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Synthesis of Configurationally Defined Sexi- and Octinaphthalene Derivatives

Kaoru Fuji,* Takumi Furuta, and Kiyoshi Tanaka[†]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

fuji@scl.kyoto-u.ac.jp

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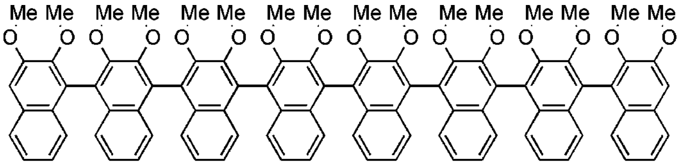
ABSTRACT



(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-isomer
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-isomer
(*S*,*S*,*S*,*S*,*S*,*R*,*S*)-isomer

Configurationally defined optically active octinaphthalenes were synthesized using the oxidative coupling of optically active quaternaphthalenes with a 2-hydroxynaphthol moiety as a key reaction. The absolute configuration was determined by comparison with products of [6 + 2] coupling.

Monodisperse π-conjugated oligomers have recently attracted attention due to their potential application in material sciences.[1] Oligo(*p*-phenylene)s have received special attention and have been used as backbones for artificial proton channels[2] and β-barrels[3] and as rigid spacer units in an artificial receptor of cyclic dipeptides.[4] Oligo(*p*-phenylene)s are also important model compounds for poly(*p*-phenylene)s, since some poly(*p*-phenylene)s are remarkable organic conductors upon doping[5] and are also used as laser materials.[6] The rod can contain 15[7] or even 16[8] phenyl rings. On the other hand, little attention has been paid to rod-shaped oligonaphthalenes connected at the 1,4-positions. The longest monodisperse oligonaphthalene is a sexinaphthalene.[9,10] It has been reported that a stereochemically defined quaternaphthalene shows characteristics of an organic zeolite.[11] It would be interesting to determine whether higher oligonaphthalenes also show such characteristics. We report here the synthesis of optically active sexi- and octinaphthalenes.

The synthesis of sexinaphthalenes started from the optically active ternaphthalene **1**[12] (Scheme 1). Methylation of (*S*,*S*)-**1** afforded (*S*,*S*)-**2**, which was converted into monohydroxy ternaphthyl (*S*,*S*)-**3** by hydrogenolysis, in 82% overall yield. Oxidative coupling[13] of **3** afforded sexinaphthalenes **4** and **8** in respective yields of 31% and 38%. The

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[†] Present address: School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan.

(1) For an extensive review, see: (a) Pu. L. *Chem. Rev.* **1998**, *98*, 2405−2494. (b) Martin, R. E.; Diederich F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377. (c) Berresheim, A. J.; Muller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1786.

(2) Weiss, L. A.; Sakai, N.; Ghebremariam, B.; Ni, C.; Matile, S. *J. Am. Chem, Soc.* **1997**, *119*, 12142−12149.

(3) (a) Baumeister, B.; Matile, S. *Chem. Eur. J.* **2000**, *6*, 1739−1749. (b) Baumeister, B.; Sakai, N.; Matile, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1955−1958. (c) Baumeister, B.; Matile, S. *Chem. Commun.* **2000**, 913−914. (d) Winum, J.-Y.; Matile, S. *J. Am. Chem. Soc.* **1999**, *121*, 7961−7962.

(4) Cristofaro, M. F.; Chamberlin, A. R. *J. Am. Chem. Soc.* **1994**, *116*, 5089−5098.

(5) Tour, J. M. *Adv. Mater.* **1994**, *6*, 190−198.

(6) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430−436.

(7) Galda, P.; Rehahn, M. *Synthesis* **1996**, 614−620.

(8) Liess, P.; Hensel, V.; Schlüter, A.-D. *Liebigs Ann.* **1996**, 1037−1040.

(9) Koch, K.-H.; Müllen, K. *Chem. Ber.* **1991**, *124*, 2091−2100.

(10) A 9-mer of naphthalene connected at 1,5-positions was reported. See: Marin, G. H.; Horak, V. *J. Org. Chem.* **1994**, *59*, 4267−4271.

(11) Fuji, K.; Furuta, T.; Otsubo, T.; Tanaka, K.; *Tetrahedron Lett.* **1999**, *7*, 3001−3004.

(12) Tanaka, K.; Furuta, T.; Fuji, K.; Miwa, Y.; Taga, T.; *Tetrahedron: Asymmetry* **1996**, *7*, 2199−2202.

