Pergamon

Tetrahedron Letters 42 (2001) 441–444

TETRAHEDRON LETTERS

Synthesis, molecular structure and fluxional behavior of (*R*)-7-*p*-tolyldinaphtho[2,1-*b*;1′,2′-*d*]stibole: the first isolated example of optically active group 15 dinaphthoheteroles

Shuji Yasuike,[a] Tomoyasu Iida,[a] Kentaro Yamaguchi,[b] Hiroko Seki[b] and Jyoji Kurita[a,*]

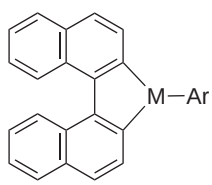
[a]*Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa 920-1181, Japan*
[b]*Chemical Analysis Center, Chiba University, 1-33, Yayoicho, Inage-ku, Chiba 263-8322 Japan*

Received 13 October 2000; accepted 2 November 2000

Abstract—The condensation of dibromo-*p*-tolylstibane with 2,2′-dilithio-1,1′-binaphthyl **3**, generated in situ from optically active 2,2′-dibromo-1,1′-binaphthyl (*R*)-(+)-**2** by treatment with *tert*-butyllithium, afforded optically active (*R*)-(−)-7-*p*-tolyldinaphtho[2,1-*b*;1′,2′-*d*]stibole **1c**, which is fluxional in the NMR time scale at elevated temperatures. The energy barrier ($\Delta G^{\ddagger}$) resulting from the flipping of the two naphthalene rings was estimated to be 85±1 kJ mol^{-1} and its half life ($t_{1/2}$) for racemization was determined to be 5.2 h in benzene at 20°C.

The chemistry of various optically active compounds comprising of a 1,1′-binaphthyl system has been one of the most active fields in synthetic chemistry, because the atropisomeric nature of the 1,1′-binaphthyl core and its C_2-symmetry make a highly advantageous chiral environment in a variety of stoichiometric and catalytic asymmetric syntheses.[1] Among these, 1,1′-bi-2-naphthol (BINOL) derivatives used in a variety of asymmetric reactions and transition metal complexes of 2,2′-bis-(diphenylphosphano)-1,1′-binaphthyl (BINAP) used in catalytic enantioselective reactions are the prominent examples of this kind of chiral reagent.[1–3] In connection with these studies, dinaphthoheteroles having group 15 heavier elements such as phosphorous **1a**[4–6] and arsenic **1b**[6] have been synthesized to investigate the possibility of such compounds as monodentate chiral ligands for asymmetric syntheses. However, it has been reported that their energy barriers for racemization are too low to achieve their optical resolution at room temperature; thus, they could be obtained only in racemic form. On the other hand, we have recently reported efficient resolutions of racemic Sb-chiral stibindoles[7] and C_2-disymmetric 2,2′-(diarylstibano)-1,1′-binaphthyls (BINASb),[8] via the separation of mixtures of their diastereoisomeric Pd-complexes using optically active *ortho*-palladated benzylamine derivatives, and the latter are the first examples of chiral auxiliaries containing antimony for transition metal-catalyzed asymmetric reactions. In the course of our continuing studies on the synthesis of optically active organoantimony compounds, we were interested in the preparation and the optical behavior of the group 15 dinaphthoheteroles. Here we present the synthesis, molecular structure and fluxional behavior of the title 1,1′-dinaphthostibole **1c**, which is the first isolated example of optically active C_2-symmetric group 15 dinaphthoheteroles (Scheme 1).

Treatment of (*R*)-(+)-2,2′-dibromo-1,1′-binaphthyl (DBBN) (*R*)-**2**[9] with *tert*-butyllithium in dry ether at −80°C, and subsequently with dibromo-*p*-tolylstibane[10] resulted in ring closure, giving the desired product {$[\alpha]_D^{23}$ −20.0} containing 7-*p*-tolyldinaphtho[2,1-*b*;1′,2′-*d*]stibole (−)-**1c** in 35% yield,[11] via 2,2′-dilithio-1,1′-binaphthyl intermediate **3**. Recrystallization of the product from ether gave racemic (±)-**1c** as crystals, and



a: M = P
b: M = As
c: M = Sb

1

Scheme 1.

Keywords: antimony and compounds; dinaphthostibole; optical properties; thermodynamics.

