganate in a two phase system with phase transfer catalysis[7] did not provide disulfone 6 in satisfactory yield. However, oxidation of dithioether 1 with ruthenium tetraoxide[18] provided disulfone 6 in 70% yield.

Structural Studies

The structure and conformation of monosulfone 3 in the solid state were established by X-ray crystallographic analysis. The crystal data for this compound are listed in Table I. Monosulfone 3 crystallized in the monoclinic space group $P2_{1/c}$ (No. 14), with a=13.184(4), b=13.182(5), c=7.106(1) Å, β=104.14°, and Z=4. The structure was solved by direct methods. Full-matrix least-squares refinement led to a conventional R factor of 0.034. The final atomic parameters and thermal parameters are listed in Table II. An ORTEP drawing[19] of the molecule is shown in Figure 1. The X-ray structure reveals that monosulfone 3 adopts a boat conformation but it is not a perfect boat. There is a twisting from an ideal boat conformer presumably to relieve repulsion between the oxygen atom of the sulfone group directed into the ring and the lone pair of electrons on the thioether sulfur atom. Data on the magnitude of this twist is found in the C(1) -S(1)-C(11)-C(12) and C(8)-S(2)-C(13)-C(12) torsional angles, which are -14 and 71° respectively. In a perfect boat conformation the former angle would be -60° and the latter would be 60°. The steric strain between the sulfur moieties is also relieved by increasing the *peri* bond angles. The bond angles C(9)-C(8)-S(2) and C(9)-C(1)-S(1) are 125.9 and 126.2°, which significantly deviate from the "ideal" 120° bond angle. Finally the steric strain is also relieved by displacing the sulfur atoms above and below the least-squares plane of the naphthalene ring. S(1) is displaced 0.44 Å on one side of the naphthalene plane while S(2) is displaced 0.21 Å on the other side. The nonbonded S...S distance in monosulfone 3 is 3.27Å which is significantly greater than this distance of 3.00Å in monosulfoxide 2[4] and only slightly larger than that of 3.23Å for dithioether 1.[3] Thus any S...S attractive interaction such as may exist in monosulfoxide 2[6] is absent in monosulfone 3[20] perhaps, due to the overwhelming of this weak interaction by repulsion between the endodentate oxygen atom of the sulfone moiety and the thioether sulfur electron pair.

The structure and conformation of disulfoxide 4 in the solid state was determined by X-ray crystallographic techniques. Disulfoxide 4 crystallized in the orthorhombic space group P_{bca} (No. 61), with a=17.931(2), b=13.108(3), c=20.280(4) Å, and Z=16. The structure was solved by direct methods. Full-matrix least-squares refinement led to a conventional R factor of 0.046 after several cycles of anisotropic refinement. The final atomic parameters and thermal parameters are given in Table III. An ORTEP drawing[19] of the molecule is shown in Figure 2. This crystal structure study showed that the relative stereochemistry of the sulfoxide oxygen atoms is cis-diequatorial[21] and that the molecule adopts an almost perfect boat conformation. The only deviation is the C(9)-C(1)-S(1) and C(9)-C(8)-S(2) bond angles which are 124.3 and 124.5° (average of molecule a and b). This increase in angle over the "ideal" 120° bond angle places the sulfur atoms 3.05Å apart, which is short compared to the S...S intramolecular distance of 3.23Å in dithioether 1.[3] In addition, the sulfur atoms in disulfoxide 4 are displaced from the naphthalene least squares plane by only 0.08, and 0.20Å on the same side of the naphthalene ring unlike the sulfur atoms in dithioether 1 which are

Table I. Crystal Data[a] for Monosulfone 3, Disulfoxide 4, Sulfoxide-sulfone 5, and Disulfone 6.

