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A new method for optical resolution of BINOL by molecular complexation with (*S*)-5-oxopyrrolidine-2-carboxanilide

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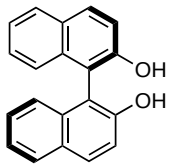
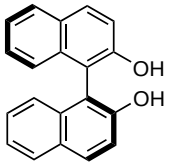
Abstract—A new method for optical resolution of racemic 1,1′-bi-2-naphthol (BINOL) has been developed through molecular complexation with a cheap and readily accessible (*S*)-5-oxopyrrolidine-2-carboxanilide, affording the enantioenriched BINOL in up to 70.4% ee and 74% yield. X-Ray structural analysis of a molecular crystal formed between (*R*)-BINOL and (*S*)-5-oxopyrrolidine-2-carboxanilide indicates that the hydrogen bonding interactions between the carbonyl groups of amides and the hydroxyl groups of (*R*)-BINOL predominate in the molecular complex formation. The chiral features of the amide and the complementary molecular packing in the crystal lattice control the stereochemistry of the guest in the molecular crystal. © 2002 Published by Elsevier Science Ltd.

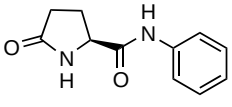
Optically active 1,1′-bi-2-naphthol (BINOL, **1**) and its derivatives have found many applications, ranging from chiral ligands in catalysts for asymmetric reactions[1] to hosts for molecular recognition and enantiomer separation,[2] and as intermediates for the synthesis of chiral materials.[3] Several protocols have been developed to access its enantiopure form, including classical crystallization of diastereoisomeric derivatives,[4] enantioselective formation of inclusion crystals with chiral host molecules,[5] enzymatic hydrolysis of esters,[6] and asymmetric coupling of 2-naphthol derivatives.[7] So far, the enantioselective formation of inclusion crystals with chiral host molecules is one of the most practical methods because of its very high efficiency[5,8] and the ready availability of racemic BINOL.[9] In the present work, we wish to report a new practical method for the large-scale resolution of BINOL by molecular complexation with a cheap and readily accessible resolving agent, (*S*)-5-oxopyrrolidine-2-carboxanilide **2**, and its novel molecular recognition pattern in the molecular crystals.



(*R*)-**1**



(*S*)-**1**



2

Natural amino acids are abundant and cheap chiral sources. Periasamy et al. reported that (*S*)-proline could be utilized as a resolving agent for obtaining enantiomerically enriched BINOL in moderate to good enantioselectivity.[5j] However, one equivalent of (*S*)-proline is necessary under the optimized conditions though the molecular complex was formed in a molar ratio of 2:1 ((*S*)-BINOL:(*S*)-proline). It is known that amide host compounds are able to form crystalline molecular complexes with a variety of organic molecules, particularly with phenols and alcohols through hydrogen bonding. Accordingly, a cheap and readily accessible amide, (*S*)-5-oxopyrrolidine-2-carboxanilide **2** which contains two amide moieties, was selected as a chiral host for enantioselective complexation with BINOL.

Amide **2** was easily prepared on a large scale via a one-step reaction of L-glutamic acid with aniline in high yield (85%) according to an improved literature procedure.[10] The resolution was carried out by dissolving 4 mmol of racemic **1** and 2 mmol of **2** in various solvents with heating (Scheme 1), followed by precipitating on cooling. It appears that the crystallization solvents are

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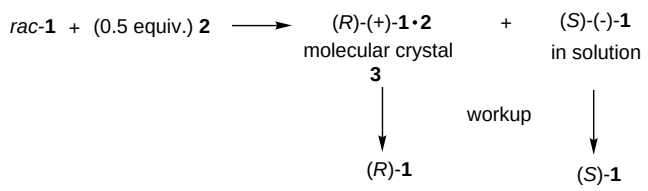

Scheme 1. The resolution of *rac*-BINOL **1** by molecular complexation.

