

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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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 efficiently 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.

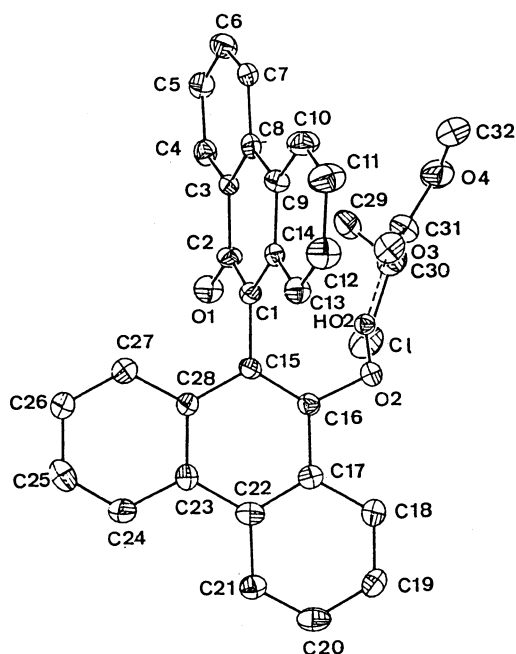
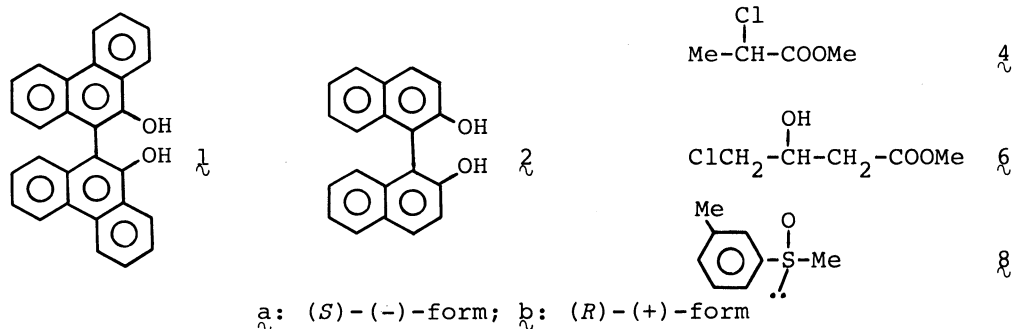


Fig. 1. A perspective view of $\mathbf{3}$ with the atomic numbering and the $-\text{OH}\cdots\text{O}=\text{C}-$ hydrogen bond.⁹⁾

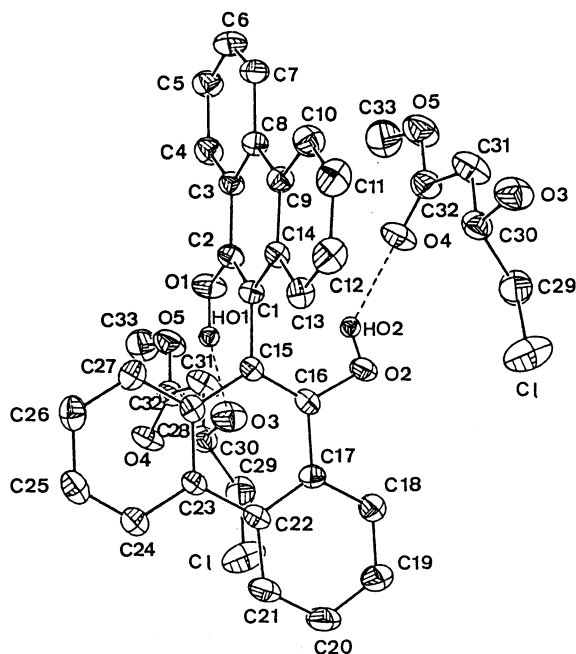


Fig. 2. A perspective view of $\mathbf{5}$ in parallel with that of $\mathbf{3}$ with the atomic numbering and the $-\text{OH}\cdots\text{O}=\text{C}-$ and $-\text{OH}\cdots\text{OH}-$ hydrogen bonds.⁹⁾ In order to show both hydrogen bonds, one extra guest molecule is included.

Apparently, the hydrogen bond between the host and guest molecules plays an important role in the crystal packing (Figs. 1 and 2). In β , there is one hydrogen bond per one host molecule, between O2 and O3 atoms (O2...O3 distance 2.791 Å) (Fig. 1). The dihedral angle between the two phenanthrol planes is 68.2°. Whereas γ forms two hydrogen bonds per one host molecule through O1...O3 (2.880 Å) and O2...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°.

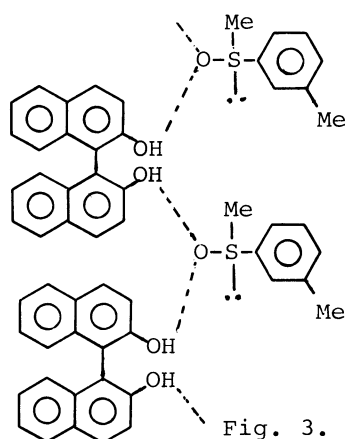
In the case of γ , strongly polarized sulfoxide oxygen of β forms two hydrogen bonds with the hydroxyl group of γ (Fig. 3), and the components get close enough to recognize chirality each other.⁶⁾ No complexation between γ and β or δ is probably due to the less polarized carbonyl oxygen of the guest compound.

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

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

Guest compound	Host compound			
	β	β	γ	γ
	H:G Ratio	Mp θ m/°C	H:G Ratio	Mp θ m/°C
MeOH	1:1	nc ^a	---	---
	1:2	108-114	1:1	nc
	---	---	1:2	82-84
	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 ₆ H 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 **7**.

Furthermore, **1a** includes **4a** and **6a** but not **4b** and **6b**. This very high chiral recognition ability of **1** is the reason for the efficient optical resolution by the complexation with **1**.

References

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- 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 reflections in 2θ range 20.4 to 24.2°, $2\theta_{\max} = 50^\circ$, 2523 unique reflections, 1123 observed with $I > 2\sigma(I)$. No absorption correction, $R(F) = 0.038$, $R_w(F) = 0.037$, $S = 1.95$. Weighting from counting statistics. 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 $\pm 0.14 \text{ e}\text{\AA}^{-3}$. Atomic scattering factors from International 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 2θ range 21.1 to 27.5°, $2\theta_{\max} = 50^\circ$, 2463 unique reflections, 1721 observed with $I > 3\sigma(I)$, No absorption correction, $R(F) = 0.037$, $R_w(F) = 0.031$, $S = 2.75$. Structure was solved by direct method using MULTAN, with 368 E's. $(\Delta/\sigma)_{\max} = 0.37$. Peaks in final ΔF within $\pm 0.19 \text{ e}\text{\AA}^{-3}$. 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.

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