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Synthesis of enantiomerically pure helicene like bis-oxazines from atropisomeric 7,7'-dihydroxy BINOL: Preliminary measurements of the circularly polarized luminescence

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Abstract

Racemic sample of 2,2',7,7'-tetrahydroxy-1,1'-binaphthyl was resolved with (*S*)-proline and the separated enantiomers were independently converted to atropisomeric bis-oxazines by aromatic Mannich reaction. These chirally pure oxazines were then converted to the helicene like cyclic ethers. The Circularly Polarized Luminescence (CPL) profile was consistent with the isolation of the targeted helical-like molecules in optically pure form, prepared from the achiral primary amines. The compounds of interest displayed active and opposite CPL activities for each sets of the helicene like isomers (*P*)-/(*M*)-**3** and (*P*)-/(*M*)-**5**.

Keywords

Resolution; bis-oxazine; CD and CPL study

Design, synthesis and application of structurally diverse chiral molecules is an extremely important field of contemporary organic chemistry. The correlation of structural features of chiral molecules and their specific properties is now a well established field. Novel chiral molecules have found many useful applications in the areas from medicine to material science.¹ The large number of naturally occurring and artificial chiral molecules possess either a chiral element; chiral center, chiral axis or chiral plane.

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Optically active molecules with chiral axis are categorized as atropisomeric,² helical³ or allene.⁴ These well studied molecules have some of the unique optical properties linked with their structural architecture. It would be useful if methods are made available for the precise synthesis of optically pure helical or atropisomeric molecules and will be helpful for further evaluation of their specific chiroptical properties. In our ongoing project of the synthesis and study of helicene or helicene-like compounds, we have previously described the synthesis of bis-1,3-oxazines in optically pure forms.⁵ In the study we had converted the racemic sample of 2,2',7,7'-tetrahydroxy 1,1'-binaphthyl **1** to diastereomeric mixture of bis-oxazines. The diastereomers of bis-oxazine were then separated by physical means such as crystallization or column chromatography and eventually converted to helicene like molecules (Figure 1). This approach has a limitation of selecting optically pure primary amine as one of the reactants for the synthesis of diastereomeric 1,3-oxazine unit.⁶ It is envisaged that if the synthesis of bis-oxazine is based on enantiomerically pure 2,2',7,7'-tetrahydroxy-1,1'-binaphthyl **1** as the starting material, one may obtain optically pure (*P* or *M*) bisoxazine with the use of achiral primary amine. In the present work we describe the synthesis of enantiomerically pure helicene like bis-oxazine from optically pure tetrol **1**.

Structurally similar 2,2'-dihydroxy-1,1'-binaphthyl (BINOL) possessing a C_2 -symmetric axis and its derivatives are widely utilized in asymmetric chemistry.⁷ In comparison to BINOL, the chemistry of 2,2',7,7'-tetrahydroxy-1,1'-binaphthyl **1** is relatively less investigated, although its synthesis is known.^{8,9} Resolution of racemic BINOL by separation of its complexes with naturally occurring (*S*)-proline was first attempted by Periasamy¹⁰ and recently reinvestigated by Hu.¹¹ The latter work¹¹ also establishes the formation of inclusion complex of two molecules of BINOL with one molecule of (*S*)-proline. In the present work the sample of racemic **1**,¹² was treated with (*S*)-proline in hot acetonitrile, the precipitated mixture was separated and extracted with ethyl acetate to furnish optically pure (*aR*)-**1** in high yield (Figure 2). The mother liquid was concentrated to access (*aS*)-**1** in 47 % yield (91 % ee), which was further enriched by recrystallization (99.6 % ee).

