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An improved and practical approach to essentially enantiopure BINOLs: enantioselective inclusion complexation of (*S*)-proline

Xiaoyun Hu [a,*], Zixing Shan [b], Qing Chang [a]

[a] College of Chemistry and Materials, South-Central University for Nationalities, Wuhan, China
[b] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China

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ABSTRACT

An improved and practical approach to (*R*)- and (*S*)-BINOLs has been developed. The *rac*-BINOL and (*S*)-proline were refluxed in acetonitrile for several hours, and the resulting white precipitate was recrystallized in ethanol to afford colorless crystals consisting of (*S*)-BINOL and (*S*)-proline, which were analyzed by single crystal X-ray structural analysis. Essentially enantiopure (*S*)- and (*R*)-BINOLs were obtained in high yields after decomposition of the colorless crystalline complex and evaporation of the acetonitrile mother liquor removed from the complex precipitate and successive crystallization. The (*S*)-proline can be recovered and reused without any decrease in efficiency.

1. Introduction

Enantiopure 1,1′-bi-2-naphthols (BINOLs) possessing a C_2-symmetric axis and their derivatives have been extensively used as chiral ligands, auxiliaries, and catalysts in many asymmetric processes because of their highly stable chiral structure and high levels of chiral inducing ability.[1] Therefore a large number of preparation methods for enantiopure (*R*)- and (*S*)-BINOL have been developed, including asymmetric oxidation coupling,[2] fractional crystallization of diastereoisomers,[3] resolution with enzymes or microorganisms,[4] and enantioselective complexation.[5] Among them, enantioselective complexation is one of the most simple, convenient, and efficient methods. However, most of chiral including agents used[5] were prepared from an expensive alkaloid, chiral amines, chiral epichlorohydrin, or a chiral sulfoxide as a chiral starting material. As a result, developing a more simple and efficient method for resolving *rac*-BINOLs is of practical significance.

(*S*)-Proline is an easily available natural amino acid. In 1995, Periasamy[6] et al attempted to resolve racemic BINOL via inclusion complexation of (*S*)-proline in benzene; however, the authors could not separate the pure inclusion complex from the reaction, and only 65% ee of (*S*)-BINOL and 44% ee of (*R*)-BINOL were obtained. In order to obtain enantiopure (*R*)- and (*S*)-BINOLs, the authors[6] carried out three successive repetitions of the above operation, utilizing an equimolar amount of (*S*)-proline for each operation [the overall yield of enantiopure (*S*)-BINOL was ca. 21.8% after three successive repetitions]. The authors also tested the enrichment of the excess enantiomer of the BINOLs in lower ee via inclusion complexation of (*S*)-proline, improving the enantiomeric purity of (*S*)-BINOL from 69% ee to 85% ee.[7] Confusingly, Periasamy[6] ever reported that the inclusion complex formed from *rac*-BINOL and (*S*)-proline in refluxing benzene would decompose in CH_3OH, while in next year,[7] Periasamy chose methanol instead of benzene as the optimized inclusion medium. However, Periasamy did not indicate whether the precipitate formed in benzene was the same as in methanol. In 2000, Shan et al.[8] explored the possibility of resolving *rac*-BINOL via an inclusion reaction of (*S*)-proline under solid state and solid-liquid conditions, and enantiopure (*R*)- and (*S*)-BINOLs were obtained after 'kinetic' crystallization, although the yields were low. In order to establish a practical procedure for preparing enantiopure BINOLs, we recently examined the complexation between (*S*)-proline and *rac*-BINOL, finally realizing enantioselective inclusion complexation of (*S*)-proline to *rac*-BINOL, and easily prepared essentially enantiopure (*R*)- and (*S*)-BINOLs in high yields. Herein we report an improved procedure for preparing essentially enantiopure BINOLs via inclusion complexation of (*S*)-proline.