cmpd	3	4	5	6
mol formula	$C_{13}H_{12}O_2S_2$	$C_{13}H_{12}O_2S_2$	$C_{13}H_{12}O_3S_2$	$C_{13}H_{12}O_4S_2$
mol wt	264.37	264.37	277.34	296.37
space group	$P2_{1/c}$ #14	P_{bca} #61	$P2_{1/n}$ #14	P_{bca} #61
a,Å	13.184(4)	17.931(2)	9.298(1)	12.258(3)
b,Å	13.182(5)	13.108(3)	10.264(2)	9.997(2)
c,Å	7.106(1)	20.280(4)	13.396(2)	20.168(4)
α,deg	90	90	90	90
β,deg	104.14(5)	90	110.06(1)	90
γ,deg	90	90	90	90
Z	4	16	4	8
d_{obsd}[b] (g/cm^{-3})	1.43	1.52	1.54	1.58
d_{calcd} (g/cm^{-3})	1.47	1.47	1.53	1.59
cryst color, shape	colorless, trapezoidal block	colorless, block	colorless, irregular	colorless, rectangular
cryst dimens (mm)	0.25 x 0.42 x 0.47	0.09 x 0.15 x 0.50	0.63 x 0.17 x 0.37	0.25 x 0.20 x 0.24
no. obsd data	2613	4276	3095	3663
no. unique data	2276	4224	2754	3235
abs. coeff. $[\mu(\lambda)]$cm^{-1}	4.1	4.1	4.2	4.2

[a] Standard deviation of the least significant figure is given in parentheses.
[b] Density was determined by the flotation method using aqueous sodium iodide solution

displaced on either side of the naphthalene ring by 0.34 and 0.07Å.[3] These geometric factors are consistent with the results from vibronic analysis of disulfoxide 4 in which evidence was adduced for a weak attractive S...S interaction.[6]

The structure and conformation of sulfoxide-sulfone 5 in the solid state was unequivocally determined by single crystal X-ray analysis. Sulfoxide-sulfone 5 crystallized in the monoclinic space group $P2_{1/n}$ (No. 14) with a=9.298(1), b=10.264(2), c=13.396(2) Å, β=110.06(1)°, and Z=4. The structure was solved by direct methods. Full matrix least-squares refinement led to a conventional R factor of 0.041 after several cycles of anisotropic refinement. The final atomic parameters and thermal parameters are listed in Table IV. An ORTEP drawing[19] of the molecule is shown in Figure 3. The molecule has an almost perfect boat conformation and the sulfoxide group is equatorial.[21] The structure, however, has a disorder. The axial oxygen atom was found to have an occupancy of two-thirds

Table II. Fractional Atomic Coordinates and Thermal Parameters for Monosulfone 3.

Atom	x^a	y^a	z^a	$B^{a,b}$Å^2
S(1)	0.34976(5)	0.10252(5)	0.20015(9)	3.06(1)
S(2)	0.14773(5)	0.10996(5)	0.39107(9)	3.16(1)
O(11)	0.2733(2)	0.1749(2)	0.1041(3)	4.17(4)
O(12)	0.4476(1)	0.1033(2)	0.1419(3)	4.76(5)
C(1)	0.2958(2)	-0.0222(2)	0.1498(3)	2.65(5)
C(2)	0.3587(2)	-0.0847(2)	0.0721(4)	3.66(6)
C(3)	0.3252(3)	-0.1807(3)	-0.0010(4)	4.72(7)
C(4)	0.2272(3)	-0.2119(2)	-0.0025(4)	4.44(7)
C(5)	0.0566(2)	-0.1871(2)	0.0651(4)	4.06(6)
C(6)	-0.0104(2)	-0.1341(2)	0.1444(4)	3.99(6)
C(7)	0.0237(2)	-0.0447(2)	0.2436(4)	3.38(6)
C(8)	0.1225(2)	-0.0046(2)	0.2571(3)	2.58(5)
C(9)	0.1928(2)	-0.0547(2)	0.1631(3)	2.55(5)
C(10)	0.1586(2)	-0.1503(2)	0.0739(4)	3.26(5)
C(11)	0.3877(2)	0.1193(2)	0.4602(4)	3.77(6)
C(12)	0.3460(2)	0.0433(2)	0.5846(4)	3.76(6)
C(13)	0.2387(2)	0.0702(2)	0.6119(4)	3.78(6)

[a] Estimated standard deviations in the least significant digits are in parenthesis

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) +bc(cos alpha)*B(2,3)].

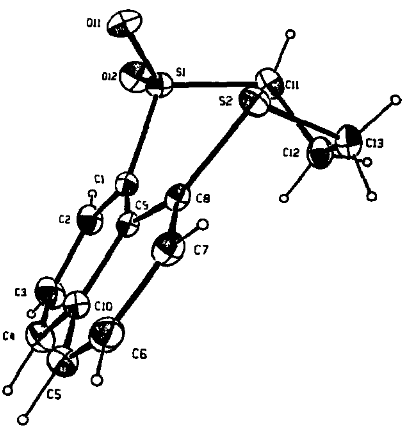


Figure 1. ORTEP drawing[19] of monosulfone 3. Thermal ellipsoids are drawn at the 50% probability level.

