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Crystal Structure and Absolute Configuration of (−)-2,2′-Bisbromomethyl-1,1′-binaphthyl

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Crystals of (−)-2,2′-bisbromomethyl-1,1′-binaphthyl have been subjected to crystal structure analysis in order to determine the absolute configuration of optically active 1,1′-binaphthyl derivatives. The crystals are orthorhombic, space group $P2_12_12_1$ with $Z=4$ and the lattice constants are; $a=10.360$, $b=13.052$, $c=13.178$ Å. The structure was solved by the heavy atom method and the final R index was 0.064. The absolute configuration was determined as (*S*)-configuration by utilizing the anomalous dispersion effect of bromine atom.

The absolute configuration of optically active substituted 1,1′-binaphthyl molecules is of great interest since the molecule has a C_2 symmetry and the rotational strength is very large in spite of simple chromophore structure. The chemical investigations revealed that the rotation around the 1,1′-single bond is restricted when the 2,2′-positions are substituted by the bulky groups.[1,2] Correlation of the absolute configuration with the optical activity of substituted binaphthyls will be important in developing the theory of the optical activity of coupled chromophore systems. The present investigation was undertaken to find the absolute configuration of one of the simplest hindered binaphthyls. The molecular structure and the absolute configuration will be discussed with a reference to the results of binaphthyl[3] and (+)-2,2′-dihydroxy-1,1′-bisnaphthalene-3,3′-dicarboxylic acid dimethyl ester.[4]

Experimental

Optically active (−)-1,1′-bisnaphthalene-2,2′-dicarboxylic acid was prepared according to the method of Hall and Turner[1] and the resolution was performed by successive recrystallization of diastereoisomer with quinine until the value of optical rotation gave an agreement with the reported one. The acid groups were reduced to hydroxymethyl groups and then transformed into bromomethyl groups. The configurations were retained throughout these reactions and it was confirmed by the CD spectral measurement.

The crystals used for crystallographic study were colorless thick plates or transparent prisms obtained from methylethylketone solution. The density was measured by the flotation method. The lattice constants were refined by a least-squares method using twelve reflections on Hilger-Watt four circle diffractometer with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å).

1) D. M. Hall and E. E. Turner, *J. Chem. Soc.*, **1955**, 1242.
2) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).
3) K. A. Kern and J. M. Robertson, *J. Chem. Soc.* (*B*), **1969**, 1146.
4) H. Akimoto and Y. Iitaka, *Acta Crystallogr.*, **B25**, 1941 (1969).

Crystal Data

(*S*)-(−)-2,2′-bisbromomethyl-1,1′-binaphthyl, $C_{22}H_{16}Br_2$, Mol. Wt. 440.2, orthorhombic,

$a=10.360\pm0.002$, $b=13.052\pm0.001$, $c=13.187\pm0.001$ Å

$D_m=1.625$, $D_c=1.639\ g\cdot cm^{-3}$, $Z=4$;

Absent spectra, $h00$, $0k0$, and $00l$ when h, k, or l is odd. Space group, $P2_12_12_1$. The intensity data were collected on the diffractometer using Cu–$K\alpha$ radiation and 2083 independent non-zero reflections were obtained.

Determination of the Structure

From the Patterson map the positions of bromine atom were determined and all of 22 carbon atoms were revealed from an electron density map calculated by the heavy atom method. Positional and thermal parameters were refined by the block-diagonal least-squares method. In the calculation of the structure factors, the anomalous dispersion effect was taken into account. The final R index was 0.064 for 1607 observed reflections with $|F_o|>3\sigma$. The atomic parameters with standard deviations are listed in Table 1, and observed and calculated structure factors are given in Table 2. Least-squares planes of naphthyl groups and the deviations of atoms from these planes are shown in Table 4. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[5]

TABLE 1. FINAL ATOMIC PARAMETERS WITH THEIR STANDARD DEVIATIONS

(1) THE ATOMIC COORDINATES

	x	y	z		x	y	z
Br	0.7492(2)	0.7294(1)	0.2718(1)	Br′	0.9705(2)	0.4481(1)	0.5063(1)
C(1)	0.8271(13)	0.4525(12)	0.2248(10)	C(1′)	0.9664(15)	0.4823(10)	0.2255(11)
C(2)	0.7383(17)	0.5111(10)	0.2793(10)	C(2′)	0.1834(15)	0.4810(11)	0.2950(13)
C(3)	0.6053(15)	0.4823(13)	0.2713(12)	C(3′)	0.0543(13)	0.4493(10)	0.2964(10)
C(4)	0.5627(15)	0.3923(20)	0.2190(13)	C(4′)	0.2259(14)	0.5446(12)	0.2206(13)
C(5)	0.6124(18)	0.2525(13)	0.1103(13)	C(5′)	0.1878(19)	0.6460(12)	0.0613(14)
C(6)	0.6956(20)	0.1868(14)	0.0584(13)	C(6′)	0.1033(18)	0.6772(12)	0.9873(14)
C(7)	0.8362(19)	0.2156(12)	0.0625(12)	C(7′)	0.9759(20)	0.6471(11)	0.9893(13)
C(8)	0.8777(16)	0.3030(11)	0.1188(12)	C(8′)	0.9215(17)	0.5844(12)	0.0679(11)
C(9)	0.7883(14)	0.3649(10)	0.1668(18)	C(9′)	0.0110(15)	0.5498(11)	0.1439(10)
C(10)	0.6518(15)	0.3402(11)	0.1649(12)	C(10′)	0.1421(16)	0.5786(11)	0.1423(11)
C(11)	0.7778(16)	0.5984(10)	0.3420(11)	C(11′)	0.0119(17)	0.3701(12)	0.3768(12)

