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## Synthesis and Chiroptical Properties of Axially Chiral, Binaphthol-based Oligomers

Man-Kit Ng, Hak-Fun Chow,\* Tze-Lock Chan and Thomas C. W. Mak

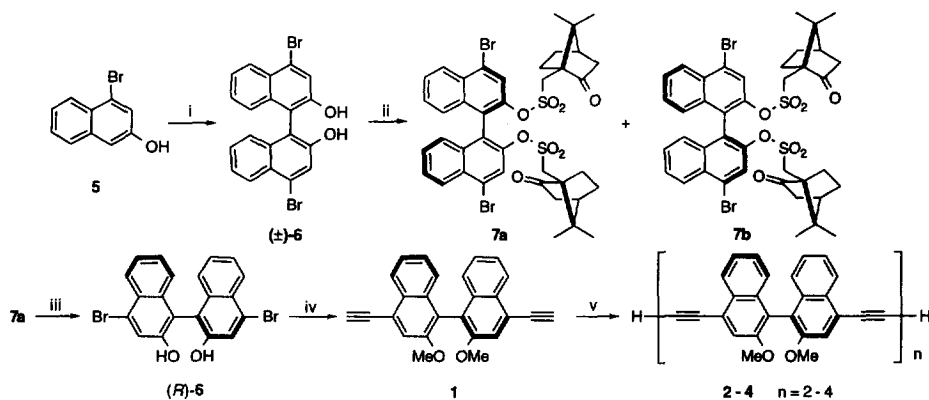
Department of Chemistry, The Chinese University of Hong Kong,  
Shatin, N.T., HONG KONG

**Abstract:** Optically active, axially chiral binaphthol-based oligomers **2** to **4** were synthesized *via* Hay's coupling from the monomer **1**. These oligomers exhibited moderate optical rotation enhancement but the effect quickly reaches a plateau with the tetramer **4**.  
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**Keywords:** binaphthol, optical active oligomers, optical activity

The potential use of optically active polymers for ferroelectric and nonlinear optical applications, enantiomeric resolutions and asymmetric syntheses has sparked extensive research to study their structure-property relationships.<sup>1</sup> One particular intriguing aspect in this context is the relationship between the optical rotation strength and the stereospatial arrangement of the constituent chiral units embedded inside the polymer matrix. For example, large optical rotation enhancements have been observed if a chiral polymer main chain can adopt a helical conformation.<sup>2</sup> Unfortunately, up to now very little data are available to establish a qualitative picture of the structural-optical rotation relationship. In this connection, homochiral, optically active, monodisperse oligomers provide the perfect models for this type of study. Inside these matrix, the repeating chiral elements are distributed in a pre-defined and orderly manner and thus allow us to evaluate the chiroptical properties of macromolecules in a systematic manner. Recently, Vasella<sup>3</sup> and Diederich<sup>4</sup> reported two different series of optically active bis(acetylene)-containing linear and cyclic oligomers having chiral sugar and binaphthol units, respectively, as part of the main chain, but there is little correlation between the molar rotation power and the number of chiral units. We reported herein the synthesis of a series of linearly-aligned, axially chiral, optically pure binaphthyl-based monomer **1** and oligomers **2** - **4** and showed that these oligomers exhibited moderate optical activity enhancement. It should be mentioned here that Tours recently reported the preparation of a diastereomeric mixture of axially chiral conjugated polymers based on binaphthyl units.<sup>5</sup> Unfortunately, no enhancement of optical rotation was observed for the resulting polymer.

The synthesis of the optically pure monomer (*R*)-**1** started from the known 4-bromo-2-naphthol **5**.<sup>6</sup> Copper(I) catalyzed oxidative coupling<sup>7</sup> of **5** gave racemic ( $\pm$ )-binaphthol **6**. Resolution of ( $\pm$ )-**6** could be accomplished by silica gel column chromatography of their respective diastereomeric bis-(*S*)-10-camphor-sulfonates **7a** and **7b**, followed by base-catalyzed desulfonylation to regenerate the enantiomeric pure (>98%



Reagents: i) CuCl(OH)-TMEDA, O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 90%; ii) (*S*)-camphorsulfonylchloride, NEt<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 95%, then chromatographic separation of 7a and 7b (silica gel, eluent: toluene-EtOAc (50:1)); iii) NaOH, aq. MeOH, 70%; iv) MeI, Cs<sub>2</sub>CO<sub>3</sub>, acetone, then TMSCH, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, NEt<sub>3</sub>, 70°C then K<sub>2</sub>CO<sub>3</sub>, MeOH/THF, 70%; v) CuCl-TMEDA, O<sub>2</sub>, CHCl<sub>3</sub>.

e.e. by <sup>1</sup>H-NMR<sup>8</sup>) *(R)*-6 and *(S)*-6 binaphthols, respectively. The more polar bis-sulfonate 7a has an *(R)*-chiral axis, whose absolute configuration was determined on the basis of X-ray crystallographic analysis.<sup>9</sup> The enantiomerically pure *(R)*-6 was then converted to the monomer bis(ethynyl)binaphthol (*R*)-1 via *O*-methylation, palladium(0)-catalyzed coupling<sup>11</sup> with trimethylsilylacetylene and desilylation.

