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The Use of Benzamide Derivatives of Secondary Amines for Stereochemical Studies by Circular Dichroism

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ABSTRACT The benzamide chromophore is widely used as a Cottonogenic derivative of *primary* amines for stereochemical studies by circular dichroism. The assignments based on the exciton chirality method are reliable since the benzamide group has well-defined geometry and conformation. A recent report (J.D. Chisholm, J. Golik, B. Krishnan, J.A. Matson, D.L. Van Vranken, *J. Am. Chem. Soc.* 1999, 121: 3801–3802) claimed a caveat in the application of the exciton chirality method to benzamides derived from *secondary* amines. By the use of benzoyl derivatives of amino alcohols (**1–4**) and diamines (**5**, **6**) of known absolute configuration we demonstrate that the 250–210 nm range exciton Cotton effects due to secondary and tertiary benzamides are generally of opposite sign. The origin of such disparity is traced to different conformational equilibria of the amide C–N bond in secondary and tertiary benzamides, as shown by semiempirical molecular modelling and NMR data. This feature can be useful in the determination of absolute configuration by analysis of the CD spectra due to exciton coupling of tertiary benzamides.

KEYWORDS absolute configuration, conformation, circular dichroism, benzamides, exciton Cotton effects, amino alcohols, diamines

INTRODUCTION

Exciton coupling between the electric dipole-allowed transitions of two or more chromophores has been successfully applied as a method of stereochemical analysis, particularly for absolute configuration determination of a wide variety of organic synthetic and natural compounds [1,2]. Chiral non-chromophoric diols and polyols have been studied as the corresponding benzoates [3], whereas in the case of the primary amino group in amino alcohols and diamines the benzamide [1,4] as well as the phthalimide [5–8] chromophoric derivatives have been applied. The success of the exciton chirality method, when applied to benzoates, secondary benzamides and phthalimides, rests on the well-established

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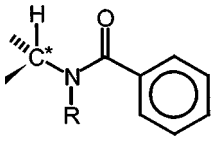
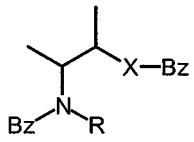
structure, electronic properties and conformational preferences of the chromophore. Whereas secondary amides (**I**, R = H) strongly prefer a conformation **I** with *Z* planar amide group and the amide carbonyl *syn* to the C–H bond of the chiral center, tertiary amides (**I**, R = alkyl) are conformationally more labile. In particular two conformers, *E* and *Z*, of the amide bond are of importance [9] since exciton coupling due to each of the two conformers could lead to opposite-sign Cotton effects, making the assignment of the absolute configuration ambiguous. In fact, configurational predictions based on the circular dichroism of tertiary amides are considered difficult [10], and recently a caveat in the application of the exciton chirality method to *N,N*-dialkyl amides has been reported [11]. Moreover, unlike *N*-phthaloyl derivatives, mixed imide derivatives of amines (**I**, R = Ac) also present difficulty in interpreting the CD spectra due to contributions of several conformers [12].



I



II

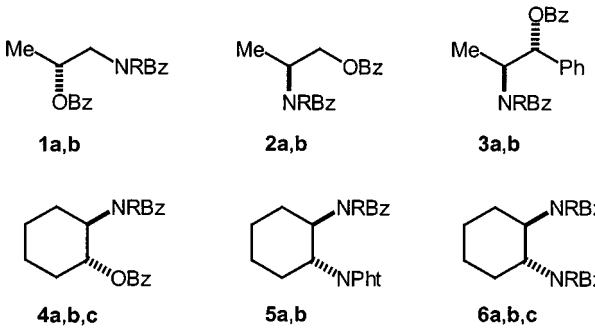
a R = H, X = O, NH
b R = Bn, X = O, NBn

Chiral *N*-benzylamines are important products of asymmetric synthesis. They can be obtained by either asymmetric nucleophilic addition to or by reduction of *N*-benzyl imines. Therefore, it is compelling to investigate more thoroughly the application of the exciton chirality method to dibenzoyl derivatives of *N*-benzyl amino alcohols and diamines **IIb**, in comparison to the CD data of dibenzoyl derivatives of primary amino alcohols and diamines **IIa**. As a result of the study we expect to be able to answer the following question: Can the *N,O*- or *N,N*-dibenzoyl exciton chirality method be reliably used to determine the absolute configuration of secondary amines, despite the contributions from several conformers and the presence of an additional benzyl chromophore?

