

Crown-6.K)⁺ complexed cations. This sandwich structure are aligned along the *a* axis. The anions connect with one after another through eight water molecules to a [001] direction (see Figure 2). All oxygen atoms in the anion coordinated to a water molecule or potassium ion. The stable packing arrangement is found in the crystal lattice.

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Crystal Structure of Bithionol, $C_{12}H_6Cl_4O_2S$

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The crystal structure of Bithionol, $C_{12}H_6Cl_4O_2S$, has been determined from X-ray intensity data measured by Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo- K_α radiation. The crystal data as follows; triclinic space group $P\bar{1}$, $a = 8.879(2)$, $b = 10.782(1)$, $c = 8.511(1)\text{\AA}$, $\alpha = 115.43(1)$, $\beta = 115.22(1)$, $\gamma = 74.44^\circ(1)$. $\mu = 9.51\text{ cm}^{-1}$, $F(000) = 356$, $Z = 2$. Final R value is 0.036 for independent 2669 observed reflections. Each six-membered benzene rings are coplanar within experimental errors and the dihedral angle between these planes is $81.28^\circ(1)$. The S-(1) and S-C(7) distances are 1.787(2) and 1.791(3) $\text{\AA}$, respectively.

Introduction

Bithionol and their different substituted derivatives are well known drugs and are particularly effective in human fascioliasis. Other flukicides of overall analogous structure contain -CONH and -CSNH bridges as well as bulky and different electron-withdrawing substituents. The geometrical configuration of the sulfur groups, X-S-Y and X-SO₂-Y, have been studied in several molecules. In the X-SO₂-Y, bond distribution about sulfur atom is found to depart significantly from that of a regular tetrahedron, with some dependence on substituent atoms X and Y. The sulfonyl group is of particular interest when linked to two aromatic rings, in view of the molecular orbital investigation of diphenyl sulfone by Koch & Moffitt¹. These authors predicted overlap of 3d orbitals of sulfur atom with adjacent carbon atom 2p orbitals, resulting in an angle of 90° between the normals to the aromatic rings and common C-S-C plane.

Experimental

The title compound was provided by Dongkwang Chemicals Co.. Colorless rectangular crystals were grown from acetone solution. Weissenberg photographs showed them to be triclinic, space group $P\bar{1}$, the crystal density was measured by flotation method in 2,3-dibromopro-

pene/iso-propyl alcohol. A crystal of $0.4 \times 0.4 \times 0.41\text{ mm}$ was used for reflection data collection with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo- K_α radiation. Unit cell parameters were determined from 25 reflections having $20 < 2\theta < 26^\circ$. Intensities were measured for 2754 reflections with $\sin\theta/\lambda < 0.70\text{\AA}^{-1}$, indices in the range $-10 < h < 10$, $-14 < k < 12$, $0 < l < 11$ using $\omega/2\theta$ scans with a scan width $\Delta\omega = (0.7 + 0.35 \tan\theta)^\circ$ and scan rate $8.24^\circ/\text{minute}$. Three monitor reflections ((3,6,2), (1,7,3), (4,4,0)) showed deviations less than 2% from their average intensities. No absorption corrections were applied. 2754 measured reflections of which 2669 with $|F_o| > 2\sigma(F_o)$ were used in structure determination and refinement. The crystal structure was solved by direct methods (SHELXS-86²) and refined by full-matrix least squares (SHELX-76³) with anisotropic temperature factor for non-hydrogen atoms and isotropic for hydrogen atoms. Atomic scattering factors for non-hydrogen atoms were taken from Cromer & Waber⁴, and those for hydrogen atoms from Stewart, Davidson & Simpson⁵. Refinement minimized was $\sum w\Delta^2$, $\Delta = |F_o| - |F_c|$ and $w = 1/[\sigma^2(F_o) + 0.001F_o^2]$. All hydrogen atoms were located in a difference Fourier map. Final positional parameters with e.s.d.s are Table 1. In the final cycle of refinement the largest parameter shift $(\Delta/\sigma)_{\max}$ was 0.01. The agreement indices were $R = 0.036$ and $R_w = 0.037$. Maximum residual electron density in final difference Fourier syn-

