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An economic, practical access to enantiopure 1,1′-bi-2-naphthols: enantioselective complexation of *threo*-(1*S*,2*S*)-*N*-benzyl-*N*,*N*-dimethyl[1,3-dihydroxy-1-(4′-nitrophenyl)]-2-propylammonium chloride

Wuzu Ha and Zixing Shan*

Department of Chemistry, Wuhan University, Wuhan 430072, China

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Abstract—An economic, convenient access to enantiopure (*R*)- and (*S*)-1,1′-bi-2-naphthol (BINOL) has been discovered. Racemic 1,1′-bi-2-naphthol was reacted with *threo*-(1*S*,2*S*)-*N*-benzyl-*N*,*N*-dimethyl-[1,3-dihydroxyl-1-(4′-nitrophenyl)]-2-propylammonium chloride (BDDNPAC) in water-containing acetonitrile under reflux until the solid dissolved completely, and then cooled to ambient temperature to isolate a yellow-greenish crystal consisting of BDDNPAC, (*S*)-BINOL, and water, which was analyzed by single crystal X-ray structural analysis. Enantiopure (*S*)- and (*R*)-1,1′-bi-2-naphthols were obtained in high yield after decomposition of the colored crystalline complex and evaporation of the acetonitrile solution removed from the complex crystals and successive crystallization. The chiral quaternary ammonium salt BDDNPAC can be recovered and reused without any decrease in efficiency.

1. Introduction

Enantiomerically pure 1,1′-bi-2-naphthols (BINOLs) possessing a C_2-symmetric axis and their derivatives are very important chiral ligands and auxiliaries, and have been extensively used in catalytic and stoichiometric asymmetric synthesis.[1,2] To meet this progressive need, a large number of preparative methods for enantiopure (*S*)- and (*R*)-BINOL have been reported, including fractional crystallization of diastereoisomers,[3,4] resolution with enzymes or microorganisms,[5] asymmetric oxidation coupling,[6] and enantioselective complexation.[7–13] As far as the complexation method is concerned, *N*-benzylcinchonidinium chloride,[7] *N*-benzylcinchonidinium chloride,[8] (*S*)-5-oxopyrrolidine-2-carboxanilide,[9] (*S*,*S*)-1,2-diaminocyclohexane,[10] chiral sulfoxide[11] *N*-(3-chloro-2-hydroxy-propyl)-*N*,*N*,*N*-trimethylammonium chloride,[12] and ethers of tartaric acid derivatives[13] have been used as chiral complexing agents. However, most of these chiral compounds were prepared from an expensive alkaloid, chiral amine, chiral epichlorohydrin or chiral sulfoxide, as a basic chiral starting material. Therefore, the cost for the preparation is higher, and from a practical point of view, most of them are not economic.

threo-(1*S*,2*S*)-2-Amino-1-(4′-nitrophenyl)-1,3-propanediol [*threo*-(1*S*,2*S*)-ANP], a 'chiral waste' in the production of chloromycetin, is one of the least expensive artificial chiral materials available. Investigation into reaction and application of *threo*-(1*S*,2*S*)-ANP is of significance for the development of new varieties of chiral materials. Recently, we conveniently prepared a number of ionic or non-ionic chiral compounds[14] using *threo*-(1*S*,2*S*)-ANP as a chiral starting material, two of which have been successfully applied to the resolution of racemic ibuprofen[15] and the preparation of enatiomerically pure BINOLs.[4h] Herein, we report the enantioselective complexation of a quaternary ammonium salt derived from *threo*-(1*S*,2*S*)-ANP, *threo*-(1*S*,2*S*)-*N*-benzyl-*N*,*N*-dimethyl-[1,3-dihydroxyl-1-(4′-nitrophenyl)]-2-propylammonium chloride (BDDNPAC, Scheme 1) to racemic BINOL and an economic, practical preparation of enantiopure (*S*)- and (*R*)-BINOL.