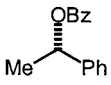
RESULTS AND DISCUSSION

We set out to compare the CD spectra of benzamide derivatives of four chiral amino alcohols (**1–4**) and one diamine (**5**, **6**) of known absolute configuration, all bearing another chromophore: benzoate, benzamide or phthalimide. These model compounds were obtained in two series: one with secondary benzamide group (**1a-6a**) and the other with tertiary benzamide group (*N*-benzyl derivatives **1b-6b,c**). *N*-Benzyl benzamides **1b-6b,c** were obtained by Schiff base formation of the amine with benzaldehyde, followed by $NaBH_4$ reduction to the corresponding *N*-benzylamine prior to benzoylation with benzoyl chloride (see Experimental section).

a R = H **b** R = Bn



4c R = Me **6c** R, R = H, Bn



7

Δε +5.9 (226 nm)
in dioxane

The CD and UV spectra of six pairs of benzamide derivatives **1a,b-6a,b,c** are shown in Figures 1 and 2.

Inspection of the data in Figure 1 indicates that the Cotton effects in the range 250–210 nm are of opposite sign for the pairs of compounds of the **a** and **b** series (the difference is less significant in the case of **1a** and **1b**). In the case of secondary benzamides (**a** series), the dominant if not exclusive conformation of the amide bond is *Z*. Also, the sign of the exciton Cotton effect reflects the sign of the N–C–C–O(or N) torsion angle in the dominant conformer, since the directions of the electric dipole transition moments in the benzamide or benzoate group are approximately parallel to the directions of the C–O or C–N bond, while that of the phthalimide chromophore is exactly in the direction of the C–N bond [5,6]. The Cotton effects of **2a**, **4a** and **6a** are similar to those reported in methanol solution [13]. The dominant conformers in the **a** series are g^+ for **2a** and g^- for **1a**, **4a**, **5a** and **6a** (g^+ and g^- refer to gauche conformation of the N–C–C–O or N–C–C–N bonds). The

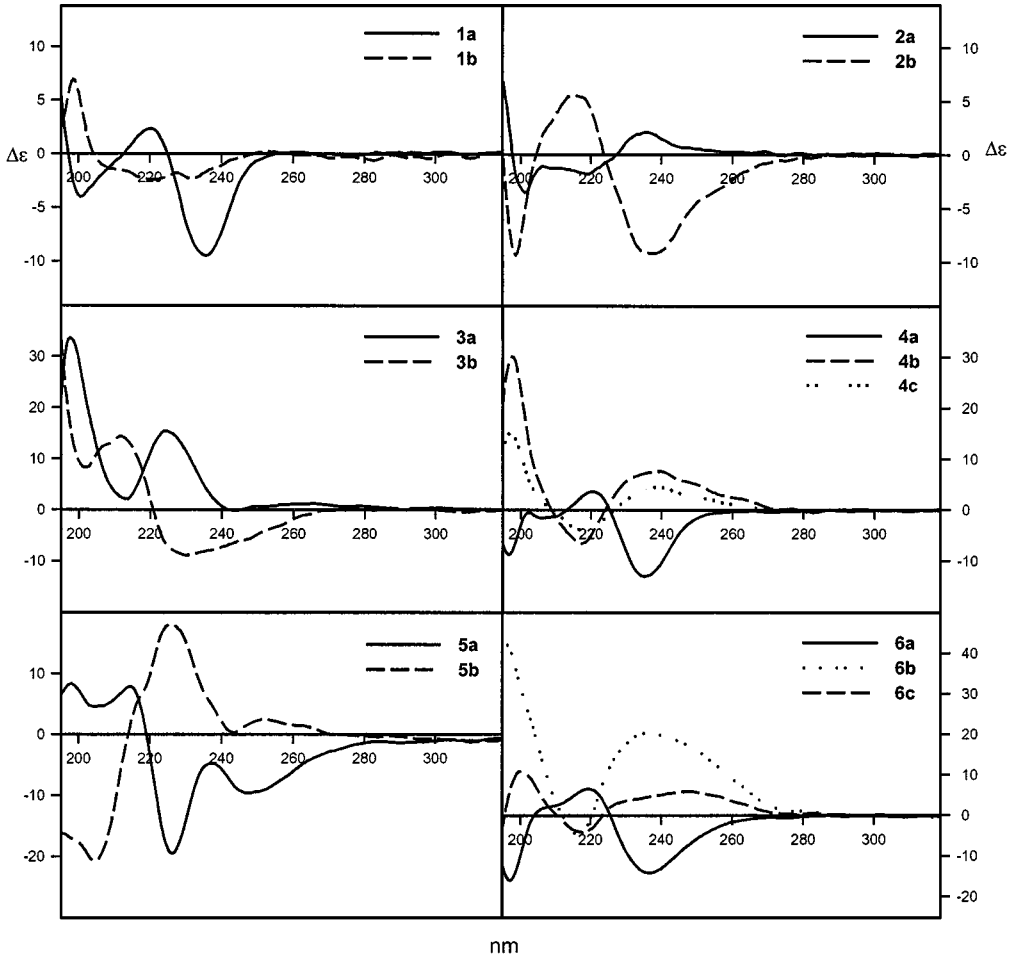
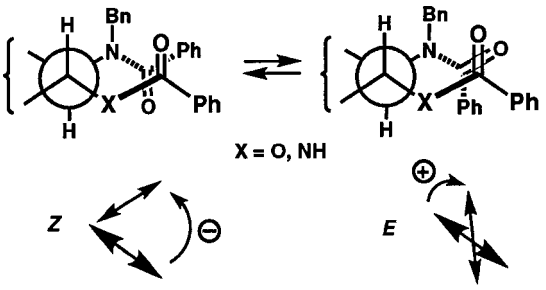