The salt of (*aR*)-**1** and (*S*)-proline was recrystallized from methanol and its structure was investigated by single crystal X-ray diffraction analysis (Figure 3). The sample of tetrol has '*R*' configuration as compared with the '*S*' of proline. It is also noteworthy to observe a stoichiometric ratio (1:1) of (*aR*)-**1** and (*S*)-proline in the molecular complex.¹³

The pure isomers of tetrol **1**, were separately subjected to the aromatic Mannich reaction with and formaldehyde or with benzyl amine and formaldehyde by the established procedure.⁵ Reaction of (*aR*)-**1** with methyl amine/formaldehyde furnished atropisomerically pure bis-oxazine dihydroxy compound (*aR*)-**2**. It was converted to the helicene like bis-oxazine (*M*)-**3** by building an ether bridge with diiodomethane in the presence of Cs_2CO_3 . Similarly the other set of compounds (*aR*)-**4** and (*M*)-**5** were synthesized using benzyl amine as the primary amine in the aromatic Mannich reaction step (Figure 4). The strategy was then repeated with the other enantiomer of tetrol, (*aS*)-**1** and isomers (*P*)-**3** and (*P*)-**5** were synthesized.

The process involves conversion of axially chiral open structure of **2** or **4** to helicene like chiral molecules **3** or **5** possessing the close structure. The isomers of helicene like bis-oxazine were synthesized from (*aR*)-**1** and (*aS*)-**1** by the above scheme to measure their optical properties (Figure 5).

The observed optical rotation (OR) of the close helicene like structure was expected to be much higher than the open atropisomeric structure.¹⁴ This phenomena is due to the screw like arrangement of helicene like framework. It is quite common for such type of molecules to have high OR values.^{3a,15-17} For example, the OR of (*aR*)-**2** was observed to be -135,

which got enhanced to -747 when it was converted to helicene like compound (*P*)-**3**. The comparison of the values of OR and molar OR for the series of molecules under the present study is summarized in Table 1.

The structure of helicene like bis-oxazine (*M*)-**5** was further established by its single crystal X-ray diffraction analysis (Figure 6).¹⁸ The dihedral angle between the two planes passing through flat naphthalene units was measured to be 66.13°, while the two oxazine rings assume half chair like conformation¹⁹ flipping outside the helical axis. This enables the two benzyl groups to orient along the helical axis of the structure.

The helicene like bis-oxazines **3** and **5** show characteristic circular dichroism (CD) spectra (Figure 7).⁵ The presence of opposite bisignate couplets, a positive one at 265 nm and a negative one at 291 nm, are attributed to the *P* isomer of **5**. As expected the identical but opposite CD curve was observed for (*M*)-**5**. Similar pattern was also seen for the other pair of bis-oxazine **3**.

We have resorted to Circularly Polarized Luminescence (CPL), the emission analog to CD, to further investigate the influence of the helical like structure of the compounds of interest on the chiroptical properties. The circularly polarized luminescence (ΔI) and total luminescence (I) spectra measured for the helicene like bis-oxazine (*P*)-/(*M*)-**3** and (*P*)-/(*M*)-**5** in acetonitrile solutions at 295 K are shown in Figure 8.

