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The Crystal and Molecular Structure of (+)-1-Bromo-2-hydroxy-2-phenylethyl *p*-Tolyl Sulfoxide: The Bromohydrin of (+)-*trans*-β-Styryl *p*-Tolyl Sulfoxide

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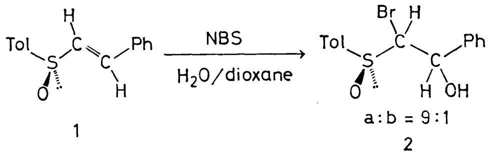
The crystal structure of (+)-1-bromo-2-hydroxy-2-phenylethyl *p*-tolyl sulfoxide, a major isomer formed by the electrophilic addition of BrOH to (+)-*trans*-*β*-styryl *p*-tolyl sulfoxide (**1**), has been determined by the X-ray diffraction method. The crystal is hexagonal; space group, $P6_2$; $a=15.61$, $c=10.82$ Å, and $Z=6$. The final R value is 0.079. A helical chain of the hydrogen bond between hydroxyl and sulfinyl groups (O···O, 2.63 Å) is formed around the threefold screw axis. The absolute configuration has been determined to be S_S, $S_{C(1)}$, $S_{C(2)}$ from the Mo Kα anomalous scattering of bromine and sulfur atoms. The bromine atom is *gauche* to the sulfinyl oxygen across the C(1)–S bond and *trans* to the hydroxyl oxygen across the C(1)–C(2) bond. Based on the established absolute configuration of the title compound, a mechanism which involves the preferential formation of an intermediary bromonium ion is proposed for the addition of BrOH to **1**.

The electrophilic addition of BrOH to (+)-*trans*-*β*-styryl *p*-tolyl sulfoxide (**1**) results in a dominant formation of a diastereomer, (+)-1-bromo-2-hydroxy-2-phenylethyl *p*-tolyl sulfoxide (**2a**) as shown in Scheme 1. The absolute configuration of **2a** was determined chemically.[1] We have recently reported the crystal structure and the absolute configuration of 1,2-dibromo-2-phenylethyl *p*-tolyl sulfoxide (**3**), a dominant isomer formed by the ionic bromination of **1**, by X-ray analysis.[2] The high selectivity of these additions is attributed to the preferential formation of a bridged bromonium ion by the electronic demand of the adjacent chiral sulfinyl group.



Scheme 1.

An X-ray diffraction study was undertaken to establish the absolute configuration and the molecular conformation of **2a** in order to elucidate such a specific reaction mechanism.

Experimental

The dominant isomer of **2** was recrystallized from hexane-ethanol solution. The crystals are colorless needles elongated along the c axis. They are unstable in air, and more unstable in a thin glass capillary. Therefore the intensity measurement was carried out without coating.

The cell dimensions were calibrated with copper powder lines superposed on Weissenberg photographs (Cu K, $\bar{\alpha}=1.5418$, $\beta=1.3920$ Å). The crystal data are: $C_{15}H_{15}BrSO_2$, MW=339.25; hexagonal, $a=15.61\pm0.01$, $c=10.82\pm0.01$ Å, $U=2281$ Å^3, $Z=6$, $D_x=1.48$, $D_m=1.50$ g cm^{-3}; $F(000)=1032$, μ(Mo Kα)$=27.8$ cm^{-1}; mp 149—151 °C; $[\alpha]_D^{26}$ +222.4° (*c* 0.526, MeOH). Laue symmetry and systematic absences ($l\neq3n$ for $00l$) indicated the possible space group $P6_2$ or $P6_4$. The former was proved to be correct by the analysis for the absolute configuration.