FIGURE 1 CD spectra of **1a–6c** in acetonitrile solution.

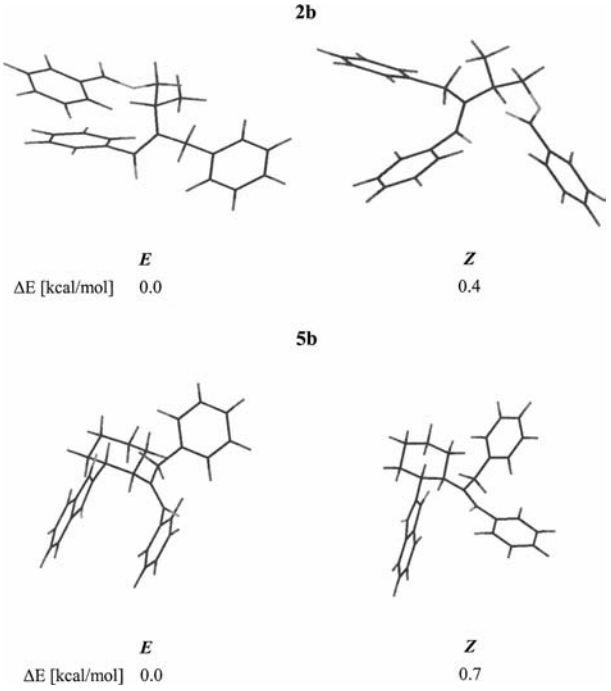
case of **3a** is more complex. From the magnitude of $J_{1,2}$ coupling constant (3.6 Hz) it appears that in addition to the *trans* conformer, a typical one for the *erythro* (*anti*) configuration [14], there is a contribution of hydrogen-bonded conformers g^+ and g^-; the positive exciton Cotton effect results mainly from the contribution of the phenyl (^1L_a transition)–benzamide coupling in the *trans* conformer and from the contribution due to the Ph-C-OBz unit, as in structure **7**. The reversal of the exciton Cotton effects in the **b** series compared to **a** can be traced to the change of conformer population in tertiary benzamides, as shown in Scheme 1.



SCHEME 1

The dominant *E* conformer of the tertiary benzamide group produces positive exciton Cotton effect, whereas a negative exciton Cotton effect is due to the *Z* conformer. Indeed, examination of the ^{1}H NMR spectra of two tertiary benzamides, **2b** (acyclic) and **5b** (cyclic), reveals that at ambient temperature the resonance signals are broadened due to a slow rate of exchange (see the ^{1}H NMR data on esters of *N*-benzoyl-*N*-benzyl-α-amino acids [15]). At lower temperatures, separate signals are observed due to the presence of two (*E*, *Z*) conformers (Figure 3).

For example, the methyl group resonance doublets of **2b** are seen in the ratio $E{:}Z = 2.5{:}1$ (at -20°C), whereas in the case of **5b** the resonance signals of the benzyl $-CH_2-$ group (doublets of doublets) are in the ratio $E{:}Z = 3.5{:}1$ (at -40°C). These findings are supported by the results of computational studies of conformational equilibria of **2b** and **5b**. Semiempirical computations (AM1) indicate that in both cases *E* conformer is of lower energy (Scheme 2).



SCHEME 2

It is noteworthy that other conformers, with the N–Bn bond eclipsing the vicinal C–H bond, according to computations are of significantly higher energy and are not further considered as significant contributors to the CD spectra.

The computed steric energy differences between *E* and *Z* conformers correspond to *E:Z* conformer ratio of 1.9:1 in the case of **2b** and 3.2:1 in the case of **5b**. The exciton Cotton effect due to the dominant *E* conformer is negative in the case of **2b** and positive in the case of **5b**. This is found experimentally for both compounds (Figure 1).