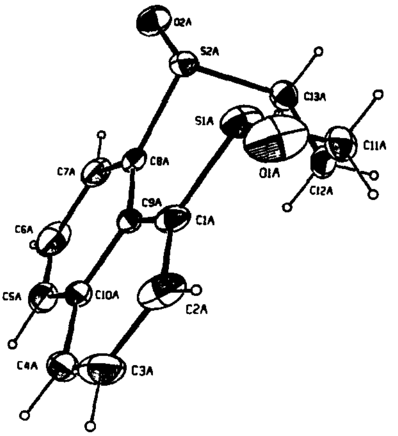


Figure 2. ORTEP drawing[19] of disulfoxide 4. Thermal ellipsoids are drawn at the 50% probability level.

on one sulfur atom and one-third on the other sulfur atom, so that the distances and angles of the sulfur and oxygen atoms are less reliable than for the other structures. In any case both sulfur atoms, S(1) and S(2), are displaced from the least-squares plane of the naphthalene ring by 0.12 and 0.17Å, respectively, on the same side of the naphthalene ring. The S(1)...S(2) intramolecular distance is 3.40Å and the C(9)-C(1)-S(1) and C(9)-C(8)-S(2) bond angles are 128.2 and 126.9° respectively (substantially increased over the "ideal" 120°

Table III. Fractional Atomic Coordinates and Thermal Parameters for Disulfoxide 4

Atom[a]	x[b]	y[b]	z[b]	B,[b,c] Å^2
S(1a)	.6983(1)	0.2221(1)	0.19691(9)	4.96(4)
S(2a)	0.65657(9)	0.0719(1)	0.08853(8)	3.77(3)
O(1a)	0.7286(3)	0.3018(4)	0.2417(3)	8.3(1)
O(2a)	0.6477(3)	0.0176(4)	0.0241(2)	5.9(1)
C(1a)	0.5987(4)	0.2164(5)	0.2127(3)	4.0(1)
C(2a)	0.5747(5)	0.2827(5)	0.2606(3)	6.0(2)
C(3a)	0.4983(5)	0.2940(6)	0.2744(4)	7.3(2)
C(4a)	0.4477(4)	0.2379(5)	0.2412(4)	7.2(2)
C(5a)	0.4156(4)	0.1077(7)	0.1592(4)	7.0(2)
C(6a)	0.4349(4)	0.0425(7)	0.1109(4)	7.3(2)
C(7a)	0.5100(4)	0.0330(6)	0.0923(3)	5.3(2)
C(8a)	0.5645(3)	0.0871(4)	0.1235(3)	3.4(1)
C(9a)	0.5475(3)	0.1572(4)	0.1760(3)	3.3(1)
C(10a)	0.4697(4)	0.1663(5)	0.1921(3)	4.8(1)
C(11a)	0.7265(4)	0.1040(5)	0.2353(3)	5.2(2)
C(12a)	0.6854(4)	0.0066(5)	0.2173(3)	4.7(1)
C(13a)	0.6915(4)	-0.0238(5)	0.1452(3)	4.5(2)

[a] These are the data for one of the unique molecules (Molecule a) in the unit cell for the other see Supplementary Material

[b] Estimated standard deviations in the least significant digits are given in parenthesis

[c] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

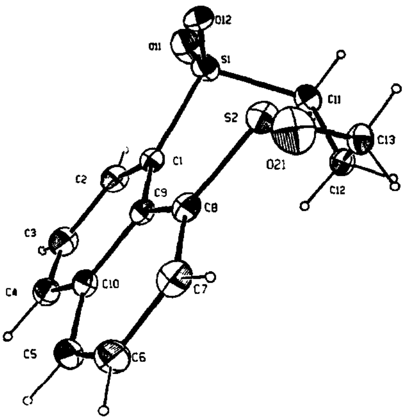


Figure 3. ORTEP drawing[19] of sulfoxide-sulfone 5. Thermal ellipsoids are drawn at the 50% probability level.

