

비치오놀 설펜사이드, $C_{12}H_6Cl_4O_3S$ 의 결정구조

申鉉昭 · 宋 鉉*

동국대학교 공과대학 화학공학과

(1993. 10. 5 접수)

Crystal Structure of Bithional Sulfoxide, $C_{12}H_6Cl_4O_3S$

Hyun-So Shin and Hyun Song*

Department of Chemical Engineering, Dongguk University, Seoul 100-715, Korea

(Received October 5, 1993)

요 약. 비치오놀 설펜사이드, $C_{12}H_6Cl_4O_3S$ 의 결정구조를 흑연으로 단색화된 Mo-K α 방사선을 이용하는 CAD-4 회절기를 사용하여 수집한 2295개의 독립된 회절반점을 이용하여 해석하였다. 결정계는 단사정계이며, 공간군은 $P2_1/n$ 이고, 격자상수는 $a=12.448(4)$, $b=9.740(1)$, $c=11.815(2)\text{\AA}$, $\beta=100.06^\circ$, $Z=4$ 이다. 구조는 직접법으로 해석하였으며, 최소자승법으로 정밀화하여 최종 신뢰도 $R=0.037$ 인 모형을 구하였다. 분자의 전체적인 형태는 비치오놀의 경우와 비교하여 2개의 페닐링 중 한 개와 설펜사이드기를 축으로 삼아 대략 180° 정도로 회전하였음을 알 수 있었으며, 이와 같은 구조적인 변화는 S-O(3)---H-O(1)형의 분자내 수소결합의 존재와 설펜사이드기와 다른 페닐링간의 입체장애 현상 때문이다. 두 개의 페닐링은 평면구조를 나타내며, 두 평면간의 이면각은 99.22° 이다. 결정구조는 O(3)---H-O(2)형 분자간 수소결합에 의해 결합되어 있다.

ABSTRACT. The crystal structure of bithional sulfoxide, $C_{12}H_6Cl_4O_3S$, has been determined from 2295 independent reflections collected on an automated CAD-4 diffractometer with a graphite-monochromated Mo-K α radiation. The crystal belongs to the monoclinic, space group $P2_1/n$, with a unit cell dimensions $a=12.448(4)$, $b=9.740(1)$, $c=11.815(2)\text{\AA}$, $\beta=100.06^\circ$, $\mu=9.02\text{ cm}^{-1}$, $D_m=1.76\text{ g/cm}^3$, $D_c=1.75\text{ g/cm}^3$, $F(000)=744$, and $Z=4$. The structure was solved by the direct method and refined by the least-squares method. The final R values was 0.037 for 2295 independent reflections. Overall conformation of the molecule is folded with respect to central sulfur atom. Comparing with the molecular conformation of bithional, one of phenyl rings was swung with about 180° . This conformational change in the molecule results in the existence of intramolecular-hydrogen bond of S-O(3)---H-O(1) type and its steric hindrance between this moiety and the other phenyl ring. The two best planes of the phenyl rings have a maximum deviation of 0.009\AA for C(1) atom. The dihedral angle between two phenyl rings is 99.22° . In the crystal structure, the molecules are packed with intermolecular-hydrogen bond of O(3)---H-O(2).

INTRODUCTION

The various structural data of crystalline molecules containing sulfur atom in different oxidation states show sulfides relatively represent the structural discontinuity compared with the corresponding sulfoxides and sulfones. The recent studies about the molecule of several simple sulfoxide

molecules have entirely confirmed the tetrahedral structures of these bonds^{1,2}. In our previous analysis of the structure containing sulfur atom, it was found that the C-S bond length of sulfides and sulfones in aromatic systems were 1.776 and 1.765 \AA , respectively. These are shorter than that of 1.800 \AA in sulfoxides. The sulfur bond angles dec-

reased in the following order, sulfone>sulfide>sulfoxide³. Objectives of this study are to establish the crystal structure of bithionol sulfoxide and to compare its bond lengths, bond angles and geometrical properties with other sulfur compounds reported in the literature. In our previous paper we have reported that the structure of bithionol has the folding conformations of the molecules and intramolecular-hydrogen bond of O---H-O type⁴.