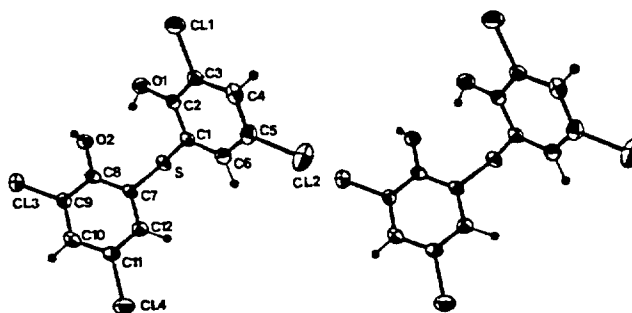
Table 1. Final Positional Parameters of Non-hydrogen Atoms (Fractional Coordinates are $\times 10^4$; U_{eq} are Isotropic Mean Square Amplitudes of Thermal Vibration ($\text{\AA}^2 \times 10^3$) given by $(U_{11} + U_{22} + U_{33})/3$ where U_{ij} are Anisotropic Thermal Parameters from the Supplementary Data.)

Atom	x	y	z	U_{eq}
S	9584(1)	2830(1)	4562(1)	35(0)
CL(1)	8674(1)	1476(1)	9548(1)	43(0)
CL(2)	5971(1)	-1418(1)	2220(1)	60(0)
CL(3)	6910(1)	7925(1)	8074(1)	49(0)
CL(4)	3547(1)	5075(1)	918(1)	48(0)
O(1)	9993(2)	2989(2)	8370(2)	43(1)
O(2)	9481(2)	5489(2)	7719(2)	42(1)
C(1)	8732(2)	1773(2)	5060(3)	32(1)
C(2)	9048(2)	2002(2)	6914(3)	30(1)
C(3)	8355(3)	1167(2)	7258(3)	32(1)
C(4)	7411(3)	129(2)	5829(3)	36(1)
C(5)	7133(3)	-96(2)	4013(3)	37(1)
C(6)	7783(3)	720(2)	3601(3)	36(1)
C(7)	7969(3)	4233(2)	4547(3)	30(1)
C(8)	8113(3)	5409(2)	6153(3)	32(1)
C(9)	6810(3)	6476(2)	6092(3)	31(1)
C(10)	5425(3)	6381(2)	4485(3)	35(1)
C(11)	5313(3)	5200(3)	2911(3)	34(1)
C(12)	6575(3)	4130(2)	2918(3)	35(1)

Table 2. Bond Distances($\text{\AA}$), Bond Angles($^\circ$) and Torsion angles($^\circ$)

Bond distances			
S-C(1)	1.787(2)	S-C(7)	1.791(3)
CL(1)-C(3)	1.735(2)	CL(2)-C(5)	1.729(2)
CL(3)-C(9)	1.725(2)	CL(4)-C(11)	1.733(2)
O(1)-C(2)	1.350(3)	O(2)-C(8)	1.355(3)
C(1)-C(2)	1.398(3)	C(1)-C(6)	1.393(3)
C(2)-C(3)	1.395(2)	C(3)-C(4)	1.375(3)
C(4)-C(5)	1.376(3)	C(5)-C(6)	1.391(2)
C(7)-C(8)	1.393(3)	C(7)-C(12)	1.394(3)
C(8)-C(9)	1.402(3)	C(9)-C(10)	1.381(3)
C(10)-C(11)	1.383(3)	C(11)-C(12)	1.381(3)
Bond angles			
C(1)-C(2)-O(1)	122.8(2)	C(2)-C(1)-S	119.4(1)
C(2)-C(3)-CL(1)	118.7(2)	C(3)-C(2)-O(1)	119.1(2)
C(3)-C(2)-C(1)	118.1(2)	C(4)-C(3)-CL(1)	119.8(2)
C(4)-C(3)-C(2)	121.5(2)	C(4)-C(5)-CL(2)	119.5(2)
C(5)-C(4)-C(3)	119.6(2)	C(5)-C(6)-C(1)	119.0(2)
C(6)-C(1)-S	119.7(2)	C(6)-C(1)-C(2)	120.8(2)
C(6)-C(5)-CL(2)	119.5(2)	C(6)-C(5)-C(4)	120.9(2)
C(7)-S-C(1)	99.8(1)	C(7)-C(8)-O(2)	119.8(2)