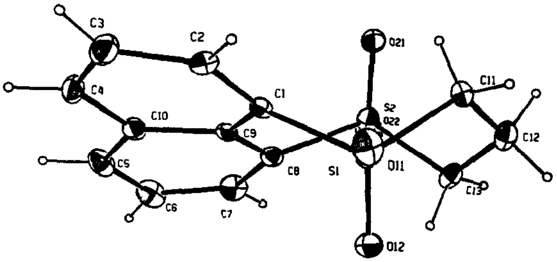


Figure 4. ORTEP drawing[19] of disulfone 6. Thermal ellipsoids are drawn at the 50% probability level.

angle). This is clear evidence that sulfoxide-sulfone 5 has a large steric strain between the inner (axial) sulfone oxygen atom and the sulfoxide sulfur atom, which is relieved by increasing the *peri* bond angles. Consistent with the view that the sulfoxide and sulfone moieties repel each other is the vibronic analysis[6] of this compound which shows no attractive interaction between the moieties.

The structure and conformation of disulfone **6** in the solid state was established by single crystal X-ray analysis. Disulfone **6** crystallized in the orthorhombic space group P_{bca} (No. 61), with a=12.258(3), b=9.997(2), c=20.168(4) Å, and Z=8. The structure was solved by direct methods. Full matrix least-squares refinement led to a conventional R factor of 0.049. The final atomic parameters and thermal parameters are compiled in Table V. An ORTEP drawing[19] of the molecule is shown in Figure 4. The conformation of this molecule in the solid state is a twist conformer. Disulfone **6** is the first reported compound of this eight-membered ring naphthalene system to have a twist conformation in the crystalline state. The twist conformation is normally a very high energy conformer because the sulfur atoms are forced to have very large displacements from the plane of the naphthalene ring (e.g. in disulfone **6** the sulfur atoms are displaced 1.02 Å above and below the naphthalene ring). In disulfone **6**, however, this strain on the naphthalene ring is more favorable than the steric strain from the close interactions of the oxygen atoms that would occur in the boat or chair conformations (perfect boat or chair conformations of **6** have the inner oxygen atoms virtually on top of each other). The twist conformation has the sulfur atoms 3.63 Å apart and allows the oxygen atoms on one sulfone group to point away from the oxygen atoms on the other sulfone group.

EXPERIMENTAL

Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model PE983 Spectrometer. ^{1}H NMR spectra at 250 MHz and ^{13}C NMR spectra at 62.9 MHz were recorded on a Bruker WM-250 FT NMR Spectrometer with 0.368 Hz/Pt digital resolution using a 5 mm tube and tetramethylsilane as the internal reference. The deuterated solvent shown for each compound was used to lock the instrument. All spectra were recorded at ambient temperature unless specified otherwise. All reagents were obtained from Aldrich Chemical Co., Milwaukee, WI and were used as delivered unless specified otherwise.

Naphtho[1,8-b,c]-1,5-dithiocin-1,1-dioxide, 3. Naphtho[1,8-*b,c*]-1,5-dithiocin, **1** (20 mg, 0.086 mmol), prepared as described previously[3] was dissolved in dichloromethane (3mL) and cetyltrimethylammonium bromide (5 mg) was added. Potassium permanganate (54 mg, 0.344 mmol) dissolved in water (3 mL) was then added. The reaction mixture was vigorously stirred overnight at room temperature. The mixture was then filtered and the purple filtrate was extracted with dichloromethane (3 x 20 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated affording a purple-brown residue. This residue was purified by preparative on silica gel eluting with 50% hexanes: ethyl acetate affording monosulfone **3** (15mg, 66% yield): mp 149.5-151°; IR (KBr) 1331(m), 1288(s), 1267(s), 1197(m), 1153(m), 1121(s), 1107(s), 984(m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.22 (2H, pentuplet, J=6 Hz), 2.93 (2H, t, J=6 Hz), 3.87 (2H, t, J=6 Hz), 7.50 (1H, dd, J=8, 8 Hz), 7.59 (1H, dd, J=8, 8 Hz), 7.96 (1H, dd, J=1, 8 Hz), 8.09 (1H, dd, J=1, 8 Hz), 8.12 (1H, dd, J=1, 8 Hz), 8.73 (1H, dd, J=1, 8 Hz); MS m/z 264. Anal. Calcd for $C_{13}H_{12}S_2O_2$: C, 59.06; H, 4.58. Found: C, 59.00; H, 4.56. Unreacted dithioether **1** (3 mg, 0.01 mmol) and monosulfoxide **2** (1 mg, 0.004 mmol, 5% yield) were also isolated from the reaction mixture.

