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A Revised Absolute Configuration of 2-Hydroxy-1,1′-binaphthyl

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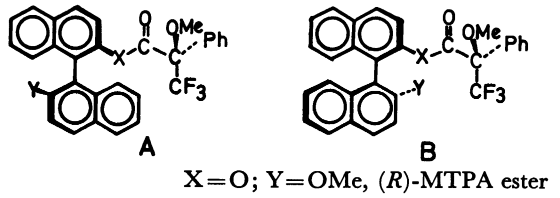
Synopsis. The absolute configuration of 2-hydroxy-1,1′-binaphthyl (**3**) has been revised to (*R*)-(+) in THF by a reexamination of the previously reported chemical correlation between **3** and 2,2′-diamino-1,1′-binaphthyl. This revised configuration agreed with that obtained from the assignment by means of the MTPA/LSR method.

In the course of the ^{1}H NMR study aimed at determining the absolute configuration of axially chiral biaryls using α-methoxy-α-trifluoromethylphenylacetic acid (MTPA, Mosher's reagent) derivatives (esters and amides) and achiral lanthanoide shift reagents (MTPA/LSR method),[1] we have found that the (*R*)-MTPA esters (amides) of a series of binaphthyls with the configuration indicated in Fig. 1A have larger lanthanoid-induced shifts of the signals due to MeO groups in the MTPA moieties ($\mathrm{LIS_{OMe}}$) than the alternate derivatives of the binaphthyls with the opposite configuration (Fig. 1B). These results can reasonably be interpreted[1] by considering the preferred coordination of the shift reagent to the diastereomeric MTPA derivatives. We faced, however, an exceptional case in correlating the relative magnitudes of $\mathrm{LIS_{OMe}}$ to the absolute configurations of the binaphthyls of this type; the reguralty described above did not hold for a fundamental binaphthol **3** if the reported configuration of **3** is correct.

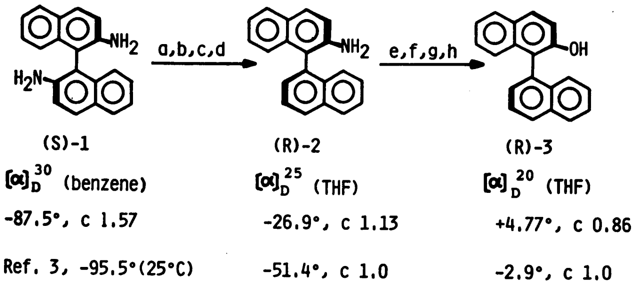
There have been two reports on the absolute configuration of **3**. In the first report, (*R*) configuration was tentatively assigned to (+)-isomer in methanol from the result of Prelog's atrolactic acid synthesis.[2] In the second, (−)-**3** was correlated chemically to (−)-2,2′-diamino-1,1′-binaphthyl (**1**), whose configuration had been known to be (*S*), thus establishing the absolute configuration as (*R*)-(−) in THF, as is shown in Scheme 1.[3,4] Although this result seems to contradict that obtained from the Prelog rule, it must be noticed that the optical rotation in each study was taken in a different solvent. We have found that the sign of the optical rotation of **3** in methanol is the opposite of that in THF. The results from these two independent studies, therefore, eventually agree and contradict the result obtained by the use of the MTPA/LSR method. This discrepancy needs to be investigated further, and so we have reexamined the reported chemical correlation between **3** and **1**.

In the reexamination of the correlation, (*S*)-(−)-**1** was correlated to (−)-**2**, in agreement with the reported result, while (−)-**2** was converted to (+)-**3**, contrary to the previous result. In order to confirm this result, the same correlation was carried out using (*R*)-(+)-**1**, and (−)-**3** was obtained by way of (+)-**2**. In addition, the CD spectra of (−)-**3** and (+)-**2** (Fig. 2) showed the same sign of the Cotton effect, indicating that the configurations of these two were the same.[5] From these new facts, the absolute configuration of **3** must be revised to (*R*)-(+) in THF and (*R*)-(−) in methanol.[6] Thus, it is clear that the MTPA/LSR method affords the correct assignment of the configuration of **3**.

Although it has been widely accepted that the Prelog rule can be extended to axially chiral biaryls[7,8] on the basis of Berson's correlation model,[9] it is now clear that the model leads to a wrong configurational assignment for **3**. Therefore, the general applicability of Berson's model must be reconsidered.



X=O; Y=OMe, (*R*)-MTPA ester
X=NH; Y=H, (*R*)-MTPA amide
Fig. 1.



Scheme 1. Configurational correlation between **1** and **3**.
a: 1 equiv. Ac_2O, b: HNO_2, c: 48% H_3PO_2, d: concd HCl, e: HNO_2, f: 42% HBF_4, g: 100 °C/AcOH, h: 5% KOH/MeOH.