C(8)-C(7)-S	119.9(2)	C(8)-C(9)-CL(3)	119.6(2)
C(9)-C(8)-O(2)	122.0(2)	C(9)-C(8)-C(7)	118.2(2)
C(10)-C(9)-CL(3)	119.0(2)	C(10)-C(9)-C(8)	121.4(2)
C(10)-C(11)-CL(4)	118.8(2)	C(11)-C(10)-C(9)	119.2(2)
C(11)-C(12)-C(6)	119.4(2)	C(12)-C(7)-S	119.3(2)
C(12)-C(7)-C(8)	120.8(2)	C(12)-C(11)-CL(4)	120.2(2)
C(12)-C(11)-C(10)	121.0(2)	Torsion angles	
C(7)-S-C(1)-C(2)	86.8(2)	C(7)-S-C(1)-C(6)	-94.1(2)
C(1)-S-C(7)-C(8)	-95.0(2)	C(1)-S-C(7)-C(12)	84.8(2)
S-C(1)-C(2)-O(1)	0.7(1)	S-C(1)-C(2)-C(3)	-179.5(2)
C(6)-C(1)-C(2)-O(1)	-178.4(3)	C(6)-C(1)-C(2)-C(3)	1.4(2)
S-C(1)-C(6)-C(5)	-179.8(3)	C(2)-C(1)-C(6)-C(5)	-0.7(2)
O(1)-C(2)-C(3)-CL(1)	-2.4(1)	O(1)-C(2)-C(3)-C(4)	178.7(3)
C(1)-C(2)-C(3)-CL(1)	177.8(3)	C(1)-C(2)-C(3)-C(4)	-1.1(2)
CL(1)-C(3)-C(4)-C(5)	-178.7(3)	C(2)-C(3)-C(4)-C(5)	0.2(2)
C(3)-C(4)-C(5)-CL(2)	-179.1(3)	C(3)-C(4)-C(5)-C(6)	0.5(2)
CL(2)-C(5)-C(6)-C(1)	179.3(3)	C(4)-C(5)-C(6)-C(1)	-0.2(2)
S-C(7)-C(8)-O(2)	-0.3(2)	S-C(7)-C(8)-C(9)	179.1(3)
C(12)-C(7)-C(8)-O(2)	179.8(3)	C(12)-C(7)-C(8)-C(9)	-0.8(2)
S-C(7)-C(12)-C(11)	-178.9(3)	C(8)-C(7)-C(12)-C(11)	1.0(2)
O(2)-C(8)-C(9)-CL(3)	1.5(2)	O(2)-C(8)-C(9)-C(10)	-179.9(3)
C(7)-C(8)-C(9)-CL(3)	-177.9(3)	C(7)-C(8)-C(9)-C(10)	0.7(2)
CL(3)-C(9)-C(10)	177.8(3)	C(8)-C(9)-C(10)-C(11)	-0.9(2)
-C(11)			
C(9)-C(10)-C(11)	-178.5(3)	C(9)-C(10)-C(11)-C(12)	1.2(2)
-CL(4)			
CL(4)-C(11)-C(12)-C(7)	178.4(3)	C(10)-C(11)-C(12)-C(7)	-1.1(2)

**Figure 1.** Stereospecific drawing of the molecular structure and atom numbering in Bithionol. Atoms are shown as 40% probability thermal ellipsoids.

thesis: $0.21(\text{e}\text{\AA}^{-3})$. The molecular bond lengths, bond angles and torsion angles are shown in Table 2.

