NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (6), 1709—1710 (1976)

The Crystal Structure and the Absolute Configuration of (+)-2,3 : 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-diyl Bis(*p*-bromobenzoate)

Tsuguhiro KANEDA, Chuji KATAYAMA, and Jiro TANAKA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

(Received February 26, 1976)

Synopsis. The crystal and the molecular structure of the titled compound was investigated by the X-ray diffraction method. The absolute configuration was determined by the Bijvoet method as 1*R*4*S*5*R*8*S*.

The titled compound was synthesized, optically resolved, and crystallized by Tatemitsu, Ogura, Nakagawa, Nakagawa, Naemura, and Nakazaki.[1] The optical properties of related compounds to it were investigated, and it was desired to determine the absolute configuration of the compound by the X-ray method.

Experimental

The space group of the crystal was determined from oscillation and Weissenberg photographs. The cell dimensions were determined by the least-squares method, using 12 reflections which had been carefully measured on a Hilger-Watts four-circle diffractometer with Ni-filtered Cu$K\alpha$ radiation (λ=1.5418 Å). Crystal data : $C_3H_{22}O_4Br_2$, *M. W.* =618.34, orthorhombic $P2_12_12_1$, a=12.391(1), b=19.802(1), c=10.595(1)Å, z=4, D_m=1.576, D_c=1.580 g·cm^{-3}, μ=46.79 cm^{-1} (for Cu$K\alpha$ radiation). Intensity data were collected with the diffractometer in the θ-2θ scanning mode ($2\theta \leqq 144°$) with the same radiation using a crystal whose size was 0.2×0.2×0.4 mm. No correction was made for absorption or extinction.

TABLE 1. ATOMIC PARAMETERS (×10^4) AND THEIR STANDARD DEVIATIONS

The anisotropic thermal factors are of the form $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	3939(2)	9820(1)	−4144(1)	133(1)	25(1)	103(1)	−1(1)	17(3)	−2(1)
Br(2)	2612(1)	2943(1)	4721(2)	100(1)	23(1)	230(3)	17(1)	24(4)	−5(2)
O(1)	3584(7)	8581(4)	1814(8)	64(6)	16(2)	78(8)	−14(6)	−34(13)	−2(7)
O(2)	4216(10)	9599(4)	2303(9)	165(13)	21(2)	119(11)	−33(9)	−145(22)	10(9)
O(3)	1961(7)	6342(4)	4439(8)	97(8)	18(2)	84(10)	0(7)	73(16)	3(8)
O(4)	1209(9)	6168(4)	6345(8)	139(11)	22(2)	94(10)	22(9)	82(19)	10(8)
C(1)	3008(12)	7349(6)	5027(11)	113(13)	22(3)	39(10)	−10(11)	40(22)	−6(11)
C(2)	3870(10)	7186(5)	4072(12)	56(8)	20(3)	88(12)	−8(9)	−8(22)	5(11)
C(3)	4141(9)	7662(6)	3147(12)	42(8)	23(3)	83(12)	−2(9)	−3(19)	−9(11)
C(4)	3683(10)	8369(5)	3129(12)	67(10)	16(3)	74(12)	−4(9)	−11(20)	−3(10)
C(5)	2597(11)	8410(5)	3792(11)	67(10)	19(3)	79(13)	−21(10)	19(21)	10(10)
C(6)	1706(10)	8046(5)	3149(13)	60(9)	12(3)	113(15)	−5(8)	28(22)	−6(11)
C(7)	1392(10)	7388(6)	3512(12)	48(9)	21(3)	84(13)	2(9)	18(19)	1(11)
C(8)	1848(11)	7067(5)	4671(13)	97(11)	12(2)	105(15)	−25(10)	44(24)	−4(11)
C(9)	2827(13)	8139(6)	5148(13)	128(15)	23(3)	80(14)	6(12)	43(27)	−15(12)
C(10)	4399(10)	6564(6)	4139(14)	55(9)	23(3)	106(14)	5(9)	−34(23)	1(13)
C(11)	5173(11)	6391(7)	3273(14)	67(10)	27(4)	122(17)	−28(11)	−30(26)	7(14)
C(12)	5427(12)	6835(7)	2291(16)	68(11)	32(4)	139(19)	14(12)	−35(26)	−23(16)
C(13)	4924(11)	7470(6)	2234(12)	62(10)	24(3)	85(15)	−15(10)	6(22)	−3(12)
C(14)	1176(11)	8368(6)	2163(13)	50(9)	22(3)	129(17)	15(10)	−13(23)	−4(13)
C(15)	313(12)	8042(8)	1517(15)	73(11)	36(5)	139(19)	27(13)	−6(27)	−1(18)
C(16)	12(13)	7380(8)	1847(18)	75(12)	35(5)	204(26)	−19(13)	13(35)	12(21)
C(17)	555(11)	7068(7)	2842(16)	72(11)	29(4)	155(21)	−23(13)	16(26)	−20(17)
C(18)	3889(11)	9193(5)	1563(12)	75(10)	15(3)	111(15)	−6(10)	−75(25)	−10(11)
C(19)	3902(10)	9332(5)	137(11)	72(9)	13(2)	82(12)	1(9)	−22(23)	−8(10)
C(20)	3148(11)	9020(6)	−639(12)	74(10)	28(4)	82(15)	−12(11)	−34(23)	−19(13)
C(21)	3119(12)	9171(6)	−1926(13)	88(12)	23(4)	91(14)	5(11)	40(24)	−7(13)
C(22)	3910(11)	9627(6)	−2354(12)	58(9)	21(3)	100(14)	3(10)	−6(23)	−13(11)
C(23)	4681(12)	9939(7)	−1643(14)	92(13)	26(4)	122(17)	−20(12)	−9(27)	14(15)
C(24)	4668(11)	9802(6)	−318(13)	88(11)	23(3)	100(14)	−13(12)	3(23)	−3(14)
C(25)	1638(10)	5956(6)	5419(13)	54(9)	22(3)	98(14)	−10(9)	−4(20)	10(12)
C(26)	1843(10)	5218(6)	5176(12)	58(8)	22(3)	89(13)	1(10)	−9(20)	29(13)
C(27)	2408(14)	5001(6)	4083(13)	99(12)	23(3)	105(14)	6(11)	35(29)	−6(12)
C(28)	2652(13)	4300(7)	3946(15)	94(13)	27(4)	130(18)	13(13)	22(3)	17(15)
C(29)	2305(10)	3868(5)	4900(12)	57(9)	18(3)	106(15)	7(9)	−13(22)	−13(11)
C(30)	1735(12)	4070(7)	5929(16)	80(11)	25(4)	138(18)	12(11)	30(28)	20(16)
C(31)	1483(11)	4752(6)	6055(12)	95(12)	25(4)	79(13)	4(12)	26(23)	13(13)

