The Crystal Structure of 1:1 Complexes of (S)-(-)-10,10'-

Dihydroxy-9,9'-biphenanthryl with (S)-(-)-Methyl 2-Chloropropionate

and (S)-(-)-Methyl 3-Chloro-2-hydroxybutyrate

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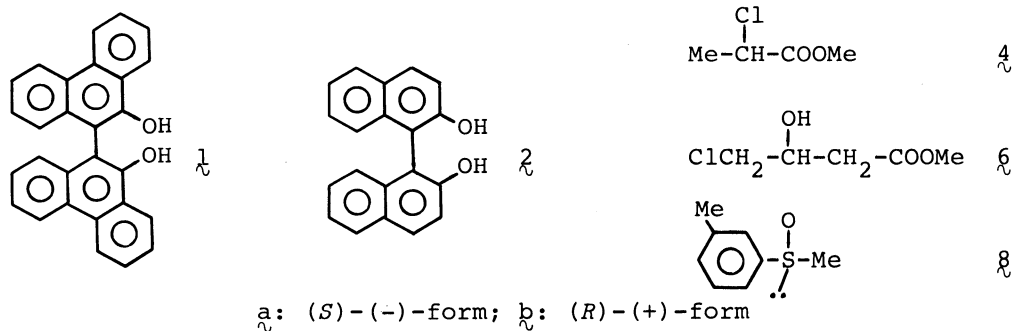
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In order to clarify the reason for high chiral recognition

ability of optically active 10,10'-dihydroxy-9,9'-biphenanthryl to

guest compounds, X-ray crystal structural study of the title

complex was carried out.

Recently, we found that optically active 10,10'-dihydroxy-9,9'-biphenanthryl

(1) forms crystalline host-guest complexes with various organic compounds and that

chiral recognition between 1 and the guest compound in the complex occurs effi-

ciently and the guest compound is resolved.[1] For example, resolution of propionic

and butyric acid derivatives and 4-hydroxycyclopent-2-en-1-one derivatives has been

reported.[2] These compounds, however, do not form complex with optically active

2,2'-dihydroxy-1,1'-binaphthyl (2), although optically active 2 includes sulf-

oxides,[2] selenoxides,[3] phosphine oxides,[4] phosphinates,[4] and arsine oxides,[5]

and these are resolved efficiently through the complex formation. Contrarily,

these compounds are not resolved with 1, although complexation occurs.

In order to clarify the reason why 1 and 2 recognize the chirality on only the

carbon and hetero atoms, respectively, crystal structures of a 1:1 complex (3) of

(S)-(-)-1 (1a) and (S)-(-)-methyl 2-chloropropionate (4a) and of a 1:1 complex (5)

of 1a and (S)-(-)-methyl 4-chloro-3-hydroxybutyrate (6a) were determined, and the

results were compared with those of a 1:1 complex (7) of (S)-(-)-2 (2a) and (S)-

(-)-methyl m-tolyl sulfoxide (8a).[6] Perspective views of 3 and 5 are shown in

Figs. 1 and 2, respectively.

Cl
|
Me-CH-COOMe   4

OH
|
ClCH$_2$-CH-CH$_2$-COOMe   6

Me   O
              ‖
⟨O⟩-S-Me   8
              ‖
              O

a: (S)-(-)-form; b: (R)-(+)-form

Crystallographic data for C$_{32}$H$_{25}$O$_4$Cl (3): FW 508.82, orthorhombic, spce group P 2$_1$2$_1$2$_1$, a = 11.705(1), b = 13.628(2), c = 15.910(1) Å, V = 2537.9(2) Å^3, Z = 4, Dc = 1.332 g cm^{-3}, μ(MoKα) = 0.18 mm^{-1}, F(000) = 1104, T = 298 K, final R = 0.038, Rw = 0.037 for 1123 observed reflections.[7]