EXPERIMENTAL

Bithionol Sulfoxide was purchased from Sigma Chemical Company and the colourless rectangular crystals were grown from saturated acetone solution by slow evaporation. The crystal system was found to be monoclinic system from X-ray Oscillation and Weissenberg photographs. The crystal density was measured in 2,3-dibromopropene and isopropyl alcohol by the flotation method. X-ray data collection was carried out using an Nonius CAD-4 diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.71069 \text{ \AA}$) with a crystal dimension $0.31 \times 0.39 \times 0.28 \text{ mm}$. The lattice constant was refined by least-squares method with 2θ ($<25^\circ$) values for 25 reflections. The reflection data were collected using $\omega-2\theta$ scan mode over a scan width $\Delta\omega=(0.8+0.3\tan\theta)^\circ$ and the ranges of indices were $0 < h < 15$, $0 < k < 12$, $-13 < l < 13$. The three standard reflections $(-1 \ -3 \ 6)$, $(3 \ 0 \ -7)$, $(-4 \ 4 \ -3)$ were measured periodically during the data collection. There was no significant crystals decay ($<2\%$) and no decay correction was applied to the reflection data. The reflection data were reduced to structure factors by applying Lorentz and polarization effects, but the absorptions were ignored. The independent reflections of 2469 were measured by scanning in 2θ ($2\theta_{\max}=48^\circ$). The 2295 reflections with $I > 3\sigma(I)$ were used in the solution and the refinement of the structure. The crystal structure was solved by the direct method (SHELXS)⁵ and refined by the full-matrix least squares method (SHELXL)⁶. The E map computed with the best set of phase shown the all non-hydrogen atoms. All hydrogen atoms were obtained from the different Fourier map. The bond

lengths for the C-H bond are in the ranges of $0.75 \sim 1.09 \text{ \AA}$. The structure was refined with anisotropic thermal parameters for non-hydrogen atoms and for the hydrogen atoms with isotropic thermal parameters. The final R value for 2295 independent reflections was 0.037. No significant residual density was shown on the final difference Fourier map. In the final cycle of the refinement, the largest parameter shift $(\Delta/\sigma)_{\max}$ for non-hydrogen atoms was 0.01. The residual density in the final difference map was 0.02 e\AA^{-3} (0.48 e\AA^{-3} near heavy atoms (S and Cl)). No weight scheme were applied. The thermal parameters of the two hydrogen atoms of the two hydroxy groups were found to be very highly. The atomic scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974)⁷, and those for hydrogen atoms from the article of Stewart, Davidson and Simpson (1965)⁸. All computations are performed on a Cyber 930 NOS/VE computer system at Dongguk University.

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters (coordinates are $\times 10^4$; $U_{eq}=(U_{11}+U_{22}+U_{33})/3$ are $(\text{\AA}^2 \times 10^3)$ with e.s.d.'s in parentheses

Atom	x	y	z	U_{eq}
S	8006(1)	2062(1)	1202(1)	35
Cl(1)	8311(1)	494(1)	-3165(1)	58
Cl(2)	9232(1)	-3085(1)	325(1)	58
Cl(3)	4590(1)	-488(1)	2571(1)	55
Cl(4)	3830(1)	3307(1)	-765(1)	64
O(1)	7903(3)	2413(3)	-1423(2)	47
O(2)	6962(2)	119(3)	2487(3)	42
O(3)	8128(2)	3455(3)	678(2)	44
C(1)	8294(3)	837(4)	178(3)	32
C(2)	8200(3)	1162(4)	-986(3)	34
C(3)	8417(3)	124(4)	-1727(3)	36
C(4)	8718(3)	-1172(4)	-1335(4)	40
C(5)	8826(3)	-1464(4)	-164(3)	37
C(6)	8619(3)	-471(4)	599(3)	36
C(7)	6565(3)	1788(4)	1048(3)	32
C(8)	6198(3)	827(4)	1765(3)	32
C(9)	5074(3)	658(4)	1673(3)	35
C(10)	4363(4)	1407(5)	897(4)	42
C(11)	4745(3)	2354(4)	196(3)	39
C(12)	5846(3)	2567(4)	272(3)	38

