The Crystal and Molecular Structure of (+)-1,2-Dibromo-2-phenylethyl *p*-Tolyl Sulfoxide

Fujiko Iwasaki, Shuichi Mitamura,* and Gen-ichi Tsuchihashi*

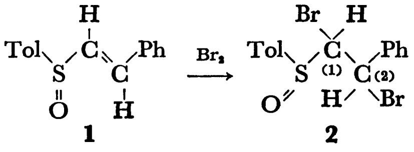
Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182

**Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229*

(Received November 11, 1974)

The crystal structure of (+)-1,2-dibromo-2-phenylethyl *p*-tolyl sulfoxide, a dominant isomer formed by the ionic bromination of (+)-*trans*-*β*-styryl *p*-tolyl sulfoxide, has been determined by the X-ray diffraction method. The crystal is monoclinic; space group, P2$_1$; a=16.193, b=5.706, c=8.541 Å, β=93.51°, and Z=2. The final R value is 0.087 for 792 observed reflections. The absolute configuration has been established to be $S_S, S_{C(1)}, S_{C(2)}$ from the Cu$K\alpha$ anomalous scattering of the bromine and sulfur atoms. The sulfinyl oxygen is *gauche* to the bromine atom across the S–C(1) bond, and the non-bonding distance between the both atoms is 3.13 Å. The bromine atom is *trans* to another bromine across the C(1)–C(2) bond. Based on the assigned structure, a mechanism which involves the preferential formation of an intermediary bromonium ion is elucidated for the bromination. The configuration at the sulfur atom is retained during the reaction.

The ionic bromination of (+)-*trans*-*β*-styryl *p*-tolyl sulfoxide (**1**) results in a dominant formation of one isomer in four diastereomers of (+)-1,2-dibromo-2-phenylethyl *p*-tolyl sulfoxide (**2**). The high selectivity of the addition is attributed to the preferential formation of a bridged bromonium ion by the electronic demand of the adjacent chiral sulfinyl group.[1] In order to elucidate such a specific reaction mechanism, it is important to study the stereochemistry of sulfur centers; however, the steructures of relatively few sulfoxides have been determined. An X-ray study was, therefore, undertaken to establish the absolute configuration and the molecular conformation of **2**.



1 **2**

Experimental

The dominant isomer of **2** was recrystallized from a *n*-hexane–ethanol solution. The crystals are colorless needles and are stable in air. The cell dimensions were calibrated with copper powder lines superposed on Weissenberg photographs (CuK, α=1.5418, α_1=1.5405 Å).

The crystal data are: $C_{15}H_{14}Br_2SO$, M.W.=402.14; monoclinic, a=16.193 (8)[2], b=5.706 (12), c=8.541 (8) Å, β=93.51 (5)°, V=787.6 Å^3, Z=2, D_X=1.695 g cm^{-3}, D_m=1.68 g cm^{-3}; F(000)=396; μ=75.7 cm^{-1} (Cu$K\alpha$); Spase group, $p2_1$; $[\alpha]_D^{22}$ +261.8° (c 0.527, CHCl$_3$); mp 161—163 °C.

The intensity data were collected from integrated equi-inclination Weissenberg photographs around the b and c axes, *h0l*—*h3l* and *hk0*—*hk5*, using Cu$K\alpha$ radiation. The intensities were estimated visually by comparison with a standard scale. A total of 792 non-zero reflections were observed. Lorentz, polarization and spot-shape corrections were made, but because of the size of specimens (max. μR=0.2) no absorption corrections were applied.