(13) (a) Brussee, J.; Groenendijk, J. L. G.; Te Koppele J. M.; Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313−3319. (b) Hovorka, M.; Scigel, R.; Gunterová, J.; Tichy, M.; Závada, J. *Tetrahedron* **1992**, *48*, 9503−9516. (c) Smrcina, M.; Polákova, J.; Vyskocil, S.; Kocovsky, P. *J. Org. Chem.* **1993**, *58*, 4534−4538. (d) Noji, M.; Nakajima, M.; Koga, K.; *Tetrahedron Lett.* **1994**, *35*, 7983−7984.

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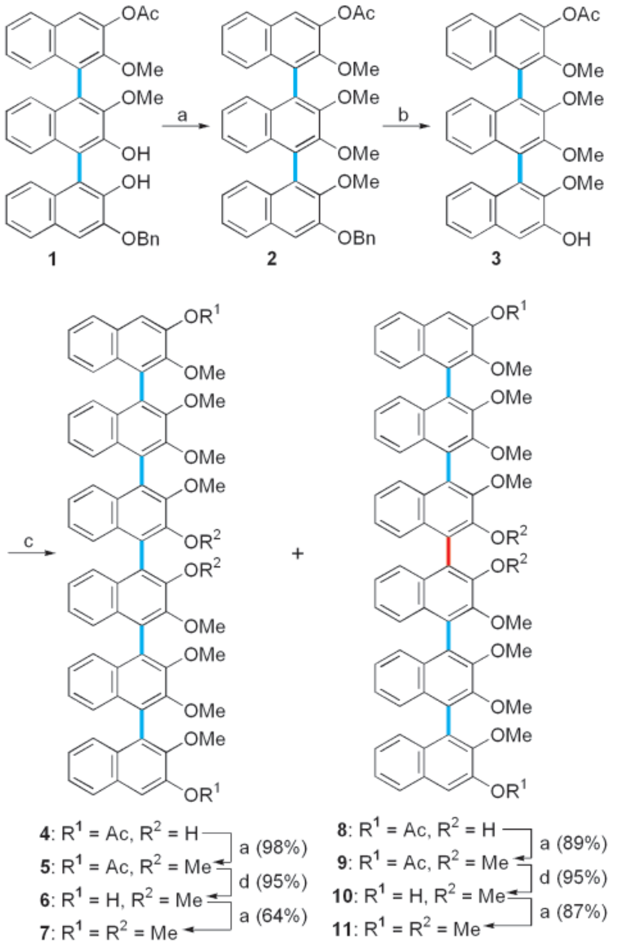
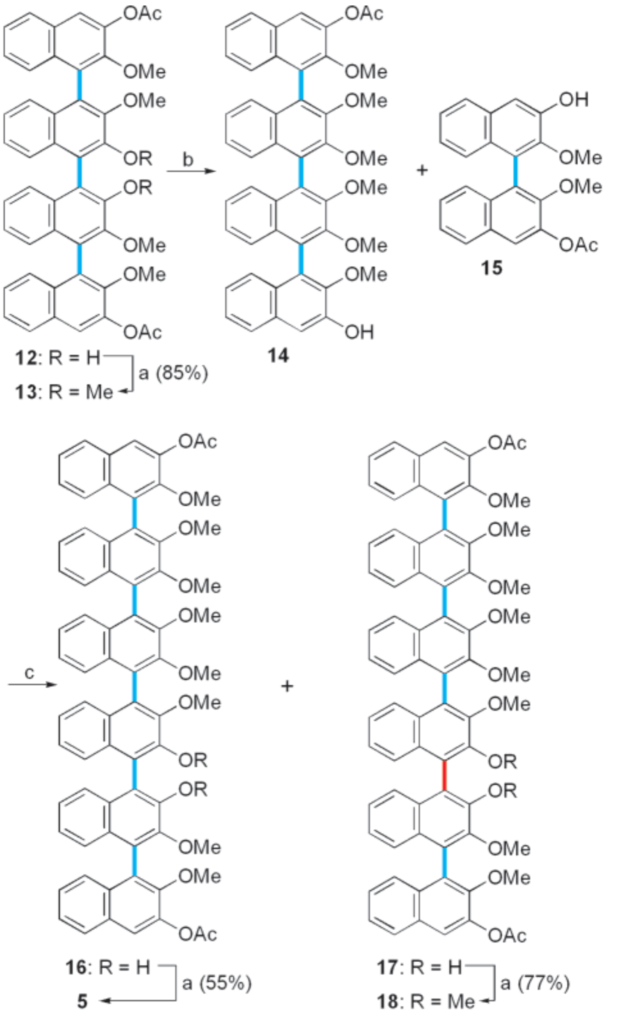
Scheme 1. The [3 + 3] Construction of Sexinaphthalene