critical for the formation of molecular crystals. In single component solvents, such as methanol ethanol, propanol, isopropanol, ethyl acetate, 1,4-dioxane, THF, acetonitrile, benzene or toluene, the crystals of **1** or **2** were formed and precipitated separately. The solubility of **2** in dichloromethane, chloroform or diethyl ether was too poor to be used as the solvent for the crystallization. Fortunately, a mixed solvent of THF and ethanol was found to be a suitable solvent. The effects of concentration, ratio of THF and ethanol, and amount of resolving agent used for crystallization were found to be evident. The use of **1** and **2** in a 1:0.5 molar ratio in THF:ethanol (1:1.5, 3.5 mL) gave best results (Table 1, entry 5). The molecular crystals **3** (containing one molecule of THF with 1:1 molar ratio of (*R*)-**1** and **2**) can be easily decomposed in acetone to precipitate **2** and recover enantioenriched (*R*)-**1** from the mother liquid. This procedure was also applied to large-scale resolution of **1** (28.6 g, 0.1 mol) by using **2** (10.2 g, 0.05 mol) in 87.5 mL of THF:ethanol (1:1.5), affording the molecular crystals of (*R*)-**1** and **2** (21.5 g, 76% yield) with 70% ee of (*R*)-**1**. After decomposition of the molecular crystals obtained above in acetone, (*R*)-**1** could be obtained in 75% yield without racemization and which can be further enriched by recrystallization from benzene to give enantiomerically pure (*R*)-**1** in 43% yield (6.2 g).

Thus, a new and practical resolution of BINOL has been successfully achieved. In order to elucidate the molecular recognition pattern between host and guest molecules in the solid state, the structure of the molecular complex of (*R*)-**1** and **2** has been determined by X-ray crystallography.

The single crystals of molecular complex **3** were obtained by slow evaporation from THF:ethanol (1:1.5) mixed solvent. The intermolecular organization and association in the molecular complex are shown in Fig. 1. The structural parameters exhibited for the host and guest molecules are in good agreement with standard values.[11]

As shown in Fig. 1, the structure of the molecular complex network between (*R*)-**1** and **2** can be described as infinite chains of interlinked species that are aligned in an alternating manner through hydrogen bonds. The hydrogen bonding pattern includes the two OH groups of BINOL as the proton donors and the two carbonyl groups of (*S*)-5-oxopyrrolidine-2-carboxanilide as the proton acceptors (at O1···O4 and O2···O3 of 2.718(5) and 2.993(5) Å, respectively), which forms a 14-membered ring. Simultaneously, one hydrogen-bonded OH group of BINOL with the pyrrolidone oxygen provides

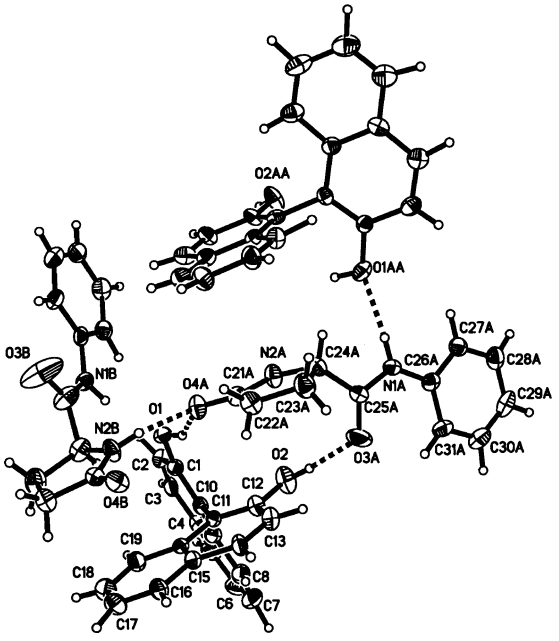

Figure 1. Perspective view of molecular complex **3**, THF has been omitted for clarity.

Table 1. Optical resolution of (±)-**1** with **2** through molecular complexation

Entry	(±)-**1**:**2**[a]	THF:ethanol	Volume (mL)	Yield of **3** (%)	% ee of (*R*)-**2**[b]	Recovery of (*S*)-**1** and its % ee[b]
1	4:2	1:1	4	66	62.4	32.0
2	4:2	1:1	6	58	53.3	18.4
3	4:2	1:1	2.8	69	67.1	34.2
4	4:2	1:1.5	2.8	72	65.0	39.7
5	4:2	1:1.5	3.5	74	70.4	39.2
6	4:2.5	1:1	8	–[c]	–	–
7	4:4	1:1	8	–[c]	–	–
8	4:2	1:2	3.0	50.2	55.7	nd
9	4:2	1:3	3.2	–[c]	–	–

[a] In mmol scale.
[b] Determined by HPLC on a Chiralcel OD column, the absolute configuration of the product was assigned by comparison with the literature.
[c] No molecular crystals were formed.

