The Crystal Structure of (+)-2,5-Dimethoxy-8-Chlorotriptycene

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(Received November 16, 1973)

The crystal structure of (+)-2,5-dimethoxy-8-chlorotriptycene has been investigated by the X-ray method. The crystal system is monoclinic, and the space group is $P2_1$. The cell dimensions are $a=8.231$, $b=13.320$, $c=8.156$ Å, and $\beta=96.49°$. The structure was deduced from the Patterson map and from the calculation of the R-factor minimized by varying the rotational and translational parameters. The structure parameters were refined by the block-diagonal least-squares method by using 1227 independent reflections; the final R-value was 0.073. The absolute configuration was determined to be 1R6S from the Cu$K\alpha$ anomalous scattering of the chlorine atom.

Triptycene has a rigid molecular skeleton, with a three-fold symmetry axis. The crystal structures of several triptycene derivatives have been investigated,[1–5] and the high symmetry of the molecular structure has been characterized. A series of optically-active substituted triptycenes were synthesized by Ogura, Nakagawa, and their co-workers,[6–8] and the theoretical analysis of their circular dichroism spectra was carried out by the exciton method.[9–11] It was found that the absolute configuration of (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide, as determined by the X-ray method, was not in agreement with that deduced by the analysis of the CD spectra.[5,9–11] The disagreement between the X-ray and CD analysis is serious problem for the foundation of stereochemistry; further investigation with other derivatives is earnestly desired.

The triptycene derivatives thus far studied have substitutents at the 2, 5, and 7-carbon atoms; however, other derivatives with substituents at different positions are also of much interest. The present investigation was undertaken in order to determine the absolute configuration of (+)-2,5-dimethoxy-8-chlorotriptycene in order to confirm the absolute configuration by the X-ray method.

Experimental

The (+)-2,5-dimethoxy-8-chlorotriptycene was synthesized and crystallized from the petroleum ether by Dr. Ogura. The space group was determined from oscillation and Weissenberg photographs. The density was measured by the flotation method in a mixed solution of cyclohexane and carbon tetrachloride. 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 ($\lambda=1.5418$ Å). The intensity data were also measured on the diffractometer in the ω-2θ scanning mode ($\theta \leq 72°$) with the same radiation, using a crystal whose size was $0.3 \times 0.3 \times 0.5$ mm^3.

Table 1. Crystal data

M. F. : $C_{22}H_{17}O_2Cl$
M. W. $=348.83$
Crystal system: monoclinic
Systematic absences: $0k0$ when k is odd.
Space group: $P2_1$
$a=8.231 \pm 0.002$, $b=13.320 \pm 0.002$,
$c=8.156 \pm 0.001$ Å; $\beta=96.49 \pm 0.01°$
$V=886.5$ Å^3, $Z=2$,
$D_m=1.280$, $D_c=1.284$ g·cm^{-3},
$F(000)=364$, $\mu=21.29$ cm^{-1} (for Cu$K\alpha$)

1378 independent reflections were obtained, and no correction was made for absorption or extinction. The crystal data are shown in Table 1.

Structure Analysis

Since the molecule is rigid and since the bond lengths of related molecules are known,[5] the position of each atom may be easily estimated when the translational and rotational parameters of the molecule in the unit cell can be determined. The direction of the pseudo-three-fold axis could be easily found from the Patterson map, because the carbon-carbon vectors with lengths of ~1.4 Å and ~2.8 Å were superposed six and four times respectively along the axis. This implies that two of the rotational parameters, ω and χ, can be determined and that only the ϕ parameter remains to fix the rotational freedom (see Fig. 1).

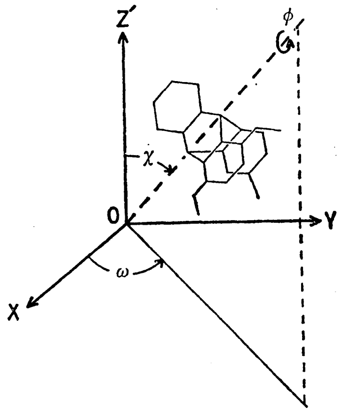

Fig. 1. Definition of rotational parameters with respect to the Cartesian coordinate axes.[12]

The translational and rotational searches were performed by the calculation of the R-values on the basis of the assumed model, which is rotated around the ϕ-axis and translated in the ac plane. Twenty-three $h0l$ reflections within $\theta < 30°$ were selected for this calculation. The angle of the ϕ parameter was changed in the range from 0 to 2π with an interval of $\pi/90$ radian. At each setting of ϕ, the molecule was successively

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translated in the *ac* plane by 1/50 for both Δx and Δz, and the *R*-value was calculated at each point. The position of the minimum *R*-value(0.30) was easily found on the *R*-map thus prepared. The calculation could be done within ten minutes machine time on the FACOM 230-60. Further refinement, using all the three-dimensional reflection data, confirmed that the position was actually adequate. The origin was adjusted so as to put all the *y*-parameters of atoms belonging to one molecule in the range from 0 to one.

