

## Preparation for Supramolecular Complexes of Chiral Diols BDPDD, DMBDPD and BINOL with Some Prochiral Compounds

De Jun LIU, Zi Xing SHAN\*, Rong WANG, Jin Gui QIN

College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072

**Abstract:** Interaction between chiral diols BDPDD, DMBDPD and BINOL with prochiral compounds was examined and some new supramolecular complexes were prepared. It was found that these chiral hosts could include prochiral guests,  $\alpha$ ,  $\beta$ -unsaturated compounds or piperazinedione derivatives to give inclusion crystals in different molar ratio. Formations of these supramolecular complexes were characterized by the data of IR and  $^1\text{H}$  NMR spectra.

**Keywords:** Chiral diols, prochiral compounds, supramolecular complexes, preparation.

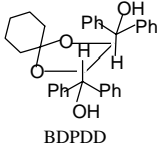
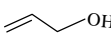
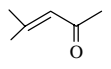
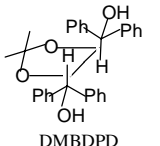
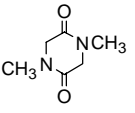
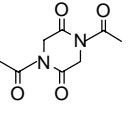
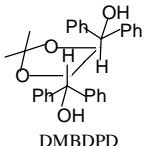
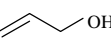
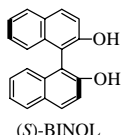
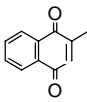
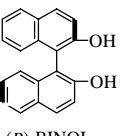
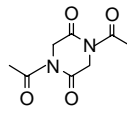
Supramolecular chemistry based on noncovalent interactions between chemical entities is one of the front fields of current chemistry. It is offering wide applications in various fields such as medicinal chemistry, host-guest chemistry, catalysis, and molecular electronics. Formation of supramolecular system possesses important significance for preparation of chiral compounds. For example, a chiral host molecule can selectively include one enantiomer of a racemic guest, resulting in enantiomeric separation of the racemic compound<sup>1</sup>. It has been known that a chiral host can include various achiral guest to offer inclusion complexes in different molar ratio<sup>2</sup>; if an inclusion complex is generated from a chiral host and a prochiral guest, under appropriate conditions, the prochiral guest included will be transformed into an optically active compound. It has been reported that some prochiral alkylaryl ketones included by (*S,S*)-1,6-di(2-chlorophenyl)-1,6-diphenyl-2,4-hexadiyn-1,6-diol can be reduced by ethylenediamine-borane to offer optically active (*R*)- secondary alcohols<sup>3</sup>. And, the inclusion compound of (*R,R*)-4,5-*trans*-bis(diphenylhydroxymethyl)-1,3-dioxaspiro[4,5]decane and cyclohexenone react with arylthol under supersonic wave irradiation at room temperature to furnish optically active Micheal addition products<sup>4</sup>. Asymmetric photocyclization reactions occurred in the inclusion crystal environment have also been reported<sup>5</sup>. For example, a 1 : 1 inclusion complexes of *S*, *S*)-1,6-di(2-chlorophenyl)-1,6-diphenyl-2,4-hexadiyn-1,6-diol and *N,N*-dimethylphenylglyoxylamide furnished enantiopure  $\beta$ -lactam in 90% yield by irradiation with a 400 W high-pressure Hg lamp at room temperature<sup>6</sup>.

To provide materials for investigating asymmetric reactions mediated by a chiral

---

\*E-mail: [Kenshan@public.wh.hb.cn](mailto:Kenshan@public.wh.hb.cn)

**Table 1** Composition and IR spectra of supramolecular complexes of chiral diols BDPDD, DMBDPD and BINOL with some prochiral compounds

Inclusion complexes	Chiral diols (A)	Prochiral compounds (B)	A / B	m.p.(°C) <sup>a</sup>	IR (ν cm <sup>-1</sup> )
1			3 / 1		3346, 3190 1639
2			2 / 1	190-192	3285, 1674 1612
3		CH <sub>2</sub> =CHCOOCH <sub>3</sub>	3 / 2	192-194	3365, 3321 1710, 1614
4		CH <sub>2</sub> =C(CH <sub>3</sub> )COOCH <sub>3</sub>	3 / 2		3371, 3327 1699, 1634
5			1 / 1	157-158	3306, 1657
6			1 / 1	146-150	3263, 1724 1688
7			1 / 1		3354, 3196 1640
8		CH <sub>2</sub> =CHCN	3 / 2		3314, 2230
9		CH <sub>2</sub> =C(CH <sub>3</sub> )COOCH <sub>3</sub>	2 / 1	194-196	3325, 3207 1720, 1701 1632, 1603
10	 ( <i>S</i> )-BINOL		1 / 1	153-155	3360, 1667 1651, 1619 1593
11	 ( <i>R</i> )-BINOL		1 / 1		3371br 1738, 1728 1704, 1695