(2) THE TEMPERATURE FACTORS

The temperature factors are expressed in the form: $T=\exp(-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl))$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.0148(2)	0.0055(1)	0.0065(1)	0.0036(4)	0.0024(3)	0.0025(2)
C(1)	0.0068(14)	0.0062(9)	0.0038(8)	0.0002(22)	0.0012(19)	0.0033(17)
C(2)	0.0082(15)	0.0059(9)	0.0031(8)	0.0015(23)	0.0013(23)	0.0017(14)
C(3)	0.0080(16)	0.0095(14)	0.0055(10)	0.0052(26)	0.0017(23)	0.0076(21)
C(4)	0.0088(18)	0.0067(11)	0.0071(12)	−0.0005(25)	0.0006(26)	0.0026(21)
C(5)	0.0136(23)	0.0065(12)	0.0069(12)	−0.0052(30)	−0.0055(29)	0.0025(20)
C(6)	0.0178(28)	0.0082(13)	0.0056(11)	−0.0023(34)	−0.0031(31)	0.0021(21)
C(7)	0.0173(25)	0.0044(9)	0.0053(10)	0.0028(29)	0.0007(28)	0.0012(17)
C(8)	0.0109(19)	0.0047(9)	0.0055(10)	0.0014(24)	0.0020(25)	−0.0010(17)
C(9)	0.0081(17)	0.0039(8)	0.0045(9)	−0.0024(20)	−0.0007(20)	0.0003(14)
C(10)	0.0080(17)	0.0046(9)	0.0061(11)	−0.0011(22)	−0.0000(24)	0.0032(16)
C(11)	0.0121(22)	0.0037(8)	0.0052(10)	0.0023(24)	0.0050(24)	0.0005(15)
Br′	0.0121(2)	0.0068(1)	0.0045(1)	0.0030(3)	0.0009(3)	0.0009(2)
C(1′)	0.0085(16)	0.0048(9)	0.0045(9)	−0.0015(21)	0.0030(24)	0.0013(15)
C(2′)	0.0080(16)	0.0054(10)	0.0072(12)	−0.0012(23)	−0.0010(25)	−0.0011(18)
C(3′)	0.0075(15)	0.0042(8)	0.0043(8)	−0.0008(21)	0.0013(19)	0.0009(15)
C(4′)	0.0068(17)	0.0064(10)	0.0077(12)	0.0008(24)	0.0004(24)	−0.0025(20)
C(5′)	0.0152(24)	0.0053(10)	0.0086(14)	0.0002(28)	0.0131(32)	−0.0002(20)
C(6′)	0.0160(24)	0.0060(10)	0.0069(12)	0.0015(28)	0.0076(34)	−0.0006(21)
C(7′)	0.0228(28)	0.0047(9)	0.0043(9)	0.0062(30)	0.0027(34)	−0.0005(16)
C(8′)	0.0136(21)	0.0063(11)	0.0032(8)	0.0037(27)	0.0018(23)	−0.0009(15)
C(9′)	0.0108(18)	0.0046(8)	0.0026(7)	0.0013(25)	0.0023(19)	0.0015(14)
C(10′)	0.0107(18)	0.0052(10)	0.0046(10)	−0.0007(24)	0.0029(24)	−0.0023(16)
C(11′)	0.0131(22)	0.0060(10)	0.0045(9)	0.0058(28)	0.0030(25)	0.0017(16)

5) "International Tables for X-ray Crystallography," The Kynoch Press, Birmingham, (1968), Vol. III, pp. 201, 213.