The computed structures of **2b** and **5b** indicate rather high degrees of non-planarity of the benzoyl group in tertiary benzamides. Non-planarity of tertiary benzamides is well documented [16,17]. It is of interest to note that non-planarity brings about a blue shift of the benzamide π-π^* absorption band (ca 20 nm in ethanol solution) [16]. We observe that such a blue shift results in negative electronic absorption between 220 and 240 nm in the differential UV spectra **1b-1a**, **2b-2a**, **3b-3a**, **6b-6a** and

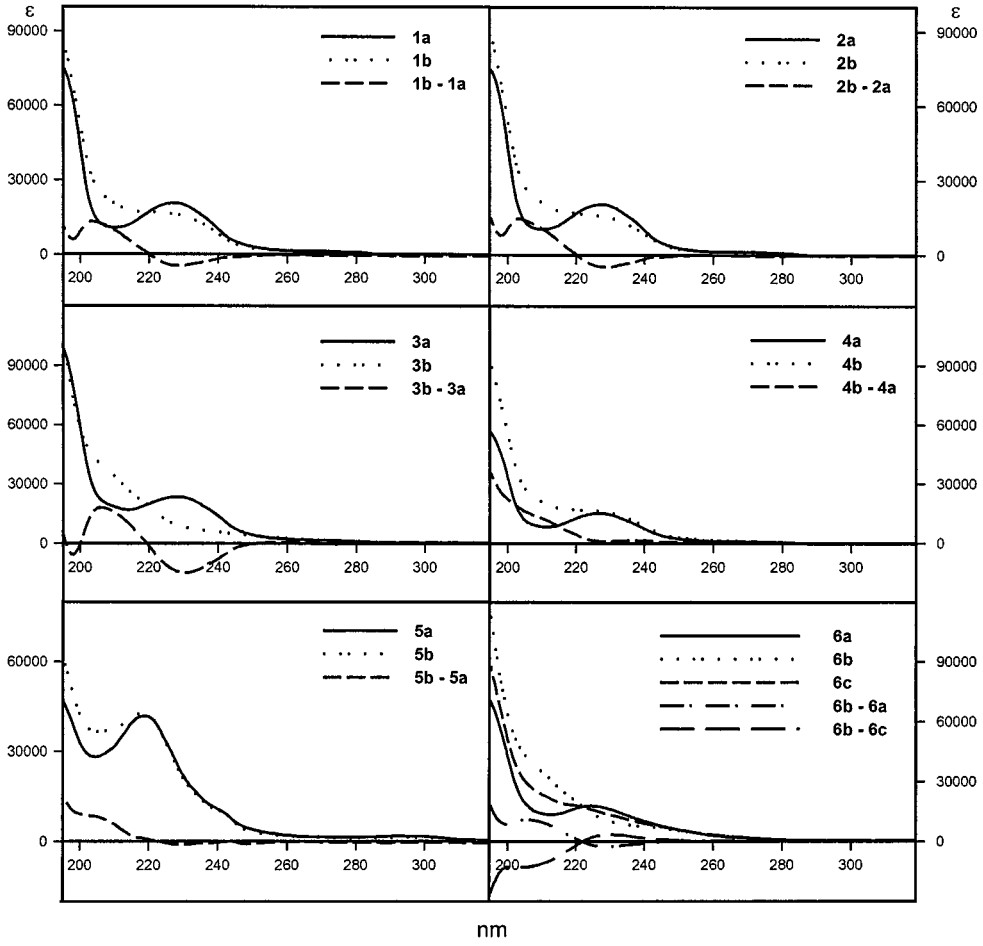


FIGURE 2 UV spectra of **1a-6c** and the differential UV spectra, in acetonitrile solution.