<sup>a</sup> Clear melting points are not observed, except those listed. The thermometer was uncorrected.

supramolecular system, we examined inclusion complexation between (*R,R*)-4,5-*trans*-bis(diphenylhydroxymethyl)-1,3-dioxaspiro[4.5]decane(BDPDD)<sup>7</sup>, (*R,R*)-2,2-dimethyl-4,5-*trans*-bis(diphenylhydroxymethyl)-1,3-dioxolane (DMBDPD)<sup>8</sup>, (*S*)- and (*R*)-1,1'-bi-2-naphthol (BINOL)<sup>9</sup> with some prochiral compounds such as allyl alcohol, acrylnitrile, methyl acrylate, methyl methacrylate, 4-methyl-3-pentene-2-one, 1,4-dimethylpiperazine-2,5-dione, 1,4-diacetylpiperazine-2,5-dione and 2-methyl-1,4-naphthoquinone, respectively, and prepared eleven new chiral inclusion complexes.

**Preparation for Supramolecular Complexes of Chiral Diols BDPDD, 377  
DMBDPD and BINOL with Some Prochiral Compounds**

The composition and spectral data of the inclusion complexes **1**~**11** were summarized in **Table 1** and **Table 2**.

**Table 2** <sup>1</sup>HMR spectra of supramolecular complexes of chiral diols BDPDD, DMBDPD and BINOL with some prochiral compounds

Inclusion complexes	Chemical shifts (CDCl <sub>3</sub> , δ ppm) <sup>a</sup>
<b>1</b>	7.52-7.12 (m, 2OH), 5.88 (m, 1/3H), 5.21 (m, 1/3H), 5.12 (m, 1/3H), 4.52 (s, 2H), 4.08 (m, 2/3H), 3.4 (m, 2/3H), 1.56-1.08 (m, 10H)
<b>2</b>	7.52-7.12 (m, 2OH), 6.08 (s, 1/2H), 4.52 (s, 2H), 3.36 (m, 2H), 2.12 (s, 3H), 1.88 (s, 3/2H), 1.56-1.08 (m, 10H)
<b>3</b>	7.52-7.12 (m, 2OH), 6.48-6.08 (m, 4/3H), 5.88-5.68 (m, 2/3H), 4.52 (s, 2H), 3.80 (m, 2H), 3.72 (s, 2H), 1.56-1.08 (m, 10H)
<b>4</b>	7.52-7.12 (m, 2OH), 6.08 (m, 1/3H), 5.48 (m, 2/3H), 4.52 (s, 2H), 4.08(m, 2/3H), 3.72 (s, 2H), 3.60 (m, 2H), 1.92 (m, 2H), 1.08-1.56 (m, 10H)
<b>5</b>	7.60-7.10 (m, 2OH), 5.20 (m, 2H), 4.50 (s, 2H), 3.80 (s, 4H), 2.90 (s, 6H), 1.50-1.10 (m, 10H)
<b>6</b>	7.52 (d, <i>J</i> =7.8, 4H), 7.40-7.25 (m, 16H), 4.60 (s, 4H), 4.55 (s, 2H), 2.59 (s, 6H), 2.60 (s, br, 2H), 1.50-1.10 (m, 10H)
<b>7</b>	7.56-7.12 (m, 2OH), 5.88 (m, 1H), 5.21 (m, 1H), 5.07 (m, 1H), 4.52 (s, 2H), 4.00 (m, 2H), 3.56-3.12 (m, 5H), 1.00 (s, 6H)
<b>8</b>	7.56-7.12 (m, 2OH), 6.21 (s, 2/3H), 6.10-5.40 (m, 4/3H), 4.52 (s, 2H), 3.98 (s, 2H), 1.00 (s, 6H)
<b>9</b>	7.61-7.22 (m, 2OH), 6.13 (s, 1/2H), 5.59 (s, 1/2H), 4.59 (s, 2H), 3.90 (s, br, 2H), 3.75 (s, 3/2H), 1.96 (s, 3/2H), 1.06 (s, 6H)
<b>10</b>	8.07 (m, 2H), 7.96 (d, 2H, <i>J</i> =8.7), 7.88 (d, 2H, <i>J</i> =7.5), 7.75-7.70 (m, 2H), 7.40-7.26 (m, 6H), 7.15 (d, 2H, <i>J</i> =8.7), 6.81 (s, 1H), 5.15 (s, 2H), 2.18 (s, 3H).
<b>11</b>	7.98 (d, 2H, <i>J</i> =8.7), 7.90 (d, 2H, <i>J</i> =7.5), 7.40-7.028 (m, 6H), 7.16 (d, 2H, <i>J</i> =8.1), 5.15 (s, 2H), 4.59 (s, 4H), 2.59 (s, 6H)