TABLE 2. OBSERVED AND CALCULATED SRTUCTURE FACTORS

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H=K= 0	0		3	24	24	1	123	136	9	22	23	4	69	67	5	17	16	3	32	35	2	64	66	2	24	23
			4	20	22	2	101	96	10	7	5	5	60	56	6	15	14	4	18	20	3	28	30	3	25	21
			5	4	6	3	167	165	11	16	16	6	68	66	7	12	12	5	46	47	4	28	27	4	42	39
			6	29	29	4	26	22	12	7	4	7	20	19	8	22	22	6	37	39	5	84	83	5	17	15
			7	18	14	5	81	77	H=K= 1		11	8	15	15	H=K= 2		15	7	18	20	6	43	41	6	24	23
2	81	81	8	14	13	6	15	15	0	37	35	9	30	29	1	13	11	8	10	9	7	11	6	7	9	8
4	208	208	10	28	27	7	60	57	1	34	34	10	11	11	2	9	10	9	27	28	8	34	32	8	44	41
6	25	24	11	7	7	8	15	15	2	30	29	15	9	9	3	2	7	10	16	16	9	59	58	14	8	9
8	99	95	12	17	18	9	32	31	3	27	25	H=K= 2		5	H=K= 3		0	11	15	16	10	28	29	H=K= 5		1
H=K= 0		1	H=K= 0		10	10	15	14	4	34	32	0	19	21	1	13	13	12	5	9	11	6	6	0	79	81
1	12	13	0	60	60	11	35	35	5	22	20	1	71	75	2	87	83	13	9	10	12	18	18	1	99	94
2	36	43	1	28	26	12	18	20	6	9	8	2	27	27	3	8	9	H=K= 3		8	13	23	25	2	50	46
3	152	144	2	29	26	13	7	7	7	16	14	3	46	43	4	43	44	0	21	20	14	8	8	3	55	50
4	22	21	3	35	33	14	16	18	8	17	17	4	28	30	5	28	26	1	6	4	H=K= 4		4	4	64	58
5	10	7	4	45	41	15	11	15	9	16	16	5	83	84	6	77	73	2	16	15	0	60	62	5	47	44
6	7	1	5	33	33	H=K= 1		4	11	12	12	6	42	42	7	33	29	3	19	20	1	42	42	6	35	34
7	95	93	6	39	37	0	82	90	H=K= 1		12	7	8	7	8	65	59	4	30	28	2	53	53	7	37	35
8	30	31	7	13	14	1	15	17	0	10	11	8	35	35	9	11	9	5	10	10	3	21	24	8	33	32
13	9	11	8	23	24	2	92	97	1	8	8	9	59	60	10	53	52	6	11	11	4	76	75	9	24	22
14	13	15	9	9	7	3	50	46	2	17	15	10	26	25	11	17	15	7	25	24	5	9	7	10	19	17
15	22	26	10	23	24	4	137	135	3	14	14	11	8	9	12	19	19	8	22	24	14	9	12	11	18	18
H=K= 0		2	12	9	11	5	19	18	4	19	18	12	16	18	13	11	10	9	8	8	H=K= 4		5	12	17	19
0	51	56	H=K= 0		11	6	93	91	5	16	14	13	30	33	14	14	19	10	13	14	0	27	30	13	4	6
1	6	6	1	26	24	7	12	12	6	15	12	14	10	11	15	10	12	11	17	19	1	49	50	14	14	17
2	34	42	3	22	20	8	60	60	7	23	21	H=K= 2		6	H=K= 3		1	12	14	16	2	51	54	H=K= 5		2
3	44	41	4	12	11	9	24	24	8	11	10	0	15	15	0	56	55	13	7	9	3	65	68	0	41	41
8	26	25	5	10	8	10	61	62	9	9	7	1	53	55	1	147	144	H=K= 3		9	4	33	34	1	56	51
9	15	13	6	9	8	11	5	5	10	9	10	2	64	66	2	60	57	0	60	60	5	9	11	2	42	39
10	44	42	11	4	3	12	34	35	H=K= 1		13	3	69	69	3	114	108	1	38	39	10	22	23	3	59	56
11	17	16	H=K= 0		12	13	9	10	0	27	25	4	27	27	4	63	59	2	18	16	11	31	32	4	34	32
12	16	17	0	22	20	14	20	22	1	15	13	5	41	40	5	69	66	3	37	38	12	16	17	5	15	13
13	4	3	1	38	34	15	3	4	2	28	26	6	31	31	6	17	17	4	45	44	14	7	9	6	38	36
14	24	26	2	14	13	H=K= 1		5	3	12	11	7	28	29	7	63	59	5	40	38	H=K= 4		6	7	43	44
15	8	8	3	28	25	0	28	30	4	24	23	8	13	13	8	24	24	6	12	13	0	46	47	8	28	25
H=K= 0		3	4	18	16	1	67	72	H=K= 1		14	9	26	26	9	52	49	7	12	11	1	66	65	9	7	7
1	166	190	5	29	30	2	76	75	0	26	25	14	3	4	10	21	20	8	25	25	2	27	29	10	29	28
2	3	2	6	10	9	3	40	43	1	6	7	H=K= 2		7	11	21	19	9	19	18	3	33	35	11	21	21
3	42	39	7	17	16	4	40	37	2	16	16	0	35	35	12	12	15	10	4	1	4	41	41	12	9	10
