Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2,5-Bis(methylthio)-1,4-benzoquinone and 2-methyl-3-(methylsulfonyl)-benzo[*b*]thiophene

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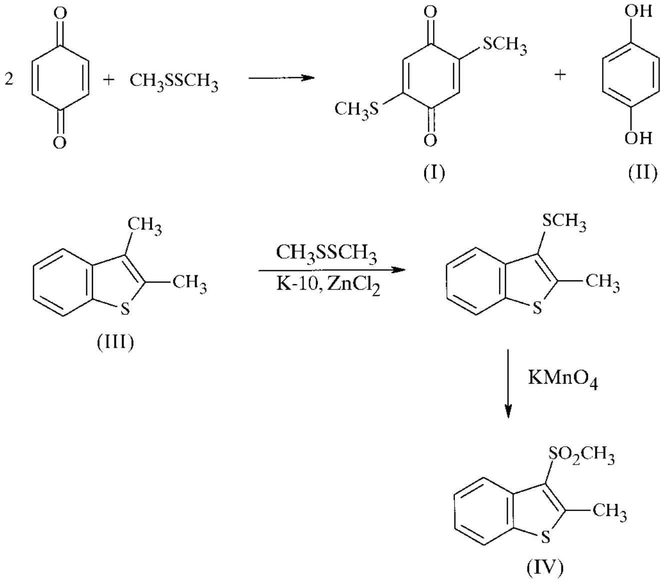
Received 11 October 1999
Accepted 25 January 2000

The structure of 2,5-bis(methylthio)-1,4-benzoquinone, $C_8H_8O_2S_2$, is composed of an essentially planar centrosymmetric benzoquinone substituted with two methylthio groups. The important bond distances are S—Csp^3 1.788 (2) and S—Csp^2 1.724 (2) Å, and the two Csp^2—Csp^2 distances are 1.447 (3) and 1.504 (3) Å, which differ significantly. There are short S···S interactions of 3.430 (1) Å and Csp^2—H···O-type contacts forming a dimeric motif with graph set $R_2^2(8)$. The structure of 2-methyl-3-(methylsulfonyl)benzo[*b*]thiophene, $C_{10}H_{10}O_2S_2$, is composed of an essentially planar benzothiophene moiety substituted with methyl and methylsulfonyl groups. The mean values of the important bond distances are endocyclic S—Csp^2 1.734 (3), S═O 1.434 (4) and C—C$_{\rm aromatic}$ 1.389 (10) Å. The exocyclic S—Csp^2 and S—Csp^3 distances are 1.759 (4) and 1.763 (5) Å, respectively.

Comment

Recently, 2,5-bis(methylthio)-1,4-benzoquinone, (I), has been used to prepare sulfur-quinone polyurethane coatings which are applied to protect iron surfaces. Surprisingly, the synthesis of (I) was not reported until 1998 and then was obtained in only 15% yield by reaction of 1,4-benzoquinone with sodium thiomethoxide (Hu & Nikles, 1998). Using a clay-catalyzed one-step thioalkylation procedure developed in our laboratories (Clark *et al.*, 1996), we have been able to make compound (I) in good yield and on a large scale. Conveniently, one half of the quinone reagent re-oxidizes the intermediate product to yield the product, (I) (see scheme). ^{1}H NMR analysis of (I), which is obtained from ethanol as brilliant red crystals, does not allow differentiation of (I) from its 2,3-bis(methylthio) isomer. X-ray analysis showed, however, that the clay-catalyzed synthesis reported herein yielded the 2,5-isomer as the sole product.

A one-step thioalkylation procedure developed in our laboratory allows addition of –S*R* groups to aromatics and heteroaromatics (Clark *et al.*, 1996). However, it was clear that reaction of 2,3-methylbenzo[*b*]thiophene, (III), with dimethyl disulfide over a clay catalyst did not yield the expected 5,6-disubstituted product, but an oily compound in which one of either the 2- or 3-methyl groups had been replaced by an –SCH$_3$ substituent (see scheme). Since an *ipso*-substitution of this type is quite rare and because other spectroscopic methods could not differentiate whether substitution had occurred at the 2- or 3- positions, the product was oxidized to its crystalline sulfonyl derivative using a literature procedure (Aitken *et al.*, 1994) and was subjected to X-ray crystallographic analysis. This analysis showed that the 3-thiomethyl derivative, (IV), had been produced, suggesting that a sulfur-assisted *ipso*-substitution had taken place.