* Corresponding author. Tel.: +00 81 76 229 1165; fax: +00 81 76 229 2781; e-mail: j-kurita@hokuriku-u.ac.jp

0040-4039/01/$ - see front matter
PII: S0040-4039(00)01977-8

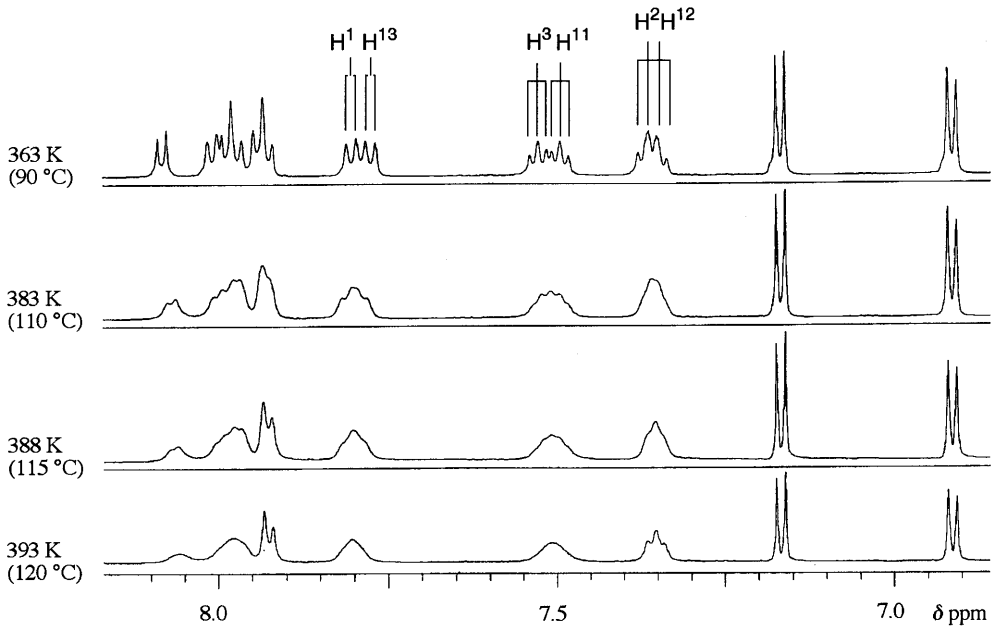


Figure 1. Variable temperature ^{1}H NMR data of aromatic region of (±)-**1c** in DMSO-d_6.

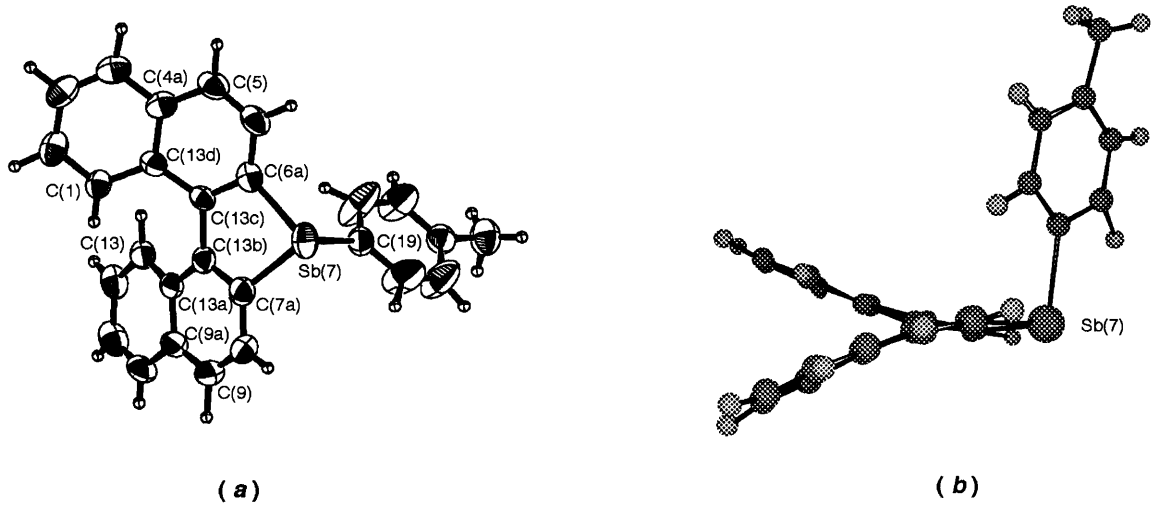
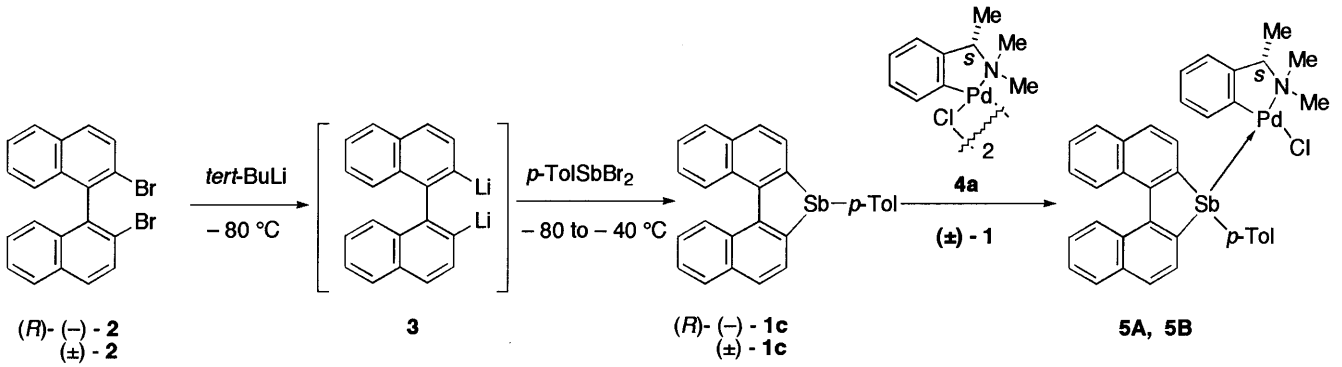