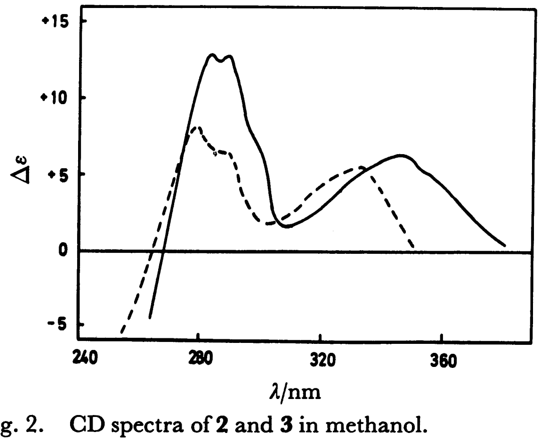


Fig. 2. CD spectra of **2** and **3** in methanol.
——: **2**, ------: **3**; The spectra were determined on the partially active **2** [$[\alpha]_D^{25}$ +24.7° (*c* 0.96, THF), 38% e.e., based on the maximum rotation (+65.2°) estimated by NMR[13)]] and **3** [$[\alpha]_D^{20}$ −12.6° (*c* 1.45, THF), 98% e.e.] and corrected for enantiomeric purities.

Experimental

Instruments. The ^{1}H NMR spectra were determined on a Hitachi R-22, 90 MHz spectrometer. The optical rotations were taken on a Perkin-Elmer 241 electronic polarimeter using a 1-dm thermostated microcell. The CD spectra were taken on a JASCO J-20 spectropolarimeter using a 1-cm cell.

(±)-2-Hydroxy-1,1′-binaphthyl (3). A mixture of 2-methoxy-1,1′-binaphthyl (1.42 g, 5 mmol, mp 113—114 °C, lit,[2] 110—111 °C) and lithium iodide (1.34 g, 10 mmol, dried at 300 °C under nitrogen) in collidine (8 ml) was refluxed for 10 h. After cooling, the mixture was poured into ice–water (60 ml) and extracted with benzene. The extract was washed with 2 M HCl, saturated $NaHCO_3$, water, and dried (Na_2SO_4), and then concentrated to give colorless crystals, which were subsequently recrystallized from methanol; 0.97 g (72%), mp 93—95 °C,[10] M+ 270. Found: C, 88.99; H, 5.38%. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22%. ^{1}H NMR ($CDCl_3$) 4.89 (s, OH), 6.9—8.0 (m, aromatic H); IR ($CHCl_3$) 3540, 3050, 3000, 1615, 1595, 1380, 1190 cm^{-1}.

Resolution of 3. The racemic **3** (81 mg, 0.3 mmol) was esterified with acid chloride of (*R*)-MTPA [88 μl, $[\alpha]_D^{24}+134.5°$ (*c* 5.6, CCl_4)] in pyridine (1 ml) in the presence of 4-dimethylaminopyridine (24 mg, 2 mmol) overnight at room temperature. After a usual work-up, the crude product was purified by column chromatography (silica gel, 7% AcOEt in hexane); the resulting diastereomeric mixture of (*R*)-(+)-MTPA esters (105 mg, 72%) was subsequently resolved by HPLC; Lichrospher SI 100 (Merk) 7.8 mm × 30 cm, 3% diisopropyl ether in hexane, Flow rate, 4 ml/min, $\alpha=1.15$. Less polar (*R*)-MTPA ester; 53 mg, ^{1}H NMR ($CDCl_3$) 2.72 (s, OMe), 6.9—8.0 (m, aromatic H), IR ($CHCl_3$) 1772 cm^{-1}. More polar (*R*)-MTPA ester; 39 mg, ^{1}H NMR ($CDCl_3$) 2.82 (s, OMe), 6.9—8.0 (m, aromatic H), IR ($CHCl_3$) 1772 cm^{-1}.

A solution of less polar (*R*)-MTPA ester (50 mg) in 5% methanolic KOH (1 ml) was refluxed for 1/2 h. After acidification with 2 M HCl, the mixture was extracted with benzene, and the extract was washed with saturated $NaHCO_3$ and water, and then dried (Na_2SO_4). The solvent was removed, and the residue was purified by TLC (silica gel, 20% AcOEt in hexane) to give 23.5 mg of **3**; mp 160—163 °C (recrystallized from MeOH), $[\alpha]_D^{30}$ +1.9°, $[\alpha]_D^{20}$ +5.6° (*c* 1.0, MeOH), $[\alpha]_D^{20}$ −12.9° (*c* 1.34, THF); M+ 270. Found: C, 88.96; H, 5.26%. Calcd for $C_{20}H_{14}O$: C, 88.86, H, 5.22%.

By the same procedure, the more polar (*R*)-MTPA ester (39 mg) afforded 18.3 mg of **3**; mp 161—164 °C[11] (recrystallized from MeOH); $[\alpha]_D^{30}$ −1.8°,[11] $[\alpha]_D^{20}$ −5.2° (*c* 1.03, MeOH); $[\alpha]_D^{20}$ +13.0° [11] (*c* 1.12, THF).

