NOVEL INTRAMOLECULAR INDUCTION OF AXIAL CHIRALITY BY A CENTRALLY CHIRAL ELEMENT IN THE BIPHENYL SERIES*

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The title induction has been observed in the reaction of achiral 2,2′,6,6′-tetrakis(bromomethyl)biphenyl with centrally chiral (*R*)-1-phenylethylamine, (*R*)-1-(1-naphthyl)ethylamine and (*R*)-1-(2-naphthyl)-ethylamine. The ratio of the arising diastereomeric doubly bridged diamines and their thermodynamic stability have been determined. The diastereomer excess in the kinetically controlled reaction is solvent-dependent. The absolute configuration of the biphenyl twist in the products has been assigned on the basis of CD spectra and comparison with singly bridged biphenyl models of known sense of the twist.
Key words: Induction of axial chirality; Bridged biphenyls.

Biphenyls bearing four identical substituents in the positions 2, 2′, 6 and 6′ are achiral (provided there are no other substituents attached to the aromatic rings). On the other hand, biphenyl systems with two identical 2,6- and 2′,6′-bridges are chiral, being exceptional in that they possess, instead of a plane of symmetry, three mutually perpendicular C_2 axes (D_2 point group[1,2]).

Conversion of achiral tetrasubstituted biphenyls into chiral doubly bridged derivatives poses a delicate stereochemical problem. As a part of our broader interest in chirality induction involving biaryl axis[3] we have now investigated the steric course of the cyclization reaction of achiral tetrabromo derivative **1** with three centrally chiral amines **2a**–**2c** (Scheme 1).

RESULTS AND DISCUSSION

On the Mechanism of the Axial Chirality Induction

As seen from a closer analysis of the multistep reaction of the tetrabromide **1** with chiral amines **2** (in Scheme 2 depicted for the amine **2a**), the cyclization step **A** → **B** is the sole axial chirality-forming step in the whole transformation. The intermediate **A** is unique in that it represents a *nonplanar, conformationally frozen species with a stereo-*

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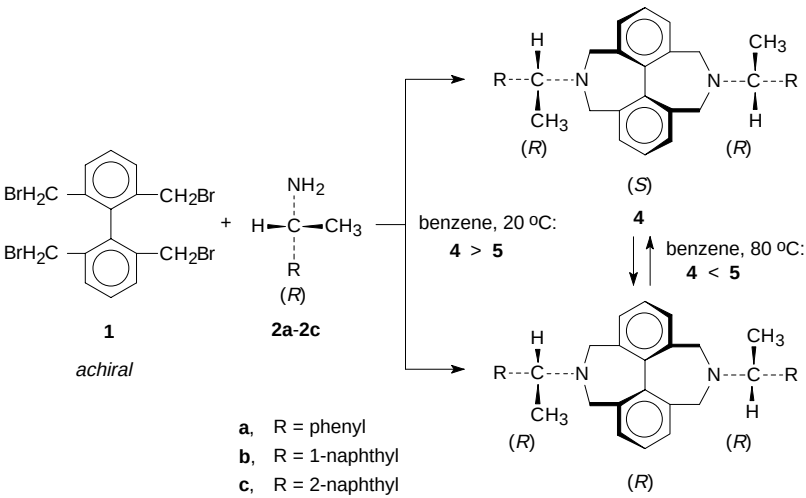
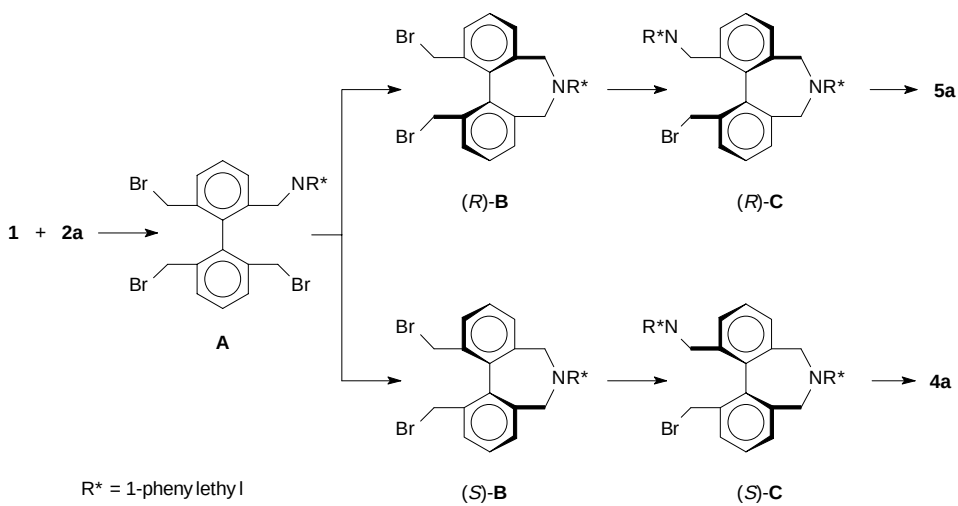
chemically undefined (prostereogenic[4]*) biaryl axis*. The stereochemical definition is attained in the *diastereoselective cyclization step* **A** → **B**. The diastereoselectivity of the cyclization is given by differing reactivities of the two alternative conformers of **A** arising by rotation about the $ArCH_2$–N bond, underlying the axial chirality induction by a centrally chiral element.