The bis(ethynyl) monomer (*R*)-1 was then subjected to oxidative Hay's coupling<sup>12</sup> (CuCl-TMEDA, O<sub>2</sub>) in CHCl<sub>3</sub> (0.05 M) at 25°C for 1 h to give a dark green mixture from which the starting material 1 (20%), dimer 2 (30%), trimer 3 (10%) and tetramer 4 (4%) together with some intractable higher molecular weight oligomers were isolated after column chromatography. We were unable to obtain the pentamer and hexamer from the reaction mixture either by changing the catalyst or reaction temperature. The structural identities of these oligomers were supported by their <sup>1</sup>H-NMR and mass spectral data.<sup>13</sup> The polarity and solubility properties of these oligomers decrease steadily with increasing number of binaphthol units. Thus, the monomer is readily soluble in THF and chlorinated solvents, whereas the trimer and especially the tetramer are poorly soluble. The optical rotation properties of these compounds were first studied by polarimetry measurements (Table 1). The specific rotations [α] as well as the molar rotations [M], are all positive and increase steadily on going from the monomer 1 to the tetramer 4.<sup>14</sup> Although monomer 1 has a different chromophore structure than those of the oligomers 2-4 and direct comparison is difficult,<sup>15</sup> Nevertheless, it was noticed that the molar rotation values increased moderately from the dimer 2 towards the tetramer 4 on a per binaphthol chiral unit basis. Due to dependence of optical rotations on the increasing bathochromic shift of the absorptions with oligomer length, we decided to look at the circular dichroism (CD) spectra of these compounds (Figure 1). The inherently dissymmetric binaphthol chromophores gave rise to extremely high molar ellipticity values ([θ] ≈ 10<sup>5</sup>). Compounds 1 to 4 all showed similar CD pattern with a negative Cotton effect at λ = 240 nm and a positive effect at λ = 226 nm. There was an additional positive dichroism maximum at 340 nm which was not apparent in the UV spectra. Most interestingly, dimer 2 exhibits consistently larger [θ] than the monomer 1 in the 200 -

Table 1. Optical rotation<sup>a</sup> and UV<sup>b</sup> data of compounds 1 - 4.

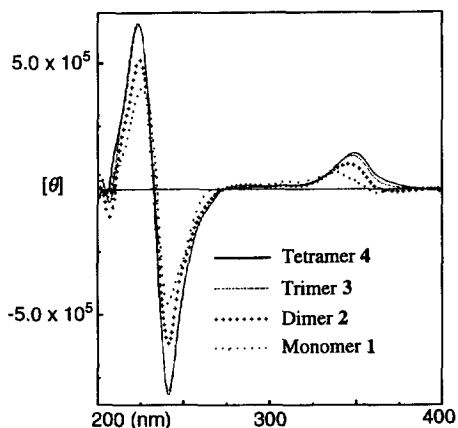
	Monomer 1 (c = 1.18)	Dimer 2 (c = 0.55)	Trimer 3 (c = 0.28)	Tetramer 4 (c = 0.20)
[ $\alpha$ ] (589 nm)	92	111	115	127
[M] (589 nm)	333	802	1246	1833
[ $\alpha$ ] (578 nm)	98	119	124	133
[M] (578 nm)	355	860	1343	1920
[ $\alpha$ ] (546 nm)	122	149	153	164
[M] (546 nm)	442	1077	1657	2368

$\lambda_{\max}$  (nm) 356 380 409 411

$\epsilon$  (mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>) 2.0 x 10<sup>4</sup> 4.5 x 10<sup>4</sup> 9.8 x 10<sup>4</sup> 22.5 x 10<sup>4</sup>

<sup>a</sup> In CHCl<sub>3</sub> solution at 25.0°C. <sup>b</sup> In ClCH<sub>2</sub>CH<sub>2</sub>Cl solution at 22°C.

Figure 1. CD spectra of compounds 1 - 4.