Structure Determination

The positions of the two bromine atoms in an asymmetric unit were found by an inspection of a three-dimensional Patterson map. For the heavy atoms alone, the R value was 0.31. The calculation of Fourier synthesis allowed coordinates to be assigned to all the other atoms. The atomic parameters were refined by least-squares methods, first with isotropic temperature factors to an R value of 0.15 and then with anisotropic temperature factors for all the non-hydrogen atoms to an R value of 0.090. The positions of the hydrogen atoms, other than those of the methyl group, were calculated with a C–H distance of 1.08 Å. These hydrogen parameters were included in the structure-factor calculations, though they were not refined. The isotropic thermal parameters for hydrogen atoms were assumed to be 5.0 Å^2. Further refinement of atomic parameters was carried out for all the non-hydrogen atoms with anisotropic temperature factors. The final R value was 0.087 for all the observed reflections. The weighting scheme used was: w=0.7 if $|F_o|<6$, w=1 if $6\leq|F_o|\leq25$ and $w=(25/|F_o|)^2$ if $|F_o|>25$. The atomic scattering factors for non-hydrogen atoms were taken from "International Tables for X-ray Crystallography".[3] For the bromine atom, the scattering factor was corrected for dispersion using the expression: $|f|=\sqrt{\{(f_0+\Delta f')^2+(\Delta f'')^2\}}$. For hydrogen, the values given by Stewart, Davidson, and Simpson[4] were used.

The 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]

Absolute Configuration. The absolute configuration has been determined by the anomalous dispersion method, with Cu$K\alpha$ radiation. The values of the real and imaginary dispersion correction terms of the scattering factor were taken as $\Delta f'_{Br}=-0.96$, $\Delta f'_S=0.31$, $\Delta f''_{Br}=1.46$, and $\Delta f''_S=0.58$.[6] The calculated values of the intensity ratio between the Friedel pair of reflections agreed with those observed on the b-axis oscillation photographs if one takes the right-handed coordinate system. A comparison of the observed and calculated intensity ratios is given in Table 3. The figures shown in this paper are drawn with the correct absolute configuration obtained above.

TABLE 1. FINAL ATOMIC PARAMETERS

(a) Atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) of non-hydrogen atoms with their estimated standard deviations.a) The anisotropic temperature 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(1)	3100(2)	2250(9)	3246(4)	83(2)	69(2)	69(2)	−21(2)	−3(1)	18(2)	5.8
Br(2)	531(2)	0(10)	1124(3)	64(1)	99(3)	43(1)	0(2)	5(1)	−6(2)	5.4
S	2117(5)	3429(16)	126(7)	90(5)	39(5)	42(3)	19(5)	25(3)	20(4)	4.4
O	2113(18)	5736(38)	868(22)	246(30)	10(13)	64(10)	20(18)	76(15)	16(11)	8.2
C(1)	2164(17)	1337(52)	1733(25)	84(18)	5(16)	44(12)	−1(14)	9(11)	−6(11)	3.5
C(2)	1373(15)	1405(51)	2615(24)	66(15)	28(18)	37(11)	3(14)	3(9)	19(11)	3.5
C(3)	1378(12)	74(52)	4125(22)	45(11)	20(13)	47(10)	−11(15)	9(8)	6(14)	2.9
C(4)	890(15)	986(56)	5316(25)	59(14)	37(18)	44(11)	−38(15)	17(9)	−6(12)	3.6
C(5)	823(14)	−290(61)	6756(21)	71(14)	61(22)	27(8)	7(20)	15(9)	−18(15)	4.1
C(6)	1267(15)	−2129(65)	6951(27)	55(14)	83(32)	60(14)	−21(18)	18(11)	43(18)	5.2
C(7)	1712(17)	−3213(58)	5846(26)	82(17)	58(24)	46(11)	4(17)	33(11)	44(16)	4.8
C(8)	1776(16)	−2062(47)	4387(32)	65(16)	11(20)	85(17)	13(15)	22(13)	2(14)	4.2
C(9)	3055(17)	2792(62)	−686(28)	74(10)	52(26)	58(14)	4(18)	26(12)	8(15)	6.0
C(10)	3151(22)	757(64)	−1639(36)	108(25)	26(21)	95(21)	22(21)	25(18)	−27(19)	6.0
C(11)	3857(19)	548(58)	−2441(33)	107(23)	31(23)	79(17)	27(20)	25(15)	−21(18)	5.6
C(12)	4513(16)	2045(71)	−2361(32)	58(15)	61(24)	77(16)	−9(20)	11(12)	24(19)	5.2
C(13)	4399(23)	4073(72)	−1351(30)	152(31)	70(29)	56(15)	−76(26)	29(10)	9(18)	7.3
C(14)	3675(20)	4494(77)	−645(29)	130(26)	90(33)	56(15)	−63(29)	39(16)	13(19)	7.2
C(15)	5225(21)	1590(80)	−3330(44)	77(20)	103(40)	121(26)	10(24)	47(19)	−7(26)	7.8