The degree of circularly polarized luminescence is given by the luminescence dissymmetry ratio, $g_{\text{lum}}(\lambda) = 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R refer, respectively, to the intensity of left and right circularly polarized emissions.^{20,21,22} The solid lines in the CPL plot are presented to show the luminescence spectral line shape. As usual for most chiral organic chromophores and transition metal complexes,^{21,22,23,24} $|g_{\text{lum}}|$ that were obtained are small: +0.0015/+0.0009 and +0.0014/-0.0013 for (*P*)-/(*M*)-**3** and (*P*)-/(*M*)-**5**, as determined at the maximum emission wavelength, respectively. Although the g_{lum} values are very small (a value equal to ~0.001 corresponding to light that is only 0.1% circularly polarized), almost opposite CPL signals were measured for the two sets of pairs of helically pure bis-oxazine enantiomers. These results confirm that the helicene like bis-oxazine solutions in acetonitrile exhibit an active CPL signal and also that the emitted light is polarized in opposite directions for the two enantiomeric forms for each set of these helicene like structures. It must be pointed out that the CPL activity observed for the two sets of **3** and **5** corroborates the objective of this work that one can prepare the targeted helical-like molecules in optically pure form from the use of the achiral primary amines (active and opposite CPL response for each enantiomeric form of the two sets of **3** and **5**). It is worth noting that **3** and **5** give a relatively similar CPL response, which is in accordance with the slight structural differences between these two compounds. The only difference is the alkyl group attached to the *N* atom of oxazine (*N*-methyl and *N*-benzyl for **3** and **5**, respectively). Although it is well established that the CPL activity is dependent on the structural properties of the chiral compounds of interest,^{20,22} it can be concluded from the CPL results (i.e. similar g_{lum} magnitudes) that the structural changes are not sufficient to considerably influence in a different manner the chiroptical properties of these two compounds. The structural changes resulting from the replacement of the *N*-methyl by the *N*-benzyl substituent does not lead to a more pronounced interplanar or dihedral angle of the helical compound, which would have resulted most likely on a more chiral system and, thus, a larger CPL signal. This is in line with the fact that the CPL response is more influenced by the chiral arrangement surrounding the luminescent/phosphorescent/fluorescent center than the contribution of chiral atoms present into the organic skeleton of a system of interest.^{20,22}

Thus in this communication we present our efforts to synthesize optically pure helicene like bis-oxazines from chiral starting material. We have fully characterized the compounds and measured their optical properties. The present set of molecules are in addition to the few other examples of small organic molecules to show CPL responses, although to a different degree.^{23,27} We believe this work will open options to access optically pure, structurally rigid helicene like molecules which can be fine-tuned by selecting appropriate primary amines, achiral or chiral, for specific aspects of chiroptical assessments.²⁸

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at room temperature for 2 h. The solid crystals were completely dissolved, the organic layer was separated, and the water phase extracted with ethyl acetate (2 X 50 mL). The organic layer was dried over anhydrous Na₂SO₄, concentrated at reduced pressure, to give (aR)-2,2',7,7'-tetrahydroxy-1,1'-binaphthyl (0.998 g, 48 %), M.p.122-124 °C, $[\alpha]_D^{28} = -116$ ($c = 0.10$, acetonitrile). [99.8 % ee based on HPLC on chiralpak OD-H].

The mother liquor acetonitrile was evaporated under reduced pressure to get (aS)-2,2',7,7'-tetrahydroxy-1,1'-binaphthyl as off white powder (0.99 g, 47 %), M.p.122-124 °C. This sample was 91.0 % optically pure, which was enhanced by a single crystallization Page 5

(MeOH:toluene, 1:1) to 99.6 % ee $[\alpha]_D^{28} = +114$ ($c = 0.10$, acetonitrile).
(aR)-(-)-2,2'-Dimethyl-2,3,2',3'-tetrahydro-1H,1'-binaphthyl-1,2-diol, 1,3-oxazinyli-9,9'-diol [(aR)-**3**]:

A solution of formaldehyde (0.324 g, 0.87 mL, 37 % w/v, 10.8 mmol) and methylamine (0.167 g, 0.42 mL, 40 % w/v, 6.91 mmol) in methanol (10 mL) was stirred at room temperature (30 min) under nitrogen atmosphere. This solution was treated with (aR)-2,2',7,7'-tetrahydroxy-1,1'-binaphthyl (0.715 g, 2.24 mmol) and the solution was stirred at 60 °C (48 h). After the completion of the reaction, the mixture was concentrated and the crude product was purified by column chromatography on silica gel using light petroleum

ether:ethyl acetate (100:0 to 60:40) as eluent to obtain a white solid (0.902 g, 94%), M.p.190-192 °C, $[\alpha]_D^{28} = -135$ ($c = 0.10$, CHCl₃).