2. Results and discussion

2.1. Separation of both enantiomers of BINOL via the formation of a molecular complex

During an unsuccessful experiment[9] to prepare a chelated chiral spiroborate derived from *rac*-BINOL, we accidently found that enantiopure BINOLs could be obtained in high yields using (*S*)-proline as the chiral resolving agent and CH_3CN as the solvent through a simple operation. A 1:1 mixture of *rac*-BINOL and (*S*)-proline was allowed to reflux in CH_3CN for 3 h, and then cooled to isolate a white precipitate from aceonitrile solution. The precipitate was

* Corresponding author.
E-mail address: homewhu@yahoo.com.cn (X. Hu).

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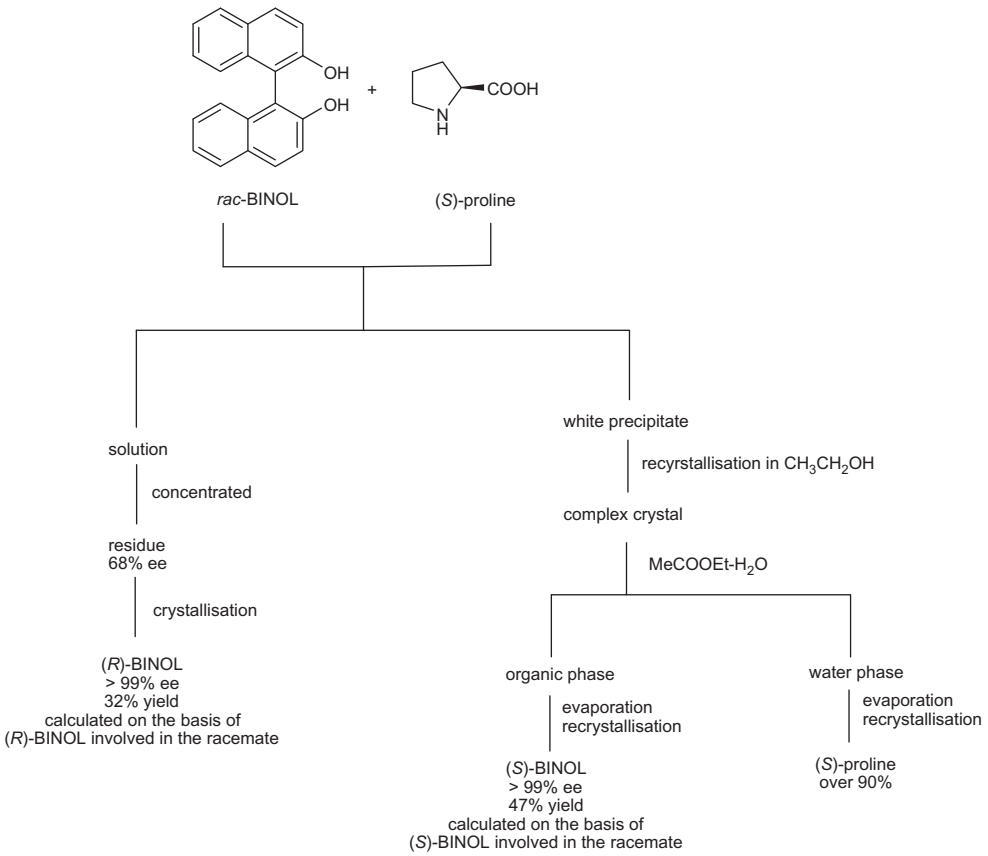
recrystallized in CH_3CH_2OH to give colorless crystals with mp 220–225 °C. The ^1H NMR spectra showed that there were 24 aromatic protons in the region of 6.93–7.85 ppm; four non-aromatic protons at 9.33 ppm disappeared after the addition of D_2O, which correspond to the two molecules of BINOL; there were seven non-aromatic protons in the region of 1.66–3.66 ppm, which is consistent with the proline skeleton resonances; furthermore, the ^{13}C NMR spectra also corresponded to one carbonyl carbon, four types of aliphatic carbons, and several types of aromatic carbons. These spectroscopic data indicated that the crystals were a molecular complex consisting of two molecules of BINOL and one molecule of (*S*)-proline although Periasamy was reported to have obtained the molecular complex, no spectroscopic data for the complex was reported.[6,7]

