Enantiopure Dendrimers Derived from the 1,1′-Binaphthyl Moiety: A Correlation Between Chiroptical Properties and Conformation of the 1,1′-Binaphthyl Template

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The absorption and CD spectra of a series of Fréchet (compounds **7**–**10**) and backfolding (compounds **11**–**12**) dendrimers derived from enantiopure (*S*)-2,2′-dihydroxy-1,1′-binaphthalene have been recorded (THF) in the range 200–350 nm. All the compounds examined show a positive couplet between 200 and 240 nm (^{1}B transition of the 2-naphthol chromophore), the intensity of which ($\Delta\varepsilon_{max}$ of the low-energy branch) ranges between 100 and 40. By means of the DeVoe polarizability model the intensity of the ^{1}B couplet has been calculated vs. the dihedral angle θ. This analysis provides θ angles of 95–110° for the Fréchet dendrimers and 100–110° for the backfolding compounds. These values clearly indicate that the torsional angle θ, defined by the two naphthalene planes, never exceeds the critical value of 110°. This investigation confirms the wide utility of CD spectroscopy to provide geometrical information that cannot be obtained by other types of structural analysis.

Introduction

The enantiopure binaphthyl moiety constitutes the common structural motif of several efficient ligands, auxiliaries, and catalysts for asymmetric synthesis.[1] More recently, new binaphthyl compounds showing interesting nonlinear optical properties have been prepared.[2] In addition, two papers have appeared[3] describing new chiral dendrimers with axial chirality, which were prepared starting from enantiopure 2,2′-dihydroxy-1,1′-binaphthalene. Noyori and Takaya[4a] demonstrated that the efficiency of the binaphthyl derivatives as chiral ligands can be ascribed to their pliancy, i.e. to the possibility of a certain rotation around the $C_{Ar}-C_{Ar}$ bond that, on changing the dihedral angle θ between the naphthalene rings, allows it to accommodate metal centers of different sizes.[4] The same parameter also determines the nonlinear optical properties of the aforementioned derivatives[2] as well as the properties of new ferroelectric liquid crystals.[5] Moreover, it has also been shown that the optical properties of the dendrimer system are linked to the torsional angle θ and a qualitative correlation between the CD spectra and θ of these compounds has recently been reported.[3b] The aim of this paper is to establish a *quantitative correlation* between the circular dichroism (CD) spectrum (i.e. the exciton couplet[6] in the ^{1}B spectral region at ca. 230 nm of the 2-naphthol chromophore[7]) and the dihedral angle θ in the binaphthyl series shown in Chart 1. The work described here follows an approach largely inspired by a seminal investigation[8] by Mason et al. on the optical activity of biaryl compounds. Although the aforementioned paper,[3b] in which the CD spectra were qualitatively studied, appeared when the present investigation was carried out, the present quantitative analysis of the CD data will more clearly show the direct dependence of the optical properties on the torsional angle θ.

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Results and Discussion

Synthesis

The two sets of compounds **1**, **3**−**6**[9] and **2**, **7**−**10**[3a] have already been described. For the synthesis of dendrimers **11** and **12**, the backfolding wedges[10] had to be synthesized first. 2,6-Dihydroxybenzoic acid was used as the starting material for the synthesis of the first and second generation backfolding dendritic wedges (Scheme 1). The first generation was synthesized by reaction of 2,6-dihydroxybenzoic acid with 3 equivalents of benzyl bromide, yielding benzyl 2,6-dibenzyloxybenzoate (**13**), followed by a reduction with $LiAlH_4$ to give 2,6-dibenzyloxybenzyl alcohol (**14**). Subsequent bromination of **14** was accomplished by a reaction with PBr_3, yielding 2,6-dibenzyloxybenzyl bromide (**15**), the first generation brominated backfolding dendrimer. In the synthesis of the second generation backfolding dendritic wedge, 2,6-dihydroxybenzoic acid was firstly converted into methyl 2,6-dihydroxybenzoate (**16**) by a reaction with methyl iodide in DMF in the presence of $NaHCO_3$. In our first approach to backfolding, the normal Fréchet-type[11] dendritic wedge of the first generation was reacted with **16** to give **17**. After reduction to the corresponding benzyl alcohol **18**, the desired benzyl bromide **19** was obtained by reaction with PBr_3. The crystalline benzyl bromides **15** and **19** proved to be rather acid-