¹H-NMR (CDCl₃, 400 MHz) Δ 7.84-7.82 (d, $J = 8.8$ Hz, 2H), 7.69-7.67 (d, $J = 8.8$ Hz, 2H), 7.15-7.13 (d, $J = 8.8$ Hz, 2H), 6.96-6.94 (d, $J = 8.8$ Hz, 2H), 5.07 (s, 2H, -OH), 4.74-4.72 (d, $J = 9.6$ Hz, 2H), 4.61-4.58 (d, $J = 9.6$ Hz, 2H), 3.64-3.60 (d, $J = 16.8$ Hz, 2H), 3.21-3.17 (d, $J = 16.8$ Hz, 2H), 2.28 (s, 6H).

MS (EI): m/z , (%) 429 (20), 428 (100), 427 (88), 426(82), 384 (31), 383 (36), 369 (42), 368 (54), 367 (43), 366 (50), 325 (37), 324 (33), 323 (30), 313 (69), 311 (50), 297 (35), 297 (35), 296 (44), 255 (30), 239 (32), 238 (40), 97 (31).

Synthesis of helicene like (M)-bis-oxazine [(M)-**3**]:

A solution of pure (aR)-**2** (0.70 g, 1.63 mmol) and Cs₂CO₃ (2.66 g, 8.16 mmol) in dry DMF (10 mL) was added CH₂I₂ (0.656 g, 2.44 mmol) and the mixture was stirred for 48 h at room temperature under nitrogen atmosphere. After the completion of the reaction (monitored by tlc) the mixture was poured in ice cold water. The aqueous layer was extracted with chloroform (3 X 100 mL) and the combined extract was washed with water (2 X 100 mL) and the organic layer was dried over Na₂SO₄ and evaporated to obtain brown viscous oil. The crude product was purified by column chromatography over silica gel using light petroleum ether:ethyl acetate

(100:00 to 70:30) as eluent to get a white solid (0.220 g, 31 %); M.p.196-198 °C, $[\alpha]_D^{28} = 747$ ($c = 0.10$, CHCl₃).

¹H NMR (CDCl₃, 400 MHz) Δ 7.88-7.85 (d, $J = 8.8$ Hz, 2H), 7.73-7.61 (d, $J = 8.8$ Hz, 2H), 7.31-7.29 (d, $J = 8.8$ Hz, 2H), 6.99-6.96 (d, $J = 8.8$ Hz, 2H), 5.67 (s, 2H), 4.56-4.54 (d, $J = 9.2$ Hz, 2H), 4.53-4.50 (dd, $J = 2.4$ Hz, 9.2 Hz, 2H), 2.70-2.66 (d, $J = 16.4$ Hz, 2H), 2.43-2.39 (d, $J = 16.4$ Hz, 2H), 2.06 (s, 6H).

MS (EI): m/z , (%) 440 (35), 439 (100), 410 (16), 408 (12), 396 (09), 382 (18), 380 (22), 354 (07), 353 (12), 352 (08), 323 (10), 312 (15), 311 (11), 278 (08), 239 (09), 238 (07).

HPLC condition: Observed one peak of single enantiomer at $R_t = 10.38$ min. Solvent System: Hexane: Iso-propanol (70:30), Flow rate: 0.5 mL/min, column: Lux Amylose 2, UV: 254 nm. (aR)-(-)-2,2'-dibenzyl-2,2',3,3'-tetrahydro-1H,1'-[10,10'-binaphtho[1,2-e][1,3]oxazine]-9,9'-diol [(aR)-**4**]:

A solution of formaldehyde solution (0.27 g, 37% w/v, 0.734 mL, 9.04 mmol) and benzylamine (0.49 g, 4.52 mmol) in methanol was stirred for 30 min under nitrogen atmosphere, to this solution (aR)-2,2',7,7'-tetrahydroxy-1,1'-binaphthyl (0.60 g, 1.88 mmol) was added in one portion. The solution was stirred for 48 h at 60 °C. After the completion of the reaction the mixture was concentrated and the crude product was purified by column chromatography on silica gel using light petroleum ether:ethyl acetate (100:0 to 60:40) as

eluent to obtain a white solid which was dried in vacuum (0.96 g, 87 %); M.p.152-154 °C, $[\alpha]_D^{28} = -257$ ($c = 0.10$, CHCl₃).