The crystalline complex obtained was easily disassembled in a H_2O–CH_3COOEt mixture at room temperature; the upper layer organic phase was separated and the water phase extracted with ethyl ether; the organic layers were combined, dried over anhydrous Na_2SO_4, evaporated to remove the solvents, and the residue was recrystallized in toluene to give transparent, heavy crystals of enantiopure (*S*)-BINOL in 47% yield [calculated on the basis of (*S*)-BINOL involved in the racemate; the same below]. The water layer was concentrated under reduced pressure to recover (*S*)-proline in over 90% yield [calculated on the basis of (*S*)-proline in the complex; the same below]. It should be noted that when the white precipitate isolated in MeCN was directly dissociated in a H_2O–CH_3COOEt mixture, (*S*)-BINOL was obtained in 76% ee and 89% yield, indicating that co-precipitation of a small amount of *rac*-BINOL took place. The acetonitrile filtrate was concentrated to furnish (*R*)-BINOL in 68% ee, which was recrystallized in toluene to furnish transparent, heavy crystals of enantiopure (*R*)-BINOL in 32% yield and a small amount of white needles of *rac*-BINOL.[10] The process for resolving *rac*-BINOL via enantioselective inclusion complexation with (*S*)-proline is summarized in Scheme 1.

2.2. Molecular and crystal structure of the complex

By taking into consideration that X-ray crystallographic analytical data for the complex of (*S*)-BINOL and (*S*)-proline (2:1) were previously obtained from the reaction of enantiopure (*S*)-BINOL and (*S*)-proline by Periasamy,[7] we attempted to grow single crystals of the complex directly from the reaction of *rac*-BINOL and (*S*)-proline. Fortunately, the single crystals of the complex could be readily obtained in CH_3CH_2OH. *rac*-BINOL and (*S*)-proline were allowed to reflux in acetonitrile for 3 h to furnish a white precipitate. The white precipitate was dissolved in hot CH_3CH_2OH and then slowly cooled to room temperature to offer a colorless single crystal suitable for X-ray crystallographic analysis with dimensions of $0.16 \times 0.12 \times 0.10$ mm. The crystallographic data were consistent with Periasamy's data. Figure 1 is the perspective view of the molecular complex consisting of (*S*)-proline and (*S*)-BINOL. It can be seen in Figure 1 that (*S*)-proline exists in the form of the zwitterion in the crystal. The structural parameters exhibited for the host and guest molecules are in good agreement with standard values.

As shown in Figures 2 and 3, there is a complicated hydrogen-bonding system in the molecular complex, where the carboxylic-O atoms and the N–H of (*S*)-proline, as well as the hydroxylic-H atoms of (*S*)-BINOL are all in a hydrogen-bonding environment. Each OH group of the two BINOLs acts as the proton donor and the carbonyl oxygen of (*S*)-proline serves as the proton accepters



Scheme 1. Separation of both enantiomers of racemic BINOL via enantioselective inclusion complexation of (*S*)-proline.