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

Atom	x	y	z	Atom	x	y	z
H(1)	225	−42	126	H(7)	213	−279	349
H(2)	126	319	297	H(8)	269	−62	−170
H(3)	55	266	511	H(9)	389	−93	−322
H(4)	46	46	769	H(10)	492	522	−116
H(5)	128	−304	808	H(11)	360	610	−3
H(6)	201	−487	605				

a) The e.s.d.'s are in parentheses and refer to the last significant digits of the respective values in Tables 1 and 5 and in Fig. 1. b) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

TABLE 3. DETERMINATION OF THE ABSOLUTE CONFIGURATION

h	k	l	Calculated $\lvert F(hkl)\rvert^2/\lvert F(h\bar{k}l)\rvert^2$	Observed $I(hkl)/I(h\bar{k}l)$
4	1	2	1.31	>1
6	1	2	1.06	>1
4	1	3	1.06	>1
−4	1	3	0.91	<1
2	1	4	0.87	<1
3	1	4	0.86	<1
−5	1	4	0.90	<1
0	1	5	1.08	>1
4	1	5	0.96	<1
2	2	1	1.16	>1
4	2	1	1.17	>1
−1	2	2	1.15	>1

Results and Discussion

The bond distances and angles are shown in Fig. 1. The three sulfur bonds form a shallow pyramid. The dihedral angle between the planes defined by the C(1)–S–C(9) and O–S–C(9) atoms is 109°. The C(1)–S–O and C(9)–S–O angles are 105 and 107° respectively; the corresponding angles in (+)-methyl *p*-tolyl sulfoxide (**3**) have been reported to be 105.5 and 106.5° respectively.7) The C(1)–S–C(9) angle is 100°, which agrees well with the values for symmetrical sulfoxides8) and **3**.7) The S–O distance is 1.47 Å, which is slightly shorter than those (1.49 and 1.53 Å) in other sulfoxides.7,8) The S–C(1) and S–C(9) distances are 1.82 and 1.75 Å. They are slightly different from each other, while in **3** the corresponding values for the S–C lengths are 1.796 and 1.797 Å respectively.

The C(1)–C(2) distance is 1.53 Å, and the C(2)–C(3) distance is 1.50 Å. They are similar to the accepted values for single C(sp^3)–C(sp^3) (1.526 Å) and C(sp^3)–C(sp^2) (1.501 Å) bonds.9) The lengths for C(1)–Br(1) and C(2)–Br(2) are 2.00 and 1.98 Å respectively. They are slightly longer than those for ethyl bromide (1.950 Å),10) for 2-bromopropane (1.957 Å)11) in the gas phase, and for hexabromoethane (1.944 Å)12) in the solid phase.

The average values for C–C bonds in aromatic rings are 1.39 (phenyl) and 1.40 Å (tolyl) respectively. The length of C(12)–C(15), 1.48 Å, is close to the corresponding value for toluene.13) The least-squares planes are listed in Table 4. The dihedral angle between these planes is 69°.