the hydrogen acceptor which associates with the proton of the NH group of the adjacent carboxanilide moiety (at O1AA···N1A of 2.894(4) Å). Two neighbouring host molecules were linked by hydrogen bonding between the pyrrolidone oxygen of one molecule and the NH group of another host molecule at pyrrolidone moiety (at O4A···N2B of 2.918(6) Å). The dihedral angle of the binaphthyl unit is 85.16(7)° and its absolute configuration was found to be *R*, unambiguously through relation with the absolute configuration of (*S*)-**2**. THF is present in the crystal lattice but without additional hydrogen bonding interactions. It appears that the phenyl group in the host molecule is less important for molecular recognition. Therefore, it can be expected that a variety of amide derivatives of **2** should be able to function as resolving reagent for the optical resolution of **1**. The studies on the further improvement of the efficiency of optical resolution of various BINOL derivatives by using the analogous compounds of **2** are currently in progress in this laboratory.

In conclusion, a new method for the optical resolution of racemic 1,1′-bi-2-naphthol (BINOL) has been developed through molecular complexation with cheap and readily accessible (*S*)-5-oxopyrrolidine-2-carboxanilide, affording enantio-enriched BINOL in up to 70.4% ee and 74% yield. X-Ray structural analysis of the molecular crystal formed between (*R*)-BINOL and (*S*)-5-oxopyrrolidine-2-carboxanilide indicates that the hydrogen bonding interactions between the carbonyl groups of the amide and the hydroxyl groups of (*R*)-BINOL predominate in the molecular complex formation. The chiral features of the amide and the complementary molecular packing in the crystal lattice operate the stereochemistry of the guest in the molecular crystal.

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References

1. For comprehensive reviews on asymmetric catalysis, see: (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994; (b) Ojima, I. *Asymmetric Catalysis*; VCH: New York, 1993; (c) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503; (d) Mikami, K.; Motoyama, Y. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 1, pp. 397–403; (e) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1236–1256; (f) Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2494; (g) Lin, G. Q.; Li, Y. M.; Chan, A. S. C. *Principles and Applications of Asymmetric Synthesis*; Wiley: New York, 2001.
2. For examples of molecular recognition and enantiomer separation, see: (a) Kyba, E. P.; Gokel, G. W.; De Jong, F.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173–4184; (b) Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930–1946; (c) Reeder, J.; Castro, P. P.; Knobler, C. B.; Martinborough, E.; Owens, L.; Diederich, F. *J. Org. Chem.* **1994**, *59*, 3151–3160; (d) Judice, J. K.; Keipert, S. J.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1323–1325.
3. For the application to the synthesis of materials, see: Ref. 1e. For other examples, see: (a) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683–1686; (b) Brunner, H.; Schiessling, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 120–121; (c) Zhang, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 4852–4857; (d) Deussen, H.-J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjornholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841–6852; (e) Musick, K. Y.; Hu, Q. S.; Pu, L. *Macromolecules* **1998**, *31*, 2933–2942; (f) Wong, M. S.; Nicoud, J.-F. *J. Chem. Soc., Chem. Commun.* **1994**, 249–250; (g) Meng, Y.; Slaven, W. T.; Wang, D.; Liu, T. J.; Chow, H. F.; Li, C. J. *Tetrahedron: Asymmetry* **1998**, *9*, 3693–3707.
4. For the resolution of **1** through formation of diastereoisomers, see: (a) Jacques, J.; Fouquey, C.; Viterbo, R. *Tetrahedron Lett.* **1971**, *7*, 4617–4620; (b) Jacques, J.; Fouquey, C. *Org. Synth.* **1988**, *67*, 1–12; (c) Gong, B.; Chen, W.; Hu, B. *J. Org. Chem.* **1991**, *56*, 423–425; (d) Brunel, J. M.; Buono, G. *J. Org. Chem.* **1993**, *58*, 7313–7314; (e) Wang, M.; Liu, S.; Hu, B. *J. Org. Chem.* **1995**, *60*, 7364–7265; (f) Fabbri, D.; Deloga, G.; De Lucchi, O. *J. Org. Chem.* **1995**, *60*, 6599–6601; (g) Pakulski, Z.; Zamojski, A. *Tetrahedron: Asymmetry* **1995**, *6*, 111–114; (h) Chow, H. F.; Wan, C. W.; Ng, M. K. *J. Org. Chem.* **1996**, *61*, 8712–8714; (i) Kim, H. C.; Choi, S.; Kim, H.; Ahn, K. H.; Koh, J. H.; Park, J. *Tetrahedron Lett.* **1997**, *38*, 3959–3962; (j) Shan, Z.; Xiong, Y.; Zhao, D. *Tetrahedron* **1999**, *55*, 3893–3896; (k) Shan, Z.; Wang, G.; Duan, B.; Zhao, D. *Tetrahedron: Asymmetry* **1996**, *7*, 2847–2850; (l) Shan, Z.; Cheng, F.; Huang, S.; Zhao, D.; Jing, Z. *Tetrahedron: Asymmetry* **1997**, *8*, 1175–1177; (j) Periasamy, M.; Venkatraman, L.; Sivakumar, S.; Sampathkumar, N.; Ramanathan, C. R. *J. Org. Chem.* **1999**, *64*, 7643–7645.
5. For the resolution of **1** through molecular complexation, see: (a) Tanaka, K.; Okada, T.; Toda, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1147–1148; (b) Toda, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *J. Org. Chem.* **1994**, *59*, 5748–5751; (c) Toda, F.; Tanaka, K. *Chem. Commun.* **1997**, 1087–1088; (d) Cai, D. W.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Tetrahedron Lett.* **1995**, *36*, 7991–7994; (e) Hu, Q. S.; Vitharana, D.; Pu, L. *Tetrahedron: Asymmetry* **1995**, *6*, 2123–2126; (f) Wang, Y.; Sun, J.; Ding, K. *Tetrahedron* **2000**, *56*, 4447–4451; (g) Kawashima, M.; Hirayama, A. *Chem. Lett.* **1990**, 2299–2300; (h) Kawashima, M.; Hirata, R. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2002–2005; (i) Periasamy, M.; Prasad, A. S. B.; Kanth, J. V. B.; Reddy, Ch. K. *Tetrahedron: Asymmetry* **1995**, *6*, 341–344; (j) Periasamy, M.; Venkatraman, L.; Thomas, K. R. J. *J. Org. Chem.* **1997**, *62*, 4302–4306.
6. Kazlauskas, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4953–4959.