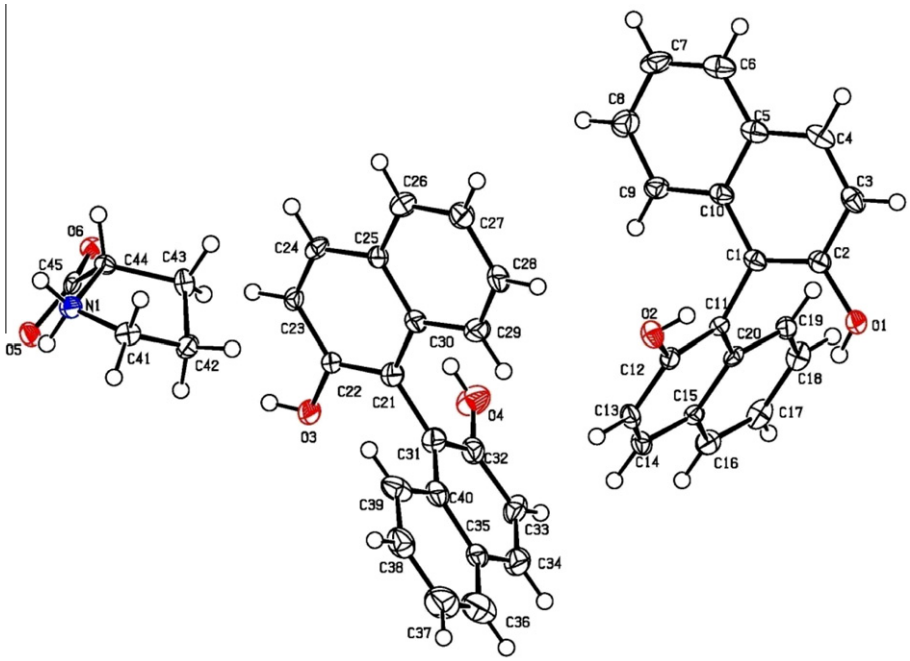


Figure 1. Perspective view of the molecular complex of (*S*)-BINOL and (*S*)-proline.

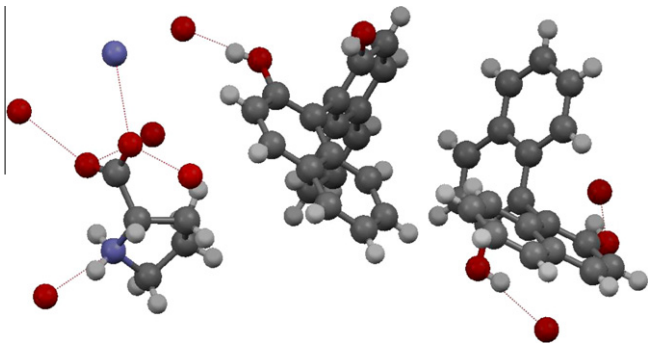


Figure 2. Hydrogen bonding in the molecular complex consisting of (*S*)-BINOL and (*S*)-proline. Hydrogen bonds are shown as dotted lines.

(O(3)-H(3A)...O(5), O(2)-H(2)...O(6), and O(1)-H(1)...O(5)). Simultaneously, hydrogen bonding interactions also occur between the carbonyl-O atom and N–H of (*S*)-proline (N(1)-H(1B)...O(5) and N(1)-H(1A)...O(6)). The molecular complex network between (*S*)-BINOL and (*S*)-proline can be described as infinite chains of interlinked species, which are aligned in an alternating manner through hydrogen bonds.

2.3. Examination of the chiral recognition ability of (*S*)-proline to *rac*-BINOL

It can be deduced based on the studies of Periasamy that (*S*)-proline only has a moderate chiral recognition ability to *rac*-BINOL. However, our experimental results show that (*S*)-proline is an effective chiral recognition agent to *rac*-BINOL in CH_3CN. We noted that in the studies of Periasamy, many solvents, CH_3OH, CH_2Cl_2, $CHCl_3$, and CH_3CN had been tested as the resolving medium. However, according to the report of Periasamy, *rac*-BINOL and (*S*)-proline were heated at 60 °C for 10 min in CH_3CN and then left at 25 °C for 12 h to furnish corresponding precipitate. We deduced that a co-crystallization of *rac*-BINOL with the resulting molecular complex could take place during the precipitation process. Under our experimental conditions, refluxing both the reactants for 3 h in MeCN (bp 81 °C) certainly would be favorable for the host–guest reaction and reducing the co-crystallization of *rac*-BINOL. Our tests proved that single crystallization of the resulting precipitate in CH_3CH_2OH could completely remove the *rac*-BINOL included in the molecular complex. It appeared that raising the host–guest reaction efficiency and lowering the co-crystallization degree of *rac*-BINOL were key to improving the practical applicability for this resolution.

For confirming our ideas, the following experiments (Scheme 2) were conducted. Enantiopure (*S*)-BINOL and (*S*)-proline were allowed to reflux in CH_3CN for 3 h to furnish almost quantitatively a 2:1 complex of (*S*)-BINOL and (*S*)-proline. In contrast, no inclusion complexation between enantiopure (*R*)-BINOL and (*S*)-proline took place under similar conditions, and (*R*)-BINOL was almost completely recovered. These results clearly show that enantioselective inclusion complexation between (*S*)-BINOL and (*S*)-proline is able to occur in high efficiency in CH_3CN.