RESULTS AND DISCUSSION

The atomic fractional coordinates for non-hydrogen atoms with equivalent isotropic thermal parameter are list in Table 1. The molecular conformation of bithionol sulfoxide with numbering scheme, which is drawn by the ORTEP⁹ program, is shown in Fig. 1. The bond lengths and bond angles of non-hydrogen atoms are given in Table 2. The molecular packing with PLUTO¹⁰ is shown in Fig. 2. The selected torsion angles and the hydrogen bonds are shown in Table 3. The overall conformation of the molecule is folded with respect to central sulfur atoms. The two phenyl rings are planar with maximum deviation 0.009 Å for C(7) atom. Four Cl atoms are out of the best planes of phenyl rings by -.024(1), -.025(1), .057(1), .054(1)Å. The C-C bond lengths in the phenyl ring A[C(1), ---, C(6)] vary from 1.374(6)Å to 1.401(5)Å with an average value of 1.383(5)Å and in the phenyl ring B[C(7), ---, C(12)], the C-C distances vary from 1.369(6)Å to 1.394(5)Å with an average value of 1.391 Å. The average C-C bond length in the two phenyl rings are in good agreement with that values of bithionol. In the two phenyl rings, the internal C-C-C angles vary from 117.6 (3)° (<C(3)-C(2)-C(1), <C(9)-C(8)-C(7)) to 121.8 (3)° (<C(12)-C(11)-C(10)) are 119.9°(3) and 120.0 (3). The internal angles of C atoms (C(2), C(8)) as the substituted hydroxyl group are smaller than 120°, these effects connected with the electron withdrawing and relasing characters by the intra-

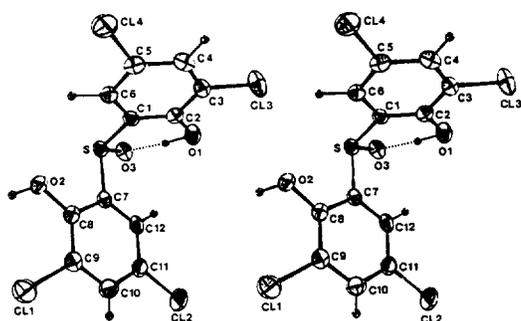


Fig. 1. An ORTEP drawing of the molecule with numbering scheme in bithionol sulfoxide. The dotted line showing the hydrogen bond.

intermolecular hydrogen bonds. The average C-S bond length is 1.787(2)Å, which is slightly larger than that proposed by Domenicano, Vaciago and Coluson[1.781(3)Å]¹¹. However, this value is in good agreement with that suggested by Cox, Gillot and Jeffrey [1.79 Å]² and that of the our previous report on bithionol[1.789(3)Å]⁴. The sulfur valence angle C(1)-S-C(7) is 98.5(2)°. Hauback and Winthen have suggested that in the bond length of sulfur atom with the aromatic system in solid states the C-S bond length in sulfoxides is significantly larger than both those in sulfides and sulfones³. They also reported that the sulfur bond angles decreased in the following order, sulfone>sulfide>sulfoxide. The results so far obtained from experiment are in good agreement with those pre-

Table 2. The bond lengths (Å) and bond angles (°) for non-hydrogen atoms.