* Corresponding author. Tel.: +86 027 68764768; fax: +86 027 68754067; e-mail addresses: kenshan@public.wh.hb.cn; zxshan@whu.edu.cn

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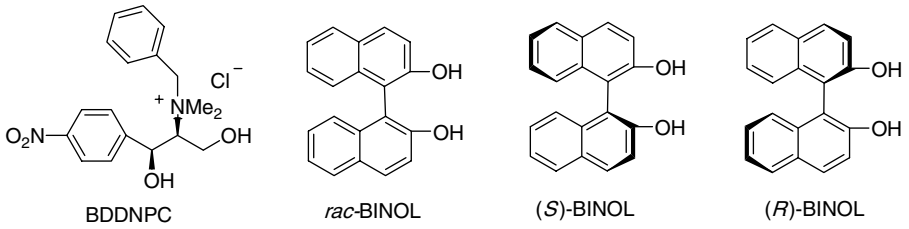


Scheme 1. Chiral including agent BDDNPAC and 1,1′-bi-naphthalene-2,2′-diol (BINOL).

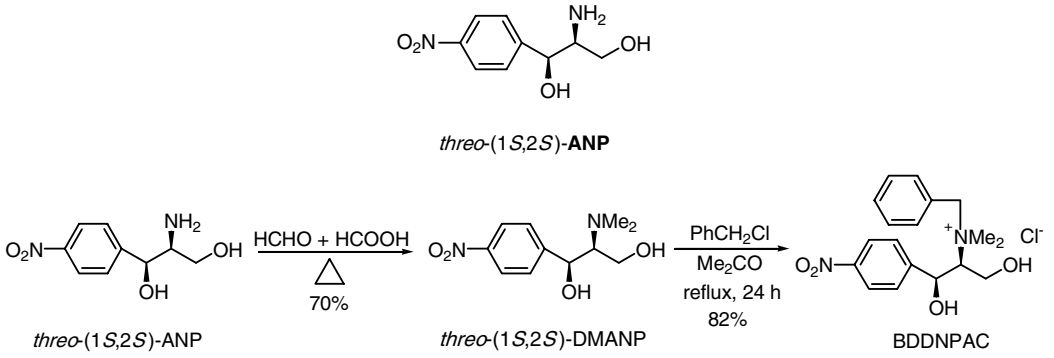
2. Results and discussion

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

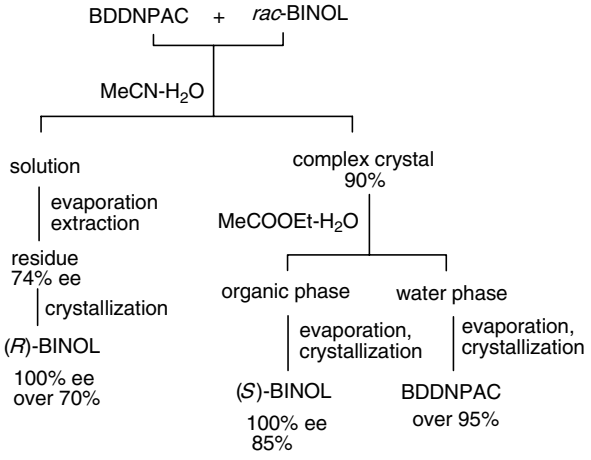
The chiral quaternary ammonium salt *threo*-(1*S*,2*S*)-*N*-benzyl-*N*,*N*-dimethyl-[1,3-dihydroxyl-1-(4′-nitrophenyl)]-2-propylammonium chloride, BDDNPAC has never been reported, although its analogous *N*-alkyl bromide and iodide has been prepared.[16] We found that it could be conveniently synthesized in high yield from *threo*-(1*S*,2*S*)-ANP via methylation with formic acid and formaldehyde and sequential quaternization with benzyl chloride (Scheme 2). The basic chiral starting material *threo*-(1*S*,2*S*)-ANP, from a pharmaceutical factory can be efficiently purified via recrystallization in a mixed solvent of MeOH and H_2O. BDDNPAC as prepared above was allowed to reflux with consistently stirring with racemic BINOL in water-containing acetonitrile, until the solid completely dissolved, and then cooled to room temperature. A large amount of yellow-greenish crystals was isolated from the system. The crystals were then separated from the mother liquor to be treated later. The IR spectra of the crystal showed the characteristic absorption of BINOL and BDDNPAC, and the absorption of the OH groups of BINOL shifted to a lower frequency field. Its ^{1}H NMR spectra clearly indicated that it included equimolar BINOL and BDDNPAC. It can be seen by comparison of the ^{1}H NMR spectra with those of BDDNPAC and BINOL that the hydroxylic protons of BINOL shifts considerably downfield (to 9.23 ppm) as well as that of the hydroxylic protons in the salt shift slightly upfield, meaning that the crystal can be a molecular complex, and where all the hydroxylic protons are in hydrogen-bonding environment. Its single crystal X-ray diffraction analysis result showed that BDDNPAC and BINOL were connected together via a complicated hydrogen-bonding network including a water molecule (see later section). This molecular complex was difficult to dissolve in water and most of the familiar organic solvents; however, it could be cleaved in certain cases. When the complex was heated and refluxed in a mixture of a polar organic solvent (e.g., ethyl acetate) and water, a two-phase solution was formed. The organic phase was separated, evaporated, and the residue recrystallized in toluene to give transparent, heavy crystals of enantiopure (*S*)-BINOL in 95% yield based on the complex, the overall yield, 85%. The water layer was evaporated to dryness under a reduced pressure and the residue was recrystallized in ethanol. The BDDNPAC was recovered almost quantitatively, and could be reused in the formation of the molecular complex to furnish the desired product in nearly the same yield as above. The acetonitrile mother liquor removed from the molecular complex was evaporated to provide an enriched (*R*)-BINOL, which was extracted with Et_2O (it has been proven that the insoluble solid was a mixture of BDDNPAC and the molecular complex), evaporated and recrystallized in toluene to offer transparent, heavy crystals of enantiopure (*R*)-BINOL in over 70% yield and a small amount of white, needle racemic BINOL.[17] It appears that the cheap chiral quaternary ammonium salt can discriminate with high enantioselectivity both the enantiomers of racemic BINOL and form a molecular complex crystal with (*S*)-BINOL. The process of chiral separation of BINOL via enantioselective complexation of the chiral host to racemic guest was summarized in Scheme 3.