Using ethyl acetate or toluene as the inclusion medium for the resolution of *rac*-BINOL with (*S*)-proline were also attempted, but the resolving efficiency was low.

Periasamy previously liberated the (*S*)-BINOL in the precipitate by acid hydrolysis with dilute HCl.[6] We have demonstrated that an H_2O–MeCOOEt mixture is a practical, environmentally friendly medium for the liberation of (*S*)-BINOL from the complex.

3. Conclusion

An improved approach to prepare essentially enantiopure (*R*)- and (*S*)-BINOL's via enantioselective inclusion complexation with (*S*)-proline has been developed. *rac*-BINOL and (*S*)-proline were allowed to reflux in CH_3CN for 3 h and the resulting precipitate was crystallized in CH_3CH_2OH to furnish a complex crystal consisting of two molecules of (*S*)-BINOL and one molecule of (*S*)-proline, which had been analyzed by single crystal X-ray diffraction analysis. This complex was disassembled in a H_2O–CH_3COOEt mixture to give essentially enantiopure (*S*)-BINOL in 47% yield. The CH_3CN mother liquor removed from the precipitate was evaporated to dryness, and then recrysatllized in toluene to afford essentially enantiopure (*R*)-BINOL in 32% yield.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were performed on a Varian Mercury VS 300. MS was recorded on a VG ZAB-HF-3F spectrometer. Optical rotations were measured on a PE-341 Mc polarimeter. Melting points were determined on a VEB Wagetechnik Rapio PHMK05 instrument and are uncorrected. Ee values were analyzed by HPLC on a Chiralcel AD column (4.6 × 250 mm) at room temperature with *n*-hexane/*i*-propanol (4:1) as eluent.

(*S*)-Proline was purchased from *Wuhan University Bio-chemical Co.* and used directly without further purification. Racemic 1,1′-bi-2-naphthol was purchased from Guangxi Xinjing Science and Technology Co. Ltd China, and recrystallized from Et_2O, Mp 218–220 °C; IR: 3507, 3436 (O–H). The THF, MeCN and ethanol used were of AR grade. Other reagents are purchased and used directly without special treatment.

4.2. Resolution of *rac*-BINOL via enantioselective inclusion complexation

rac-BINOL (1.43 g, 5 mmol) and (*S*)-proline (0.575 g, 5 mmol) were added to acetonitrile (20 mL). The mixture was refluxed for 3 h, and then cooled to room temperature to give a white precipitate from the solution. The precipitate was recrystallized in ethanol (about 35 mL) to furnish 0.653 g of colorless crystals of the molecular complex, 76% yield (based on (*S*)-BINOL involved in the racemate); Mp 220–225 °C, ^{1}H NMR (DMSO-d_6): δ 9.33 (s, 4H, disappeared after adding D_2O), 7.85 (d, J = 8.1 Hz, 8H), 7.33 (d, J = 9 Hz, 4H), 7.25–7.14 (m, 8H), 6.93 (d, J = 8.1 Hz, 4H), 3.66 (t, J = 8.1 Hz, 1H), 3.24–3.16 (m, 1H), 3.05-–2.96 (m, 1H), 2.02–1.91(m, 2H), 1.80-1.66 (m, 2H). ^{13}C NMR (DMSO-d_6): δ 171.6, 152.1, 133.3, 128.2, 127.6, 126.9, 125.0, 123.8, 121.6, 117.7, 113.9, 59.9, 44.7, 28.7, 23.4. The crystal was added to a 3:2 (v/v) mixture of ethyl acetate and water and stirred at room temperature for about 2 h. The solid was completely dissolved, the organic layer was separated, and the water phase extracted with ethyl ether (10 ml × 3). The organic layers were combined and dried over anhydrous Na_2SO_4, evaporated to remove the solvents, the residue was recrystallized in toluene to offer 0.336 g of a transparent, heavy crystal of (*S*)-1,1′-bi-2-naphthol, overall yield, 42%; Mp: 206–208 °C {lit.[5e] 207–210 °C}; $[\alpha]_D^{20} = -35.4$ (*c* 1, THF), 99.98% ee based on HPLC on a chiral column.