Crystallographic data for C$_{33}$H$_{27}$O$_5$Cl (5): FW 538.84, monoclinic, space group P 2$_1$, a = 8.894(2), b = 15.639(4), c = 9.713(2) Å, β = 93.62(2)°, V = 1348.3(4) Å^3, Z = 2, Dc = 1.328 g cm^{-3}, μ(MoKα) = 0.18 mm^{-1}, F(000) = 564, T = 298 K, final R = 0.037, Rw = 0.031 for 1721 observed reflections.[8]
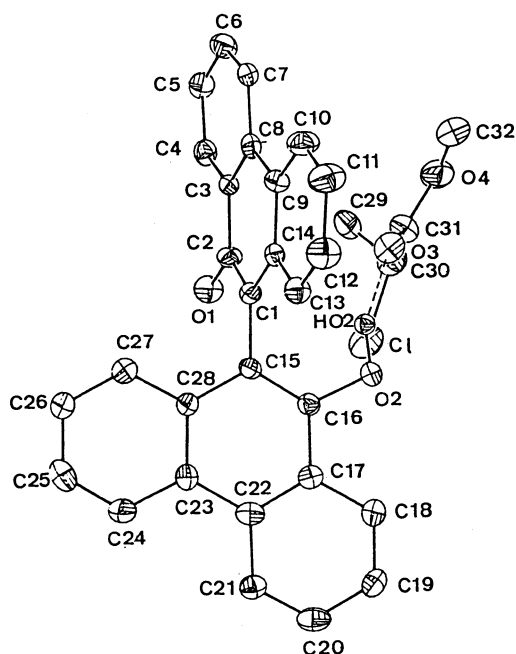
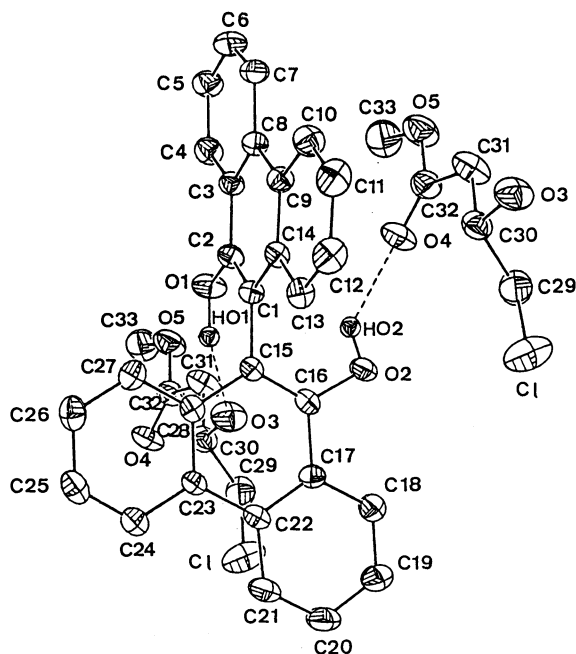Fig. 1. A perspective view of 3 with the atomic numbering and the -OH···O=C- hydrogen bond.[9]

Fig. 2. A perspective view of 5 in parallel with that of 3 with the atomic numbering and the -OH···O=C- and -OH···OH- hydrogen bonds.[9] In order to show both hydrogen bonds, one extra guest molecule is included.

Apparently, the hydrogen bond between the host and guest molecules plays an important role in the crystal packing (Figs. 1 and 2). In 3, there is one hydrogen bond per one host molecule, between O2 and O3 atoms (O2$\cdots$O3 distance 2.791 Å) (Fig. 1). The dihedral angle between the two phenanthrol planes is 68.2°. Whereas 5 forms two hydrogen bonds per one host molecule through O1$\cdots$O3 (2.880 Å) and O2$\cdots$O4 (2.777 Å). So it packs as a chain throughout the crystal. In this case, the dihedral angle between the two phenanthrol planes is 87.7°.

In the case of 7, strongly polarized sulfoxide oxygen of $8a$ forms two hydrogen bonds with the hydroxyl group of 2 (Fig. 3), and the components get close enough to recognize chirality each other.[6] No complexation between 2 and 4 or 6 is probably due to the less polarized carbonyl oxygen of the guest compound.

In the case of 3 and 5, relatively larger phenanthrol group of 1 surround the guest molecule more effectively than does naphthol group of 2, and the surrounding makes easy to accommodate the guest molecule in crystal lattice in the complex. The stronger accommodation ability of 1 to various guest compounds is shown in Table 1. Although 1 includes almost all of the guest compound shown in Table 1, 2 includes a half of them.