SCHEME 1



SCHEME 2

Such type of intramolecular axial chirality induction has not been hitherto demonstrated. A "mirror-like" case, *i.e. a diastereoselective ring opening in a "quasi-planar", conformationally mobile species with a prostereogenic biaryl axis*, has already been reported[5,6].

Steric Course of the Cyclization Reactions

In the cyclization of the achiral tetrabromide **1** with the centrally chiral amines **2a–2c** any induction of axial chirality should manifest itself as an excess of one of the two possible diastereoisomeric products **4** and **5**. Treatment of tetrabromide **1** with (*R*)-1-phenylethylamine (**2a**) in benzene at 20 °C afforded products **4a** and **5a** in the ratio 3 : 2 proving thus a chirality induction. The percentage of **4a** (**4a** + **5a** taken as 100%) differed according to the solvent employed, amounting to 58% in benzene, 58% in ethanol, 52% in dioxane, 46% in dimethylformamide and 45% in acetonitrile (see Table I)*.

The individual products **4a** and **5a** were separated by crystallization. Whereas at room temperature their solutions were virtually stable, at elevated temperatures they interconverted, the equilibrium being shifted in favour of **5a** (77% at 80 °C, see Experimental). The isomer **4a** is thus preferred *kinetically* whereas the isomer **5a** *thermodynamically*. Practically the same results were obtained with the isomeric 2-naphthyl derivatives **4c** and **5c** (Table I); thus, in benzene the reaction gave about 56% of isomer **4c** whereas an equilibrium mixture at 80 °C contained only 24% of this isomer.

We expected that with the 1-naphthyl derivatives **4b** and **5b** there should be a greater diastereomer excess because the 1-naphthyl moiety should have greater steric require-

TABLE I
Percentages of isomers **4** in the reaction mixtures from tetrabromide **1** and amines **2a–2c** (20 °C, 1 day)[a]

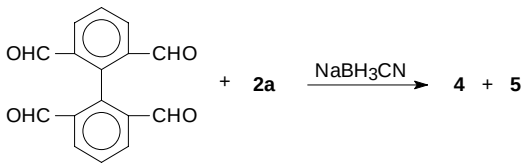
Compound	Benzene	Ethanol	Dioxane	CH_3CN	DMF
4a	58	57	52	45	46
4b	53	51	51	45	51
4c	56	58	63	45	46

[a] Sum of isomers **4** and **5** taken as 100%. Analyzed on a 250-mm Purosphere RP-18 (Merck) column in 90% aqueous methanol, 0.8 ml/min.

* The accompanying change in the absolute sense of the biaryl twist strongly suggests that the solvent effect is of an entropic origin.

ments than the phenyl or 2-naphthyl substituents. However, the kinetically controlled isomer ratio **4b** : **5b** in benzene (53 : 47) was close to that in the phenyl and 2-naphthyl series whereas under the conditions of thermal equilibrium the population of isomer **4b** was slightly lower (19%).