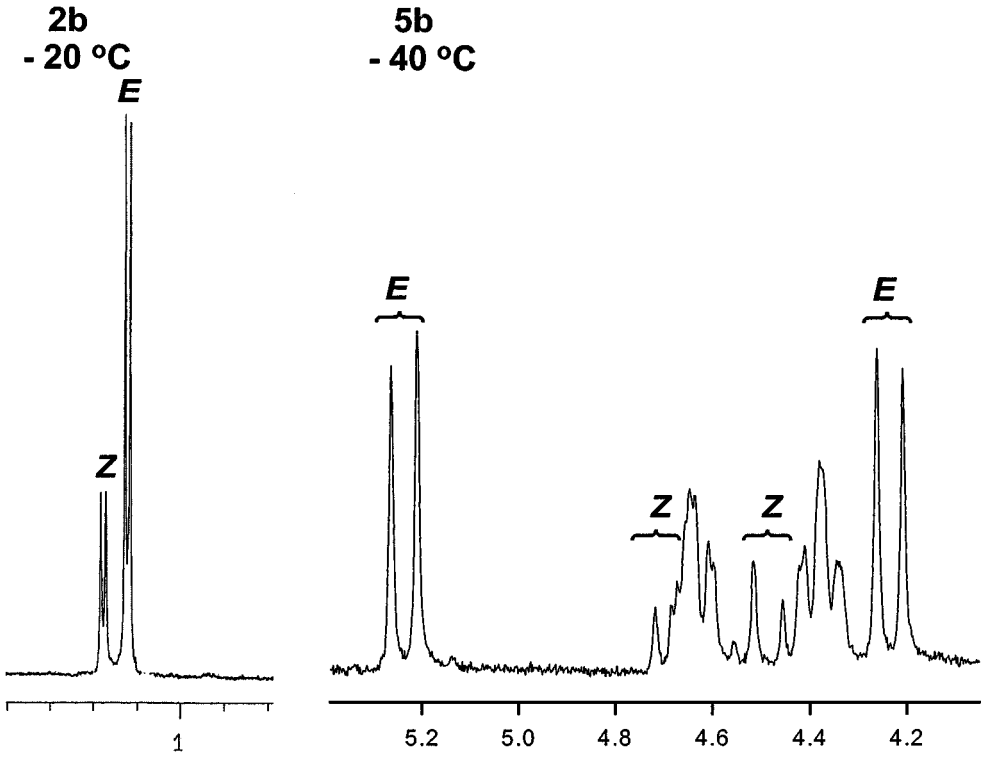


FIGURE 3 Portions of the ^{1}H NMR spectra of benzamides **2b** and **5b** in $CDCl_3$ solution.

6b-6c shown in Figure 2. This negative absorption corresponds to the position of the benzamide π-π^* band at ca. 225 nm. Non-planarity of the benzamide group can contribute to the CD spectrum, if it is biased toward one of the two enantiomeric conformers in the chiral molecule.

Finally, we briefly examined the effect of the *N*-benzyl chromophore on the CD spectra of benzamides of the **b** series. Direct comparison of the CD spectrum of **6b** with the reported CD of its *N,N′*-dimethyl analogue [10] reveals that the Cotton effects in the 240–210 nm region are of the same sign, although they differ in magnitude. Similarly, the Cotton effects of *N*-benzyl derivative **4b** are of the same sign but are of higher amplitude compared with those of the *N*-methyl analogue **4c** (Figure 1). In addition, we measured the CD spectra of derivatives **8–10** (Figure 4).

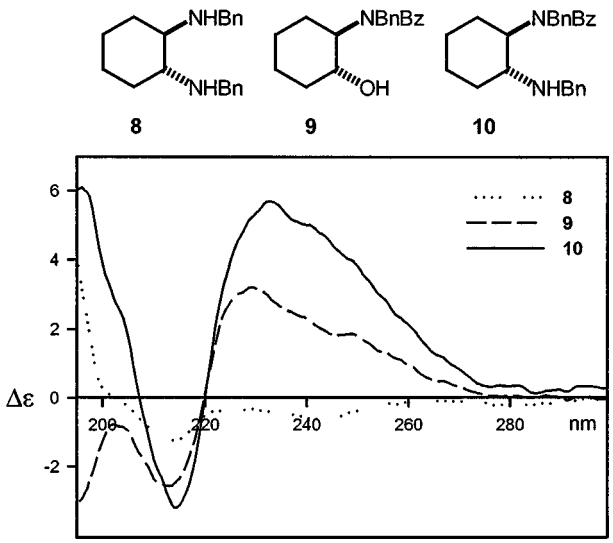


FIGURE 4 CD spectra of *N*-benzyl derivatives **8–10** (in acetonitrile).

Bichromophoric interaction of the benzyl chromophores in **8** results in very weak Cotton effects, probably due to conformational averaging. The interaction of the benzyl and benzoyl chromophores attached to the same nitrogen atom, as in **9**, gives a weak, bisignate Cotton effect. Only slightly larger Cotton effects are obtained in the case of monobenzoyl derivative **10** of *N,N′*-dibenzyl diamine **8**. Thus, chromophoric contribution of the *N*-benzyl group to the CD spectra of *N*-benzyl benzamides can be neglected for the purpose of qualitative stereochemical analysis.

CONCLUDING REMARKS

The leading conclusion from the present work is that exciton coupling can be used for stereochemical assignments involving tertiary benzamides

if augmented by suitable analysis of the *E*,*Z* amide conformer population, for example, by NMR spectroscopy or semiempirical computations.

The practical conclusion drawn from inspecting the CD data is that in the cases studied the sign of the Cotton effects due to the interactions of the benzamide/benzoate π-π^* transitions are opposite, when comparing the data for R-NH-Bz and R-N(Bn)-Bz derivatives. The sign of the exciton Cotton effect due to the vicinal benzoate/benzamide or benzamide/benzamide interactions is of the same sign as the sign of the N–C–C–O(N) torsion angle in the case of -NHBz amides, but of opposite sign in the case of -NBnBz amides.