only difference between **4** and **8** is the absolute stereochemistry of the newly created bond, which was unambiguously determined by synthesis via another route that included the [4 + 2] construction of sexinaphthalenes (Scheme 2). The known quaternaphthalene **12**[12] was methylated to give **13**, partial hydrolysis of which afforded **14** in 40% yield. The oxidative coupling of **14** and **15** afforded sexinaphthalenes **16** and **17** in respective yields of 18% and 16%, along with **12** and its isomer with an *R*-configuration at the central bond.[14] Methylation of **16** gave **5**, which is identical to one of the products of the homocoupling of **3**, while methylation of **17** gave **18**, which is distinct from both **5** and **9**. These findings clearly support the absolute configurations of the coupling products **4**, **8**, **16**, and **17**.

A similar strategy was used to synthesize octinaphthalenes and to determine their absolute stereochemistry (Scheme 3). Oxidative coupling of quaternaphthalene **14** gave **19** (14%) and **23** (18%). Methylation of **19** followed by hydrolysis gave **21**. Treatment of **21** with CH_3I/K_2CO_3 in acetone converted **21** into **22**, which has a methoxy group as a uniform substituent. The diastereomer **23** was transformed to **26** through the same sequence of reactions as those for **19**. The [6 + 2] construction of octinaphthalenes is also shown in Scheme 3. Partial hydrolysis of **5** gave **27**, which was then oxidatively coupled with **15** to give **28** (13%) and **29** (22%). Methylation of **28** gave **20**, while that of **29** gave **30**, which determined the absolute configuration of the products **28** and **29** as shown in Scheme 3.

Scheme 2. The [4 + 2] Construction of Sexinaphthalene



Another interesting aspect of oligonaphthalenes is their molecular shape, which is reminiscent of the banisters of a spiral staircase, and their π-system, which is totally different from that of helicenes.[15] An interesting question is how many naphthyl rings are required to complete a full turn of the helix. An X-ray crystal structural analysis of a quaternaphthalene revealed that four naphthyl units are insufficient.[12] Since none of the sexi- or octinaphthalenes gave crystals

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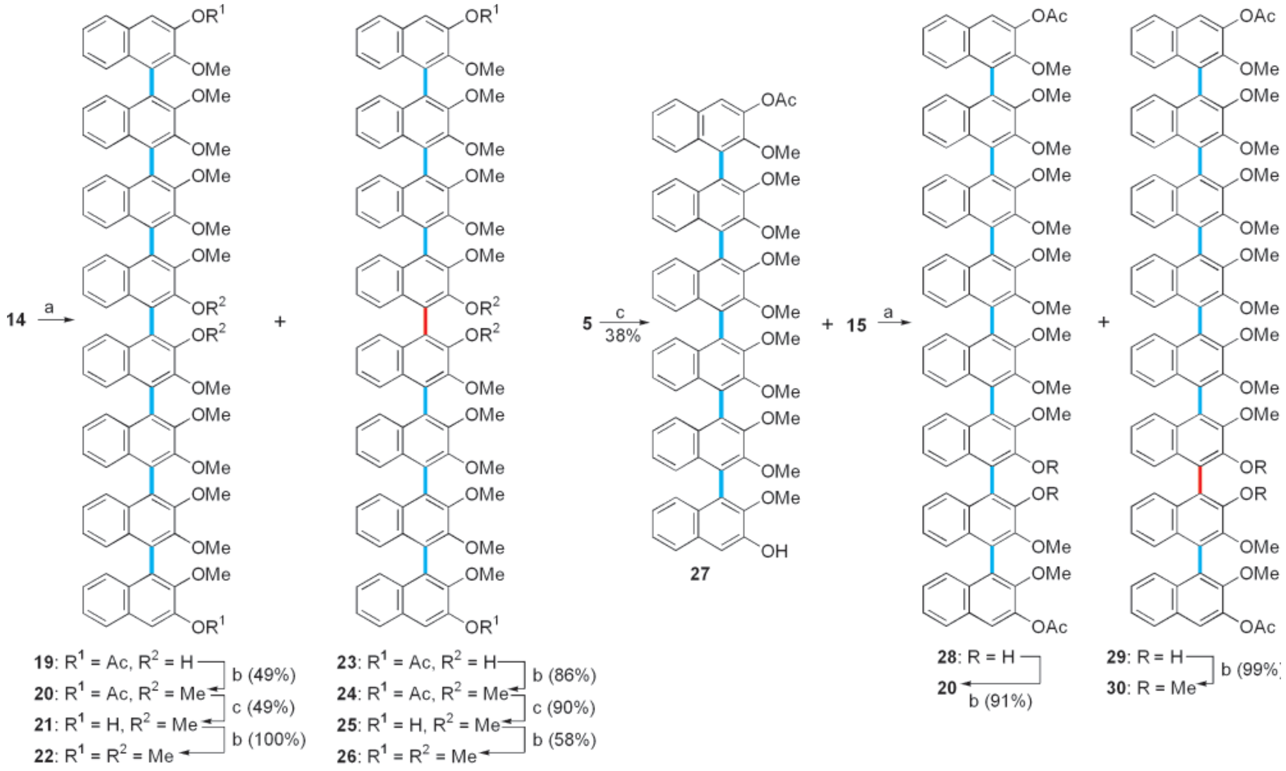
(14) To save more valuable quaternaphthalene **14**, a large excess of **15** was used. Thus, a solution of **14** (96 mg, 0.13 mmol) and **15** (252 mg, 0.65 mmol) in CH_2Cl_2(12 mL) was added into a mixture of $CuCl_2$ (210 mg, 16 mmol) and α-phenylethylamine (0.25 mL, 2.0 mmol) in MeOH (0.6 mL) and the mixture was stirred for 27 h at room temperature under N_2. After addition of 2 N HCl to decompose the copper−amine complex the mixture was condensed under reduced pressure. Extractive workup followed by preparative TLC gave **16** (27 mg), **17** (24 mg), **12** (66 mg), and its isomer with *S*,*R*,*S*-configuration (51 mg).