H=K= 0		4	8	16	14	5	34	36	3	10	9	1	40	42	13	16	17	11	12	12	5	30	30	13	7	10
0	103	114	9	9	8	6	41	40	4	13	12	2	39	41	14	9	12	12	12	13	6	8	10	14	9	12
1	29	34	10	5	5	7	2	3	5	13	15	3	62	63	15	9	11	H=K= 3		10	7	17	19	H=K= 5		3
2	111	113	H=K= 0		13	8	34	34	6	12	11	4	17	16	H=K= 3		2	5	32	32	8	15	15	0	6	3
3	96	92	1	22	22	9	23	24	H=K= 1		15	5	18	17	0	57	63	6	18	17	9	28	29	1	53	56
4	117	118	3	9	7	14	7	10	0	16	15	6	19	18	1	43	37	7	19	20	10	8	4	2	33	36
5	77	77	4	14	12	H=K= 1		6	1	5	7	7	50	50	2	60	55	8	8	9	H=K= 4		7	3	62	60
6	65	63	5	18	18	0	85	84	2	15	15	8	22	21	3	23	21	H=K= 3		11	0	34	33	4	4	5
7	40	39	6	18	18	1	20	18	3	11	11	9	8	9	4	35	35	0	23	21	1	35	37	5	44	44
8	37	36	7	13	14	2	59	62	4	8	10	H=K= 2		8	5	37	33	1	21	18	2	39	36	6	34	34
9	25	28	8	15	17	3	39	39	H=K= 2		0	0	73	73	6	42	39	2	48	46	3	11	8	7	32	30
10	14	15	H=K= 0		14	4	97	96	0	23	25	1	59	56	7	16	12	3	16	14	4	26	27	8	18	16
11	12	14	0	6	4	5	30	30	1	59	58	2	9	9	8	44	43	4	12	12	5	44	42	10	15	16
12	8	9	1	21	21	6	49	48	2	228	238	3	37	40	9	14	14	5	23	22	6	23	24	11	14	14
13	17	17	2	3	2	7	36	39	3	50	47	4	53	53	10	33	30	6	30	30	7	8	10	H=K= 5		4
14	12	13	3	15	13	8	34	33	4	10	8	5	33	33	11	13	14	7	9	9	8	26	27	0	32	33
15	11	14	4	3	1	9	42	42	5	20	19	6	36	39	12	21	23	H=K= 3		12	9	23	22	1	43	46
H=K= 0		5	5	8	7	10	42	43	6	134	124	7	22	22	13	21	24	0	16	15	10	12	14	2	38	39
1	60	63	6	9	5	11	27	29	7	72	63	8	23	24	14	11	12	1	18	17	11	9	9	3	51	50
2	26	29	7	12	11	12	22	22	8	65	59	9	20	20	15	7	5	2	15	14	12	17	18	4	36	37
3	50	52	H=K= 0		15	13	9	7	9	5	5	10	17	19	H=K= 3		3	H=K= 3		13	13	16	17	5	37	37
4	12	11	1	13	10	14	16	17	10	62	58	11	7	8	0	57	60	0	27	24	H=K= 4		8	6	32	30
5	51	46	2	6	7	H=K= 1		7	11	19	18	12	13	13	1	85	89	1	17	15	0	12	11	7	17	18
6	71	67	3	8	6	0	45	45	12	23	24	13	11	12	2	23	18	2	23	24	H=K= 4		9	8	41	40
7	96	94	4	7	9	1	67	67	13	8	8	H=K= 2		9	3	72	64	3	10	10	0	4	1	9	29	30
8	35	34	H=K= 1		0	2	32	32	14	15	16	0	12	12	4	70	64	H=K= 3		15	1	17	17	10	28	29
9	10	10	1	72	68	3	64	66	15	1	5	1	12	12	5	78	76	0	13	15	2	18	14	11	8	9
10	12	14	2	20	19	4	49	49	H=K= 2		1	2	17	17	6	18	18	1	13	12	3	18	15	12	20	22
11	51	52	3	26	16	5	61	60	0	20	21	3	9	7	7	40	38	2	7	7	4	12	14	13	18	21
12	23	25	4	80	71	6	30	31	1	119	117	4	35	36	8	32	31	H=K= 4		0	5	17	17	H=K= 5		5
13	9	9	5	46	39	7	24	22	2	44	41	5	30	28	9	22	21	0	146	151	6	15	17	0	15	19
H=K= 0		6	6	44	42	8	25	25	3	31	30	6	37	35	10	8	7	1	32	33	7	26	25	1	48	47
0	63	63	7	28	26	9	28	28	4	21	19	7	9	10	11	22	21	2	49	42	8	10	11	2	37	35
1	60	60	8	54	52	10	21	22	5	88	82	8	40	42	H=K= 3		4	3	52	50	9	5	5	3	30	30
2	21	25	9	20	21	11	20	22	6	28	29	9	20	21	0	62	66	4	130	125	10	23	24	4	40	40
3	17	17	10	46	45	12	9	9	7	18	18	10	15	16	1	58	62	5	54	54	11	10	11	5	34	37
4	25	28	11	21	22	13	11	15	8	20	18	11	5	2	2	67	68	6	18	15	H=K= 4		10	6	30	30
5	38	36	12	35	36	14	8	10	9	50	49	12	21	23	3	60	59	7	42	41	0	38	38	7	8	8
