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Absolute Configuration of 3,3'-Dihydroxy-4,4'-biphenanthryl as Determined by the Stereochemistry of Cyclic Diester Formation with 1,1'-Binaphthyl-2,2'-dicarboxylic Acid

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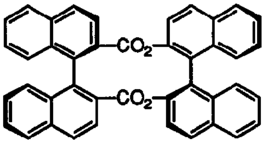
Abstract: Condensation of racemic 3,3'-dihydroxy-4,4'-biphenanthryl [(±)-**2**] with (*R*)-1,1'-binaphthyl-2,2'-dicarboxylic acid dichloride (**5**) allows cyclization of only (−)-**2** to give the 12-membered cyclic diester (**7**), the absolute configuration of which can be assigned (*R,R*) from steric reasons. Thus, absolute stereochemistry of (−)-**2** is determined to be (*R*).

Previously we reported that in order to assemble a 12-membered cyclic diester containing two sets of biaryl units joined by ester–CO_2–linkages between the *ortho,ortho'*-positions, *e. g.* a compound **1**, the directions of axial twist of the two biaryl units must be same for steric reasons as the CPK molecular models clearly indicate.[1] Thus, this provides a convenient method for recognizing axial chirality of biaryls because by knowing one of the configurations of the two biaryl units of cyclic diesters such as **1** one can assign the configuration of the other.[2,3]

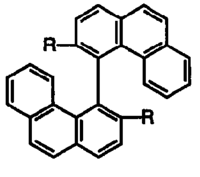
Yamamoto *et al.* applied this method for the determination of the configuration of 3,3'-dihydroxy-4,4'-biphenanthryl (**2**) *via* the intramolecular Ullmann coupling of a diester of 1-bromo-2-naphthoic acid derived from (−)-**2** to give the cyclic diester **7**.[4] They claimed that hydrolysis of the diester **7** afforded (*S*)-(−)-1,1'-binaphthyl-2,2'-dicarboxylic acid (*S*)-**4**, and thus assigned (−)-**2** to be (*S*). On the contrary, Hayashi *et al.*[5] have recently pointed out that (−)-**2** should be (*R*) based on CD spectrum reported by Yamamura *et al.*, who also had done an X-ray crystallographic analysis on a related compound **3**.[6]

These contradictory reports prompted us to make sure whether the axial chirality recognition method can be applied to biphenanthrol **2** or it is an exceptional compound where the method can not be applied. Herein we report that the method still holds for **2**, giving the result contrary to that of Yamamoto *et al.*[4] and in agreement with Hayashi *et al.*[5]

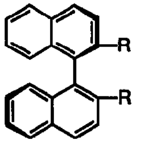
To a well stirred, refluxing solution of benzene (160 ml), pyridine (5.0 ml) and 4-(dimethylamino)-pyridine (379 mg, 3.10 mmol) were added slowly (1 h) a solution of (±)-**2**[7] (600 mg, 1.55 mmol) in benzene