Intensity data were collected on a RIGAKU automatic diffractometer, using MoKα radiation monochromatized with a graphite monochromator. An ω-2θ scan technique was used to obtain the intensities with width of $\Delta\omega=1.0°+0.5°\tan\theta$ and a scanning speed of 2° min^{-1}. At both ends of the scan range for each reflection, 10 s background counts were taken. The intensities of three standard reflections, measured after every 50 reflections, decreased over the period of data collection. Their final intensities were 85% of the original values. The data were corrected for decomposition. Reflections in the range $2\theta<55°$ and $-13\leq l\leq7$ were measured, and 1043 of these had $F_o>3\sigma(F)$, which were considered as observed reflections. This set included the reflections with indices hkl and $hk\bar{l}$ which were treated as independent because of the anomalous scattering of Mo Kα radiation by bromine and sulfur atoms.

Structure Determination

The position of the bromine atom was found by inspection of a three-dimensional Patterson map. For a heavy atom alone, the R value was 0.43. Successive cycles of Fourier syntheses revealed the location of the remaining non-hydrogen atoms. The atomic parameters were refined by block-diagonal least-squares method, first with isotropic temperature factors to an R value of 0.17 and then with anisotropic temperature factors for all the non-hydrogen atoms to an R value of 0.10. A difference Fourier map showed positive density at the expected hydrogen atom positions except those of the methyl group. The coordinate of the hydroxyl-hydrogen atom H(O1) was estimated from this map. But the positions of other hydrogen-atoms, except those of the methyl group, were calculated with C–H distance of 1.08 Å. These parameters were included in the structure-factor calculations though they were not refined. The isotropic thermal parameters for hydrogen atoms were assumed to be 7.0 Å^2. Further cycles of refinement were carried out on two enantiomorphic structures taking the anomalous dispersion effect into consideration. The lowest R values for the two enantiomers were 0.079 and 0.089, respectively. The former corresponded to the space group $P6_2$ and the latter to $P6_4$. The difference of the R values is significant,[3] so that the true space group is assigned as $P6_2$ and the molecule has an absolute configuration illustrated in Fig. 1.

The weighting scheme used was: $w=0.3$ if $|F_o|<15$, $w=1.0$ if $15\leq|F_o|\leq60$ and $w=(60/|F_o|)^2$ if $|F_o|>60$. The atomic scattering factors were taken from "International Tables for X-ray Crystallography".[4] The

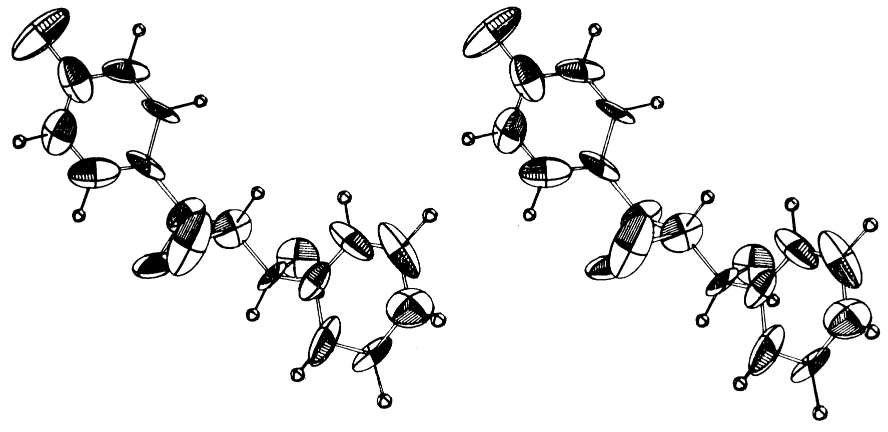


Fig. 1. Stereoscopic view of the molecule.

Table 1. Final atomic parameters

(a) Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^3$) of non-hydrogen atoms with their estimated standard deviations.[a] The anisotropic temterature factors are of the form:

$$\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}$$

The B_{eq} values are the equivalent isotropic temperature factors.[b]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Br	1700(3)	3463(3)	3333(4)	285(5)	154(3)	81(2)	171(3)	−58(2)	−31(2)	11.5
S	1327(5)	4664(4)	1344(5)	106(5)	68(4)	37(3)	10(4)	1(3)	7(3)	6.7
O(1)	2404(11)	5115(14)	1060(14)	55(10)	140(15)	91(12)	−40(11)	18(9)	−45(11)	10.7
O(2)	1351(11)	5918(10)	3427(15)	103(12)	72(10)	111(12)	57(10)	−8(10)	19(10)	7.1
C(1)	1244(16)	4363(16)	3042(17)	100(19)	87(16)	23(10)	14(14)	21(12)	31(10)	6.7
C(2)	1788(15)	5317(15)	3737(14)	72(15)	86(17)	20(11)	−4(13)	−2(10)	−35(10)	6.2
C(3)	1593(15)	5032(13)	5132(18)	106(17)	49(12)	63(13)	42(13)	−17(13)	−27(12)	5.6
C(4)	713(16)	4501(18)	5723(26)	45(15)	111(21)	137(22)	28(15)	42(14)	28(16)	8.1
C(5)	566(19)	4327(22)	6992(25)	98(19)	163(27)	114(23)	52(19)	100(18)	65(19)	10.3
C(6)	1425(17)	4755(16)	7676(21)	86(18)	54(16)	98(17)	13(14)	3(14)	7(12)	7.1
C(7)	2343(16)	5306(13)	7171(19)	96(17)	23(12)	85(15)	15(12)	−29(13)	−43(11)	5.9
C(8)	2465(22)	5446(18)	5868(19)	166(26)	114(23)	40(13)	56(21)	2(16)	−35(13)	8.9
C(9)	638(14)	3449(17)	722(16)	26(12)	122(19)	52(12)	20(13)	28(10)	42(12)	5.9
C(10)	−328(13)	2931(18)	646(17)	14(12)	137(21)	67(14)	29(14)	−4(10)	7(13)	6.1
C(11)	−818(14)	2015(16)	66(22)	42(14)	91(17)	79(15)	−18(13)	8(13)	26(15)	7.4
C(12)	−333(17)	1539(18)	−353(20)	105(19)	157(23)	67(15)	102(19)	13(13)	28(15)	7.4
C(13)	666(18)	2019(16)	−248(22)	136(20)	96(17)	88(17)	94(17)	−24(16)	−8(15)	7.2
C(14)	1179(17)	2990(17)	237(22)	78(16)	86(17)	90(18)	16(14)	−34(14)	28(14)	7.7
C(15)	−887(28)	525(17)	−869(27)	256(39)	35(15)	126(23)	48(20)	−70(23)	−14(14)	11.9

(b) Atomic coordinates for hydrogen atoms ($\times 10^3$).

Atom	x	y	z	Atom	x	y	z
H(O1)	183	645	400	H(7)	298	565	778
H(1)	48	402	332	H(8)	321	588	547
H(2)	258	576	360	H(10)	−77	323	104
H(4)	4	417	518	H(11)	−161	166	−4
H(5)	−14	393	746	H(13)	108	167	−56
H(6)	141	458	855	H(14)	198	339	26

a) The e.s.d.'s are in parentheses and refer to the last significant digits of the respective values in Tables 1 and 3 and in Fig. 3. b) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