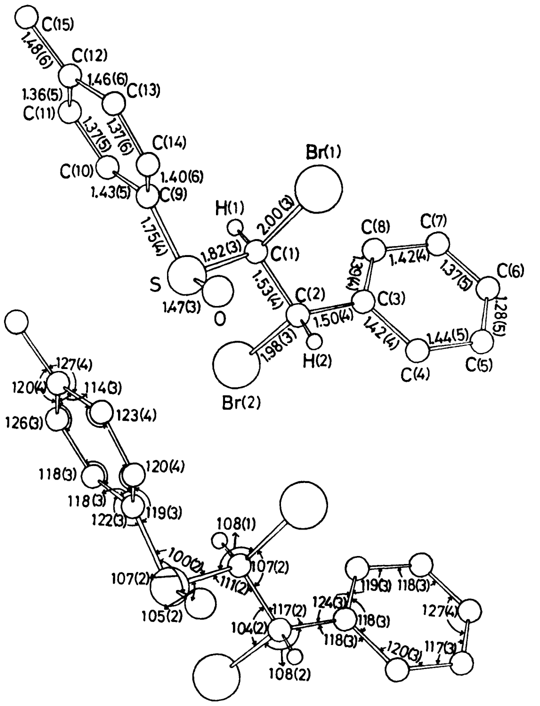


Fig. 1. Bond lengths (Å) and angles (°) with their estimated standard deviations in parentheses.

TABLE 4. LEAST-SQUARES PLANES

Equation of the plane: $AX+BY+CZ=D$, 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)	0.777	0.502	0.380	2.904
(2) *p*-Tolyl ring C(9)—C(14)	0.378	−0.482	0.791	0.645

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

Plane 1		Plane 2	
C(3)	−19	C(9)	−9
C(4)	−4	C(10)	−4
C(5)	39	C(11)	30
C(6)	−48	C(12)	−12
C(7)	15	C(13)	−46
C(8)	18	C(14)	51
C(2)[a]	34	C(15)[a]	60
		S[a]	208

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

The conformation of groups across the bonds, C(1)–C(2), S–C(1), S–C(9), and C(2)–C(3), are shown in Fig. 2. The oxygen atom is *gauche* to Br(1) across the S–C(1) bond, and the torsion angle, O–S–C(1)–Br(1), is 45°. The lone-pair orbital of the sulfur atom is *trans* to Br(1). Br(2) is *trans* to Br(1) across the C(1)–C(2) bond. The non-bonding distances, Br(1)···O, Br(1)···C(8), Br(1)···C(9), and O···C(14), are 3.13, 3.44, 3.37, and 2.86 Å respectively.

The absolute configuration is rigorously 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 ionic bromination of (+)-*trans*-β-styryl *p*-tolyl sulfoxide (**1**) is (+)-(S_S, $S_{\mathrm{C}(1)}$, $S_{\mathrm{C}(2)}$)-1,2-dibromo-2-phenylethyl *p*-tolyl sulfoxide (**2**).

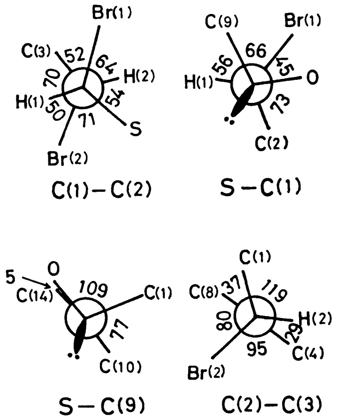
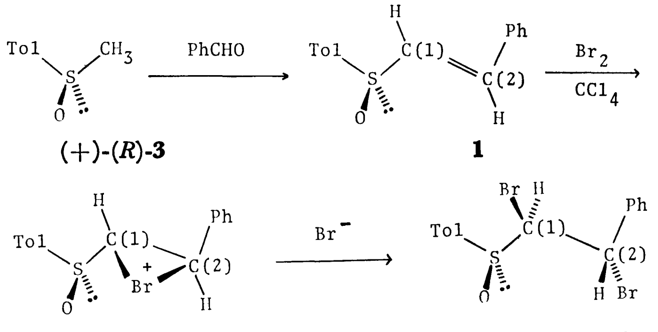


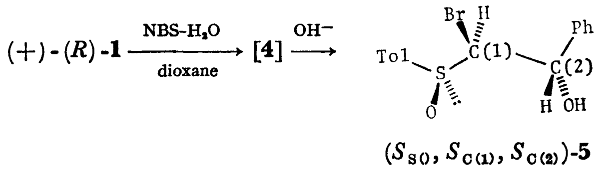
Fig. 2. Torsion angles in the molecule.