2.2. Molecular and crystal structure of the complex

A hot water-containing acetonitrile solution of the molecular complex was slowly cooled to room temperature to furnish a yellow-greenish single crystal suitable for X-ray crystal structure analysis with dimensions of



Scheme 2. Preparation of *threo*-(1*S*,2*S*)-*N*-benzyl-*N*,*N*-dimethyl-[1,3-dihydroxyl-1-(4′-nitrophenyl)]-2-propylammonium chloride, BDDNPAC.



Scheme 3. Separation of both the enantiomers of racemic BINOL via enantioselective inclusion complexation of BDDNPAC.

0.20 mm × 0.18 mm × 0.17 mm. Final atomic coordinates of the crystal, along with 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-287999. Data 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.cn; web: http//www.ccdc.cam.ac.uk). Figure 1 shows the numbering scheme of the molecular complex. The intermolecular organization and association in the complex are depicted in Figure 2. The structural parameters exhibited for the various moieties in the complex are in good agreement with the standard values.

As shown in Figure 2, there is a complicated hydrogen-bonding system in the molecular complex, where all the hydroxylic H atoms are in a hydrogen-bonding environment, and H_2O and Cl^- are used as bridges between the chiral quaternary ammonium salt molecules or between a quaternary ammonium salt molecule and a BINOL molecule. For a BINOL, it is connected directly or indirectly with three quaternary ammonium salt molecules via three hydrogen bonds. More accurately, one of the hydroxyl groups of BINOL is used as proton donor in a H bonding [O(6)–H(6F)–Cl(1)], while the other plays a different role in the formation of hydrogen bond, that is, it is used as a proton donor in one instance [O(7)–H(5F)–O(5)] and as a proton acceptor in another instance [O(5)–H(4F)–O(4)]. For a quaternary ammonium salt BDDNPAC molecule, it can simultaneously connect directly or indirectly with two BINOL molecules and three BDDNPAC molecules via hydrogen bonds, of which three connections include hydrogen bonds generated from two hydrogen atoms of a water molecule, respectively. It appears that the existence of a water molecule is a key factor in the formation of the molecular complex. It not only makes bonding occur efficiently between the salt molecules via hydrogen bond interaction and the salt molecules arrange in head-to-head mode along the *c*-axis to form layer structure, but also provides appropriate connectors for the embedding of BINOL and the formation of the hydrogen-bonding network.