Figure 2. Molecular structure of (±)-**1c**. (a) Front view. Selected bond distances (Å) and angles (°): C(6a)–Sb(7) 2.116(9), C(7a)–Sb(7) 2.128(8), C(19)–Sb(7) 2.161(7), C(13b)–C(13c) 1.504(9); C(6a)–Sb(7)–C(7a) 80.5(3), C(6a)–C(13c)–C(13b)–C(7a) 21.1(8), C(13a)–C(13b)–C(13c)–C(7d) 37.6(9). (b) Side view.

the desired more optically active (−)-**1c** $\{[\alpha]_D^{23}$ −51.7$\}$ could be obtained from the mother liquid as an oil. The optically active (−)-**1c** (Sb) isolated here is far more optically stable than **1a** (P) and **1b** (As), but racemizes gradually at room temperature ($t_{1/2}$ 5.2 h at 20°C, benzene).

The structure of **1c** was elucidated by its MS (EI), ^{1}H NMR spectral and single-crystal X-ray analyses. In the ^{1}H NMR of (±)-**1c** (DMSO-d_6, 50°C), all of the corresponding signals on the two naphthalene rings are non-equivalent and appear as two sets of signals; e.g. δ 7.34 and 7.36 for 2- and 12-H, δ 7.49 and 7.52 for 3- and 11-H, and δ 7.73 and 7.76 for 1- and 13-H. These magnetic features of naphthyl protons on **1c** are different from those of dinaphthophospholes **1a**[4,5] and dinaphthoarsoles **1b**,[6] for which all of the corresponding signals are seen to be equivalent. The results suggest the presence of some restriction on flipping between the naphthalene rings on **1c** at ambient temperature in the NMR time scale. The variable-temperature ^{1}H NMR spectral analysis for 1-H and 13-H signals on **1c** revealed that the energy barrier ($\Delta G^{\ddagger}$) resulting from the flipping of the two naphthalene rings was 85±1 kJ mol^{-1} ($\Delta\nu = 9.7$ Hz, $T_c = 393$ K, DMSO-d_6), which was larger than those reported for the corresponding phosphorus **1a** (56 kJ mol^{-1}) and arsenic **1b** (59 kJ mol^{-1}) analogs (Fig. 1).[6]

The ORTEP structure of **1c** having *S*-configuration (a) and its side view (b) obtained by single-crystal X-ray analysis of (±)-**1c** are illustrated in Fig. 2.[12] The result



Scheme 2.