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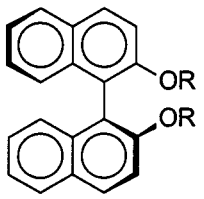


Class	R	R	R	R
A (Δε 200)	Me **1**	Bn **2**		
B (Δε 300-350)	**3**	**4**	**5**	**6**
C (Δε 100-140)	**7**	**8**	**9**	**10**
D (Δε 40-60)	**11**	**12**		

Chart 1. Modified binaphthols **1**−**12**

sensitive and compound **19** even decomposes upon standing in chloroform solution.

For the synthesis of axially chiral dendrimers **11** and **12**, enantiomerically pure (*S*)-(−)-2,2′-dihydroxy-1,1′-binaph-

thalene[1] was used as the core and was reacted[3a] with the first (**15**) and second (**19**) generation backfolding wedge. The synthesis of the dendrimers is rather straightforward, but small amounts of impurities proved to be very difficult to remove, leading to lower yields. All spectroscopic data in terms of ^{1}H NMR and ^{13}C NMR spectroscopy as well as IR spectroscopy, elemental analysis and MALDI-TOF-MS are in full agreement with the structures assigned to the compounds obtained.

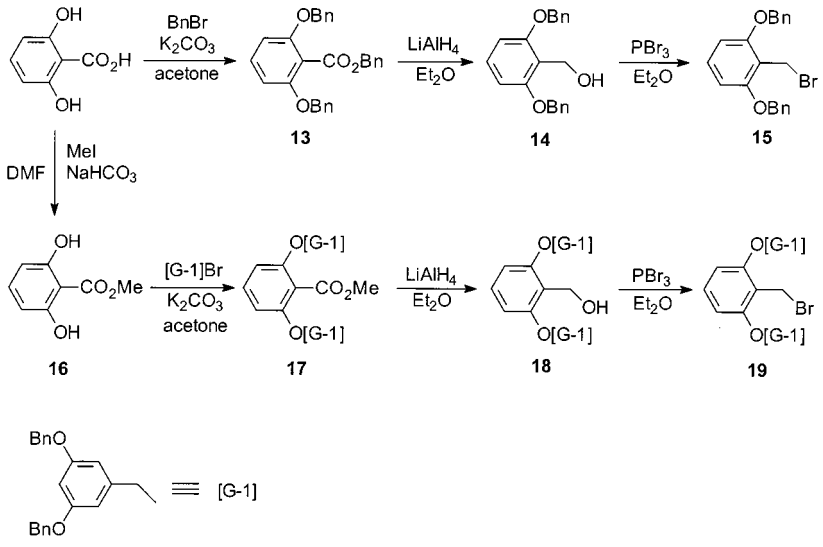
Optical Properties

The molar rotations $[\Phi]_D$ of compounds **1**−**12** are reported in Table 1. As has been previously pointed out,[3a] there is a correlation between the molar optical rotation and the value of the dihedral angle θ: for (*S*)-binaphthyls a positive sign corresponds to small angles whilst large angles are related to negative rotations. This trend has been confirmed by means of a simple analysis of the CD data.[3b]

We were interested in providing a more quantitative analysis of the chiroptical data and evaluating the θ values of **1**−**12** from the above spectral data only. Taking into account that the optical rotation measured at a single wavelength results from the contributions of all the Cotton effects over the whole spectrum,[12] we decided to measure the CD spectra of the compounds **1**−**12** and to analyze them in order to point out the most important Cotton effects contributing to the overall optical rotatory power. This approach would then allow us to relate spectra and structures in a simple and reliable way. The CD spectra of **1**−**12** were recorded in THF solution between 350 and 200 nm. The relevant absorption and CD features of compounds **1**−**12** are collected in Table 2. The absorption and CD spectra of compounds **1**, **3**, **8**, and **12**, chosen as representative examples, are depicted in Figures 1−4.