a) Bond length (Å)			
S-O(3)	1.510(3)	S-C(1)	1.780(4)
S-C(7)	1.791(4)	Cl(1)-C(3)	1.721(4)
Cl(2)-C(5)	1.726(4)	Cl(3)-C(9)	1.720(4)
Cl(4)-C(11)	1.731(4)	O(1)-C(2)	1.350(5)
O(2)-C(8)	1.351(5)	C(1)-C(2)	1.397(5)
C(1)-C(6)	1.401(5)	C(2)-C(3)	1.395(5)
C(3)-C(4)	1.374(6)	C(4)-C(5)	1.397(6)
C(5)-C(6)	1.377(5)	C(7)-C(8)	1.392(5)
C(7)-C(12)	1.390(5)	C(8)-C(9)	1.394(5)
C(9)-C(10)	1.369(6)	C(10)-C(11)	1.379(6)
C(11)-C(12)	1.373(5)		
b) Bond angle (°)			
C(1)-S-O(3)	106.1(2)	C(1)-C(2)-O(1)	123.5(3)
C(2)-C(1)-S	121.7(3)	C(2)-C(3)-Cl(1)	118.6(3)
C(3)-C(2)-O(1)	118.9(3)	C(3)-C(2)-C(1)	117.6(3)
C(4)-C(3)-Cl(1)	119.7(3)	C(4)-C(3)-C(2)	121.7(4)
C(4)-C(5)-Cl(2)	119.4(3)	C(5)-C(4)-C(3)	119.7(4)
C(5)-C(6)-C(1)	118.8(3)	C(6)-C(1)-S	116.6(3)
C(6)-C(1)-C(2)	121.7(3)	C(6)-C(5)-Cl(2)	120.0(3)
C(6)-C(5)-C(4)	120.7(4)	C(7)-S-O(3)	105.2(2)
C(7)-S-C(1)	98.5(2)	C(7)-C(8)-O(2)	117.3(3)
C(8)-C(7)-S	117.9(3)	C(8)-C(9)-Cl(3)	118.9(3)
C(9)-C(8)-O(2)	125.1(3)	C(9)-C(8)-C(7)	117.6(3)
C(10)-C(9)-Cl(3)	120.3(3)	C(10)-C(9)-C(8)	120.8(4)
C(10)-C(11)-Cl(4)	119.8(3)	C(11)-C(10)-C(9)	120.6(4)
C(11)-C(12)-C(7)	118.8(3)	C(12)-C(7)-S	120.2(3)
C(12)-C(7)-C(8)	121.8(3)	C(12)-C(11)-Cl(4)	119.8(3)
C(12)-C(11)-C(10)	120.5(4)		

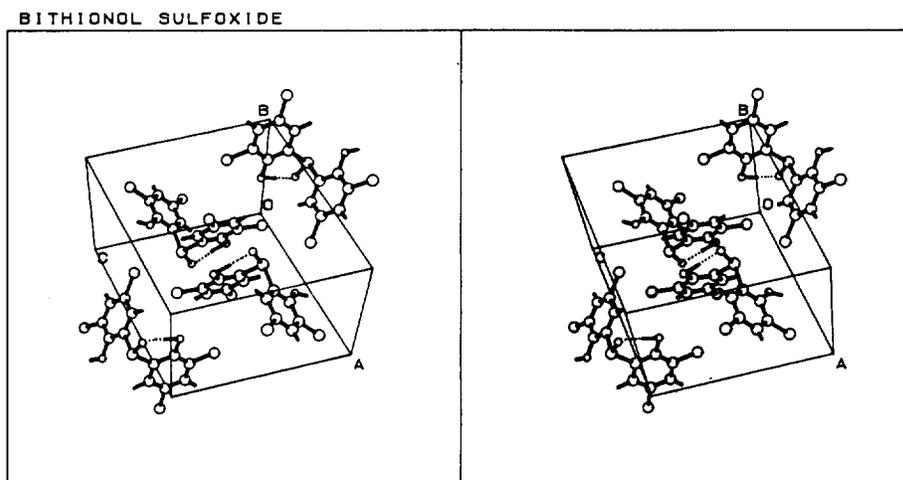


Fig. 2. The molecular packing in the unit cell by PLUTO.