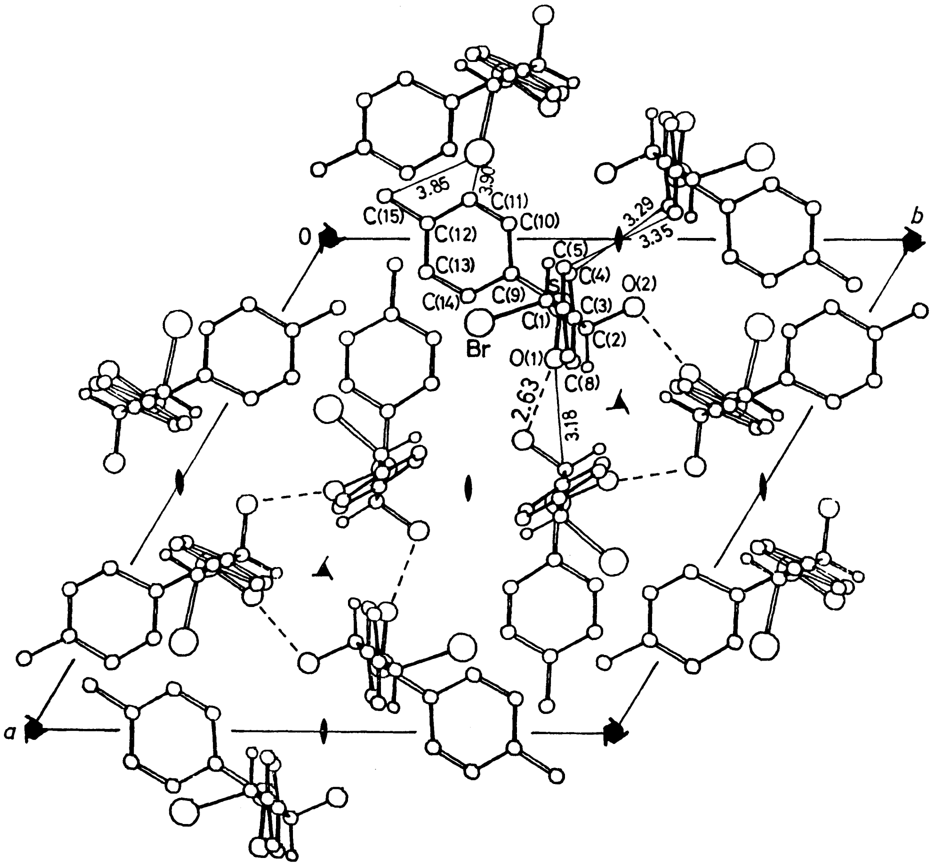


Fig. 2. Projection of the structure along the c axis.

Table 3. Intermolecular distances less than 4.0Å

Symmetry code Superscript			
None	x	y	z
i	x	y	$z-1$
ii	y	$y-x$	$z-1/3$
iii	y	$y-x$	$z+2/3$
iv	$-x$	$-y$	z
v	$-x$	$1-y$	z
vi	$y-x$	$1-x$	$z-2/3$
vii	$1-y$	$1-y+x$	$z-1/3$

S···C(6$^{\mathrm{i}}$)	3.97 (3) Å	O(2)···C(1$^{\mathrm{v}}$)	3.87 (3) Å
O(1)···C(6$^{\mathrm{i}}$)	3.90 (3)	O(2)···C(4$^{\mathrm{v}}$)	3.86 (3)
C(9)···C(6$^{\mathrm{i}}$)	3.74 (4)	C(4)···C(4$^{\mathrm{v}}$)	3.29 (3)
C(14))···C(6$^{\mathrm{i}}$)	3.79 (4)	C(4)···C(5$^{\mathrm{v}}$)	3.59 (5)
Br···C(5$^{\mathrm{ii}}$)	3.90 (4)	C(5)···C(5$^{\mathrm{v}}$)	3.35 (4)
C(13)···C(11$^{\mathrm{ii}}$)	3.75 (4)	O(1)···C(7$^{\mathrm{vi}}$)	3.66 (3)
Br···C(11$^{\mathrm{iii}}$)	3.90 (3)	O(1)···C(8$^{\mathrm{vi}}$)	3.96 (4)
Br···C(15$^{\mathrm{iii}}$)	3.85 (4)	O(1)···O(2$^{\mathrm{vii}}$)	2.63 (3)
C(6)···C(11$^{\mathrm{iii}}$)	3.71 (4)	O(1)···C(2$^{\mathrm{vii}}$)	3.18 (3)
C(7)···C(10$^{\mathrm{iii}}$)	3.74 (4)	O(1)···C(3$^{\mathrm{vii}}$)	3.57 (3)
C(7)···C(11$^{\mathrm{iii}}$)	3.67 (4)	O(1)···C(8$^{\mathrm{vii}}$)	3.56 (4)
C(8)···C(11$^{\mathrm{iii}}$)	3.90 (4)	C(2)···C(7$^{\mathrm{vii}}$)	3.95 (3)
C(15)···C(15$^{\mathrm{iv}}$)	3.86 (4)	C(2)···C(8$^{\mathrm{vii}}$)	3.99 (4)
O(2)···O(2$^{\mathrm{v}}$)	3.73 (4)	C(8)···C(7$^{\mathrm{vii}}$)	3.80 (4)
		O(1)···H(3$^{\mathrm{vii}}$)	1.68

final atomic parameters and their estimated standard deviations are given in Table 1. The observed and calculated structure factors are listed in Table 2.[5]