6	11	8	13	32	34	H=K= 1		8	10	22	21	H=K= 2		10	4	69	68	8	55	53	1	40	35	8	3	3
8	23	24	14	18	19	0	36	36	11	21	21	0	31	30	5	13	13	9	39	37	2	17	18	9	10	11
9	31	30	15	10	10	1	11	10	H=K= 2		2	1	52	49	6	58	57	10	18	18	3	39	37	10	8	9
10	5	6	H=K= 1		1	2	16	17	0	157	197	2	51	48	7	43	43	11	20	21	4	27	26	11	12	12
11	2	0	0	55	66	3	13	13	1	68	61	3	37	36	8	57	55	H=K= 4		1	5	25	24	12	7	8
13	11	9	1	92	91	4	25	23	2	33	31	4	20	18	9	3	5	0	11	13	6	18	17	13	4	3
14	13	14	2	59	54	5	18	21	3	46	44	5	33	31	10	46	46	1	30	30	7	27	28	H=K= 5		6
H=K= 0		7	3	175	170	6	29	31	4	132	123	6	39	39	11	27	27	2	28	28	8	16	17	0	33	32
1	69	66	4	41	37	7	7	8	5	33	28	7	25	25	12	21	23	3	36	31	9	10	9	1	24	25
2	4	1	5	107	102	8	21	22	6	10	6	8	25	26	13	5	5	4	14	13	10	13	15	2	24	24
3	15	16	6	18	16	9	26	28	7	54	48	9	10	9	14	15	16	5	44	43	H=K= 4		11	3	39	38
4	16	18	7	79	72	10	22	22	8	56	55	10	10	12	H=K= 3		5	6	36	31	2	5	7	4	50	50
5	82	86	8	25	24	11	15	16	9	6	1	11	4	4	0	34	37	7	58	53	3	7	4	5	10	11
6	31	30	9	52	49	12	14	13	10	19	17	H=K= 2		11	1	64	65	8	17	16	4	17	16	6	19	19
7	12	13	10	9	8	13	12	15	11	11	11	3	14	13	2	22	23	9	17	18	5	8	8	7	47	49
8	20	22	11	48	46	H=K= 1		9	12	20	21	4	10	9	3	45	44	10	13	11	10	11	11	8	24	24
9	47	50	12	16	16	0	52	52	13	11	12	5	26	26	4	61	60	11	34	33	H=K= 4		12	9	6	5
10	7	9	13	8	8	1	36	34	14	17	21	6	15	15	5	21	24	12	12	12	0	23	21	10	15	16
11	10	8	14	10	10	2	62	59	H=K= 2		3	7	6	5	6	25	26	13	17	17	1	23	22	11	24	26
12	15	17	15	15	19	3	43	40	0	14	17	8	2	6	7	30	30	14	10	9	2	13	10	12	16	16
13	20	22	H=K= 1		2	4	34	32	1	90	91	9	12	14	8	17	13	H=K= 4		2	3	23	23	H=K= 5		7
H=K= 0		8	0	15	16	5	42	40	2	36	35	10	19	18	9	5	7	0	22	19	4	4	5	0	50	52
0	19	18	1	64	63	6	32	31	3	79	75	H=K= 2		12	10	13	13	1	50	50	5	16	17	1	32	31
1	79	78	2	40	38	7	21	22	4	12	10	0	20	19	H=K= 3		6	2	115	114	H=K= 4		13	2	17	19
2	87	88	3	108	98	8	13	11	5	12	12	1	20	19	0	35	36	3	48	45	0	5	7	11	9	12
3	49	48	4	66	64	9	22	23	6	31	30	2	14	14	1	27	27	4	23	21	1	19	19	12	14	17
4	17	19	5	36	37	10	9	10	7	118	112	3	26	23	2	62	62	5	44	41	2	19	18	H=K= 5		8
5	29	26	6	72	69	11	22	23	8	44	41	4	8	6	3	19	17	6	74	70	3	7	5	0	14	16
6	49	51	7	14	12	12	5	6	9	2	6	5	20	20	4	65	65	7	28	27	4	11	12	1	27	28
7	16	16	8	64	60	H=K= 1		10	10	12	12	6	23	20	5	48	48	8	17	16	5	14	14	2	11	8
8	22	22	9	15	13	0	12	10	11	56	55	7	13	14	6	55	53	9	24	23	6	14	15	3	9	9
9	5	4	10	50	48	1	7	9	12	19	18	8	13	10	7	11	14	10	30	29	7	6	5	4	16	13
10	12	14	11	19	19	2	8	8	14	9	7	9	7	0	12	22	24	11	15	15	H=K= 4		14	5	26	28
11	15	18	12	18	17	3	25	24	15	19	23	H=K= 2		13	13	15	19	12	16	17	1	15	15	6	22	23
12	18	19	13	16	17	4	8	9	H=K= 2		4	0	22	21	14	11	13	13	12	12	2	4	5	7	2	5
13	3	3	14	14	16	5	27	28	0	65	70	1	20	19	H=K= 3		7	14	9	8	3	15	17	8	9	10
H=K= 0		9	15	9	11	6	13	12	1	32	32	2	7	4	0	21	23	H=K= 4		3	4	5	4	9	15	15
1	16	15	H=K= 1		3	7	29	30	2	87	92	3	11	10	1	53	52	0	8	5	H=K= 5		0	10	13	13
2	38	35	0	19	22	8	12	13	3	32	29	4	17	15	2	68	67	1	42	40	1	59	55	11	5	5