Table 1. Ratios and Melting Points of the Inclusion Complexes of 1 and 2 with Various Guest Compounds

| Guest compound | Host compound | | | |
| | 1 | | 2 | |
	H:G Ratio	Mp θm/°C	H:G Ratio	Mp θm/°C
MeOH	1:1	nc[a]	---	---
(cyclohexanone)	1:2	108–114	1:1	nc
(γ-butyrolactone)	---	---	1:2	82–84
(tetrahydrofuran)	1:2	100–110	1:2	nc
CCl_4	1:1	124–129	---	---
MeC≡N	1:2	75–77	---	---
DMSO	1:2	139–146	1:2	155–158
DMF	1:2	nc	1:2	117–125
C_6H_5-NO_2	1:1	119	---	---
Pyridine	1:2	99–107	1:2	nc
PhCH(NH_2)Me	1:1	105–106	---	---
Acetone	1:1	nc	---	---

a) Not clear.
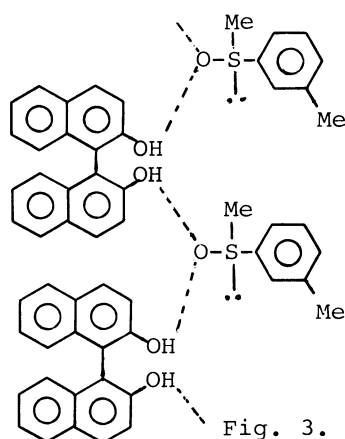
Fig. 3. Hydrogen bonds in $\underset{\sim}{7}$.

Furthermore, $\underset{\sim}{1a}$ includes $\underset{\sim}{4a}$ and $\underset{\sim}{6a}$ but not $\underset{\sim}{4b}$ and $\underset{\sim}{6b}$. This very high chiral

recognition ability of $\underset{\sim}{1}$ is the reason for the efficient optical resolution by the

complexation with $\underset{\sim}{1}$.

References

1) F. Toda and K. Tanaka, Tetrahedron Lett., in press.

2) F. Toda, K. Tanaka, and S. Nagamatsu, Tetrahedron Lett., 25, 4929 (1984).

3) F. Toda and K. Mori, J. Chem. Soc., Chem. Commun., 1986, 1357.

4) F. Toda, K. Mori, Z. Stein, and I. Goldberg, J. Org. Chem., 53, 308 (1988).

5) F. Toda and K. Mori, J. Chem. Soc., Chem. Commun., submitted.

6) F. Toda, K. Tanaka, and T. C. W. Mak, Chem. Lett., 1984, 2085.

7) Crystal size 0.3 x 0.3 x 0.3 mm, CAD4-4 diffractometer, Unit cell: 25 re-
flections in 2θrange 20.4 to 24.2°, $2\theta_{max}$ = 50°, 2523 unique reflections, 1123
observed with $I > 2\sigma$ (I). No absorption correction, R(F) = 0.038, Rw(F) = 0.037, S
= 1.95. Weighting from counting statics. Structure was solved by direct method
using MULTAN, with 248 E's. All the non-phenyl H atoms were located by difference
Fourier, phenyl H atoms were calculated according to sp^2 approximation. $(\Delta/\sigma)_{max}$ =
0.33. Peaks in final ΔF within ± 0.14 $e\overset{\circ}{A}^{-3}$. Atomic scattering factors from Inter-
national Tables for X-ray crystallography (1974). Computing programs NRCVAX,
MULTAN from Enraf-Nonius SDP.

8) Crystal size 0.25 x 0.25 x 0.25 mm, Unit cell: 25 reflections in 2θrange 21.1 to
27.5°, $2\theta_{max}$ = 50°, 2463 unique reflections, 1721 observed with $I > 3\sigma$(I), No absorp-
tion correction, R(F) = 0.037, Rw(F) = 0.031, S = 2.75. Structure was solved by
direct method using MULTAN, with 368 E's. $(\Delta/\sigma)_{max}$ = 0.37. Peaks in final ΔF
within ± 0.19 $e\overset{\circ}{A}^{-3}$. Other details are same as those described in the reference 7.

9) The atomic coordinates have been deposited with the Cambridge Crystallographic
Data Centre, Structure factors are obtainable from the first two authors.