The diagonal least-squares method was applied for the refinement of structure parameters by using 1227

TABLE 2. ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS

	x	*y*	*z*
C (1)	0.4281(12)	0.4415(8)	0.3635(12)
C (2)	0.7310(11)	0.4379(8)	0.2961(12)
C (3)	0.8900(12)	0.4587(8)	0.3461(13)
C (4)	0.9373(12)	0.5042(8)	0.5005(13)
C (5)	0.8153(11)	0.5312(8)	0.5988(11)
C (6)	0.5095(12)	0.5350(8)	0.6413(12)
C (7)	0.3878(13)	0.3929(9)	0.8085(11)
C (8)	0.3108(13)	0.3022(9)	0.8033(12)
C (9)	0.2677(12)	0.2499(10)	0.6602(12)
C (10)	0.2993(13)	0.2939(8)	0.5129(12)
C (11)	0.2424(12)	0.5876(9)	0.2469(13)
C (12)	0.1775(13)	0.6829(9)	0.2753(14)
C (13)	0.2189(14)	0.7324(9)	0.4226(14)
C (14)	0.3270(12)	0.6882(8)	0.5457(13)
C (15)	0.6089(11)	0.4610(7)	0.3958(11)
C (16)	0.6560(11)	0.5108(7)	0.5488(12)
C (17)	0.4241(11)	0.4361(7)	0.6624(11)
C (18)	0.3788(11)	0.3845(8)	0.5124(11)
C (19)	0.3477(11)	0.5459(8)	0.3704(12)
C (20)	0.3899(10)	0.5958(8)	0.5209(11)
C (21)	0.7886(16)	0.3721(13)	0.0349(15)
C (22)	1.0172(14)	0.5977(12)	0.8079(16)
O (1)	0.6712(9)	0.3902(6)	0.1487(8)
O (2)	0.8467(7)	0.5790(6)	0.7495(8)
Cl	0.2712(5)	0.2452(4)	0.9903(4)

Atomic coordinates of hydrogen atoms

	x	*y*	*z*
H(C1)	0.370	0.401	0.254
H(C3)	0.987	0.447	0.265
H(C4)	1.076	0.515	0.541
H(C6)	0.555	0.571	0.760
H(C7)	0.416	0.419	0.915
H(C9)	0.212	0.174	0.648
H(C10)	0.278	0.260	0.427
H(C11)	0.222	0.545	0.147
H(C12)	0.065	0.725	0.200
H(C13)	0.175	0.793	0.445
H(C14)	0.349	0.719	0.631

TABLE 3. ANISOTROPIC THERMAL FACTORS* ($\times 10^4$) AND THEIR STANDARD DEVIATIONS

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C (1)	126(17)	41(7)	97(15)	−13(16)	42(25)	−13(16)
C (2)	149(18)	41(7)	111(16)	23(17)	110(28)	15(17)
C (3)	105(17)	55(8)	151(18)	7(18)	106(28)	−1(20)
C (4)	115(16)	50(7)	141(17)	−27(18)	71(28)	−40(19)
C (5)	95(15)	50(7)	98(16)	−19(16)	19(24)	14(17)
C (6)	126(17)	43(6)	106(16)	−27(17)	75(25)	−55(17)
C (7)	149(18)	58(8)	78(15)	−31(19)	34(25)	0(18)
C (8)	171(21)	66(9)	97(16)	−56(21)	87(30)	50(20)
C (9)	132(18)	66(8)	147(18)	−61(22)	94(29)	42(23)
C (10)	156(19)	62(8)	98(17)	−11(20)	14(29)	−34(19)
C (11)	105(16)	66(8)	134(18)	8(20)	24(27)	41(20)
C (12)	135(19)	46(7)	173(21)	14(19)	−12(31)	47(21)
C (13)	158(21)	50(8)	203(20)	−21(21)	64(33)	18(24)
C (14)	104(17)	36(6)	175(20)	31(17)	26(29)	−29(18)
C (15)	95(15)	42(6)	96(14)	12(15)	52(23)	−17(16)
C (16)	89(14)	36(6)	115(15)	21(15)	31(23)	−4(16)
C (17)	100(16)	41(6)	102(15)	−3(16)	28(24)	−19(16)
C (18)	101(15)	46(7)	105(15)	−30(17)	37(24)	5(17)
C (19)	92(15)	41(7)	116(16)	19(16)	12(24)	18(17)
C (20)	58(13)	60(7)	107(16)	12(16)	−3(22)	−19(18)
C (21)	214(27)	136(14)	149(22)	57(32)	176(38)	−89(30)
C (22)	127(20)	135(15)	191(24)	−66(30)	−36(43)	−133(32)
O (1)	180(14)	76(6)	93(11)	−9(16)	77(19)	−64(14)
O (2)	98(10)	62(5)	124(11)	1(13)	1(17)	−47(13)
Cl	335(8)	112(3)	147(5)	−175(9)	75(10)	54(7)