Result and Discussion

The structure of Bithionol is shown in Figure 1 with ORTEP⁶ drawing of 40% probability thermal ellipsoids and a stereoview of unit cell is shown in Figure 2.

The molecule consists of two planar benzene rings with largest deviation from least-squares plane being $0.007(2)\text{\AA}$ for C(2). The L.S. planes benzene rings were calculated and displacements of atoms from L.S planes are listed in Table 3. In the benzene rings, the average C-C bond length and bond angle are $1.388(2)\text{\AA}$ and $119.9(1)^\circ$, respectively. In

*Tables of anisotropic thermal parameters, H atom parameters, distances and angles involving H atoms, molecular least squares planes and the observed and calculated structure amplitudes have been deposited with British Library Document Supply Centre as Supplementary Publication No. SUP 43625 (11 PP.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

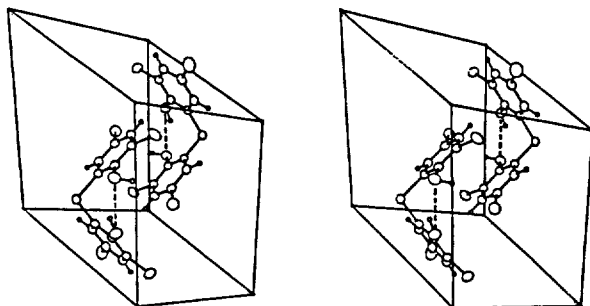


Figure 2. Stereoscopic drawing of the crystal packing. Dotted lines indicate intramolecular hydrogen bonding.

Table 3. Least-squares Planes in Bithionol

(A) Plane of benzene ring A		
$(0.713X - 0.701Y + 0.037Z = -4.416)$		
C(1)	0.006(2)	
C(2)	-0.007(2)	
C(3)	0.004(2)	
C(4)	0.003(2)	
C(5)	-0.005(2)	
C(6)	-0.001(2)	
(B) Plane of benzene ring B		
$(0.777X + 0.559Y - 0.289Z = -5.960)$		
C(7)	0.003(2)	
C(8)	-0.002(2)	
C(9)	0.002(2)	
C(10)	-0.003(2)	
C(11)	0.004(2)	
C(12)	-0.004(2)	

the substituent of benzene ring. C-Cl bond lengths vary from 1.725(2) to 1.735(2) Å with an average 1.731(2) Å. This value is similar to such bonds in Phenyls⁷. The two C-O bond lengths vary from 1.350(3) to 1.355(3) Å, with an average 1.353(3) Å. These value are slightly shorter than 1.385(4) Å of 4-hydroxy biphenyl⁸, and are closely to 1.355(4) Å of 3,3', 5,5'-tetrachloro-4,4'-dihydroxy biphenyl⁹. Cox, Gillot & Jeffrey¹⁰ have suggested that 1.79 Å be regard as the standard length of a single covalent C-S bond and 1.60 Å as the length of a standard double bond.

The C(1)-S and C(7)-S bond lengths are the same within an experimental error, and the average bond length is

1.789(3) Å. These values are slightly larger than other aromatic sulfides and are slightly shorter than 1.800 Å in the sulfoxide¹¹. The sulfur valence angle C(1)-S-C(7) is 99.8(1)°. The structure is found to be stabilized by intra-molecular hydrogen bond of the type O(1)-H-O(2). The hydrogen bond length and angle are 2.864(3) Å and 147.9(5)° respectively.

The dihedral angles between two benzene rings is 81.28°, in agreement with Koch & Moffitt's prediction of 90°, assuming overlap of the 3*r* orbital of S atom with the 2*p* orbitals of C(1) atoms¹. It is also very close to the corresponding dihedral angle of 82° found in diphenyl sulfoxide and 84.7(3)° in 4,4'-dichloro diphenyl sulfone¹². This value is larger than di-*p*-bromo phenyl sulfide and di-*p*-tolyl sulfide¹³. The molecular packing in unit cell is maintained by van der waals forces.

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