Monosulfoxide **2** (50 mg, 0.20 mmol) prepared as described previously[4] was dissolved in dichloromethane (3 mL) and cetyltrimethylammonium bromide (10 mg) was added. A solution of potassium permanganate (48 mg, 0.30 mmol) in water (10 mL) was added and the mixture stirred vigorously for 4 h at room temperature. Analysis of the reaction mixture by TLC indicated that the reaction was complete. The layers were separated and the aqueous layer extracted with dichloromethane (3 X 20 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated to a brown residue by rotary evaporation. The residue was purified by

Table IV. Fractional Atomic Coordinates and Thermal Parameters for Sulfoxide-Sulfone 5.

Atom	x[a]	y[a]	z[a]	B[a,b] Å^2
S(1)	0.51933(7)	0.00231(6)	0.73687(5)	3.87(1)
S(2)	0.43965(7)	0.22164(7)	0.53524(4)	3.73(1)
O(11)	0.5525(2)	-0.981(2)	0.8199(2)	6.00(5)
O(12)	0.4124(6)	-0.0052(5)	0.6376(4)	5.0(1)
O(21)	0.3952(2)	0.3012(2)	0.4399(1)	5.67(5)
O(22)	0.3639(3)	0.1035(3)	0.5380(2)	4.43(6)
C(1)	0.4921(2)	0.1539(2)	0.7985(2)	2.85(4)
C(2)	0.5133(3)	0.1360(3)	0.9043(2)	3.77(5)
C(3)	0.4825(3)	0.2335(3)	0.9673(2)	4.35(6)
C(4)	0.4309(3)	0.3498(3)	0.9223(2)	4.16(5)
C(5)	0.3753(3)	0.5056(3)	0.7783(2)	4.17(6)
C(6)	0.3648(3)	0.5412(3)	0.6796(2)	4.52(6)
C(7)	0.3884(3)	0.4478(3)	0.6106(2)	4.09(6)
C(8)	0.4250(2)	0.3207(2)	0.6420(2)	3.00(4)
C(9)	0.4437(2)	0.2785(2)	0.7486(2)	2.75(4)
C(10)	0.4155(2)	0.3768(2)	0.8157(2)	3.33(5)
C(11)	0.7021(3)	0.0292(3)	0.7210(2)	3.71(5)
C(12)	0.7331(2)	0.1623(2)	0.6837(2)	3.29(5)
C(13)	0.6411(3)	0.1981(3)	0.5688(2)	3.58(5)

[a]Estimated standard deviations in the least significant digits are in parenthesis.
[b]Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

preparative layer chromatography on silica gel eluting with 50% hexanes in ethyl acetate to give monosulfone 3 (39 mg, 73% yield) identical with the material prepared above.

Naphtho[1,8-b,c]-1,5-dithiocin-1,5-dioxide, 4. Sodium metaperiodate (100 mg, 0.467 mmol) dissolved in water (5 mL) and methanol (5 mL) was added dropwise to dithioether 1 (27.0 mg, 0.116 mmol) dissolved in methanol (5 mL) at 0°C. The reaction mixture was stirred at room temperature for 72 h at which time TLC analysis showed the reaction to be complete. Themethanol was then removed by rotary evaporation and the remaining aqueous mixture was extracted with dichloromethane (3 X 20 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated, affording disulfoxide 4 as a white solid (29.2 mg, 95% yield): mp 253-254°; IR (KBr) 1088(m), 1050(s), 1040(s), 1001(m), 968(m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (1H, ddddd, *J*=15, 13, 13, 4, 4 Hz) 2.05 (1H, ddddd, *J*=15, 4, 4, 4, 4 Hz), 2.58 (2H, ddd, *J*=13, 4, 4 Hz), 3.72 (2H, ddd, *J*=13, 13, 4 Hz), 7.74 (2H, dd, *J*=8, 8 Hz), 8.04 (2H, dd, *J*=1, 8 Hz), 8.34 (2H, dd, *J*=1, 8 Hz); MS *m/z* 264. Anal. Calcd for $C_{13}H_{12}S_2O_2$: C, 59.06; H, 4.58. Found: C, 58.92; H, 4.41.