As a pendant to the cyclization study, we have cursorily examined the reductive cyclization of the corresponding tetraldehyde **3** with a single chiral amine (**2a**) in the presence of sodium cyanoborohydride[7,8] (Scheme 3). In methanol, under conditions of kinetic control, the diastereoisomers **4a** and **5a** arose in a nearly statistical ratio (51 : 49).



3

achiral

SCHEME 3

Assignment of Absolute Configuration to Isomers **4** *and* **5**

The absolute configuration of 1-phenylethylamine (**2a**), 1-(1-naphthyl)ethylamine[9,10] (**2b**) and 1-(2-naphthyl)ethylamine[11] (**2c**) has been known for a long time. The sense of the biaryl twist was determined by the CD spectra. As observed by Mislow and other authors[1,12–15], biphenyl derivatives of configuration *R* exhibit positive bands at about 260 nm. Since the spectra of compounds **4a** and **4c** display negative maxima in this region whereas those of isomers **5a**, **5b** and **5c** show positive maxima (Fig. 1), the

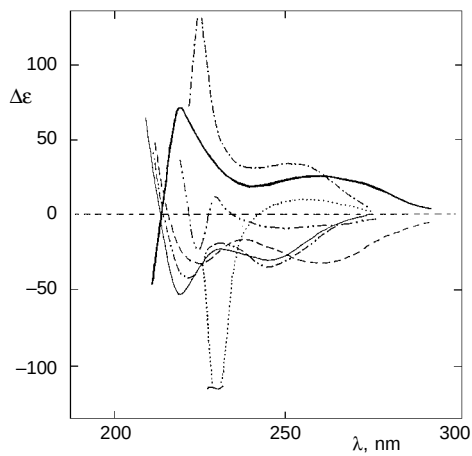
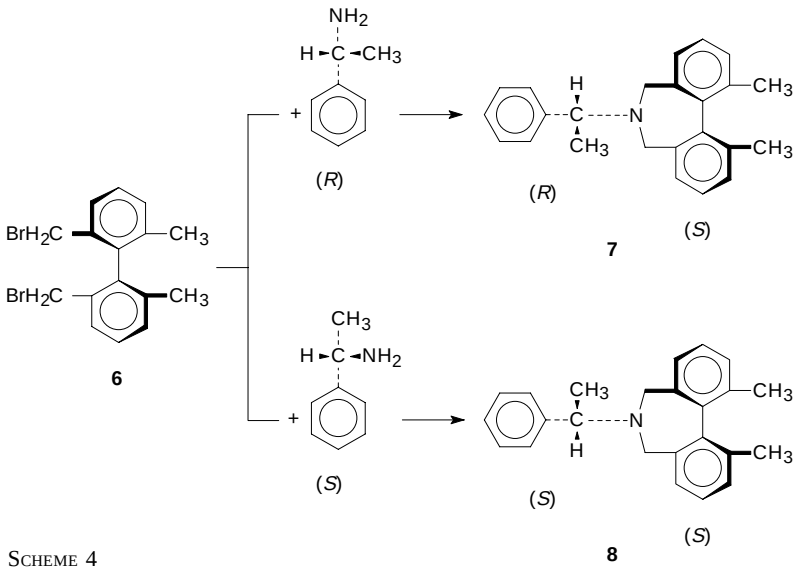


FIG. 1
Circular dichroism spectra (in methanol) of compounds **4**, **5**, **7** and **8**. **4a** – – –, **4b** – · · – · · –, **5a** ——, **5b** · · · ·, **5c** – · – · –, **7** – – · · – – **8** ——

biphenyl moiety was assigned configuration *S* in the former and configuration *R* in the latter isomers.

Supporting evidence came also from comparison of CD and ^{1}H NMR spectra of isomers **4** and **5** with those of the singly bridged diastereomeric models **7** and **8**, obtained by reaction of (+)-(*S*)-6,6′-dimethyl-2,2′-bis(bromomethyl)biphenyl (**6**) of known absolute configuration[16] with (*R*)- and (*S*)-1-phenylethylamine, respectively (Scheme 4). The CD spectra of **7** and **8** exhibited negative maxima in the 250 nm region (Fig. 1), in accord with the configuration *S* of the biphenyl residue in both compounds, and were similar to those of the isomers **4a**, **4b** and **4c**.