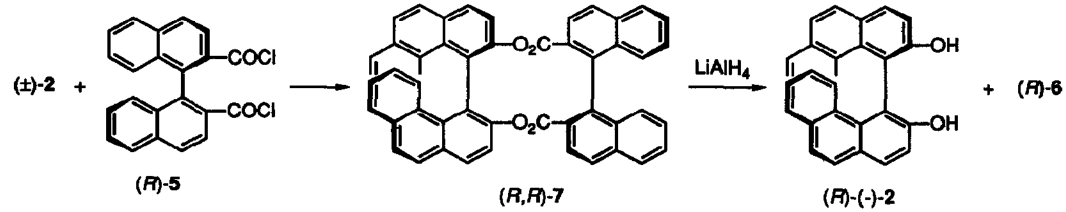
(*R,R*)-**1**



2 R = OH
3 R = OMe



(*R*)-**4** R = CO_2H
(*R*)-**5** R = COCl
(*R*)-**6** R = CH_2OH



(70 ml) and also a solution of (*R*)–**5** (588 mg, 1.55 mmol) in benzene (70 ml) at a same rate, and then, the mixture was stirred under reflux for another 12 h. After the usual workup which included aqueous washings, extractions with diethyl ether and drying over $MgSO_4$, volatiles were removed under reduced pressure to leave a pale yellow residue. This material was chromatographed on a silica–gel column with hexane – dichloromethane (1:1) to give the cyclic diester **7** as the first eluted component [153 mg, 14% based on (*R*)–**5**].[8] Diastereomeric homogeneity of **7** was confirmed by the fact that reductive cleavage of the ester linkages by treatment with $LiAlH_4$ in THF gave enantiomerically pure (–)–**2**[9] as judged by chiral HPLC analyses. It can be said that upon treatment with (±)–**2**, (*R*)–**5** serves as the template to pick up only (–)–**2** to complete a cycle of the diester **7**, the configuration of which should be (*R,R*). Thus, the absolute stereochemistry of (–)–**2** is determined to be (*R*) as suggested by Hayashi *et al.*[5]

In conclusion, we have shown here an additional example where the axial chirality recognition method can be applied, correctly assigning the configuration of 3,3'–dihydroxy–4,4'–biphenanthryl (**2**). The intramolecular Ullmann coupling route by Yamamoto *et al.*[4] should also have reached to the same conclusion but seemingly the rotation of **2** used for the Ullmann reaction after having been separated by a chiral HPLC might have been inadvertently exchanged.

References and Notes

1. (a) Miyano, S.; Handa, S.; Tobita, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.*, **1986**, *59*, 235. (b) Miyano, S.; Shimizu, K.; Sato, S.; Hashimoto, H. *ibid.*, **1985**, *58*, 1345. (c) Miyano, S.; Handa, S.; Shimizu, K.; Tagami, K.; Hashimoto, H. *ibid.*, **1984**, *57*, 1943. (d) Miyano, S.; Tobita, M.; Hashimoto, H. *ibid.*, **1981**, *54*, 3522.
2. (a) Miyano, S.; Fukushima, H.; Handa, S.; Ito, H.; Hashimoto, H. *Bull. Chem. Soc. Jpn.*, **1988**, *61*, 3249. (b) Hattori, T.; Koike, N.; Miyano, S. *J. Chem. Soc., Perkin Trans. 1*, **1994**, in press.
3. *Cf.*, (a) Wang, X.; Luh, T.-Y. *J. Org. Chem.*, **1989**, *54*, 263. (b) Yamamoto, K.; Kitsuki, T.; Okamoto, Y. *Bull. Chem. Soc. Jpn.*, **1986**, *59*, 1269. (c) Yamamoto, K.; Watanabe, K.; Chikamatsu, H.; Okamoto, Y.; Yoshida, T. *J. Chem. Soc., Chem. Commun.*, **1987**, 807.
4. Yamamoto, K.; Noda, K.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.*, **1985**, 1065.
5. (a) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y. *J. Am. Chem. Soc.*, **1994**, *116*, 775. (b) Hayashi, T.; Iwamura, H.; Uozumi, Y.; Matsumoto, Y.; Ozawa, F. *Synthesis*, **1994**, 526.
6. Yamamura, K.; Ono, S.; Ogoshi, H.; Masuda, H.; Kuroda, Y. *Synlett*, **1989**, 18.
7. Feringa, B.; Wynberg, H. *Tetrahedron Lett.*, **1977**, 4447.
8. (*R,R*)–**7**: m.p. 290 °C (decomp.); $[\alpha]_D^{20}$ +622 (*c* 1.53, $CHCl_3$); IR (KBr) 1755 cm^{-1}; ^1H NMR (250 MHz; $CDCl_3$) δ 6.83 – 7.90 (m, ArH); FD–MS *m/z* (rel intensity) 694 (13), 693 (54), 692 (M^+; 100), and 346 (M^{2+}; 10). Found: C, 86.7; H, 4.35%. Calcd for $C_{50}H_{28}O_4$: C, 86.7; H, 4.1%.
9. (–)–**2**: m.p. 144 – 145 °C; $[\alpha]_D^{20}$ –68 (*c* 0.48, $CHCl_3$) [lit.,[5] $[\alpha]_D^{20}$ –67 (*c* 0.13, $CHCl_3$)].

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