(15) This type of helix was called a Geländer-type molecule. See: Kiupel, B.; Niederalt, C.; Nieger, M.; Grimme, S.; Vögtle, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3031−3034.

Scheme 3. Synthesis of Octinaphthalenes



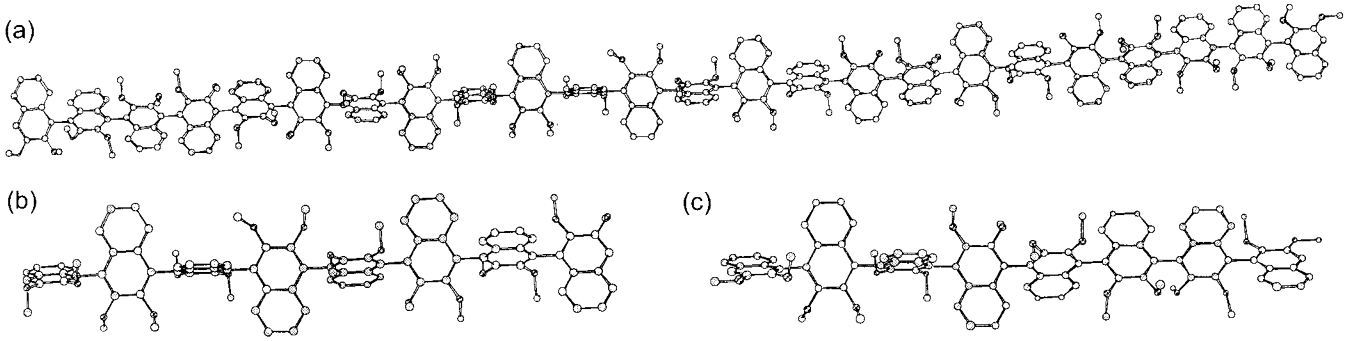


Figure 1. (a) The most stable conformation of the 24-mer calculated by MacroModel (version 6.0). (b) The central eight naphthalenes of the 24-mer. (c) The most stable conformation of octinaphthalene **22** calculated by MacroModel (version 6.0).

suitable for X-ray analysis, the most stable conformation of **22** was calculated by MacroModel/MM2 (version 6.0). The results indicated that five to six naphthyls are necessary for a turn (Figure 1c). The calculation for the corresponding 24-mer revealed that the helix repeated a full turn every five to six naphthyls (Figure 1a). The central eight naphthalene units of the 24-mer were extracted and compared with octinaphthalene **22** (Figure 1b and 1c). While the two conformations are quite similar, a slight lag was observed for a turn.

The use of optically active sexi- and octinaphthalenes for new materials and for molecular recognition is currently under investigation.

Supporting Information Available: Experimental procedures for compounds **4**, **8**, **28**, and **29** and characterization of **4**, **7**, **8**, **11**, **16**, **17**, **19**, **22**, **23**, **26**, **28**, and **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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