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

independent reflections with $|F^0|>6\sigma$, and the R-index was reduced to 0.130. Additional block-diagonal least-squares refinement was carried out with anisotropic thermal factors, and the R-index was converged to 0.097. The hydrogen atoms attached to the benzene rings and those attached to the bridge-head carbons were found on the difference Fourier map. Further refinement, including these hydrogen positions, resulted in the final R-value of 0.073, with an equal weight for each reflection. No other significant peaks were found in the final Fourier and difference Fourier maps.

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[13] The computation was carried out with the programs of UNICS coded by Dr. Ashida and those coded by ourselves on FACOM 230-60 at the Nagoya University Computation Center.

The atomic coordinates, with their standard deviations, and the anisotropic thermal factors, with their standard deviations, are listed in Table 2 and Table 3 respectively. The observed and calculated structure factors are listed in Table 4.[14]

TABLE 5. BOND LENGTHS AND THEIR STANDARD DEVIATIONS

C (2)-C (3)	1.352(15) Å	C (1)-C (15)	1.502(14) Å
C (2)-C (15)	1.395(14)	C (1)-C (18)	1.526(15)
C (3)-C (4)	1.413(16)	C (1)-C (19)	1.541(14)
C (4)-C (5)	1.400(15)	C (6)-C (16)	1.524(14)
C (5)-C (16)	1.354(14)	C (6)-C (17)	1.511(14)
C (15)-C (16)	1.428(14)	C (6)-C (20)	1.540(15)
average	1.390	average	1.524
C (7)-C (8)	1.362(17)	C (2)-O (1)	1.398(13)
C (7)-C (17)	1.387(15)	C (5)-O (2)	1.383(13)
C (8)-C (9)	1.370(17)	C (21)-O (1)	1.432(20)
C (9)-C (10)	1.387(17)	C (22)-O (2)	1.447(18)
C (10)-C (18)	1.372(16)	C (8)-Cl	1.767(13)
C (17)-C (18)	1.415(15)		
average	1.382		
C (11)-C (12)	1.407(17)		
C (11)-C (19)	1.370(16)		
C (12)-C (13)	1.378(17)		
C (13)-C (14)	1.392(17)		
C (14)-C (20)	1.358(15)		
C (19)-C (20)	1.404(15)		
average	1.385		

Results and Discussion

(+)-2,5-Dimethoxy-8-chlorotriptycene is actually a rigid molecule with a pseudo-three-fold axis. The bond lengths and angles are shown in Table 5 and Table 6 respectively. The average bond length around the C(1) and C(6) of the bridge head carbons, 1.52 Å, is in good agreement with the expected value for an sp^2-sp^3 carbon bond.[15] The bonds which form the bicyclo-2,2,2-octatriene ring are longer than the normal value of the benzene ring by 0.02∼0.04 Å. The tetrahedral angles around the bridge-head carbons are smaller by 2.4∼4.6° than the normal tetrahedral angle. The external angles made by the bicyclo-2,2,2-octatriene ring and the benzenoid ring are about 127°, while the internal angles are about 113°. These results mean that a significant strain is exerted on the part of the