*Configurational Assignment of 3 by the (*R*)-MTPA/LSR Method.* A ^{1}H NMR shift study was conducted on a carbon tetrachloride solution of the diastereomeric mixture of (*R*)-MTPA esters (49 mg) prepared from a partially active **3** ($[\alpha]_D^{20}$ −6.83° (*c* 1.61, THF)) and acid chloride of (*R*)-MTPA. The lanthanoid-induced shifts of the signals due to MeO groups in the MTPA moieties (LIS_{OMe}) were determined by the successive addition of $Eu(fod)_3$ (0.1—0.5 equivalent). The smaller MeO signal initially located at 2.82 ppm showed a larger induced shift ($LIS_{OMe}=5.8$) than the larger one at 2.72 ppm ($LIS_{OMe}=5.1$). From the consideration of the preferred coordination of the shift reagent with the diastereomeric MTPA esters,[1] (*R*) configuration was assigned to (+)-isomer in THF.

Chemical Correlation between the Absolute Configurations of 3 and 1. By the previously reported procedure,[3] a partially active (*S*)(−)-**1**[12] ($[\alpha]_D^{30}$ −87.5° (*c* 1.57, benzene)) was transformed to (*R*)-(−)-**2**; $[\alpha]_D^{25}$ −26.9° (*c* 1.13, THF); M+ 269. Found: C, 89.35; H, 5.78; N, 5.21%. Calcd for $C_{12}H_{15}N$: C, 89.18; H, 5.61; N, 5.20%.

This (−)-**2** (128 mg) was further converted to crude **3** (60 mg, $[\alpha]_D^{25}$ +1.30° (*c* 1.08, THF)) by the procedure previously described in the literature (diazotization, thermal decomposition of diazonium salt in acetic acid, and hydrolysis, successively). The crude **3** was purified by HPLC (Lichrospher SI 100 (Merk) 7.8 mm × 30 cm, 6% AcOEt in hexane) to give colorless crystals; 42.8 mg, M+ 270, $[\alpha]_D^{20}$ +4.77° (*c* 0.86, THF). The IR ($CHCl_3$) and ^{1}H NMR ($CDCl_3$) spectra of this product agreed with those of authentic racemic and optically active **3**.

By the same procedure, (R)-(+)-**1**[12] ($[\alpha]_D^{30}$ +77.6° (*c* 1.64, benzene)) was correlated to (*S*)-(+)-**2** ($[\alpha]_D^{25}$ +24.7° (*c* 0.96, THF)), which was successively correlated to (*S*)-(−)-**3**, M+ 270; $[\alpha]_D^{20}$ −2.43° (*c* 1.48, THF).

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References

1) K. Kabuto, F. Yasuhara, and S. Yamaguchi, *Tetrahedron Lett.*, **22**, 659 (1981).

2) J. A. Berson and M. A. Greenbaum, *J. Am. Chem. Soc.*, **80**, 653 (1958).

3) H. Akimoto and S. Yamada, *Tetrahedron*, **27**, 5999 (1971).

4) In Ref. 3, the authors stated that (*S*)-(−)-**3** and (*S*)-(−)-**2** were obtained from (*S*)-(−)-**1**. According to Cahn-Ingold-Prelog sequence rule, however, the configuration of **2** and **3** should be (*R*).

5) These CD spectra showed the same sign as, and a pattern similar to, those of (*R*)-2,2′-disubstituted 1,1′-binaphthyls, whose configurations correspond to (*S*)-**2** and (*S*)-**3**; K. Mislow, E. Bunnenberg, R. Records, K. Wellman, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 1342 (1963).

6) Very recently, this observation has been confirmed by Meyers and Cram. a) A. I. Meyers and K. A. Lutomski, *J. Am. Chem. Soc.*, **104**, 879 (1982); b) J. M. Willson and D. J. Cram, *ibid.*, **104**, 881 (1982).

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8) J. C. Fiaud, "Stereochemistry," ed by H. B. Kagan, Georg Thieme, Stuttgart (1977), Vol. 3, p. 31.

9) J. A. Berson and M. A. Greenbaum, *J. Am. Chem. Soc.*, **80**, 445 (1958).

10) The mp does not agree with the previously reported value (188—189 °C, Ref. 2).

11) The mp and optical rotation are different from the values reported in Ref. 2 (mp 199—199.5 °C, $[\alpha]_D^{30}$ +21.7° in MeOH). However, these values are close to those recently reported by Meyers (mp 159—161°C, $[\alpha]_D$+13.8° in THF, Ref. 6a).

12) The mistypings [(*R*)-(−) and (*S*)-(+)-**5**] in our previous communication[1] should be corrected to (*R*)-(+) and (*S*)-(−).

13) K. Kabuto, F. Yasuhara, and S. Yamaguchi, *Tetrahedron Lett.*, **21**, 307 (1980).