The water layer was concentrated under reduced pressure to give 0.257 g of (*S*)-proline in 90% recovery efficiency. The recovered (*S*)-proline could be reused for the resolution of racemic BINOL and almost the same result was obtained.

The acetonitrile filtrate was evaporated and the residue was recrystallized in toluene twice to furnish 0.236 g transparent, heavy crystal of (*R*)-1,1′-bi-2-naphthol (38% yield), Mp: 206–208 °C {lit.[5e]: 208–210 °C}; $[\alpha]_D^{20} = +35.0$ (*c* 1, THF), 99.88% ee based on HPLC on a chiral column. Furthermore 0.132 g of white, lightweight needles, of almost *rac*-BINOL (Mp 216–218 °C) was separated out.[10]

4.3. X-ray crystal structure analysis of the complex

Crystals suitable for X-ray structural analysis were obtained by slowly cooling a hot ethanol solution of the complex to room temperature. A colorless crystal of dimensions 0.16 × 0.12 × 0.10 mm was mounted on a glass fiber. X-ray diffraction intensity data collection and cell refinement were performed on Bruker APEX-II CCD. A total of 6635 unique reflections were collected using MoKa (k = 0.71073 Å) radiation by fine-focus sealed tube at 273(2) *K*, of which 6247 reflections had $I > 2\sigma(I)$ and were used in the structure solution and refinements. The corrections for *Lp* factors and empirical absorption were applied to the intensity data. All calculations were performed on Enraf-Nonius Molen/VAX Software using the program SHELXL-97. The structure was solved by direct methods and refined on F^2 using a full-matrix least-squares technique. The non-hydrogen atoms were also refined by a full-matrix least-squares technique, anisotropically, and hydrogen atoms were included but not refined. Cell dimensions were obtained by the least-squares refinement of well centered reflections in the range of $1.49 < \theta < 26°$. Convergence with unweighted and weighted agreement factors was achieved at R = 0.0641 and Rw = 0.1605 ($w = 1/[/s^2(F_o^2) + (0.0740P)^2 + 4.2576P]$ where $P = (F_o^2 + 2Fc^2)/3$, S = 0.0006(8), and $Fc^* = kFc[1 + 0.001 \times Fc^2/l^3/\sin(2/q)]^{-1/4}$). The maximum and minimum peaks on the final difference Fourier map correspond to 1.123 and −0.326 eÅ^{-3} respectively.