EXPERIMENTAL SECTION

Materials and Methods

NMR spectra were obtained using a Varian Gemini 300 spectrometer, in $CDCl_3$ solutions, with tetramethylsilane (TMS) as an internal standard. Optical rotations were determined on a Perkin-Elmer 243B polarimeter at 20°C in $CHCl_3$ solutions. Circular dichroism and UV spectra were measured using a Jasco J-810 spectropolarimeter. Melting points were measured using a Büchi B-545 apparatus and are uncorrected. All reagents were purchased from Sigma-Aldrich Chemical Co. and used without further purification.

Semiempirical computations were performed using MOPAC97.

N,N′-*Dibenzoyl Diamines and* N,O-*Dibenzoyl Amino Alcohols, Representative Procedure for 6a*

To a CH_2Cl_2 solution of (1*R*,2*R*)-*trans*-diaminocyclohexane (114 mg, 1 mmol) was added triethylamine (0.4 mL, 2.87 mmol) and benzoyl chloride (0.4 mL, 3.44 mmol) at 0°C and the mixture was stirred overnight at room temperature. The reaction was quenched by adding water (5 mL). The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with aqueous sodium bicarbonate and brine, dried and evaporated. The crude product was crystallized from benzene-hexane to give (1*R*,2*R*)-*trans-N,N′*-dibenzoyl-(1*R*,2*R*)-*trans*-diaminocyclohexane **6a**.

N,N′-*Dibenzoyl*-N,N′-*dibenzyl Diamines and* N,O-*dibenzoyl*-N-*benzyl Amino Alcohols, Representative Procedure for 4b*

A mixture of (1*R*,2*R*)-*trans*-2-aminocyclohexanol (115 mg, 1 mmol) and benzaldehyde (106 mg, 1 mmol) in 10 mL of toluene (with a drop of DMF) was refluxed for 5 h with a Dean-Stark adapter. After cooling, the solvent was evaporated to dryness and the crude (1*R*,2*R*)-*trans-N*-benzylidene-2-aminocyclohexanol was dissolved in MeOH (5 mL). Then, sodium borohydride (76 mg, 2 mmol) was added in one portion at 0°C. The mixture was allowed to warm to room temperature and was stirred overnight. After evaporation to dryness, CH_2Cl_2 (10 mL) and water (10 mL) were added and the mixture was stirred for 1 h. The aqueous phase was separated and extracted twice with CH_2Cl_2. The combined organic extracts were washed with brine, dried and concentrated in vacuum to give crude (1*R*,2*R*)-*trans-N*-benzyl-2-aminocyclohexanol which was used directly for the benzoylation reaction according to the procedure described above.

(R)-N,O-*Dibenzoyl-1-amino-2-propanol* ***(1a)***, colorless crystals, mp. 70–72°C (benzene-hexane); $[\alpha]_D = -65.4$ (c = 1); ^{1}H NMR δ: 1.5 (d, J = 6.3 Hz, 3H), 3.7–3.8 (m, 2H), 5.3–5.4 (m, 1H), 6.7 (br s, 1H), 7.4–7.5 (m, 10H), 7.7 (d, J = 11.8 Hz, 2H), 8.0 (d, J = 11.8 Hz, 2H).

(R)-N,O-*Dibenzoyl*-N-*benzyl-1-amino-2-propanol* ***(1b)***, oil, $[\alpha]_D = -37.0$ (c = 0.5); ^{1}H NMR (1:3.5 mixture of *Z* and *E* conformers) δ: 1.1 and 1.4 (br siglets, 3H), 3.3–3.9 (m, 2H), 4.6–5.1 (m, 2H), 5.4 and 5.6 (br singlets, 1H), 7.1–7.6 (m, 13H), 8.0 (br s, 1H), 8.1 (br s, 1H).

(S)-N,O-*Dibenzoyl-2-amino-1-propanol* ***(2a)***, colorless crystals, mp. 104–107°C (benzene-hexane); $[\alpha]_D = -28.7$ (c = 1); ^{1}H NMR δ: 1.4 (d, J = 6.9 Hz, 3H), 4.4–4.5 (m, 2H), 4.6–4.7 (m, 1H), 6.5 (d, J = 6.6 Hz, 1H), 7.4–7.6 (m, 6H), 7.7 (d, J = 9.6 Hz, 2H), 8.0 (d, J = 9.6 Hz, 2H).

(S)-N,O-*Dibenzoyl*-N-*benzyl-2-amino-1-propanol* ***(2b)***, colorless crystals, mp. 67–70°C (benzene-hexane); $[\alpha]_D = +15.8$ (c = 1); ^{1}H NMR δ: 1.2 (br s, 3H), 4.1–4.9 (br m, 5H), 7.2–7.5 (m, 12H), 7.6–7.7 (m, 1H), 7.9 (br s, 1H), 8.1–8.2 (m, 1H).