(+)-*trans*-β-Styryl *p*-tolyl sulfoxide (**1**)[1a] was obtained by the condensation reaction of benzaldehyde with (+)-(*R*)-methyl *p*-tolyl sulfoxide (**3**), whose configuration has been unequivocally established as *R* by the chemical transformation to sulfoxides of a known absolute configuration[14,15] and by the X-ray diffraction method.[7] Since the **3** to **1** transformation does not involve the chiral center, and since the configuration at the sulfur atom of **2** is *S*, the ionic bromination of **1** proceeds with the retention of the configuration at the sulfur atom.



Scheme 1.

An inspection of the molecular structure of (+)-(S_S, $S_{\mathrm{C}(1)}$,$S_{\mathrm{C}(2)}$)-**2** revealed that the bromination proceeds in the *trans* manner, giving a product in which the bromine atom at C(1) is in the *gauche* position to the oxygen atom in the adjacent sulfinyl group. The formation of this product can be explained in terms of the preferential formation of an intermediary bromonium ion (**4**), followed by the attack of the bromide anion at C(2), as is shown in Scheme 1. The same bromonium ion, **4**, was proposed as an intermediate of the bromo-



(S_SO, $S_{\mathrm{C}(1)}$, $S_{\mathrm{C}(2)}$)-**5** hydrin-forming reaction of **1**, which gave predominantly a product with the same configuration, *i.e.*, $(S_S, S_{C(1)}, S_{C(2)})$-1-bromo-2-hydroxy-2-phenylethyl *p*-tolyl sulfoxide (**5**).[1c,16]

It is noteworthy that the torsion angle for Br–C(1)–S–O is 45°, much smaller than the usual angle of 60°. As a result, the bomine atom at C(1) and the sulfinyl oxygen are very close together in space; the non-bonding distance between these two atoms is 3.13 Å. This suggests the existence of a strong interaction between the bromine atom and the sulfinyl group.

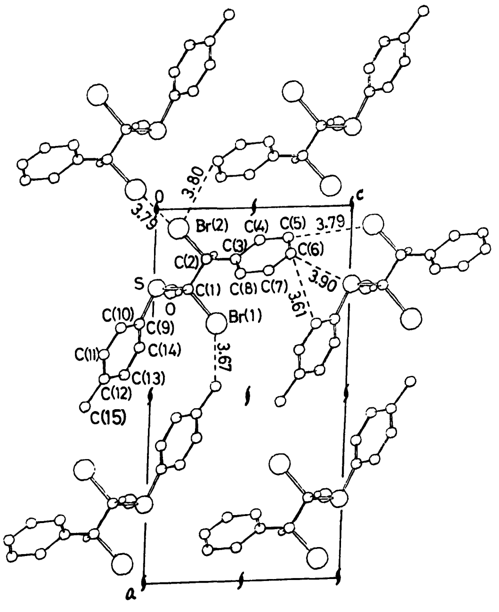


Fig. 3. Projection of the structure along the b axis.

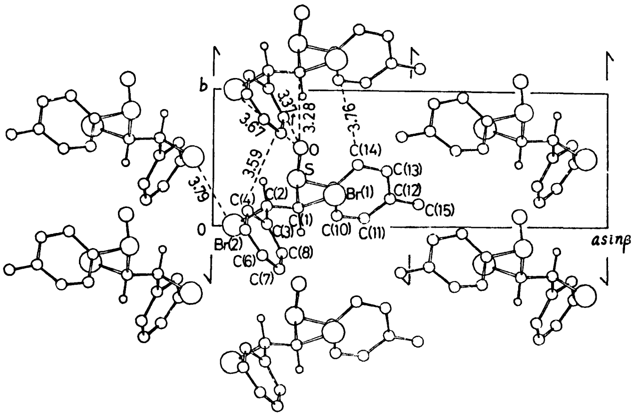


Fig. 4. Projection of the structure along the c axis.

Figures 3 and 4 show the crystal structure viewed along the b and c axes respectively. There is a rather short contact between Br(2)···Br(2$^{\mathrm{iv}}$) (3.79 Å), related by a twofold screw axis; twice the van der Waals radius is 3.90 Å.[17] Such a short Br···Br contact is also found in hexabromoethane.[12] The intermolecular contacts less than 4 Å are shown in Table 5. The molecules are packed together mainly through van der Waals forces.