Naphtho[1,8-b,c]-1,5-dithiocin-1,1,5-trioxide 5. Monosulfone 3 (20 mg, 0.076 mmol) was dissolved in methanol (3 mL). Sodium metaperiodate (32 mg, 0.15 mmol) dissolved in water (3 mL) and methanol (3 mL) was then added at 0°C. The reaction was stirred at room temperature for 48 h, at which time TLC analysis showed the reaction to be complete. The methanol was removed by rotary evaporation and the remaining aqueous mixture was extracted with dichloromethane (3 X 20 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated affording sulfoxide-sulfone 5 (21 mg, 99% yield): mp 235-236°; IR (KBr) 1334(m), 1302(s), 1279(m), 1157(m), 1131(s), 1120(s), 1040(s), 1008(m), 974(m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.13 (1H, ddd, *J*=16, 13, 13 Hz) 2.38 (1H, d, *J*=16 Hz), 2.70 (1H, d, *J*=13 Hz), 3.33 (1H, m, *J*=13 Hz), 3.62 (1H, ddd, *J*=13, 13, 4 Hz), 3.94 (1H, ddd, *J*=13, 13, 3 Hz), 7.71 (1H dd, *J*=8, 8 Hz), 7.85 (1H, dd, *J*=8, 8 Hz), 8.12 (1H, dd, *J*=1, 8 Hz), 8.29 (1H, dd, *J*=1, 8 Hz), 8.66 (1H, dd, *J*=1, 8 Hz), 8.71 (1H, dd, *J*=1, 8 Hz); MS *m/z* 280. Anal. Calcd for $C_{13}H_{12}S_2O_3$: C, 55.69; H, 4.31. Found C, 55.45; H, 4.15.

Naphtho[1,8-b,c]-1,5-dithiocin-1,1,5,5-tetraoxide, 6. Dithioether 1 (20 mg, 0.086 mmol) was dissolved in dichloromethane (2 mL). Ruthenium dioxide (1.0 mg) and cetyltrimethylammonium bromide (1.0 mg) were added. Sodium metaperiodate (80 mg, 0.373 mmol) dissolved in water (2 mL) was added. The resulting mixture was stirred vigorously at room temperature for 72 h, at which time TLC analysis showed the reaction to be complete. The layers were separated and the aqueous layer was extracted again with dichloromethane

Table V. Fractional Atomic Coordinates and Thermal Parameters for Disulfone 6

Atom	*x*[a]	*y*[a]	*z*[a]	*B*[a,b] Å^2
S(1)	0.76548(8)	0.1013(1)	0.66510(5)	2.18(2)
S(2)	0.47600(9)	0.1742(1)	0.67663(5)	2.80(2)
O(11)	0.8705(2)	0.0370(4)	0.6617(2)	3.35(7)
O(12)	0.7640(3)	0.2452(3)	0.6672(1)	3.07(6)
O(21)	0.4740(3)	0.0307(3)	0.6800(2)	3.66(7)
O(22)	0.3736(2)	0.2441(4)	0.6815(2)	4.65(8)
C(1)	0.6949(3)	0.0560(4)	0.5904(2)	1.95(7)
C(2)	0.7499(4)	-0.0357(4)	0.5529(2)	2.66(8)
C(3)	0.7298(4)	-0.0487(5)	0.4841(2)	3.7(1)
C(4)	0.6618(4)	0.0396(5)	0.4540(2)	3.03(9)
C(5)	0.5316(4)	0.2235(5)	0.4583(2)	3.6(1)
C(6)	0.4712(4)	0.3131(5)	0.4921(3)	4.0(1)
C(7)	0.4661(4)	0.3048(5)	0.5620(2)	3.4(1)
C(8)	0.5294(3)	0.2151(4)	0.5961(2)	2.34(8)
C(9)	0.6082(3)	0.1344(4)	0.5626(2)	2.00(8)
C(10)	0.6008(3)	0.1321(4)	0.4914(2)	2.52(9)
C(11)	0.6978(4)	0.0346(5)	0.7360(2)	2.65(9)
C(12)	0.6295(4)	0.1337(5)	0.7772(2)	3.2(1)
C(13)	0.5591(4)	0.2383(5)	0.7412(2)	2.99(9)