SCHEME 4

In the ^{1}H NMR spectra, the diastereomeric relation between the two chiral elements (biphenyl twist and asymmetric C-1 carbon of the amine moiety) in **7** and **8** gives rise to different chemical shifts of the methyl doublets (δ 1.57 for the *R*,*S*-isomer **7** and 1.34 for the *S*,*S*-isomer **8**). We have found analogous differences for the corresponding pairs of isomers **4** and **5** (δ, ppm: **4a** 1.60, **5a** 1.38; **4b** 1.73, **5b** 1.49; **4c** 1.68, **5c** 1.46). Knowing the absolute configuration of the amines employed, we can derive the absolute configuration of the biphenyl twist as *S* in compounds of the series **4** and as *R* for the series **5**, in accord with the results based on the CD spectra.

EXPERIMENTAL

Tetrabromide **1** and tetraldehyde **3** were obtained as described by Agranat and coworkers[17], (*R*)-1-(2-naphthyl)ethylamine (**2c**) according to Fredga[18] and dibromide **6** according to Wittig[19]. (*R*)-1-Phenyl-

ethylamine, (*S*)-1-phenylethylamine and (*R*)-1-(1-naphthyl)ethylamine were Aldrich products. Proton NMR spectra were taken on a Varian UNITY-200 (200 MHz) instrument with tetramethylsilane as internal standard, mass spectra on a ZAB-EQ (VG Analytical, Manchester) spectrometer, CD spectra were obtained with a Jobin Yvon Mark 5 instrument in methanol.

(–)-5,11-Bis((*R*)-1-phenylethyl)-(*S*)-5,6,11,12-tetrahydro-4*H*,10*H*-5,11-diazadibenzo[*ef*,*kl*]heptalene (**4a**)

Tetrabromide **1** (1 050 mg, 2 mmol) was added to a stirred solution of (*R*)-(+)-1-phenylethylamine (**2a**; 3.0 g, 24 mmol) in benzene (10 ml) and the solution was set aside at room temperature for 5 days. The mixture was concentrated *in vacuo* at room temperature and the residue (shown by NMR to contain isomers **4a** and **5a** in the ratio 3 : 2) was partitioned between water and chloroform. The solvent was evaporated and the residue chromatographed on a 1 × 30 cm column of silica gel in ether–methanol–25% aqueous ammonia (100 : 2 : 2) to remove the excess phenylethylamine. The product-containing fractions were evaporated, the oily residue was quickly dissolved in methanol (10 ml) and inoculated with pure isomer **4a** (obtained from another experiment by fractional crystallization). After 2 min the deposited crystals (283 mg, 32%) of pure (HPLC) isomer **4a** were collected and washed with cold methanol, m.p. 162–164 °C, $[\alpha]_D^{25}$ –140.2° (*c* 0.2, methanol). For $C_{32}H_{32}N_2$ (444.6) calculated: 86.44% C, 7.26% H, 6.30% N; found: 86.25% C, 7.28% H, 6.33% N. ^{1}H NMR spectrum ($CDCl_3$): 7.20–7.40 m, 16 H (H arom.); 3.71 d, 4 H, *J*(gem) = 12.6 (NCH_2); 3.52 q, 2 H, *J*(CH,CH_3) = 6.4 (CH); 3.09 d, 4 H, *J*(gem) = 12.6 (NCH_2); 1.60 d, 6 H, *J*(CH_3,CH) = 6.4 (CH_3). CD spectrum (methanol, *c* 2.72 . 10^{-3} mol l^{-1}), Δε, l mol^{-1} cm^{-1} (λ, nm): –33.67 (262), –17.95 (240), –33.22 (226), 2.020 (218), 113.1 (204, end value).