Structure Determination

The structure was determined by the symbolic addition method using the program coded by Dr. Furusaki in Hokkaido University. An E-map revealed all the atoms except hydrogen atoms. The block-diagonal least-squares refinement was proceeded with anisotropic thermal parameters for all non-hydrogen atoms by using 1929 independent reflections with $|F^\circ| > 3\sigma$. The final R-index was converged to 0.062 with an equal weight for each reflection. The program HBLS-IV coded by Prof. Ashida was utilized for the block-diagonal least-squares refinement. The final atomic parameters with their standard deviations are shown in Table 1.

The atomic scattering factors for all atoms and $\Delta f'$ and $\Delta f''$ values for bromine atom were taken from International Tables for X-ray Crystallography.[2] The computations were carried out on a FACOM 230-60 computer at Nagoya University Computation Center. The table of the observed and calculated structure factors is kept at the office of this Bulletin. (Document No. 7623).

Results and Discussion

Figure 1 shows the atomic labelings, bond distances and angles with their standard deviations. The molecule has a bicyclo[3.3.1]nonadiene ring skeleton, and the bicyclo ring seems to be distorted by the

TABLE 2. DETERMINATION OF THE ABSOLUTE CONFIGURATION

h	k	l	$100\times\{I(hkl)-I(\overline{hkl})\}/I(hkl)$ Obsd	Calcd
1	6	4	−6.0	−8.5
2	2	1	5.3	7.1
2	10	1	9.0	9.3
3	4	2	−6.7	−5.1
4	11	1	−8.7	−9.6
5	8	2	8.2	6.5
6	5	5	−9.1	−7.6
6	6	5	5.3	5.9