[a] Estimated standard deviations in the least significant digits are in parenthesis
[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + AB(cos gamma) *B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

(2 X 10 mL). The dichloromethane layers were combined and filtered through silica gel on a sintered glass funnel. The silica gel was then washed with methanol (3 X 75 mL). The methanol
washings were combined and concentrated affording a gray-white residue, which was purified by recrystallization by vapor diffusion of pentane into a solution of the residue in 1,2-dichloroethane to give white crystalline disulfone 6 (17.8 mg, 70% yield): mp 276.5-277.5°; IR (KBr) 1299(s), 1276(m), 1193(m), 1174(m), 1149(m), 1123(s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.72 (2H, pentuplet, *J*=7 Hz), 4.33 (4H, t, *J*=7 Hz) 7.68 (2H, dd, *J*=8,8 Hz), 8.12 (2H, dd, *J*=1, 8 Hz), 8.60 (2H, dd, *J*=1, 8 Hz). Anal. Calcd for $C_{13}H_{12}S_2O_4$: C, 52.68; H, 4.08. Found: C, 52.62; H, 3.87.

X-ray Single Crystal Structure Study of Monosulfone 3, Disulfoxide 4, Sulfoxide-sulfone 5 and Disulfone 6. Crystals suitable for X-ray crystallographic analysis were grown by vapor diffusion of pentane into solution of the compound in 1,2-dichloroethane. A colorless, irregular crystal [(0.25 x 0.42 x 0.47 mm), (0.09 x 0.15 x 0.50 mm), (0.63 x 0.17 x 0.37 mm) and (0.25 x 0.20 x 0.24 mm) for 3-6 respectively] was sealed to a glass capillary and mounted on a Syntex P2$_1$ autodiffractometer. Mo Kα radiation (λ=0.71073Å) was used with graphiteas monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using 25, 25, 24, and 25 reflections for 3-6 respectively. The cell constants and other parameters are given in Table I. The $\theta/2\theta$ scan technique was used and data were collected to a maximum 2θ of 55, 50, 50, and 57.7° for 3-6 respectively. The data with $\underline{F} \geq 3\sigma(\underline{F})$ were used in the calculations. The data were reduced to F_o and $\sigma(F_o)$. Lorentz and polarization corrections were applied to the data. Three representative reflections were measured every 97, 46, 97, and 97 reflections for 3-6 respectively, and indicated no decay. The structure was solved by direct methods using the SDP-PLUS program package.[22] Using default parameters a total of 9, 29, 17, and 16 atoms were found for 3-6 respectively. The remaining nonhydrogen atoms were located in succeeding difference maps. The hydrogen atoms were added at idealized positions and in all subsequent refinements all hydrogen atoms restricted to fixed isotropic thermal parameters and restrained to ride on the atom to which they are bonded. The structure was refined by full-matrix least-squares techniques[22] by using neutral scattering factors[23] with anomalous dispersion terms included.[24] The final cycle of refinement included 154, 307, 172, and 172 variable parameters for 3-6 respectively, and converged with unweighted (*R*) agreement factors of 0.034, 0.046, 0.041 and 0.049 for 3-6 respectively and weighted (R_w) agreement factors of 0.044, 0.051, 0.053, and 0.053 for 3-6 respectively. The standard deviation of an observation of unit weight was

1.53, 1.19, 1.64, and 1.31 for 3-6 respectively. The highest peak in the final difference Fourier had a height of 0.29, 0.26, 0.28, and 0.37 $e^-/\text{Å}^3$ with an estimated error based on σ(F) of 0.05, 0.06, 0.05 and 0.09 for compounds 3-6 respectively.[25]

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Supplementary Material Available: List of refined coordinates for molecule b of disulfoxide 4 has been deposited at the Cambridge Crystallographic Data Centre. Stereoscopic view of the packing of monosulfone 3, disulfoxide 4, sulfoxide-sulfone 5, and disulfone 6 in the unit cells, and table of bond lengths, bond angles, and selected torsion angles for molecule b of disulfoxide 4 and tables of bond lengths, bond angles, and selected torsion angles for monosulfone 3, disulfoxide 4 (both molecules a and b); sulfoxide-sulfone 5, and disulfone 6 and a listing of structure factor amplitudes is available from the authors.

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