The structure of (I) is composed of centrosymmetric molecules which are essentially planar [maximum deviation 0.026 (2) Å for C3]. The bond distances agree well with the corresponding values reported for bis-, tris- and tetrakis-(thiophenyl)benzoquinones (Cambridge Structural Database; Allen & Kennard, 1993). The S—Csp^3 and S—Csp^2 bond distances of 1.788 (2) and 1.724 (2) Å, respectively, differ significantly. The bonds C3═O1 [1.227 (3) Å] and C1═C2 [1.353 (3) Å] are double bonds. The Csp^2—Csp^2 bonds, C1—C3$^{\rm i}$ [1.504 (3) Å; symmetry code: (i) $-x$, $-y$, $1 - z$] and C2—C3 [1.447 (3) Å], are in excellent agreement with the values

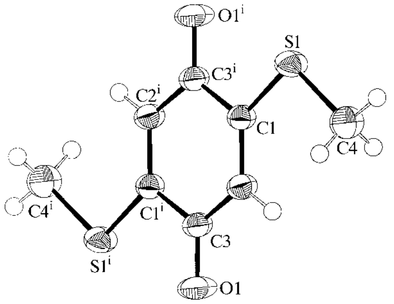


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I) with the atomic numbering scheme. Displacement ellipsoids have been plotted at the 50% probability level and H atoms assigned arbitrary radii [symmetry code: (i) $-x$, $-y$, $1 - z$].

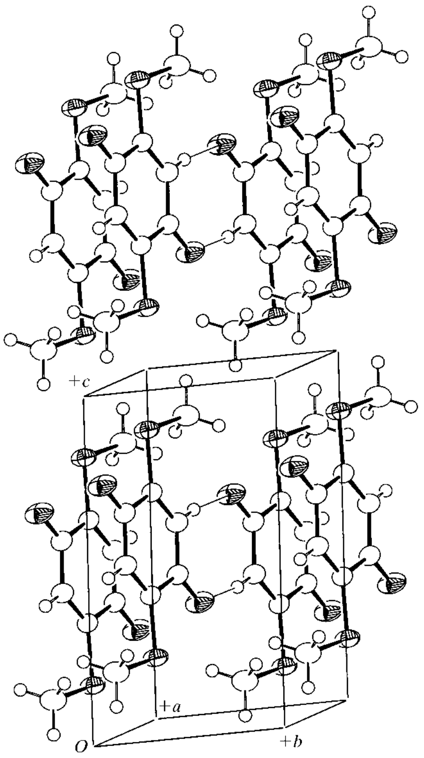


Figure 2
The unit-cell packing of (I) showing Csp^2—H···O-type contacts (thin lines) forming a dimeric motif.

reported for the thiophenylbenzoquinone structures mentioned above. The S1—C1—C3^{i} angle of 112.85 (15)° is smaller than the value of 120° expected for a Csp^2 atom, perhaps because of intermolecular methyl–methyl and methyl–carbonyl interactions.

The molecules of (I) pack in layers which lie perpendiular to the (101) plane. Within the layers there are short S···S interactions of 3.430 (1) Å between the molecules related by inversion centers. There are also short Csp^2—H···O type contacts (H···O 2.56 Å and Csp^2—H···O 164°) forming a dimeric motif with graph set $R_2^2(8)$ (Fig. 2); similar interactions in the crystal structures of quinones have been discussed by Bernstein *et al.* (1994).

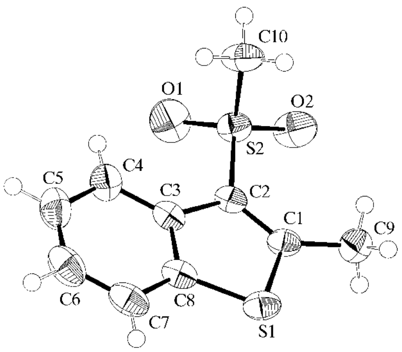


Figure 3
*ORTEP*II (Johnson, 1976) drawing of (IV) with the atomic numbering scheme. Displacement ellipsoids have been plotted at the 50% probability level and H atoms assigned arbitrary radii.

The structure of (IV) is composed of discrete molecules separated by normal van der Waals distances. The benzothiophene moiety is essentially planar [maximum deviation 0.021 (4) Å for C5], with S2 and C9 of the methylsulfonyl and methyl groups lying 0.045 (5) and 0.022 (6) Å, respectively, on the same side of the plane. The intramolecular repulsion between the two substituents is relieved by the widening of the C2—C1—C9 angle to 132.5 (4)°. The important bond distances are endocyclic S—Csp^2 (mean) 1.734 (3), exocyclic S—Csp^2 1.759 (4), S—Csp^3 1.763 (5), S═O (mean) 1.434 (4) and C—C$_{\rm aromatic}$ (mean) 1.389 (10) Å.