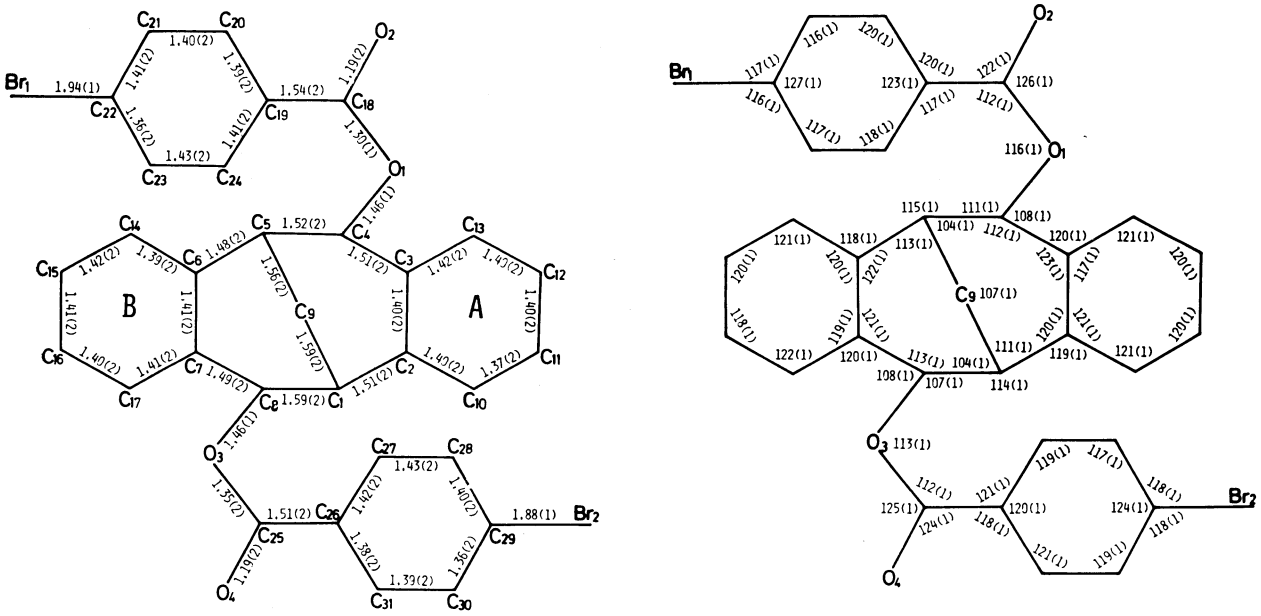

Fig. 1. Bond distances (l/Å), bond angles (ϕ/°) and atomic labelings. The e.s.d.'s are shown in the parentheses. Symbols, A and B, in the benzene rings are the names of the corresponding rings.

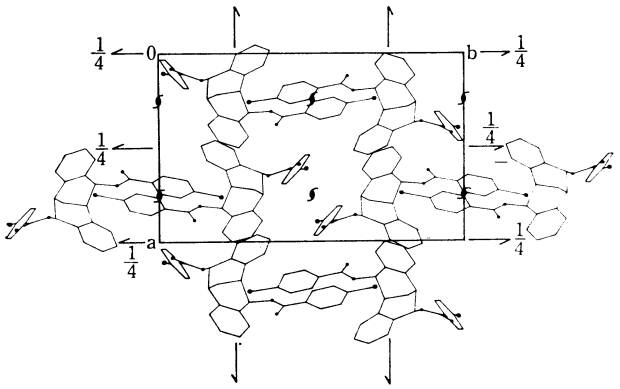

Fig. 2. Projection of the structure along c axis.

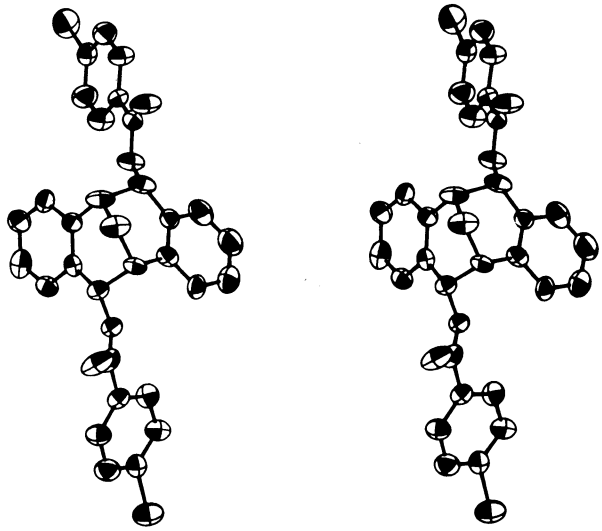

Fig. 3. Stereoscopic view of the molecule. The atoms are represented as thermal ellipsoids of a size such that the vibrating atoms have a 50% probability of being found within them.

presence of the bridge. Bond angles C(2)–C(1)–C(8) and C(4)–C(5)–C(6) are larger by 4.5° and 5.5°, respectively, than the normal tetrahedral angle. On the other hand, C(8)–C(1)–C(9) and C(4)–C(5)–C(9) are both smaller by 5.5° than the normal value. The planarities of two benzene rings, A and B, are good with the maximum deviations by 0.02 and 0.01 Å, respectively, while C(4) deviates by 0.16 Å from the A plane and C(8) by 0.19 Å from the B plane. These considerable deviations are not noticed in (−)-argemonine methiodide which also has bicyclo[3.3.1]nonadiene skeleton.[3] The bond distances and the remaining bond angles show the normal values for the respective bond types. Dihedral angle between the A and B planes is 86.9°, which was 90.4° in (−)-argemonine methiodide. Projection of the structure along the c axis is shown in Fig. 2. No particularly short intermolecular contact was found in this crystal.

The absolute configuration was determined by the Bijvoet method using the anomalous scattering by the bromine atom. The observed and calculated intensity differences between 8 pairs are listed in Table 2. The signs of observed values are in good agreement with those calculated based on the positional parameters of Table 1 in the right-handed coordinate system. The absolute configuration thus determined is 1*R*4*S*5*R*8*S* for (+)-enantiomer (Fig. 3).

References

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3) T. Kaneda, N. Sakabe, and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **49**, 1263 (1976).