¹H NMR (CDCl₃, 400 MHz) Δ 7.77-7.75 (d, $J = 8.8$ Hz, 2H), 7.64-7.62 (d, $J = 8.8$ Hz, 2H), 7.21-7.16 (m, 6H), 6.99-6.96 (m, 6H), 6.93-6.90 (d, $J = 8.8$ Hz, 2H) 4.98 (s, 2H), 4.66-4.63 (d, $J = 9.6$ Hz, 2H), 4.52-4.49 (d, $J = 9.2$ Hz, 2H), 3.55-3.54 (d, $J = 2$ Hz, 4H), 3.52-3.47 (d, $J = 16.8$ Hz, 2H), 3.24-3.20 (d, $J = 16.8$ Hz, 2H).

MS (EI): m/z , (%) 579 (09), 550 (06), 488 (11), 460 (10), 369 (09), 342 (13), 340 (07), 313 (48), 312 (52), 311 (62), 296 (24), 238 (48), 194 (78), 134 (32), 118 (94), 92 (12), 91 (100), 89 (08).

Anal. Calcd. for C₃₈H₃₂N₂O₄: C 78.60, H 5.55; N 4.82%. Found: C 78.22, H 5.19, N 4.77%. Synthesis of helicene like (M)-bis-oxazine [(M)-**5**]:

A solution of pure (aR)-**4** (0.70 g, 1.25 mmol) and anhydrous Cs₂CO₃ (2.04 g, 6.03 mmol) in dry DMF (10 mL) and CH₂I₂ (0.502 g, 1.87 mmol) was added and the mixture was stirred 48 h at room temperature under nitrogen atmosphere. After the completion of the reaction (tlc) the reaction mixture was poured in ice cold water. The aqueous layer was extracted with chloroform (3 X 100 mL) combine the extract and washed with water (2 X 100 mL) and the organic layer was dried over Na₂SO₄ and evaporated to obtained crude solid. The crude product was purified by column chromatography over silica gel using a light petroleum ether/ethyl acetate as

eluent (100:00 to 80:20) furnishing a white solid (0.385 g,54%); M.p.218-220 °C, $[\alpha]_D^{28} = -930$ ($c = 0.10$, CHCl₃).

¹H NMR (CDCl₃, 400 MHz) Δ 7.79-7.77 (d, $J = 8.8$ Hz, 2H), 7.72-7.70 (d, $J = 8.8$ Hz, 2H), 7.25-7.22 (m, 6H), 7.16-7.14 (d, $J = 8.8$ Hz, 2H), 7.01-6.97 (m, 6H), 5.61 (s, 2H), 4.61-4.58 (d, $J = 9.6$ Hz, 2H), 4.54-4.52 (dd, $J = 2$ Hz, 9.2 Hz, 2H), 3.42-3.39 (d, $J = 12.8$ Hz, 2H), 3.27-3.24 (d, $J = 12.8$ Hz, 2H), 2.75-2.71 (d, $J = 16.8$ Hz, 2H), 2.57-2.53 (d, $J = 16.4$ Hz, 2H).

¹³C NMR (CDCl₃, 100.6 MHz): Δ 152.9 (Cq), 150.9 (Cq), 137.5 (Cq), 133.8 (Cq), 131.0 (CH), 129.6 (CH), 129.1 (2 X CH), 128.3 (2 X CH), 127.8 (Cq), 127.2 (CH), 126.3 (Cq), 118.0 (CH), 117.2 (CH), 112.1 (Cq), 102.1 (O-CH₂-O), 80.4 (NCH₂O), 54.5 (ArCH₂N), 49.5 (NCH₂Ph).