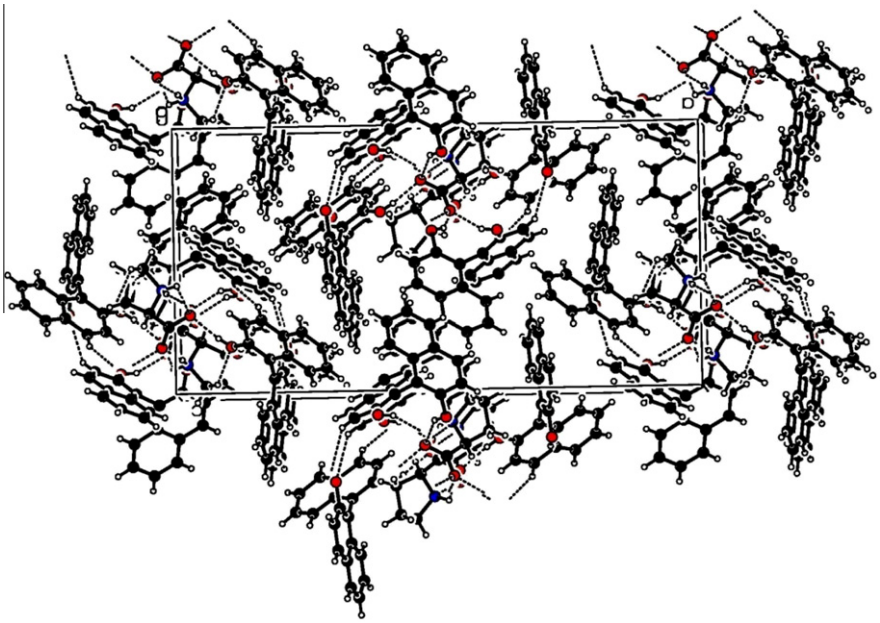
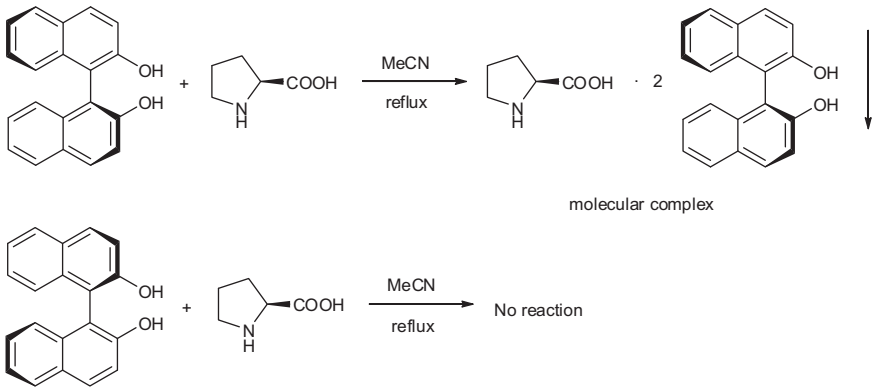


Figure 3. Packing diagram of the molecular complex of (*S*)-BINOL and (*S*)-proline. Hydrogen bonds are shown as dotted lines.



Scheme 2. Interaction of (*S*)- and (*R*)-BINOL with (*S*)-proline in MeCN.

Crystal data for the 1:2 complex of (*S*)-proline and (*S*)-BINOL: empirical formula, $C_{45}H_{37}NO_6$; formula weight, 687.76; calculated density, 1.348 g/cm^3; volume (V), 3388.75(6) Å^3; crystal system, Orthorhombic; space group, P2(1)2(1)2(1); $Z = 4$; unit cell dimensions, $a = 27.272(2)$, $b = 9.0398(8)$, $c = 13.7458(12)$, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$; absorption coefficient (μ), 0.089 mm^{-1}; index ranges $-33 \leqslant h \leqslant 32$, $-10 \leqslant k \leqslant 11$, $-16 \leqslant l \leqslant 16$; $F(000)$, 1448; GOF, 1.050.

Acknowledgments

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9. We attempted to prepare a chelated chiral spiroborate (see Ref. 3d,e,g and Periasamy, M. *Pure & Appl. Chem.* **1996**, *68*, 663–666) ester via *rac*-BINOL, butyl borate and (*S*)-proline in refluxing acetonitrile. A white precipitate isolated after refluxing for several hours. The white precipitate was recrystallized in CH_3CH_2OH. Spectroscopic analysis of the crystals obtained revealed that the product was a molecular complex consisting of BINOL and (*S*)-proline, instead of the desired spiroborate. This unsuccessful experiment may mean that inclusion complexation between (*S*)-proline and BINOL readily occurs. As a result, we decided to examine the complexation behaviour between racemic BINOL and (*S*)-proline in acetonitrile. We found that complexation between (*S*)-proline and *rac*-BINOL could take place enantioselectively. On the basis of this, a more practical approach to produce enantiopure BINOLs was established.
10. We had found that enantiopure (*R*)- and (*S*)-BINOL are different from racemic BINOL in crystalline behavior in benzene or toluene. In the two solvents, the enantiopure isomers were separated out as colorless, transparent, heavy crystals, and racemic BINOL was isolated as white, lightweight needles. This crystalline property has been successfully applied to the separation of the enantiomers and the racemate in non-racemic BINOL according to 'kinetic' crystallization.