(+)-5,11-Bis((*R*)-1-phenylethyl)-(*R*)-5,6,11,12-tetrahydro-4*H*,10*H*-5,11-diazadibenzo[*ef*,*kl*]heptalene (**5a**)

A. Mother liquors from crystallization of isomer **4a** in the preceding experiment were boiled for 6 h. After cooling, the solution was concentrated to 2 ml and inoculated with pure isomer **5a** (obtained from another experiment by fractional crystallization). Yield of pure (HPLC) isomer **5a** was 460 mg (52%; total yield of **4a** + **5a** was thus 84%); m.p. 143–145 °C, $[\alpha]_D^{25}$ +295.7° (*c* 0.4, methanol). For $C_{32}H_{32}N_2$. 1/2 CH_3OH (460.6) calculated: 84.74% C, 7.44% H, 6.08% N; found: 85.19% C, 7.41% H, 6.05% N. ^{1}H NMR spectrum ($CDCl_3$): 7.22–7.55 m, 16 H (H arom.); 3.75 d, 4 H, *J*(gem) = 12.6 (NCH_2); 3.61 q, 2 H, *J*(CH,CH_3) = 6.4 (CH); 3.07 d, 4 H, *J*(gem) = 12.6 (NCH_2); 1.38 d, 6 H, *J*(CH_3,CH) = 6.4 (CH_3). CD spectrum (methanol, *c* 2.34 . 10^{-3} mol l^{-1}), Δε, l mol^{-1} cm^{-1} (λ, nm): 25.59 (259), 20.11 (243), 69.21 (220), –134.5 (205, end value).

B. A mixture of tetrabromide **1** (1.05 g, 2 mmol), (*R*)-(+)-1-phenylethylamine (**2a**; 1.45 g, 12 mmol) and benzene (10 ml) was refluxed for 20 h. The same work-up procedure as described in the preceding experiment afforded a 1 : 3 mixture of **4a** and **5a**. Crystallization from methanol afforded 448 mg (50%) of pure isomer **5a**.

Stereoisomeric 5,11-Bis((*R*)-1-(1-naphthyl)ethyl)-5,6,11,12-tetrahydro-4*H*,10*H*-5,11-diazadibenzo[*ef*,*kl*]heptalenes **4b** and **5b**

A mixture of tetrabromide **1** (24.0 mg, 0.046 mmol), (*R*)-(+)-1-(1-naphthyl)ethylamine (**2b**; 67.5 mg, 0.39 mmol) and benzene (0.3 ml) was allowed to stand at ambient temperature for one day. Beside much unreacted material, the reaction mixture contained isomers **4b** and **5b** in the ratio 53 : 47 (HPLC; Table I). The mixture was made up to 1 ml with benzene and refluxed for 10 h. The ratio **4b** : **5b** was found to be 19 : 81, without change on further heating. Semipreparative HPLC of a part of this mixture on Purospher RP-18 gave isomer **5b** (2.3 mg), contaminated with about 10% of isomer **4b**. CD spectrum (methanol, *c* 1.84 . 10^{-3} mol l^{-1}), Δε, l mol^{-1} cm^{-1} (λ, nm): 13.16 (269),

–183.5 (226), 45.46 (216). ^{1}H NMR spectrum ($CDCl_3$): 7.18–8.36 m, 20 H (H arom.); 4.14 q, 2 H, J(CH,CH_3) = 6.4 (CH); 3.81 d, 4 H, J(gem) = 12.2 (CH_2); 3.18 d, 4 H, J(gem) = 12.2 (CH_2); isomer **4b** (10%): 1.73 d, J(CH_3,CH) = 6.2 (CH_3); isomer **5b** (90%): 1.49 d, 6 H, J(CH_3,CH) = 6.2 (CH_3). Mass spectrum (FAB), *m/z*: 545 (M + 1); HRMS calculated: 545.2956; found: 545.2909. The product prepared above by HPLC (**5b** containing 10% of **4b**; 1 mg) was isomerized in boiling benzene (0.5 ml) for 10 h, which increased the content of **4b** to 18%.