400 nm absorption region, which in turn is consistently smaller than that of the trimer 3. However, the trimer 3 and tetramer 4 gave almost identical CD spectra and it was concluded that optical rotation enhancement had reached a plateau with the tetramer. We speculated that this effect was due to the rotational freedom of the diacetylene spacer, which allowed individual chiral binaphthol units to rotate independently and not arrange in a coherent manner to exert cooperative conformational effect in order to have optical rotation enhancement.<sup>2f</sup>

We showed here that the optical rotatory properties of structurally rigid oligomers can be enhanced if the optically active units are aligned linearly, although this effect is moderate and levels off rapidly with increasing oligomer length. This is in contrast to the results of Diederich<sup>4</sup> and Tours,<sup>5</sup> in which no molar rotational enhancement is observed when the binaphthol units are arranged in a cyclic array, or when the chiral elements are not homogeneously pure. We are now testing and extending this concept by preparing other structurally related higher soluble oligomers and polymers in our laboratories.

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## References and Notes

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4. In one of the cyclic binaphthol-containing oligomer series, the molar rotation is proportional to the number of chiral binaphthol groups inside the molecule. However, in another related series, no relationship could be established, see Anderson, S.; Neidlein, U.; Gramlich, V.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1596.
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8. To ensure that no racemization took place during hydrolysis, binaphthol (*R*)-**6** obtained after base hydrolysis was treated with (*S*)-camphorsulfonyl chloride. Examination of the <sup>1</sup>H-NMR of the reaction product showed the presence of only **7a**, the other diastereomer **7b** could not be detected.
9. X-Ray structure analysis: C<sub>40</sub>H<sub>40</sub>O<sub>8</sub>S<sub>2</sub>Br<sub>2</sub> **7a**, *M<sub>r</sub>* = 872.7, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 11.973(2), *b* = 17.347(3), *c* = 18.627(4) Å, *V* = 3868.7(6) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.498 g cm<sup>-3</sup>, MoKα (*λ* = 0.71073 Å), *μ* = 2.25 mm<sup>-1</sup>, *F*(000) = 1784, *T* = 295°K. Intensity data (crystal size 0.22 x 0.36 x 0.62 mm, 2θ<sub>max</sub> = 55°, 4956 unique reflections) were collected on a Siemens P4/PC diffractometer. Structure solution and refinement were carried out using the SHELXTL/PC program package,<sup>10</sup> and final *R<sub>F</sub>* = 0.058 for 2695 observed reflections with |*F<sub>o</sub>*| > 4σ(|*F<sub>o</sub>*|).
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13. Selected physical data: **1**: white solid; m.p. 192 - 194°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.37 (d, *J* = 8.3 Hz, 2H), 7.69 (s, 2H), 7.41 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 2H), 7.25 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 6H), 3.55 (s, 2H); MS: *m/z* 362 (*M*<sup>+</sup>, 100%). **2**: yellow solid; m.p. > 230°C (decomp.); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.47 (d, *J* = 8.3 Hz, 2H), 8.39 (d, *J* = 8.2 Hz, 2H), 7.80 (s, 2H), 7.71 (s, 2H), 7.51 - 7.39 (m, 4H), 7.33 - 7.25 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 3.80 (s, 6H), 3.79 (s, 6H), 3.57 (s, 2H); MS: *m/z* 723.3 (*M* + H<sup>+</sup>, 80%). **3**: yellow solid; m.p. > 230°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.48 (d, *J* = 8.2 Hz, 2H), 8.47 (d, *J* = 8.4 Hz, 2H), 8.39 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 2H), 7.81 (s, 2H), 7.71 (s, 2H), 7.53 - 7.40 (m, 6H), 7.35 - 7.24 (m, 6H), 7.19 - 7.10 (m, 6H), 3.83 (s, 6H), 3.80 (s, 6H), 3.79 (s, 6H), 3.57 (s, 2H); MS: *m/z* 1083.4 (*M* + H<sup>+</sup>, 100%). **4**: yellow solid; m.p. > 230°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.49 (d, *J* = 8.4 Hz, 4H), 8.48 (d, *J* = 8.4 Hz, 2H), 8.39 (d, *J* = 8.5 Hz, 2H), 7.83 (s, 4H), 7.81 (s, 2H), 7.71 (s, 2H), 7.54 - 7.40 (m, 8H), 7.36 - 7.25 (m, 8H), 7.20 - 7.11 (m, 8H), 3.84 (s, 12H), 3.81 (s, 6H), 3.79 (s, 6H), 3.57 (s, 2H); MS: *m/z* 1444.5 (*M*<sup>+</sup>, 100%).
14. The specific rotation values [α]<sub>D</sub> of compounds **1** to **4** remain essential constant (± 2%) at different concentrations (*c* ranges from 0.03 to 1.18). Hence, the moderate optical activity enhancement observed here is not due to aggregation of different oligomers.
15. Monomer **1** can be considered as consisting of two 'independent' naphthol-monoacetylene chromophores due to the orthogonal disposition of the two naphthol rings. However, a new type of naphthol-diacetylene-naphthol chromophore is inserted between the two terminal naphthol-monoacetylene chromophores for oligomers **2** - **4**.

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