The chiral quaternary ammonium salt molecule layers assembled via a hydrogen bond have a specific configuration, and have a very strong chirality recognition ability with regards to racemic BINOL. As a result, only (*S*)-BINOL molecules are permitted to inset between the layers (i.e., the absolute configuration of the BINOL is limited as levorotatory) and connected with chiral quaternary

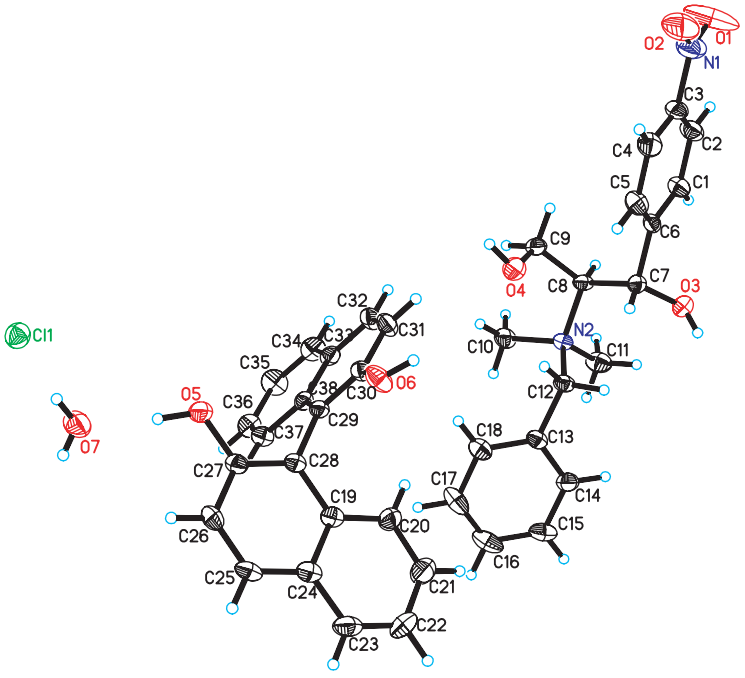


Figure 1. Perspective view of the molecular complex of BDDNPAC, (*S*)-BINOL and water showing the numbering scheme.