(+)-5,11-Bis((*R*)-1-(2-naphthyl)ethyl)-(*S*)-5,6,11,12-tetrahydro-4*H*,10*H*-5,11-diazadibenzo[*ef*,*kl*]-heptalene (**4c**)

A mixture of tetrabromide **1** (260 mg, 0.5 mmol), (*R*)-(+)-1-(2-naphthyl)ethylamine (**2c**; 553 mg, 3.3 mmol) and benzene (2 ml) was refluxed for 10 h. The reaction mixture was partitioned between dilute aqueous ammonia and ether, the organic layer was dried over sodium sulfate and the solvent evaporated. The residue, containing isomer **4c** and isomer **5c** in the ratio of about 1 : 3, was mixed with methanol, the insoluble portion was collected and washed with methanol to give pure (HPLC) isomer **4c** (55 mg; 20%); m.p. 221–223 °C, $[\alpha]_D^{25}$ +250.6° (*c* 0.15, $CHCl_3$). For $C_{40}H_{36}N_2$ (544.7) calculated: 88.19% C, 6.66% H, 5.14% N; found: 88.40% C, 6.67% H, 5.33% N. ^{1}H NMR spectrum ($CDCl_3$): 7.25–7.90 m, 20 H (H arom.); 3.73 d, 4 H, J(gem) = 12.8 (NCH_2); 3.70 q, 2 H, J(CH,CH_3) = 6.7 (CH); 3.13 d, 4 H, J(gem) = 12.8 (NCH_2); 1.68 d, 6 H, J(CH_3,CH) = 6.7 (2 × CH_3). Mass spectrum (FAB), *m/z*: 545 (M + 1). CD spectrum (methanol, *c* 2.17 . 10^{-4} mol l^{-1}), Δε, l mol^{-1} cm^{-1} (λ, nm): –12.12 (261), –6.148 (241), –7.550 (238), 9.757 (229), –27.24 (224), 41.85 (211, end value).

(–)-5,11-Bis((*R*)-1-(2-naphthyl)ethyl)-(*R*)-5,6,11,12-tetrahydro-4*H*,10*H*-5,11-diazadibenzo[*ef*,*kl*]-heptalene (**5c**)

The mother liquors from the above crystallization were concentrated and chromatographed on a silica gel column in a mixture of ether, methanol and concentrated aqueous ammonia (50 : 1 : 1). The first fractions consisted of almost pure isomer **5c** (201 mg; 75%) which was further purified on a Purospher RP-18 column in 90% methanol. Solid foam, $[\alpha]_D$ –7.8° (*c* 0.15, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$): 7.27–7.92 m, 20 H (H arom.); 3.81 d, 4 H, J(gem) = 12.2 (NCH_2); 3.79 q, 2 H, J(CH,CH_3) = 6.4 (CH); 3.13 d, 4 H, J(gem) = 12.2 (NCH_2); 1.46 d, 6 H, J(CH_3,CH) = 6.4. Mass spectrum (FAB), *m/z*: 545 (M + 1). CD spectrum (methanol, *c* 2.46 . 10^{-4} mol l^{-1}), Δε, l mol^{-1} cm^{-1} (λ, nm): 30.29 (250), 143.0 (231), –47.43 (225), –156.9 (215, end value).

(–)-1,11-Dimethyl-6-((*S*)-1-phenylethyl)-(*S*)-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine (**7**)

A solution of (*S*)-(–)-1-phenylethylamine (185 mg, 1.5 mmol) in benzene (5 ml) was added to a solution of (+)-6,6′-dimethyl-2,2′-bis(bromomethyl)biphenyl (**6**; 184 mg, 0.5 mmol) in benzene (5 ml) and the mixture was refluxed for 30 h. After evaporation, the mixture was partitioned between water and chloroform, the organic layer was washed with water and dried. Evaporation gave 160 mg (98%) of essentially pure (NMR) product, m.p. 111–113 °C (methanol); $[\alpha]_D^{25}$ –23.6° (*c* 0.4, methanol). For $C_{24}H_{25}N$ (327.4) calculated: 88.03% C, 7.70% H, 4.28% N; found: 88.32% C, 7.78% H, 4.26% N. ^{1}H NMR spectrum ($CDCl_3$): 7.10–7.50 m, 11 H (H arom.); 3.65 d, 2 H, J(gem) = 12.2 (NCH_2); 3.43 q, 1 H, J(CH,CH_3) = 6.7 (CH); 2.93 d, 2 H, J(gem) = 12.2 (NCH_2); 2.20 s, 6 H (CH_3); 1.34 d, 3 H, J(CH_3,CH) = 6.7 (CH_3). CD spectrum (methanol, *c* 3.380 . 10^{-3} mol l^{-1}), Δε, l mol^{-1} cm^{-1} (λ, nm): –28.91 (245), –21.32 (232), –54.21 (220), 126.5 (203, end value).