Table 3. a) selected torsion angles ($^{\circ}$), b) hydrogen bond length (\AA) and angles ($^{\circ}$)

a) Selected torsion angles		
	Title compound	Bithionol
O(3)-S-C(1)-C(2)	-22.3(3)	
O(3)-S-C(1)-C(6)	157.7(3)	
C(7)-S-C(1)-C(2)	86.3(3)	86.8(2)
C(7)-S-C(1)-C(6)	-93.6(3)	94.1(2)
O(3)-S-C(7)-C(8)	-159.3(3)	
O(3)-S-C(7)-C(12)	17.6(3)	
C(1)-S-C(7)-C(8)	91.4(3)	-95.0(2)
C(1)-S-C(7)-C(12)	-91.7(3)	84.8(2)
S-C(1)-C(2)-O(1)	0.9(3)	0.7(1)
S-C(1)-C(2)-C(3)	-178.4(5)	-179.5(2)
C(6)-C(1)-C(2)-O(1)	-179.1(6)	-178.4(3)
S-C(1)-C(6)-C(5)	178.5(5)	-179.8(3)
S-C(7)-C(8)-O(2)	-3.3(3)	-0.3(2)
S-C(7)-C(8)-C(9)	177.5(5)	179.1(3)
S-C(7)-C(12)-C(11)	-178.4(5)	-178.9(3)
b) Hydrogen bond		
I. Intra-hydrogen bond	Length(\AA)	Angle($^{\circ}$)
O(1)-H(01)---O(2)	2.653(3)	175.4(57)
II. Inter-hydrogen bond	Length(\AA)	Angle($^{\circ}$)
O(2)-H(02)---O(3)	2.726(4)	153.2(58)

sented by Hauback and Winthen³. Substitution of the hydrogen atoms for the aromatic ring is deduced to be induce the distortion from the ideal geometry of a benzene ring¹. These suggest that sulfoxide group and Cl atoms have a little perturbing

effect on the regular ring geometry and cause an enlargement of the internal angles at the chlorine with respect to the adjacent atoms. In the two phenyl rings, the C-Cl bond lengths vary from 1.720(4) to 1.731(4) \AA with the average value of 1.729(4) \AA . The average value shows the shortening effect compared with the value reported by Domenicano, Vaciago and Coulson¹[1.7404(11) \AA], but it is in good agreement with the value of the bithionol[1.731(2) \AA]¹. Comparing to molecular conformation of bithionol, one of phenyls rings was swinged with about 180 $^{\circ}$. This conformational change in the molecule results in the existance of intramolecular-hydrogen bond of S-O(3)---H-O(1) type and its steric hindrance between this moiety and the phenyl ring. The crystal structure consists of molecule held together by intermolecular-hydrogen bond of O(3)---H-O(2) type with the bond length and bond angle 2.736(4) \AA and 153.2(4) $^{\circ}$, respectively.

REFERENCES

1. Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Cryst.* **1975**, *B31*, 1630~1641.
2. Cox, E. G.; Gillot, R.; J. J. M.; Jeffrey, G. A. *Acta Cryst.* **1949**, *2*, 356.
3. Mo, F.; Hauback, B. C.; Winthen, S. *Acta Cryst.* **1984**, *B40*, 388~294.

4. Song, H.; Kim, E. S.; Shin, H. S. *Bull. Korean Chem. Soc.* **1990**, *11*, 19~21.
5. Sheldrick, G. M. *SHELXS. Program for Crystal Structure Determination*; Univ. of Cambridge: England, 1986.
6. Sheldrick, G. M. *SHELXS. Program for Crystal Structure Determination*; Univ. of Cambridge: England, 1976.
7. *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.
8. Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175~3187.
9. Johnson, C. K. *ORTEP Report ORNL-3794*; Oak Ridge National Laboratory; Tennessee, 1965.
10. Motherwell, W. D. S.; Clegg, W. *PLUTO Program for Plotting Molecular and Crystal Structures*; Univ. of Cambridge, England, 1978.
11. Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Cryst.* **1975**, *B31*, 221~234.