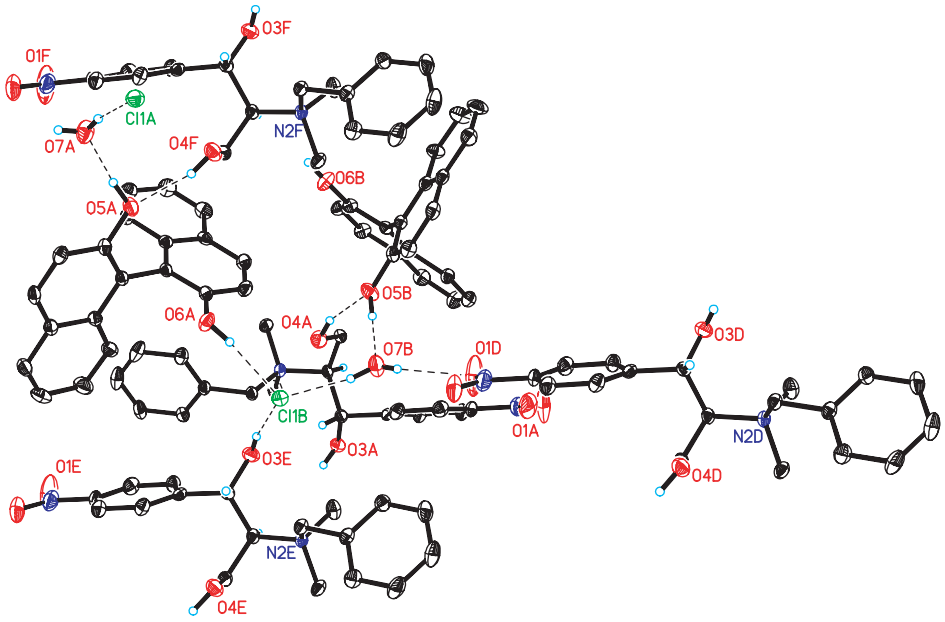


Figure 2. Hydrogen bonding in the molecular complex consisting of BDDNPAC, (*S*)-BINOL and H_2O shown as dotted lines (bond lengths: Å). O(5)–H(5F)–O(7): O(5)–H(5F), 0.93 (6); O(7)–H(5F), 1.72 (6); O(5)–O(7), 2.648 (4). O(6)–H(6F)–Cl(1): O(6)–H(6F), 0.87 (4); Cl(1)–H(6F), 2.17 (4); O(6)–Cl(1), 3.034 (3). O(3)–H(3F)–Cl(1): O(3)–H(3F), 0.81; Cl(1)–H(3F), 2.28(5); O(3)–Cl(1), 3.077 (3). O(7)–H(7F)–Cl(1): O(7)–H(7F), 0.87 (4); Cl(1)–H(7F), 2.21 (4); O(7)–Cl(1), 3.074 (4). O(7)–H(7E)–O(1): O(7)–H(7E), 0.74 (5); O(1)–H(7E), 2.25 (5); O(7)–O(1), 2.925 (5). O(4)–H(4F)–O(5): O(4)–H(4F), 0.90 (6); O(5)–H(4F), 1.94 (6); O(4)–O(5), 2.811 (4). Bond angles for hydrogen bonds (°): O(6)–H(6F)–Cl(1), 173 (4); O(5)–H(5F)–O(7), 173 (5); O(7)–H(7F)–Cl(1), 169 (4); O(7)–H(7E)–O(1), 153 (6); O(3)–H(3F)–Cl(1), 167 (5); O(4)–H(4F)–O(5), 161 (5); H(7F)–O(7)–H(7E), 118(5).

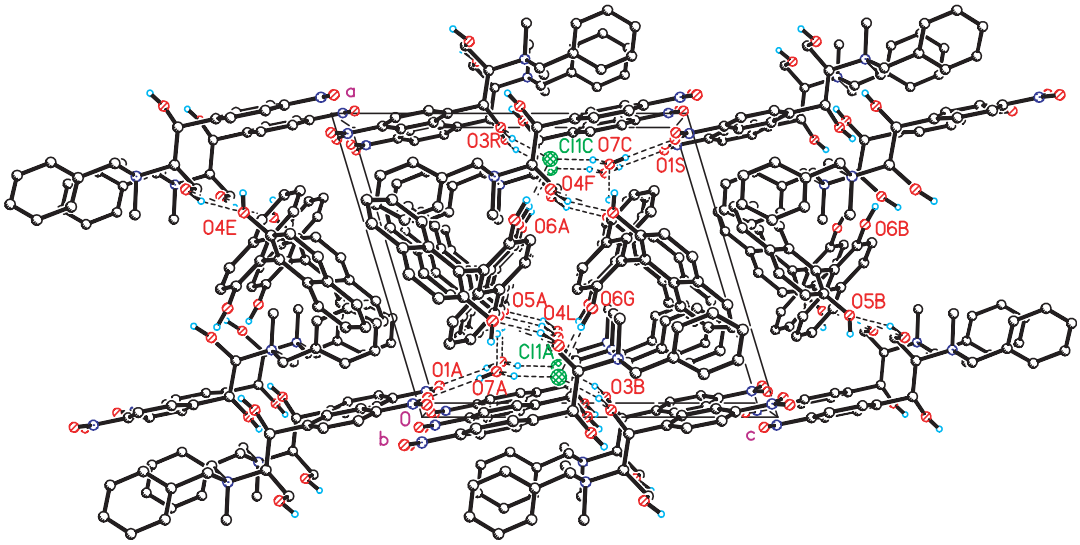


Figure 3. The packing diagram of the molecular complex of the chiral quaternary ammonium salt BDDNPAC, (*S*)-BINOL and water. Hydrogen bonds are shown as dotted lines.

ammonium salt molecules together via specific hydrogen bonds to form a supramolecular network. The ordered connection of BDDNPAC and (*S*)-BINOL molecules engenders a stable three-dimensional architecture, where the chloride ion, the oxygen atom of water molecule and the hydroxylic O(5) atom of (*S*)-BINOL are located at the node of the hydrogen-bonding network. The packing diagram of the molecular complex of the chiral quaternary ammonium salt BDDNPAC, (*S*)-BINOL and water is shown in Figure 3.