shows that the naphthalene rings are bent significantly away from each other, making the compound chiral, and the distance between H(1) and H(13) is 2.406 Å. Also apparent is that the geometry of the five-membered heterole rings in **1a**–**c** is sensitive to change in the heteroatom and some regularity exists. For instance, the values of the inner dihedral angles of the heterole rings C(6a)–C(13c)–C(13b)–C(7a) for **1a**–**c** increase in the order **1a** (P: 13.6°)<**1b** (As: 15.3°)<**1c** (Sb: 21.1°);[4c] this tendency implies that the planarity of the heterole ring in **1a**–**c** decreases as the element became heavier in the periodic table. Accompanying this alteration of the angles, the outer dihedral angles C(13a)–C(13b)–C(13c)–C13d) for **1a**–**c** increase in the order **1a** (P: 24.2°)<**1b** (As: 26.4°)<**1c** (Sb: 37.6°). These regular variations of the dihedral angles should be close to the difference in the covalent radii of the P, As, and Sb atoms.[13]

We next examined the resolution of the racemic (±)-**1c** using optically active palladium complexes. The racemic (±)-**1c** could be readily prepared from racemic DBBN **2** via 2,2′-dilithio-1,1′-binaphthyl intermediate **3** in 48% yield. Treatment of (±)-**1c** with 0.5 equiv. of dimeric optically active di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)-ethyl]phenyl-*C*,*N*}dipalladium(II) (*S*)-**4**, which has been proved to be a useful resolving agent for chiral phosphorous,[14] arsenic[15] and antimony derivatives,[7,8] resulted in coordination of antimony to palladium, giving rise to a diastereomeric mixture of **5A** and **5B** (Scheme 2). However, all attempts to separate the two diastereomers by fractional recrystallization from a variety of solvents or by column chromatography have been unsuccessful. Furthermore, the ^{1}H NMR spectrum of a mixture of optically active (−)-**1c** ($[\alpha]_D^{22}$ −19.8°) and (*S*)-**4** is essentially the same as that of a mixture of racemic (±)-**1c** and (*S*)-**4**. This result shows that the optically active **1c** should racemize with ease in the presence of palladium complex (*S*)-**4**.

In conclusion, we have disclosed that the condensation of dibromo-*p*-tolylstibane with 2,2′-dilithio-1,1′-binaphthyl generated in situ from (*R*)-2,2′-dibromo-1,1′-binaphthyl gave optically active (*R*)-(−)-7-*p*-tolyldinaphtho[2,1-*b*;1′,2′-*d*]stibole **1c**, which is optically more stable than the corresponding phosphorous **1a** and arsenic **1b** analogues and could be isolated as an optically active form.

Acknowledgements

Partial financial support for this work was provided by a Grant-in Aid for Scientific Research (No. 09672172) from the Ministry of Education, Sciences, Sports and Culture of Japan.

References

1. Rossini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503–517.
2. (a) Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709–6716; (b) Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717–6725; (c) Sakane, S.; Maruoka, K.; Yamamoto, H. *Tetrahedron*, **1986**, *42*, 2203–2209; (d) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310–312; (e) Wang, J. T.; Fan, X.; Quian, Y. M. *Synthesis* **1989**, 292–292.
3. For reviews, see: (a) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187–208 (b) Brunner, H. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Ed.; Wiley: Chichester, 1989; Vol. 5, pp. 109–146; (c) Noyori, R. *Science* **1990**, *248*, 1194–1199; (d) Narasaka, K. *Synthesis*, **1991**, 1–11; (e) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*, Wiley: New York, 1994; (f) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422.
4. (a) Dore, A.; Fabbri, D.; Gladiali, S.; De Lucchi, O. *J. Chem. Soc., Chem. Commun.* **1993**, 1124–1125; (b) Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Valle, G. *J. Org. Chem.* **1994**, *59*, 6363–6371; (c) Fabbri, D.; Dore, A.; Gladiali, S; De Lucchi, O.; Valle, G. *Gazz. Chim. Ital.* **1996**, *126*, 11–18.
5. (a) Tani, K.; Yamagata, T.; Tashiro, H. *Acta Crystallogr., Sect. C* **1994**, *50*, 769–771; (b) Tani, K.; Tashiro, H.; Yoshida, M.; Yamagata, T. *J. Organomet. Chem.* **1994**, *469*, 229–236.
6. Watson, A. A.; Willis, A. C.; Wild, B. S. *J. Organomet. Chem.* **1993**, *445*, 71–78.
7. Kurita, J.; Usuda, F.; Yasuike, S.; Tsuchiya, T.; Tsuda, Y.; Kiuchi, F.; Hosoi, S. *Chem. Commun.* **2000**, 191–192.
8. Yasuike, S.; Okajima, S.; Yamaguchi, K.; Seki, H.; Kurita, J. *Tetrahedron*: *Asymmetry* **2000**, *11*, 4043–4047.
9. Hoshi, T.; Shionoiri, H.; Suzuki, T.; Ando, M.; Hagiwara, H. *Chem. Lett.* **1999**, 1245–1246.