(+)-1,11-Dimethyl-6-((*R*)-1-phenylethyl)-(*S*)-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine (**8**)

The (+)-dibromide **6** (185 mg, 0.5 mmol) was treated with (*R*)-(+)-1-phenylethylamine (185 mg, 1.5 mmol) exactly as described in the above experiment, yielding the product, m.p. 78–81 °C (methanol); $[\alpha]_D^{25}$ +60.5° (*c* 0.4, methanol). For $C_{24}H_{25}N$ (327.4) calculated: 88.03% C, 7.70% H, 4.28% N; found: 88.15% C, 7.72% H, 4.26% N. ^{1}H NMR spectrum ($CDCl_3$): 7.05–7.40 m, 11 H (H arom.); 3.60 d, 2 H, *J*(gem) = 12.5 (NCH_2); 3.32 q, 1 H, *J*(CH,CH_3) = 6.4 (CH); 3.09 d, 4 H, *J*(gem) = 12.6 (NCH_2); 1.60 d, 6 H, *J*(CH_3,CH) = 6.4 (CH_3). CD spectrum (methanol, c 3.073 . 10^{-3} mol l^{-1}), $\Delta\varepsilon$, l mol^{-1} cm^{-1} (λ, nm): –33.79 (246), –19.48 (231), –42.74 (222), 1.39 (216), 112.9 (202, end value).

Reaction of Tetrabromide **1** with Amines **2a**–**2c** in Various Solvents

A solution of the tetrabromide **1** (15 mg) in the given solvent (0.4 ml) was mixed with the appropriate amine (70 mg) and the mixture was stirred at 20 °C. After one day, samples were withdrawn and analyzed (direct injection of the reaction mixture) on a Purosphere column (*vide infra*). In the case of dimethylformamide, the samples were diluted with ether, washed twice with water, dried, concentrated, the residue dissolved in dioxane and analyzed. As shown by a blank experiment, after one day's standing of solutions of pure isomers **4**, the extent of isomerization to the respective isomers **5** was less than 3% in all the solvents examined. The results are given in Table I.

Preparation of **4a** and **5a** from 1,1′-Biphenyl-2,2′,6,6′-tetracarboxaldehyde (**3**)

A solution of (*R*)-(–)-1-phenylethylamine (**2a**; 110 mg, 0.91 mmol) and 1,1′-biphenyl-2,2′,6,6′-tetracarboxaldehyde (**3**; 53 mg, 0.2 mmol) in methanol (2 ml) was stirred under nitrogen for 2 h. Sodium cyanoborohydride (40 mg, 0.6 mmol) was added at 0 °C and stirring was continued for additional 2 h. After standing overnight, the mixture was acidified with 1 M hydrochloric acid (hood!), stirred for 1 h, diluted with water and extracted with ether. The aqueous layer was made alkaline and the product was taken up in dichloromethane. The solution was dried, the solvent evaporated and the residue analyzed as described in the isomerization experiment. The ratio **4a** : **5a** was 49 : 51.

Epimerization of Isomers **4** and **5**

A solution of isomer **4** or **5** (3.0 mg) in benzene (3.0 ml) was refluxed for 10 h. The isomer composition was determined by chromatography on a 250-mm Purosphere RP-18 (Merck) column; mobile phase 90% methanol, flow rate 0.8 ml/min, detection at 260 nm. The same Purospher column was used for semipreparative purification of the isomers.

The percentages of isomers **4** in the epimerization mixtures are given below. For series **a**: 23% (starting from both **4a** and **5a**); for series **b**: 19% (from **4b**) and 18% (from enriched **5b**); for series **c**: 24% (from **4c**) and 24% (from **5c**).

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