MS (EI): m/z , (%) 591 (16), 501 (11), 458 (09), 354 (10), 342 (18), 341 (21), 340 (15), 324 (13), 310 (16), 298 (15), 256 (27), 255 (28), 236 (31), 182 (36), 133 (16), 118 (22), 91 (100). Anal. Calcd. for C₃₉H₃₂N₂O₄: C 79.03, H 5.44, N 4.73%. Found: C 78.64, H 5.30, N 4.65%.

HPLC condition: Observed one peak of single enantiomer at $R_t = 15.25$ min. Solvent System: Hexane: Iso-propanol (85:15), Flow rate: 0.5 mL/min, column: Lux Amylose 2, UV: 254nm.

About CPL measurements:

The circularly polarized luminescence (CPL) and total luminescence spectra were recorded on an instrument described previously,²⁵ operating in a differential photon-counting mode. The light source for excitation was a continuous wave 1000 W xenon arc lamp from a Spex Fluorolog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersion of 4 nm/mm (SPEX, 1681B). To prevent artifacts associated with the presence of linear polarization in the emission,²⁶ a high quality linear polarizer was placed in the sample compartment, and aligned so that the excitation beam was linearly polarized in the direction of emission detection (z-axis). The key feature of this geometry is that it ensures that the molecules that have been excited and that are subsequently emitting are isotropically distributed in the plane (x,y) perpendicular to the direction of emission detection. The optical system detection consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photo-counting mode. All measurements were performed with quartz cuvettes with a path length of 1.0 cm.

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Figure 1.
Synthesis of diastereomeric bis-oxazines.

Figure 2. Resolution of 2,2',7,7'-tetrahydroxy-1,1'-binaphthyl by fractional crystallization with (S)-proline

Figure 3.
ORTEP diagram of the salt of (*aR*)-**1**•(*S*)-Proline.

Figure 4. Synthesis of optically pure isomers of helicene like bis-oxazines from (*aR*)-1.

Figure 5. Synthesized enantiomers of helicene like bis-oxazine with their optical properties.

Figure 6.
ORTEP diagram of (*M*)-5.

Figure 7.
CD spectra of bis-oxazine (*P*)-**5** (blue) and (*M*)-**5** (green) [c 8.44×10^{-4} M solution in acetonitrile]

Figure 8.

CPL (upper curves) and total luminescence (lower curves) spectra of the (*M*)-**3** (left red), (*P*)-**3** (left black), (*M*)-**5** (right red), and (*P*)-**5** (right black), compounds in 1 mM acetonitrile solutions at 295 K, upon excitation at 357 nm, respectively. The solid lines in the CPL plot are presented to show the luminescence spectral line shape.

Table 1

Summary of OR and molar OR of the atropisomeric and helicene like molecules.

Compound	OR [α]	Molar OR [Φ]	Compound	OR [α]	Molar OR [Φ]
(<i>aR</i>)-1	-116	-369			
(<i>aR</i>)-2	-135	-578	(<i>aR</i>)-4	-257	-1492
(<i>M</i>)-3	-747	-3290	(<i>M</i>)-5	-930	-5512

Compound	OR [α]	Molar OR [Φ]	Compound	OR [α]	Molar OR [Φ]
(<i>aS</i>)-1	+114	+362			
(<i>aS</i>)-2	+137	+587	(<i>aS</i>)-4	+234	+1359
(<i>P</i>)-3	+787	+3467	(<i>P</i>)-5	+890	+5275

The structure of helicene like bis-oxazine (*M*)-5 was further established by its single crystal X-ray diffraction analysis (Figure 6).¹⁸ The dihedral angle between the two planes passing through flat naphthalene units was measured to be 66.13°, while the two oxazine rings assume half chair like conformation¹⁹ flipping outside the helical axis. This enables the two benzyl groups to orient along the helical axis of the structure.