3. Conclusion

A novel, inexpensive chiral quaternary ammonium salt BDDNPAC for the preparation of enantiopure (*R*)- and (*S*)-BINOL has been discovered, which was synthesized from *threo*-(1*S*,2*S*)-2-amino-1-(4′-nitrophenyl)-1,3-propanediol as a chiral starting material. A mixture of BDDNPAC and racemic BINOL was refluxed in water-containing acetonitrile and dissolved to furnish a homogeneous yellow solution, which was cooled to room temperature to isolate

a yellow-greenish crystal consisting of BDDNPAC, (*S*)-BINOL, and water in a 1:1:1 molar ratio, in which there was a complicated, but ordered H-bonding network. The complex crystal gave enantiopure (*S*)-BINOL in very high yield after simple treatment. The mother liquor removed from the complex crystal offered enantiopure (*R*)-BINOL after evaporation, extraction, and crystallization. On the other hand, the chiral quaternary ammonium salt can be conveniently recovered and reused. The procedure separating both the enantiomers of BINOL via enantioselective complexation is simple, efficient, and economic. This is perhaps one of the most practical preparative methods for enantiopure (*R*)- and (*S*)-BINOL for the time being.

4. Experimental

4.1. General

IR spectra were recorded on a *Testscan Shimadzu FTIR 8000* in KBr.^{1}H and ^{13}C NMR spectra were performed on a *Varian Mercury VS 300*, δ values (ppm) relative to Me_4Si. 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 obtained by comparison with the maximum of specific rotation.

threo-(1*S*,2*S*)-2-Amino-1-(4′-nitrophenyl)-1,3-propanediol [*threo*-(1*S*,2*S*)-ANP] was presented by Wuhan Pharmaceutical Factory as a gift, and purified via crystallization, mp 161–163 °C, $[\alpha]_D^{20} = +31.4$ (*c* 1, 6 M HCl); *threo*-(1*S*,2*S*)-*N*-Benzyl-*N*,*N*-dimethyl-[1,3-dihydroxyl-1-(4′-nitrophenyl)]-2-propylammonium chloride (BDDNPAC) was conveniently synthesized in high yield from *threo*-(1*S*,2*S*)-ANP via methylation with formic acid and formaldehyde and sequential quaternization with benzyl chloride, 176–178 °C; $[\alpha]_D^{20} = +48.8$ (*c* 1.184, EtOH); MS (FBA): 331 ($M^+_{C_{18}H_{23}N_2O_4}$, 100). Racemic 1,1′-bi-2-naphthol was purchased from Guangxi Xinjing Science and Technology Co. Ltd., and without special treatment prior to use.

4.2. Resolution of racemic 1,1′-bi-2-naphthol via enantioselective complexation

1,1′-Bi-2-naphthol (2.86 g,10 mmol) and chiral quaternary ammonium salt BDDNPAC (2.20 g, 6 mmol) were added to a water-containing acetonitrile (40 mL). The mixture was refluxed until the solid dissolved completely to form a homogeneous solution. The solution was cooled to room temperature, yellow-greenish crystals isolated out of the solution and filtered. The solid was collected and washed with acetonitrile (about 10 mL), dried, and quantified, 3.03 g, 90% yield; Mp 178–210 °C; $[\alpha]_D^{20} = -25.9$ (*c* 1.012, DMF); ^{1}H NMR (DMSO-d_6): δ 9.36 (s, 2H, disappeared after adding D_2O), 8.28 (d, $J = 8.1$ Hz, 2H), 7.86–7.86 (m, 6H), 7.67 (s, 2H), 7.54 (s, 3H), 7.39 (d, $J = 9.0$ Hz, 2H), 7.28 (s, 1H, disappeared after adding D_2O), 7.24–7.12 (m, 4H), 6.94 (d, $J = 7.8$ Hz, 2H), 5.90 (s, 1H, disappeared after adding D_2O), 5.59–5.57 (m, 1H), 5.14–4.99 (AB system, 2H), 3.87 (d, $J = 13.2$ Hz, 1H), 3.75 (d, $J = 9$ Hz, 1H), 3.47 (s, 2H, mixed together with water in the solvent, disappeared after adding D_2O), 3.26–3.31 (m, 1H), 3.26 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 153.7, 150.4, 147.9, 134.8, 134.3, 130.9, 130.0, 129.4, 129.2, 129.1, 128.8, 128.5, 126.5, 125.1, 124.4, 122.9, 119.3, 116.1, 74.4, 70.5, 69.0, 57.8, 51.0, 50.3. IR (KBr, cm^{-1}): 3418, 1603, 1520, 1479, 1437, 1348, 1294, 1257, 1098, 1009, 950, 760. The mother liquor was evaporated to dryness, and the residue treated, with stirring, with diethyl ether, filtered, and the indissoluble solid (0.65 g) combined with the above colored crystals and added to a 3:2 (v/v) mixture of ethyl acetate and water. The mixture was heated and refluxed until the solid dissolved completely (for about 1 h), and then cooled to room temperature, the organic layer was separated, and the water phase extracted with diethyl ether (20 mL × 3). The organic phases were combined and dried over anhydrous Na_2SO_4, evaporated to remove the solvents, to give 1.32 g of solid. The solid was recrystallized in toluene to afford 1.22 g of transparent, heavy crystal of (*S*)-1,1′-bi-2-naphthol, overall yield, 85%; Mp 206–208 °C; $[\alpha]_D^{20} = -35.4$ (*c* 1.78, THF), 100% ee {lit.[7a]: $[\alpha]_D^{21} = -34$ (*c* 1, THF)}. The water layer was evaporated to dryness, and the residue was recrystallized in ethanol–water to give 2.1 g BDDNPAC, 95% recovery efficiency. The recovered salt could be reused for resolution of racemic BINOL and almost same result was obtained.