<sup>a</sup> The spectra of inclusion complexes **1**, **2**, **3**, **4**, **7** and **8** were determined on a JEOL FX-90Q spectrometer; the rest were recorded on a Varian Mercury VS 300 spectrometer. *J* in Hz.

It can be seen that the chiral diols are able to form inclusion compounds with the selected prochiral compounds in required molar ratios. In the IR spectra of these inclusion complexes, stretching vibration for the hydroxyl groups of the hosts and the guests all shifted to lower wavenumber region, and, the shifts for the hydroxyl groups of the chiral hosts<sup>10</sup> are much larger than that for the guests and the maximum of the shifts is up to 250 cm<sup>-1</sup>; in most cases, they shifted by 200-80 cm<sup>-1</sup> to lower frequency region. This phenomenon is an important characteristic of the formation of the inclusion complexes; and, it means that the chiral hosts connect together with the prochiral guests through hydrogen bonding in these chiral inclusion complexes.

The general procedure:

An equal molar mixture of (*S*)-(-)-1,1'-bi-2-naphthol and 2-methyl-1,4-naphthoquin- one in benzene was heated to convert into a homogenous solution, and on cooling to room temperature to furnish a reddish orange crystal. This crystal was recrystallized from benzene twice, m.p. 153-155°C; IR (KBr, ν, cm<sup>-1</sup>): 3420, 3360, 1667,

1651, 1619, 1593, 1508, 1350, 1301, 1277, 1263, 1194, 1166, 1141, 1128, 817, 758. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, 300MHz): 8.07(m, 2H), 7.96 (d, 2H, *J*=8.7), 7.88 (d, 2H, *J*=7.5), 7.75- 7.70 (m, 2H), 7.40-7.26 (m, 6H), 7.15 (d, 2H, *J*=8.7), 6.81 (s, 1H), 5.15 (s, 2H), 2.18 (s, 3H).

### Acknowledgment

This work was supported by the National Natural Science Foundation of China (Project 29972033) and the Key Science Research Foundation of Hubei Province of China (Project 98IP1305).

### References and Notes

1. a) F. Toda, K. Tanaka, *J. Org. Chem.* **1988**, *53*, 3607; b) F. Toda, H. Takumi, K. Tanaka, *Tetrahedron: Asymmetry*, **1995**, *6* (5),1059; c) J. Zhu, Y. Qin, Z. He, F. M. Tu, Z. Y. Zhou, J. G. Deng, Y. Z. Jiang, *Chin. J. Synth. Chem.* (in Chinese) , **1997**, *5* (Zhengkan), 317.
2. Edwin Weber, Norbert Döypinghaus, Claus Wimmer, *J. Org. Chem.* **1992**, *57*, 6825
3. F. Toda, K. Mori, *J. Chem. Soc. Chem. Commun.* **1989**, 1245.
4. F. Toda, K. Tanaka, J. Sato, *Tetrahedron: Asymmetry*, **1993**, *4*, 1771.
5. K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100* (3), 1057 and the references listed therein
6. F. Toda, K. Tanaka, M. Yagi, *Tetrahedron*, **1987**, *43*, 1493.
7. F. Toda, K. Tanaka, *Tetrahedron Lett.*, **1988**, *29*, 551.
8. D. Seebach, A. K. Beck, R. Imwinkelried, S. Roggo, A. Wonnacott, *Helv. Chim. Acta*, **1987**, *70*, 954..
9. Z. X. Shan, Y. Xiong, W. Z. Li, D. J. Zhao, *Tetrahedron: Asymmetry*, **1998**, *9* (22), 3985.
10. The shifts for the hydroxyl groups of the chiral hosts: For BDPDD, 3531, 3342; For DMBDDP, 3439, 3213; For BINOL, 3507, 3436.

Received 23 May, 2002