Results and Discussion

Figure 2 shows the crystal structure viewed along the c axis. The methyl groups are arranged around the sixfold screw axis. A helical chain of the hydrogen bonds between hydroxyl and sulfinyl groups is formed around the threefold screw axis: thus the structure consists of infinite columns parallel to the c axis. The O···O hydrogen-bond distance is 2.63 Å. Intermolecular contacts between adjacent columns are of van der Waals' type; those less than 4 Å are shown in Table 3.

The bond distances and angles are shown in Fig. 3 with their estimated standard deviations. The C(1)–S–O(1), C(9)–S–O(1) and C(1)–S–C(9) angles are 104, 111, and 100°; the corresponding angles in 1,2-dibromo-2-phenylethyl *p*-tolyl sulfoxide (**3**) are 105, 107, and 100°, respectively.[2] The S–O(1) distance is 1.49 Å, which agrees well with those in other sulfoxides.[6,7] The S–C(1) and S–C(9) distances are 1.88 and 1.78 Å. They are different from each other, while in (+)-methyl *p*-tolyl sulfoxide the corresponding S–C lengths are 1.796 and 1.797 Å, respectively.[6] The longer distance of S–C(1) is attributed to the presence of the bromine atom. The corresponding length in **3** is 1.82 Å. The non-bonding intramolecular distances of S···Br is 3.09 Å in **2** and also 3.09 Å in **3**, respectively.

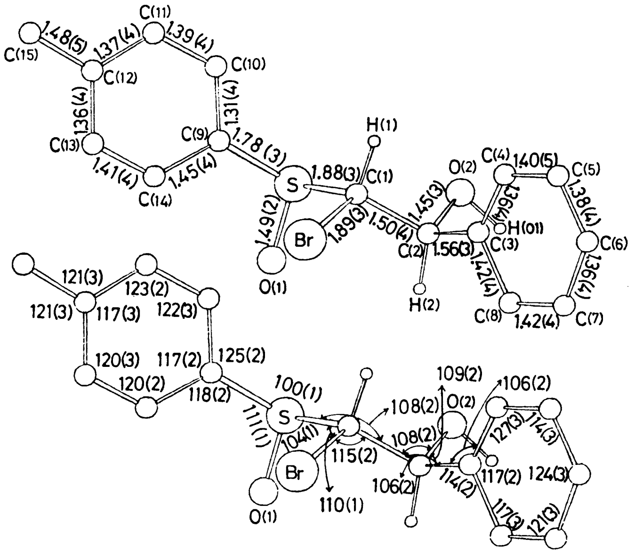


Fig. 3. Bond lengths (Å) and angles (°) with their estimated standard deviations.

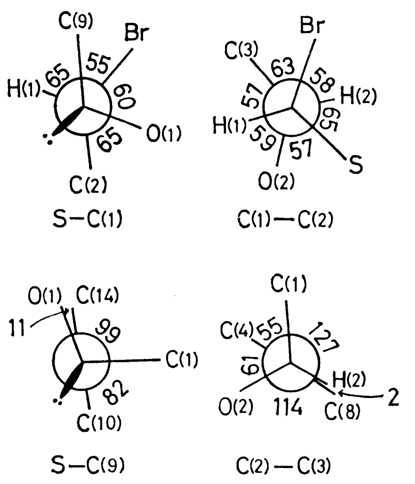


Fig. 4. Torsion angles in the molecule.