10. Millington, P. L.; Sowerby, D. B. *J. Organomet. Chem.* **1994**, *480*, 227–234.
11. Experimental procedures for (*R*)-(−)-**1c**: All operations in this procedure were performed at below 25°C. A solution of (*R*)-(+)-**2** ($[\alpha]_D^{23}$ +32.6, 474 mg, 1.15 mol) in ether (5 ml) was added to a stirred solution of *tert*-BuLi (1.6 *N* in pentane, 4.2 ml, 6.72 mmol) in ether (20 ml) at −80°C under an argon atmosphere. After stirring the mixture for 1 h at the same temperature, a solution of dibromo-*p*-tolylstibane (935 mg, 2.5 mmol) in ether (10 ml) was added dropwise to the reaction mixture. The mixture was stirred for 1 h at −80°C and for 1 h at −40°C, and then diluted with ether and water. The organic layer was separated, washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent in vacuo, the resulting residue was separated by silica gel column chromatography (*n*-pentane/dichloromethane 5:1) to furnish an optically active mixture of (*S*)-(+)-**1c** and (*R*)-(−)-**1c** ($[\alpha]_D^{23}$ −20.0, 189 mg, 35% yield). Recrystallization of the mixture from ether (1.5 ml) gave racemic (±)-**1c** (118 mg) as crystals and more optically active product {71 mg, $[\alpha]_D^{23}$ −51.7 (*c* 1.8 benzene)} as an oil. The optical purity of this product is not known at present, because no methods to determine the purity of the product have been found. *Selected data* for (±)-**1c**: yellow prisms (ether/hexane 1:5) mp 143–145°C, δ_H (600 MHz, *J* Hz, DMSO-d_6, 50°C) 2.09 (3H, s, Tol-*Me*), 6.90 and 7.17 (each 2H, each d, *J* 7.8, Tol-*H*), 7.34 (1H, t, 12-*H*), 7.36 (1H, t, 2-*H*), 7.49 (1H, t, 11-*H*), 7.52 (1H, t, 3-*H*), 7.73 (1H, d, 13-*H*), 7.76 (1H, d, 1-*H*), 7.93 (1H, d, 9-*H*), 7.95 (1H, d, 5-*H*), 7.97 (1H, d, 10-*H*), 8.01 (1H, d, 4-*H*), 8.02 (1H, d, 8-*H*), 8.12 (1H, d, 6-*H*), $J_{1,2(12,13)}$ 9.5, $J_{2,3(11,12)}$ 7.0, $J_{3,4(10,11)}$ 7.7 and $J_{5,6(8,9)}$ 7.7; *m*/*e* (HR-MS) 464.053 (calcd for $C_{27}H_{19}Sb$, 464.0525). Anal. calcd for $C_{27}H_{19}Sb$: C, 69.71; H, 4.12. Found: C, 69.74; H, 4.36.
12. *Crystal data* for (±)-**1c**: empirical formula: $C_{27}H_{19}Sb$: triclinic; space group *P*1; $a = 12.87(2)$, $b = 15.09(1)$, $c = 11.66(1)$ Å; $\alpha = 107.12(7)$, $\beta = 107.62(7)$, $\gamma = 89.60(6)°$; $V = 2053(3)$ Å^3; $T = 288$ K, $Z = 4$, μ(Mo Kα) = 13.50 cm^{-1}, 6118 reflections measured, 5539 reflections [$I > 3.00\sigma(I)$] were used in all calculations, $R = 0.072$, $Rw = 0.088$.
13. Emsley, J. *The Elements*; Clarendon Press: Oxford, 1998; 3rd ed.
14. (a) Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876–7886; (b) Pietrusiewicz, M. K.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375–1411; (c) Gladiali, S.; Dore, A.; Fabbri, D; Lucchi, O. D.; Manassero, M. *Tetrahedron: Asymmetry* **1994**, *5*, 511–514; (d) Schmid, R.; Foricher, J.; Cereghetti, M.; Schönholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370–388; (e) Alkock, N. W.; Hulmes, D. I.; Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 395–397.
15. (a) Roberts, N. K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1979**, 2015–2021; (b) Wild, S. B. *Coord. Chem. Rev.* **1997**, *166*, 291–311, and references cited therein.