7. For the asymmetric synthesis of binaphthols including enantioselective oxidation with catalytic amount of chiral ligand and second-order asymmetric transformation, see: (a) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, *64*, 2264–2271 and references 3 and 4 cited therein; (b) Smrcina, M.; Palakova, J.; Vyskocil, S.; Kocovsky, P. *J. Org. Chem.* **1993**, *58*, 4534–4537; (c) Feringa, B.; Wynberg, H. *Bioorg. Chem.* **1978**, *7*, 397–408; (d) Brussee, J.; Groenendijk, J. L. G.; te Koppele, J. M.; Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313–3319; (e) Li, X. L.; Yang, J.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 1137–1140.
8. For comprehensive reviews, see: (a) Toda, F. *Top. Curr. Chem.* **1987**, *140*, 43–69; (b) Toda, F. In *Advances in Supramolecular Chemistry*, Gokel, G. W., Ed.; JAI Press: Stamford, CT, 1992; Vol. 2, pp. 141–191; (c) Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 728–729.
9. For examples of the highly efficient synthesis of (±)-BINOL, see: (a) Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 7983–7984; (b) Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007–3009; (c) Ding, K.; Wang, Y.; Zhang, L.; Wu, Y.; Matsuura, T. *Tetrahedron* **1996**, *52*, 1005–1010; (d) Nakajima, M.; Hashimoto, S.; Noji, M.; Koga, K. *Chem. Pharm. Bull.* **1998**, *46*, 1814–1845; (e) Colonna, S.; Re, A.; Wynberg, H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 547–552; (f) Jacobs, W. A.; Heidelberger, M. *J. Am. Chem. Soc.* **1919**, *41*, 2090–2120.
10. Brunel, J. M.; Constantieux, T.; Buono, G. *J. Org. Chem.* **1999**, *64*, 8940–8942.
11. Crystal data for **3** ($C_{35}H_{36}N_2O_5$): $42.569>\theta>4.411°$; formula weight 564.66, monoclinic, space group $P2_1$, $a=11.0489(8)$, $b=8.8662(7)$, $c=14.9503(11)$ Å, $\alpha=90.00$, $\beta=94.837(2)$, $\gamma=90.00°$, $V=1459.34(19)$ Å^3, $Z=2$, $D_{calcd}=1.285$ g cm^{-3}, μ(Mo Kα)$=0.086$ cm^{-1}, $F(000)=600$, index ranges $-10\leq h\leq 13$, $-10\leq k\leq 10$, $-17\leq l\leq 17$, $1.37\leq\theta\leq 25.00°$. Final atomic coordinates of the complex **3**, along with the lists of anisotropic thermal parameters, hydrogen coordinates, bond lengths, and bond angles, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-181003. They can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).