The length for C(1)–Br is 1.89 Å, which is slightly shorter than those of **3** (2.00 and 1.98 Å). The average values for C–C bonds in aromatic rings are 1.39 (phenyl) and 1.38 Å (tolyl), respectively. The length of C(12)–C(15) is 1.48 Å. The length of C(2)–O(2) is 1.45 Å, which is very similar to the corresponding values for methanol[8] and 1-hexadecanol.[9]

The least-squares planes are listed in Table 4. The dihedral angle between these planes is 70°.

The torsion angles of groups around the bonds, S–C(1), C(1)–C(2), S(1)–C(9), and C(2)–C(3) are shown in Fig. 4. The sulfinyl oxygen atom is *gauche* to Br across the S–C(1) bond. The torsion angle, O(1)–S–C(1)–Br is 60° and non-bonding distance O(1)···Br is 3.33 Å; the corresponding values for **3** is 45° and 3.13 Å, respectively. The bromine atom is *trans* to the hydroxyl oxygen O(2) across the C(1)–C(2) bond. The non-bonding distances, Br···C(3), Br···C(9), S···O(2), and O(1)···C(14), are 3.20, 3.27, 2.97, and 3.02 Å, respectively.

Table 4. Least-squares planes

Equation of the plane: $AX+BY+CZ+D=0$, where X, Y and Z are the coordinates in Å referred to the orthogonal axes a, b* and c.

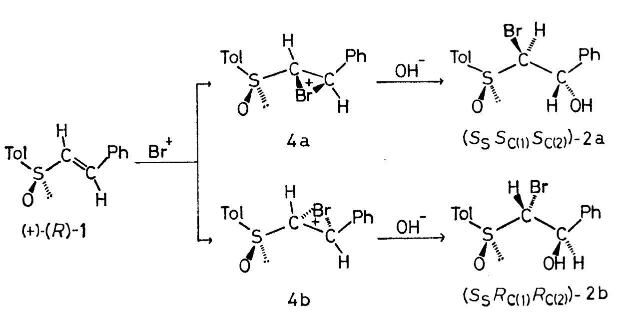
	A	B	C	D
(1) Phenyl ring C(3)—C(8)	0.548	−0.831	−0.100	6.986
(2) *p*-Tolyl ring C(9)—C(14)	0.161	−0.409	0.898	1.473

Deviations (Å×10³) of atom the least-squares planes.

Plane 1		Plane 2	
C(3)	−8	C(9)	−3
C(4)	−2	C(10)	31
C(5)	5	C(11)	−32
C(6)	2	C(12)	3
C(7)	−13	C(13)	30
C(8)	15	C(14)	−27
C(2)[a]	−132	C(15)[a]	51
		S[a]	−48

[a] Atoms not used to define the least-squares plane.

The absolute configuration was unequivocally determined to be *S* at the sulfur atom, *S* at C(1), and *S* at C(2). Therefore the structure of the dominant isomer derived from the electrophilic addition of BrOH to **1** is (+)-(S_S, $S_{C(1)}$, $S_{C(2)}$)-1-bromo-2-hydroxy-2-phenylethyl *p*-tolyl sulfoxide (**2a**). The same assignment has been made earlier on the basis of chemical evidence.[1] Based on the assigned structure of (+)-(S_S, $S_{C(1)}$, $S_{C(2)}$)-**2a**, it can be concluded that the electrophilic addition of BrOH proceeds in the *trans* manner, giving a product in which the bromine atom is in the *gauche* position to the sulfinyl oxygen atom in the adjacent sulfinyl group. A similar result has been obtained for the ionic bromination of **1**. (+)-(S_S, $S_{C(1)}$, $S_{C(2)}$)-1,2-Dibromo-2-phenylethyl *p*-tolyl sulfoxide is formed as a dominant isomer.[2] The selectivity for these additions can be explained in terms of the preferential formation of intermediary bromonium ion (**4a**) rather than **4b**, as is shown in Scheme 2.



Scheme 2.

All the crystallographic computations were performed on a HITAC 8800 computer of the Computer Center of the University of Tokyo, using the UNICS program system.[10] Figures 1, 2, and 3 were drawn by using the program ORTEP[11] on a CDC 6600 computer at the Century Research Center.

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