The etheral solution removed from the indissoluble solid was dried over anhydrous Na_2SO_4, evaporated, and the residue was recrystallized in toluene to furnish 1.0 g transparent crystal (*R*)-BINOL (70% yield). Mp 206–208 °C; $[\alpha]_D^{20} = +34.8$ (*c* 1.84, THF), 100% ee {lit.[7a]: $[\alpha]_D^{21} = -34$ (*c* 1, THF)} and 0.35 g white, lightweight needle, an almost racemic BINOL (Mp 216–218 °C).

4.3. X-ray crystal structure analysis of the complex

A single crystal suitable for X-ray structural analysis was obtained by slowly cooling a hot, water-containing acetonitrile solution of the complex to room temperature. A yellow-brownish crystal of dimensions 0.20 mm × 0.18 mm × 0.17 mm was mounted on a glass fiber. X-ray diffraction intensity data collection and cell refinement were performed on Bruker P4 four-circle diffractometer equipped with a graphite monochromator. A total of 5516 unique reflections were collected using MoK_α-($\lambda = 0.71073$ Å) radiation by the ω–2θ scan technique at 291(2) K, of which 4085 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 289 reflections in the range of $2 < \theta < 25.1°$. The final cycle of full-matrix least-squares refinement was based on 5422 observed reflections and 459 variable parameters.

Convergence with unweighted and weighted agreement factors was achieved at $R = 0.0529$ and $R_w = 0.0907$ ($w = 1/[\backslash s^2(F_o^2) + (0.0481P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$, $S = 0.0140(14)$, and $F_c^* = kF_c[1 + 0.001 \times F_c^2\backslash l^3/\sin(2\backslash q)]^{-1/4}$). The maximum and minimum peaks on the final difference Fourier map correspond to 0.224 and -0.150 eÅ^{-3}.

Crystal data for a 1:1:1 complex of BDDNPAC, (*S*)-BINOL, and water: empirical formula, $C_{38}H_{39}ClN_2O_7$; formula weight, 671.16; calculated density, 1.284 g/cm^3; volume (V), 1736.5(6) Å^3; crystal system, monoclinic; space group, *P*2(1); $Z = 2$; unit cell dimensions, $a = 12.547(3)$, $b = 10.265(2)$, $c = 14.075(3)$, $\beta = 106.98(3)°$; absorption coefficient (μ), 0.162 mm^{-1}; index ranges $0 \leqslant h \leqslant 15$, $-12 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 16$; *F*(000), 708; GOF, 1.031.

Acknowledgements

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17. Enantiopure (*R*)- and (*S*)-BINOL are different from racemic BINOL in crystalline behavior in benzene or toluene. In the two solvents, enantiopure isomers are separated out as a colorless, transparent, heavy crystal, and that racemic BINOL is isolated as a white, lightweight needle. This crystalline property has been successfully applied to the separation of the enantiomer and the racemate in a non-racemic BINOL. In our experiment, the water-containing acetonitrile solution removed from the molecular complex crystal was evaporated to dryness to furnish a solid mixture of (*R*)-BINOL and a small amount of the dissolved molecular complex, BDDNPAC and racemic BINOL (for BINOL, it is either the unchanged starting material or the result of racemization of (*R*)-BINOL during heating). The solid mixture was worked up with Et_2O, (*R*)- and racemic BINOL entered into the solution. When the ethereal solution was evaporated and the residue was crystallized in toluene, enantiopure BINOL was efficiently separated from the racemate.