TABLE 6. BOND ANGLES AND THEIR STANDARD DEVIATIONS

C (3)-C (2)-C (15)	120.8(10) °	C (15)-C (1)-C (18)	107.1(8) °
C (2)-C (3)-C (4)	121.1(10)	C (15)-C (1)-C (19)	104.9(8)
C (3)-C (4)-C (5)	118.5(10)	C (18)-C (1)-C (19)	105.4(8)
C (4)-C (5)-C (16)	120.5(10)	C (16)-C (6)-C (17)	106.0(8)
C (2)-C (15)-C (16)	118.1(9)	C (16)-C (6)-C (20)	106.1(8)
C (5)-C (16)-C (15)	120.8(9)	C (17)-C (6)-C (20)	105.1(8)
C (8)-C (7)-C (17)	118.9(11) °	C (6)-C (17)-C (18)	113.9(10) °
C (7)-C (8)-C (9)	123.6(11)	C (1)-C (15)-C (16)	113.4(8)
C (8)-C (9)-C (10)	117.8(11)	C (6)-C (16)-C (15)	112.4(8)
C (9)-C (10)-C (18)	120.7(11)	C (1)-C (18)-C (17)	112.2(9)
C (7)-C (17)-C (18)	118.8(10)	C (1)-C (19)-C (20)	113.3(9)
C (10)-C (18)-C (17)	120.2(10)	C (6)-C (20)-C (19)	112.6(9)
C (12)-C (11)-C (19)	117.7(11) °	C (1)-C (15)-C (2)	128.5(9) °
C (11)-C (12)-C (13)	120.9(11)	C (5)-C (16)-C (6)	126.8(9)
C (12)-C (13)-C (14)	120.1(11)	C (6)-C (17)-C (7)	127.3(9)
C (13)-C (14)-C (20)	119.8(10)	C (1)-C (18)-C (10)	127.6(10)
C (11)-C (19)-C (20)	121.5(10)	C (1)-C (19)-C (11)	125.2(10)
C (14)-C (20)-C (19)	119.9(10)	C (6)-C (20)-C (14)	127.5(10)
C (3)-C (2)-O (1)	125.9(10) °	Cl-C (8)-C (7)	118.9(9) °
C (15)-C (2)-O (1)	113.3(9)	Cl-C (8)-C (9)	117.4(9)
C (4)-C (5)-O (2)	123.6(9)		
C (16)-C (5)-O (2)	115.9(9)		
C (2)-O (1)-C (21)	115.9(10)		
C (5)-O (2)-C (22)	116.7(9)		

bicyclo-2,2,2-octatriene ring of the triptycene skeleton. A similar trend is found in the results of previous studies.[1-5)]

The least-squares planes of three benzene rings are given by the following equations;

(1) Benzene ring:

$$0.8201X+0.4291Y-0.3786Z'-4.0490=0$$

(2) Chlorobenzene ring:

$$0.8823X-0.4620Y+0.0906Z'-0.3395=0$$

(3) Dimethoxybenzene ring:

$$-0.0524X+0.8942Y-0.4446Z'-3.8398=0$$

where X, Y, and Z' are coordinates in Å along the a, b, and c* axes respectively. The deviations of atoms from these planes are shown in Table 7. The planarity of the three benzene rings is remarkably good. The chlorine atom is nearly on the ring plane, and bridgehead carbons are on nearly three planes, but C(21) deviates from the dimethoxybenzene-ring plane by 0.13 Å.

TABLE 7. DEVIATIONS FROM THE LEAST-SQUARES PLANE

(1) Benzene-ring plane			
C (11)	0.001 Å	C (1)[a)]	−0.026 Å
C (12)	−0.001	C (6)[a)]	−0.005
C (13)	−0.002		
C (14)	0.004		
C (19)	0.001		
C (20)	−0.004		
(2) Chlorobenzene-ring plane			
C (7)	−0.005 Å	C (1)[a)]	0.024 Å
C (8)	−0.005	C (6)[a)]	0.018
C (9)	0.015	Cl[a)]	0.043
C (10)	−0.015		
C (17)	0.005		
C (18)	0.005		
(3) Dimethoxybenzene-ring plane			
C (2)	0.008 Å	C (1)[a)]	−0.058 Å
C (3)	0.010	C (6)[a)]	0.033
C (4)	−0.018	C (21)[a)]	0.128
C (5)	0.007	C (22)[a)]	−0.031
C (15)	−0.018	O (1)[a)]	−0.010
C (16)	0.011	O (2)[a)]	0.027

a) Atoms not included in the least-squares plane calculation.

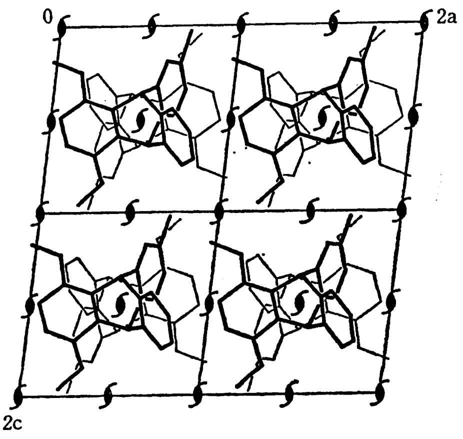

Fig. 2. Projection along the b axis.