Table 5. Intermolecular distances less than 4.0 Å

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

O···Br(2$^{\mathrm{i}}$)	3.67 (3) Å	C(6)···C(10$^{\mathrm{ii}}$)	3.61 (5) Å
O···C(1$^{\mathrm{i}}$)	3.28 (4)	C(7)···C(10$^{\mathrm{ii}}$)	3.82 (5)
O···C(2$^{\mathrm{i}}$)	3.85 (4)	C(6)···S$^{\mathrm{iii}}$	3.90 (4)
O···C(8$^{\mathrm{i}}$)	3.37 (4)	C(6)···O$^{\mathrm{iii}}$	3.79 (5)
O···C(10$^{\mathrm{i}}$)	3.94 (5)	Br(2)···Br(2$^{\mathrm{iv}}$)	3.79 (1)
C(4)···C(7$^{\mathrm{i}}$)	3.59 (5)	Br(2)···C(5$^{\mathrm{v}}$)	3.97 (4)
C(13)···C(11$^{\mathrm{i}}$)	3.90 (5)	Br(2)···C(6$^{\mathrm{v}}$)	3.80 (4)
C(14)···C(10$^{\mathrm{i}}$)	3.76 (6)	C(4)···C(5$^{\mathrm{v}}$)	3.84 (5)
C(14)···C(11$^{\mathrm{i}}$)	3.80 (6)	Br(1)···C(15$^{\mathrm{vi}}$)	3.67 (5)
Br(1)···C(11$^{\mathrm{ii}}$)	3.93 (3)	C(13)···C(12$^{\mathrm{vi}}$)	3.29 (6)
C(5)···Br(2$^{\mathrm{ii}}$)	3.79 (4)	C(14)···C(15$^{\mathrm{vi}}$)	3.92 (6)
C(5)···C(10$^{\mathrm{ii}}$)	3.98 (5)		

All the crystallographic computations were performed on the HITAC 8800 computer of the Computer Center of the University of Tokyo, using the UNICS program system.[18] Figures 1, 3, and 4 were drawn by using the program ORTEP[19] on the CDC 6600 computer at the Century Research Center.

References

1) a) G. Tsuchihashi, S. Mitamura, S. Inoue, and K. Ogura, *Tetrahedron Lett.*, **1973**, 323; b) G. Tsuchihashi, S. Mitamura, and K. Ogura, *ibid.*, **1973**, 2469; c) G. Tsuchihashi, S. Mitamura, and K. Ogura, *ibid.*, **1974**, 455.

2) The limits of error are in parentheses and refer to the last significant digits of the respective values in these data.

3) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

4) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

5) Table 2 has been submitted to, and is kept by the Office of the Chemical Society of Japan, 1-5, Kanda-Surugadai, Chiyodaku, Tokyo 101. (Document No. 7506)

6) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

7) U. de la Camp and H. Hope, *Acta Crystallogr.*, **B26**, 846 (1970).

8) S. C. Abrahams, *Quart. Rev. Chem. Soc. London*, **10**, 407 (1956); R. Thomas, C. B. Shoemaker, and K. Eriks, *Acta Crystallogr.*, **21**, 12 (1966).

9) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

10) C. Franagan and L. Pierce, *J. Chem. Phys.*, **38**, 2963 (1963).

11) R. H. Scwendeman and F. L. Tobiason, *ibid.*, **43**, 201 (1965).

12) G. Mandel and J. Donohue, *Acta Crystallogr.*, **B28**, 1313 (1972).

13) F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956).

14) K. K. Cheung, A. Kjær, and G.A. Sim, *Chem. Commun.*, **1965**, 100.

15) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green,

and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4835 (1968).

16) F. Iwasaki, unpublished results.

17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York (1960), p. 260.

18) T. Sakurai, Ed., The Universal Crystallographic Computation Program System, The Crystallographic Society of Japan (1967); T. Sakurai, T. Ito, H. Iwasaki, Y. Watanabe, and M. Fukuhara, *Rep. Inst. Phys. Chem. Res.*, **43**, 62 (1967).

19) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).