Table 2. Continued

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
12	7	3	1	14	13	1	24	23	H,K=	6	11	3	32	32	3	9	10	6	26	27	2	13	13	H,K=	10	1
H,K=	5	9	2	16	12	2	44	45	4	10	8	4	21	22	4	7	5	7	15	15	3	16	16	7	10	11
0	29	30	3	20	20	3	1	4	6	14	18	5	31	30	5	5	7	H,K=	8	6	4	12	10	8	5	5
1	15	13	4	19	19	4	45	45	7	3	2	6	23	22	6	7	7	0	11	11	5	5	6	9	9	9
2	69	69	5	36	33	5	34	31	8	10	10	11	8	7	7	8	10	1	24	26	6	12	13	H,K=	10	2
3	30	28	6	13	13	6	29	27	H,K=	6	12	H,K=	7	4	H,K=	8	0	2	14	15	7	12	10	0	7	6
4	8	7	7	14	13	7	9	9	0	17	12	0	19	19	0	32	32	3	25	26	8	8	7	1	17	18
5	21	18	8	10	8	8	40	42	1	13	17	1	24	23	1	31	31	4	4	5	9	4	2	2	20	19
6	37	36	9	32	32	9	21	20	2	10	9	2	11	11	2	24	21	5	10	12	10	10	11	3	9	9
7	10	13	10	15	15	10	24	26	3	14	18	3	44	43	H,K=	8	1	6	8	9	H,K=	9	4	4	5	6
8	11	13	11	24	24	12	12	16	4	3	5	4	31	29	2	14	14	7	8	9	0	20	23	5	12	13
9	9	10	12	12	13	H,K=	6	6	5	8	10	5	15	16	3	27	28	8	3	6	1	23	25	6	9	9
10	13	16	13	7	11	0	32	36	H,K=	6	13	H,K=	7	5	4	9	7	9	5	6	2	11	12	7	10	12
11	8	12	H,K=	6	2	1	29	31	2	9	8	0	29	32	5	18	17	H,K=	8	8	H,K=	9	5	8	0	4
H,K=	5	10	0	58	62	2	30	27	3	3	6	1	22	21	6	6	8	0	14	11	0	23	25	9	4	7
0	9	9	1	38	40	3	39	43	4	12	14	2	18	22	7	30	28	1	21	21	1	13	11	H,K=	10	3
1	20	20	2	34	33	4	16	14	H,K=	7	0	3	30	28	8	10	10	2	11	10	2	17	17	0	20	20
2	15	14	3	48	45	H,K=	6	7	4	38	39	4	19	21	9	14	15	3	20	18	3	14	15	1	8	7
3	12	12	4	49	46	0	31	31	5	2	2	5	15	13	H,K=	8	2	4	12	11	4	5	7	2	9	11
4	9	10	5	29	28	1	14	14	6	56	55	6	18	17	0	28	30	5	12	13	5	14	13	3	4	1
5	18	17	6	15	13	2	8	10	7	19	19	7	17	19	1	36	37	6	9	10	6	8	9	4	13	13
6	2	2	7	40	39	3	33	31	12	10	14	H,K=	7	6	2	34	32	7	13	18	9	7	7	H,K=	10	4
7	14	15	8	34	36	4	32	31	13	4	7	4	8	9	3	37	37	H,K=	8	10	H,K=	9	6	0	10	11
8	12	12	9	19	18	5	7	7	H,K=	7	1	5	21	24	4	24	21	0	5	5	0	15	14	1	9	11
9	12	16	10	5	5	6	15	14	0	26	25	6	16	14	5	16	16	1	15	22	1	12	13	2	11	10
10	3	2	11	20	19	7	25	25	1	46	42	7	12	12	6	18	17	2	1	1	2	11	11	3	5	6
H,K=	5	11	12	6	5	8	17	18	2	53	48	1	35	36	7	22	21	3	8	18	3	25	25	4	8	8
0	28	27	13	8	13	9	9	9	3	40	39	2	11	11	H,K=	8	3	H,K=	9	0	4	6	8	5	8	7
1	11	10	H,K=	6	3	10	14	17	4	43	41	3	25	25	0	25	29	2	6	8	5	9	9	6	8	7
H,K=	5	12	0	31	33	11	14	16	5	31	33	8	5	5	1	16	18	4	17	18	H,K=	9	7	8	3	5
1	8	10	1	23	20	H,K=	6	8	6	37	37	9	18	20	2	25	25	5	18	19	0	13	12	H,K=	10	5
2	5	4	2	38	40	0	29	28	7	5	4	10	10	11	3	22	18	6	11	13	1	14	13	0	16	19
3	16	16	3	26	27	1	36	35	8	32	31	11	9	6	4	24	25	H,K=	9	1	3	14	13	1	1	5
4	7	7	4	42	41	2	19	17	9	2	4	H,K=	7	7	5	10	9	0	29	29	4	15	16	2	17	14
5	2	6	5	15	13	3	24	24	10	20	20	0	4	3	6	20	21	1	22	20	6	2	6	3	10	10
6	9	8	6	28	29	4	20	17	11	11	12	1	18	17	7	7	7	2	22	20	7	4	5	4	13	15
7	16	19	7	51	51	5	23	22	12	13	17	2	32	32	8	20	20	3	20	19	8	9	11	5	4	3
H,K=	5	13	8	20	20	6	8	11	13	6	5	3	24	26	9	21	19	4	33	32	H,K=	9	8	6	10	12
2	19	20	9	17	17	7	19	21	H,K=	7	2	4	3	7	11	12	16	5	22	21	0	7	7	7	9	10
3	7	9	10	19	17	8	10	9	0	7	4	5	15	13	H,K=	8	4	6	18	16	1	13	12	H,K=	10	8
4	9	9	11	19	20	H,K=	6	9	1	29	28	6	20	22	0	33	33	7	3	7	2	9	9	0	1	1
5	9	10	12	12	14	4	12	12	2	10	11	7	7	7	1	9	9	8	12	14	3	4	6	1	10	14
H,K=	6	0	13	3	6	5	8	8	3	34	31	8	6	5	2	22	22	9	7	7	4	7	9	2	8	7
0	12	17	H,K=	6	4	6	8	9	4	5	6	9	2	3	3	16	17	10	12	16	5	8	10	H,K=	11	0
1	43	45	0	33	35	7	9	9	5	26	26	10	13	15	4	20	22	H,K=	9	2	6	9	12	6	0	3
2	87	83	1	22	23	H,K=	6	10	6	9	9	H,K=	7	9	5	7	8	3	25	24	7	4	3	H,K=	11	1
3	61	56	2	46	46	0	11	14	7	22	21	0	52	48	6	15	15	4	4	6	H,K=	10	0	0	6	9
4	34	32	3	21	21	1	30	29	8	7	6	1	7	7	7	11	11	5	15	14	0	22	20	1	13	12
5	31	29	4	20	18	2	16	15	9	20	19	2	8	6	8	9	10	6	18	15	1	22	21	H,K=	11	2
6	54	51	5	9	8	3	33	35	10	10	11	7	5	5	H,K=	8	5	7	9	11	2	15	16	6	5	3
7	29	28	6	27	25	4	7	6	11	12	12	8	17	21	0	43	47	8	5	5	3	16	14	H,K=	11	3
8	6	3	7	18	19	5	21	20	12	11	14	9	2	0	1	14	16	9	6	8	4	20	20	0	10	12
9	22	20	8	11	10	6	12	13	H,K=	7	3	H,K=	7	10	2	24	24	10	12	14	5	17	18	H,K=	11	7
10	8	6	9	14	16	7	12	14	0	28	31	0	5	3	3	14	15	H,K=	9	3	7	8	11	1	6	5
H,K=	6	1	H,K=	6	5	8	5	8	1	29	29	1	13	11	4	22	21	0	8	6	8	3	4	2	11	11
0	6	9	0	40	42	9	13	14	2	16	17	2	2	3	5	10	11	1	16	18	9	8	9			