The crystal structures as projected along the b axis and the c axis are shown in Figs. 2 and 3 respectively. The intermolecular distances within 3.6 Å are listed in Table 8. The closest distance occurs at 3.29 Å between the chlorine atom and the oxygen atom of the methoxyl group (0(2)).

The absolute configuration was determined by the Bijvoet method using the anomalous scattering of Cu$K\alpha$ radiation by the chlorine atom. The $\Delta f'$ and $\Delta f''$ values were taken from the International Tables for X-ray Crystallography.[13)] The observed intensity differences and calculated ones between the Bijvoet pair for twenty reflections are listed in Table 9. The signs of the observed values are in good agreement with those calculated based on the positional parameters of Table 2 in the right-handed coordinate system. The absolute configuration thus determined is 1R6S, as is illustrated in Fig. 4. This result is in good agreement with the chemical correlation of (+)-2,5-dimethoxy-8-

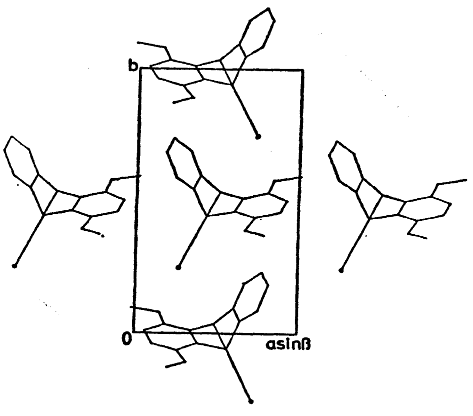

Fig. 3. Projection along the c axis.

TABLE 8. INTERMOLECULAR DISTANCES ≤ 3.6 Å

The Roman numerals represent the symmetry operators relevant to the atoms listed second.

Cl··············O (2^{iv})	3.288(9) Å
O (1) ·········C (7^{ii})	3.417(11)
C (2) ·········C (13^{iii})	3.566(16)
C (3) ·········C (11^{vii})	3.542(15)
C (7) ·········C (21^{i})	3.604(16)
C (10)·········C (14^{iii})	3.465(15)
C (11)·········C (4^{vi})	3.604(15)
C (12)·········O (21^{v})	3.604(19)

Symmetry code superscript	Symmetry operator		
i	x	y	$1+z$
ii	x	y	$-1+z$
iii	$-x$	$1/2+y$	$-z$
iv	$-x$	$1/2+y$	$1-z$
v	$-x$	$1/2+y$	$-1-z$
vi	$-1+x$	y	z
vii	$1+x$	y	z

TABLE 9. DETERMINATION OF ABSOLUTE CONFIGURATION
$100\times\{I(hkl)-I(\bar{h}\bar{k}\bar{l})\}/I(hkl)$

h	k	l	Obsd	Calcd
1	1	−3	−5.1	−4.6
1	3	−4	9.1	6.0
1	5	1	2.3	3.4
1	9	1	−22.7	−25.2
2	1	−3	13.7	6.5
2	2	−4	14.7	7.9
2	2	5	−18.5	−5.8
2	6	−5	−15.0	−17.6
2	6	−1	27.8	17.2
2	6	2	−13.5	−9.2
3	1	−2	−9.9	−5.5
3	3	−1	−11.2	−4.3
3	3	2	−9.8	−5.7
3	5	2	9.6	7.0
3	7	1	24.2	21.9
4	2	4	30.3	23.2
4	3	−4	24.5	13.8
4	3	1	−19.4	−15.9
5	2	−3	−16.0	−14.1
5	4	−3	12.3	12.5

chlorotriptycene[16] with (+)-2,5-dimethoxy-7-dimethylaminotriptycene, since the absolute configuration of the latter molecule, as determined by the X-ray method,[5] is known to be 1R6S also.

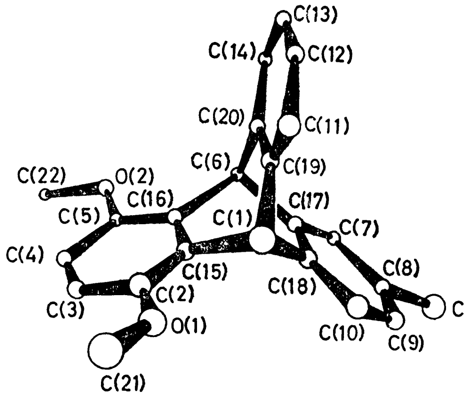

Fig. 4. Absolute configuration of (+)-2,5-dimethoxy-8-chlorotriptycene.

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