(*1*R,*2*RS)-N,O-*Dibenzoyl-2-amino-1-phenyl-1-propanol* ***(3a)***, colorless crystals, mp.165–167°C; $[\alpha]_D = +5.3$ (c = 1); ^{1}H NMR δ: 1.3 (d, J = 6.9 Hz, 3H), 4.8 (m, 1H), 6.2 (d, J = 3.6 Hz, 1H), 6.4 (d, J = 8.5 Hz,

1H), 7.3–7.5 (m, 10H), 7.6 (m, 1H), 7.7 (d, $J = 9.6$ Hz, 2H), 8.1 (d, $J = 9.6$ Hz, 2H).

(*1*R,*2* S)-N,O-*Dibenzoyl*-N-*benzyl-2-amino-1-phenyl-1-propanol* (***3b***), colorless crystals, mp. 157–159°C (benzene); $[\alpha]_D = +2.2$ (c = 1); ^{1}H NMR δ: 1.4 (d, $J = 7.1$ Hz, 3H), 3.4 (d, $J = 6.3$ Hz, 1H), 4.3 (d, $J = 15.7$ Hz, 1H), 4.6 (d, $J = 15.7$ Hz, 1H), 5.0 (s, 1H), 7.0 (d, $J = 6.3$ Hz, 2H), 7.2–7.3 (m, 8H), 7.4–7.5 (m, 10H).

(*1* R,*2* R)-trans-N,O-*Dibenzoyl-2-aminocyclohexanol* (***4a***), colorless crystals, mp. 146–152°C (benzene-hexane), (lit.[18] 153–155°C); $[\alpha]_D = -72.3$ (c = 0.5); ^{1}H NMR data in agreement with previously reported [18].

(*1*R,*2*R)-trans-N,O-*Dibenzoyl*-N-*benzyl-2-amino-cyclohexanol* (***4b***), colorless crystals, mp. 114–117°C (benzene-hexane); $[\alpha]_D = +17.4$ (c = 0.5); ^{1}H NMR δ: 1.1–1.9 (m, 8H), 3.9–4.0 (m, 1H), 4.4 (d, $J = 15.4$ Hz, 1H), 5.0 (d, $J = 15.4$ Hz, 1H), 5.1 (br s, 1H), 7.1–7.6 (m, 13H), 7.9–8.1 (m, 2H).

(*1*R,*2*R)-trans-N,O-*Dibenzoyl*-N-*methyl-2-amino-cyclohexanol* (***4c***) was obtained as follows. To a pyridine solution of (1*R*,2*R*)-*trans*-2-aminocyclohexanol (115 mg, 1 mmol) was added a solution of ethyl chloroformate (0.19 mL, 2 mmol) in CH_2Cl_2 (2 mL) at 0°C and the mixture was stirred overnight at room temperature. The reaction was quenched by adding water (5 mL). The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with aqueous sodium bicarbonate and brine, dried and evaporated to dryness. The crude (1*R*,2*R*)-*trans-N,O*-di(ethoxycarbonyl)-2-aminocyclohexanol was dissolved in anhydrous THF, then lithium aluminum hydride (76 mg, 2 mmol) was added in one portion at 0°C. The mixture was allowed to warm to room temperature and stirred overnight. After addition of ethyl acetate (1 mL), the mixture was stirred for an additional hour and the water (5 mL) was added. The aqueous phase was separated and extracted twice with Et_2O. The combined organic extracts were washed with brine, dried and concentrated in vacuum to give crude (1*R*,2*R*)-*trans-N*-methyl-2-aminocyclohexanol which was used directly for the benzoylation reaction according to the procedure described for **4b**. Product **4c** was obtained as an oil; $[\alpha]_D = +18.8$ (c = 0.6); ^{1}H NMR (1:1.8 mixture of conformers) 1.1–2.0 (m, 7H), 2.1–2.3 (m, 1H); 2.8 and 3.0 (two singlets, 1H); 3.3 and 3.6 (two broad singlets, 3H), 5.0–5.1 and 5.1–5.2 (two multiplets, 1H), 7.1–7.6 (m, 9H), 8.0–8.1 (m, 1H).

(*1*R,*2*R)-trans-N-*Benzoyl*-N′-*phtaloyldiaminocyclohexane* (***5a***), colorless crystals, mp. 260–261°C (benzene-dioxane); $[\alpha]_D = -104.7$ (c = 1); ^{1}H NMR δ: 1.3–1.4 (m, 2H), 1.5–1.6 (m, 1H), 1.8–2.0 (m, 3H), 2.2 (d, $J = 10.4$ Hz, 1H), 2.6–2.7 (m, 1H), 4.0–4.1 (m, 1H), 4.7–4.8 (m, 1H), 5.9 (d, $J = 8.0$ Hz, 1H), 7.3–7.4 (m, 4H), 7.5 (d, $J = 8.2$ Hz, 1H), 7.6–7.7 (m, 2H), 7.8 (m, 2H).