Table 3. A comparison of calculated and observed intensity ratios of the Friedel's pair

h	k	l	$I_c(hkl)/I_c(\bar{h}\bar{k}\bar{l})$	$I_o(hkl)/I_o(hkl)$
1	3	13	0.63	0.89
2	4	10	0.67	0.77
2	13	2	1.72	2.60
3	1	6	1.78	1.35
4	4	5	0.67	0.74
4	7	3	1.58	1.61
7	2	10	1.61	1.21
5	8	2	0.46	0.91
7	2	6	0.46	0.70
8	1	4	1.58	1.16

Absolute Configuration

The absolute configuration of (−)-2,2′-bisbromomethyl-1,1′-binaphthyl was determined by the Bijvoet method using the values of $\Delta f' = -0.9$ and $\Delta f'' = 1.5$ for bromine atom.[5] A comparison of calculated and observed intensity ratios for hkl and $\bar{h}\bar{k}\bar{l}$ reflections is shown in Table 3 and the coordinates given in Table 1 are shown to be the correct ones in the right-handed coordinate system. Thus the absolute configuration can be designated as (*S*). All figures are drawn with the correct absolute configuration.

Results and Discussion

The present analysis showed that the absolute configuration of (−)-2,2′-bisbromomethyl-1,1′-binaphthyl is (*S*)-configuration. The chemical studies on (−)-2,2′-dihydroxymethyl-1,1′-binaphthyl and (−)-1,1′-bisnaphthalene-2,2′-dicarboxylic acid showed that the configurations were retained, so that all these related molecules have (*S*)-configuration. This result is in good agreement with the chemical correlation studies on substituted binaphthyls[2,6] and the X-ray study of Akimoto and Iitaka[4] on (+)-2,2′-dihydroxy-1,1′-bis-

Table 4. Least-squares planes and the deviation of atoms from the planes

The planes are of the form $AX+BX+CZ+P=0$, where X,Y,Z are coordinates measured along three cell edges in Å unit.

Naphthyl group I $0.113X-0.569Y+0.814Z+0.034=0$		Naphthyl group II $0.222X+0.801Y+0.556Z+6.771=0$	
C(1)	−0.02Å	C(1′)	0.00Å
C(2)	0.03	C(2′)	−0.03
C(3)	0.00	C(3′)	0.00
C(4)	0.02	C(4′)	0.02
C(5)	−0.01	C(5′)	0.00
C(6)	0.02	C(6′)	−0.02
C(7)	0.01	C(7′)	0.00
C(8)	0.01	C(8′)	0.02
C(9)	−0.03	C(9′)	0.01
C(10)	−0.03	C(10′)	0.00
C(11)	0.10	C(11′)	0.17

6) H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Lett.* **1968**, 97.