Experimental

A mixture of 1,4-benzoquinone (54 g, 0.5 mol), dimethyl disulfide (28.2 g, 0.3 mol) and montmorillonite K-10 (*ex* Fluka) impregnated with 2 mmol g^{-1} $ZnCl_2$ (50 g; Clark *et al.*, 1996) in dichloromethane (500 ml) was stirred for 16 h at 293 K. Filtration of the reaction mixture afforded a red solid comprised of the clay catalyst and the product, (I). The filtrate contained a small amount of (I), excess dimethyl disulfide and the quinol (II), formed during re-oxidation of the reaction intermediate. Soxhlet extraction of the red solid with dichloromethane over 20 h gave (I) as a red solid (34 g, 63%). Recrystallization from ethanol afforded red plates. Compound (IV) was prepared using K-10 montmorillonite clay and the method described previously by Clark *et al.* (1996), and was oxidized to its sulfonyl derivative using a method employed by Aitken *et al.* (1994). Crystals of (IV) were obtained by slow crystallization from aqueous ethanol.

Compound (I)

Crystal data

$C_8H_8O_2S_2$
$M_r = 200.26$
Triclinic, $P\bar{1}$
$a = 4.032$ (2) Å
$b = 5.717$ (1) Å
$c = 9.626$ (1) Å
$\alpha = 86.04$ (1)°
$\beta = 80.60$ (2)°
$\gamma = 86.09$ (3)°
$V = 218.0$ (1) Å^3
$Z = 1$
$D_x = 1.525$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–20°
$\mu = 5.17$ mm^{-1}
$T = 293$ (2) K
Plate, red
0.36 × 0.28 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scan (3 reflections; North *et al.*, 1968)
$T_{\rm min} = 0.22$, $T_{\rm max} = 0.66$
1535 measured reflections
791 independent reflections
757 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 68°$
$h = -4 \rightarrow 4$
$k = -6 \rightarrow 6$
$l = -11 \rightarrow 11$
3 standard reflections every 200 reflections intensity decay: <0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.111$
$S = 1.15$
791 reflections
56 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.0706P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.060 (10)

Table 1
Selected geometric parameters (Å, °) for (I).

S1—C1	1.724 (2)	C1—C2	1.353 (3)
S1—C4	1.788 (2)	C1—C3$^{\text{i}}$	1.504 (3)
O1—C3	1.227 (3)	C2—C3	1.447 (3)
C1—S1—C4	102.83 (11)	C1—C2—C3	121.5 (2)
C2—C1—C3$^{\text{i}}$	119.5 (2)	O1—C3—C2	121.8 (2)
C2—C1—S1	127.68 (17)	O1—C3—C1$^{\text{i}}$	119.1 (2)
C3$^{\text{i}}$—C1—S1	112.84 (15)	C2—C3—C1$^{\text{i}}$	119.1 (2)
C4—S1—C1—C2	4.5 (2)	S1—C1—C2—C3	−179.95 (16)
C4—S1—C1—C3$^{\text{i}}$	−175.06 (15)	C1—C2—C3—O1	−179.4 (2)
C3$^{\text{i}}$—C1—C2—C3	−0.4 (3)	C1—C2—C3—C1$^{\text{i}}$	0.4 (3)

Symmetry code: (i) $-x, -y, 1-z$.

Compound (IV)

Crystal data

$C_{10}H_{10}O_2S_2$
$M_r = 226.30$
Monoclinic, $P2_1$
$a = 5.8228$ (5) Å
$b = 10.440$ (1) Å
$c = 8.6217$ (9) Å
$\beta = 99.57$ (1)°
$V = 516.8$ (1) Å^3
$Z = 2$

$D_x = 1.454$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–$20°$
$\mu = 0.48$ mm^{-1}
$T = 293$ (2) K
Prismatic, colorless
0.55 × 0.38 × 0.35 mm

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (3 reflections; North *et al.*, 1968)
$T_{\min} = 0.78$, $T_{\max} = 0.85$
1385 measured reflections
1268 independent reflections
1063 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$
$\theta_{\max} = 27.6°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = -11 \rightarrow 11$
3 standard reflections every 200 reflections intensity decay: 1.31%

Table 2
Selected geometric parameters (Å, °) for (IV).

S1—C1	1.731 (4)	S2—O2	1.437 (3)
S1—C8	1.736 (4)	S2—C2	1.759 (4)
S2—O1	1.431 (4)	S2—C10	1.763 (5)
C1—S1—C8	92.9 (2)	O1—S2—C10	108.0 (3)
O1—S2—O2	117.4 (2)	O2—S2—C10	107.6 (2)
O1—S2—C2	108.7 (2)	C2—S2—C10	104.4 (2)
O2—S2—C2	109.8 (2)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.109$
$S = 1.19$
1268 reflections
128 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.07 (15)

For both compounds, H atoms were treated as riding with default C—H distances and U_{iso} values. The absolute structure of compound (IV) could not be established in this analysis because no Friedel pairs were collected.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989), for (I), *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) for (IV); cell refinement: *CAD*-4 *Software* for (I), *MSC/AFC Diffractometer Control Software* for (IV); for both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL*97.

The authors thank the Natural Sciences and Engineering Research Council of Canada for providing the diffractometer through an equipment grant to the University of Calgary, and Alberta Sulphur Research Ltd, Calgary, Alberta, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1513). Services for accessing these data are described at the back of the journal.

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