(*1*R,*2*R)-trans-N-*Benzoyl*-N-*benzyl*-N′-*phtaloyldiaminocyclohexane* (***5b***), colorless crystals, mp. 157–159°C (benzene); $[\alpha]_D = -25.8$ (c = 0.5); ^{1}H NMR δ: 1.3 (br s, 2H), 1.5 (br d, $J = 12.1$ Hz, 1H), 1.7 (br s, 2H), 2.0 (br d, $J = 12.1$ Hz, 1H), 2.2 (br s, 1H), 4.2 (d, $J = 16.2$ Hz, 1H), 4.3–4.4 (m, 1H), 4.5–4.6 (m, 2H), 5.2 (d, $J = 15.7$ Hz, 1H), 7.2–7.5 (m, 10H), 7.7 (br s, 2H), 7.9 (s, 2H).

(*1* R,*2* R)-trans-N,N′-*Dibenzoyldiaminocyclohexane* (***6a***), colorless crystals, mp. 257–259°C (benzene-dioxane) (lit.[19] > 300°C); ^{1}H NMR data in agreement with previously reported [19].

(*1*R,*2*R)-trans-N,N′-*Dibenzoyl*-N-*benzyldiaminocyclohexane* (***6b***), solidified oil, mp. 69–70°C; $[\alpha]_D = +11.2$ (c = 0.5); ^{1}H NMR 1.3–1.4 (m, 4H), 1.7–1.8 (m, 2H), 1.9 (s, 1H), 2.3 (d, $J = 12.4$ Hz, 1H), 4.1 (d, $J = 12.4$ Hz, 1H), 4.6 (s, 2H), 4.9 (br s, 1H), 7.1–7.2 (m, 10H), 7.4–7.5 (m, 4H), 7.9 (d, $J = 8.0$ Hz, 1H).

(*1* R,*2* R-trans-N,N′-*Dibenzoyl*-N,N′-*dibenzyldiaminocyclohexane* (***6c***), colorless crystals, mp. 162–164°C (benzene-hexane); $[\alpha]_D = +139.3$ (c = 1); ^{1}H NMR (1:1 mixture of conformers) δ: 0.8–1.1 (m, 4H), 1.2–1.3 (m, 4H), 1.5–1.6 (m, 3H), 1.8–2.0 (m, 4H), 2.1 (d, $J = 12.6$ Hz, 1H), 3.2 (d, $J = 15.7$ Hz, 1H), 3.6 (d, $J = 17.0$ Hz, 1H), 4.0–4.1 (m, 1H), 4.2 (d, $J = 15.9$ Hz, 1H), 4.5–4.6 (m, 2H), 4.8 (d, $J = 15.1$ Hz, 1H), 5.0 (d, $J = 18.1$ Hz, 2H), 5.2–5.3 (m, 2H), 5.5 (d, $J = 15.9$ Hz, 1H), 6.8 (m, 2H), 7.0–7.6 (m, 38H).

(*1*R,*2*R)-trans-N,N′-*Dibenzyldiaminocyclohexane* (***8***), obtained according to a reported procedure [20].

(*1*R,*2*R)-trans-N-*Benzoyl*-N-*benzyl-2-aminocyclohexanol* (***9***), obtained according to general procedure using one equivalent benzoyl chloride, with no triethylamine; oil; $[\alpha]_D = -19.7$ (c = 1); ^{1}H NMR δ: 1.1–1.3 (m, 3H), 1.5–1.7 (m, 3H), 1.8–1.9 (m, 1H), 2.1 (br s, 1H), 3.5 (br s, 2H), 4.5 (d, $J = 15.6$ Hz, 1H), 4.6 (br s, 1H), 5.0 (br d, $J = 15.4$ Hz, 1H), 7.3–7.6 9 (m, 10H).

(*1*R,*2*R)-trans-N-*Benzoyl*-N,N′-*dibenzyldiaminocyclohexane* (***10***), obtained from **8** according to general procedure using one equivalent benzoyl chloride, with no triethylamine; oil; $[\alpha]_D = +2.4$ (c = 1);

^{1}H NMR δ: 0.8–1.7 (m, 8H), 2.1 (d, J = 11.3 Hz, 1H), 2.5–2.6 (m, 1H), 3.3 (d, J = 12.9 Hz, 1H), 3.6–3.7 (m, 1H), 3.7 (d, J = 13.2 Hz, 1H), 4.3 (d, J = 15.4 Hz, 1H), 4.8 (d, J = 15.4 Hz, 1H), 6.9–7.6 (m, 15 H).

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