Table 5. Comparison of bond lengths and angles

Molecule	Bond length between C(1) and C(1′)	Twist angle between two planes
1,1′-Binaphthyl[3]	1.475Å	68°
(+)-2,2′-Dihydroxy-1,1′-bisnaphthalene-3,3′-dicarboxylic acid dimethyl ester[4]	1.49Å	76.6°
(−)-2,2′-Bisbromomethyl-1,1′-binaphthyl	1.50Å	91.6°

naphthalene-3,3′-dicarboxylic acid dimethyl ester, which was shown as (*R*)-configuration.

The naphthyl groups are nearly planar (Table 4). One naphthyl group is twisted against the other one with an angle of 91.6°. The values for other related molecules are listed in Table 5. It is interesting that the present molecule exhibits the largest twist angle, which may be related to the steric repulsion of bulky substituents such as bromomethyl group.

The bond lengths and angles are shown in Figs. 1 and 2. The bond length between C(1) and C(1′) is close to the normal single bond like those in other related molecules, and the resonance effect may not be significant. The projection of molecules onto the crystallographic planes are illustrated in Figs. 3 and 4 with interatomic distances.

The absolute configuration determined as (*S*)-configuration will be used for the chiro-optical study of (−)-binaphthyl derivatives.

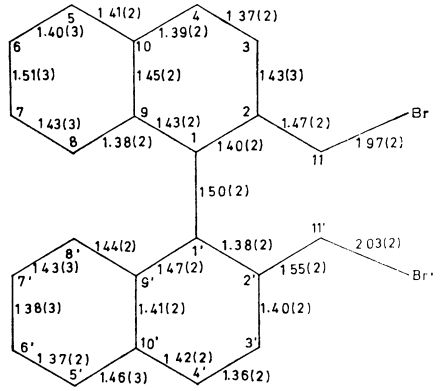

Fig. 1. Bond lengths (Å) with standard deviations.

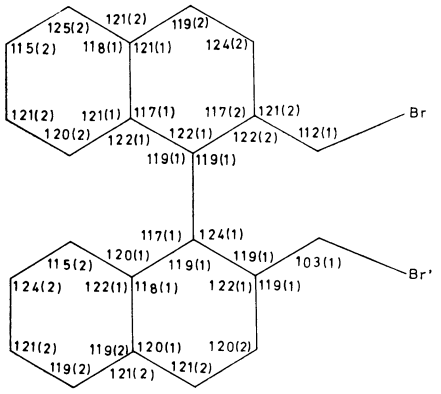

Fig. 2. Bond angles (degree) with standard deviations.

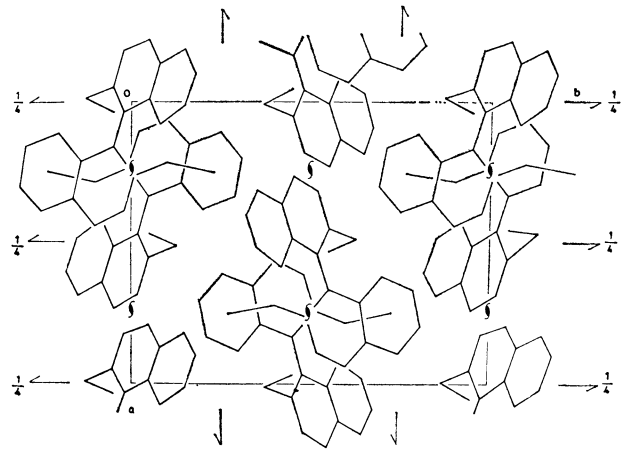

Fig. 3. Projection of the crystal structure along the c-axis.

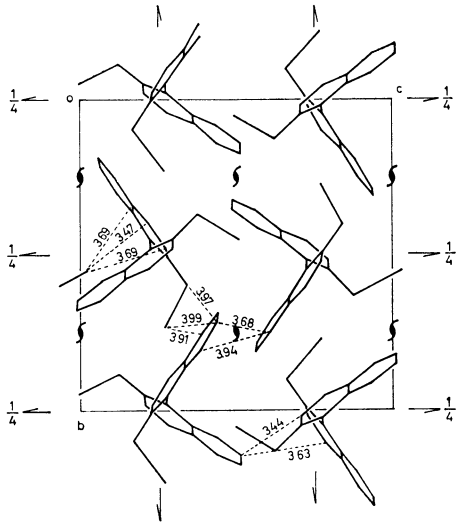

Fig. 4. Projection of the crystal structure along the a-axis.

The authors thank to Dr. Noriyoshi Sakabe in this laboratory for many helpful discussions. All calculations were carried out at the Computation Center of Nagoya University, using the programs of UNICS.[7]

7) "UNICS. A Universal Crystallographic Computation System," The Crystallographic Society of Japan, Tokyo (1967).