The absorption spectra of all compounds examined show the three distinct regions that are characteristic of the 2-naphthol chromophore:[7] 350−300 nm (^1L_b transition), 300−250 nm (^1L_a transition) and 250−200 nm (^1B transition). The CD spectra can be divided in the same way: for our (*S*)-configured compounds negative Cotton effects (Δε −10 ca.) can be measured in the ^1L_b and ^1L_a spectral ranges, whilst an intense positive couplet can be observed in the ^1B spectral range. As Mason pointed out in his 1974 paper,[8] the sign and intensity of this couplet are related to the value of the angle θ. For the (*S*) absolute configuration a positive couplet is observed for θ in the range 0° to 110°, while a further increase in θ values (i.e. passing from a cisoid to a transoid conformation[13]) leads to a change in the sign of the couplet, even if the absolute configuration of the derivative remains the same. It is noteworthy (Table 1, Figures 1−4) that all the (*S*)-configured compounds (**1**−**12**) give a positive couplet, indicating that, according to Mason′s analysis, the dihedral angle θ never exceeds the critical value of 110°.

However, it is very important to note that the intensity of the low-energy component of the couplet (at 230−240 nm ca.) ranges between a minimum value of about 50 (**12**) to a maximum value of 350 (**3**), indicating that the nature of the substituent groups at the 2- and 2′-positions strongly affects the θ value. Choosing the intensity of this component of the couplet as a discriminating criterion, compounds **1**−**12** have been divided into classes A−D as depicted in Chart 1. This choice is also determined by the fact that this band occurs in a range of wavelengths where there are no other overlapping bands. In order to formulate a quantitative correlation between CD data and structure, an approach similar to the one described by Mason has been followed.[8] However, instead of plotting a normalized Δε as a function of θ, we calculated, by means of the coupled oscillator model of DeVoe,[14] the CD spectrum in the ^1B spectral region as a function of the dihedral angle θ and we plotted the absolute intensity of the low energy branch of the calculated couplet vs. θ (*vide infra*).



Scheme 1. Synthesis of backfolding dendritic wedges

Table 1. Optical rotations for binaphthol derivatives **1**−**6** and dendrimers **7**−**12**[a]

compound	$[\alpha]_D^{20}$ (conc.)	$[\Phi]_D$	compound	$[\alpha]_D^{20}$ (conc.)	$[\Phi]_D$
1	−54 (0.06)	−170	**7**	−22.8 (0.89)	−203
2	−45.5 (0.47)	−212	**8**	−15.6 (1.74)	−271
3	779 (1.00)	2337	**9**	−12.3 (1.01)	−424
4	523 (1.00)	1642	**10**	−9.5 (0.57)	−650
5	431 (1.00)	1413	**11**	−53.3 (0.90)	−475
6	217 (1.00)	742	**12**	−23.2 (1.74)	−404

[a] Measured in CH_2Cl_2.

In the DeVoe model a molecule is considered to be composed of a set of subsystems, the chromophores. These subsystems are polarized by the external electromagnetic radiation and are coupled to each other by their own dipolar oscillating fields. The optical properties (absorption, refraction, optical rotatory dispersion, and circular dichroism) of the molecule studied can then be calculated taking into account the interaction of the subsystems. Therefore, this treatment requires to divide the molecule into a set of subsystems that have to be suitably characterized. Each group is then represented in terms of one (or more) classical oscillator(s); each oscillator represents an electric-dipole-allowed transition, defined by the polarization direction $\mathbf{e}_i$ and by the complex polarizability $\alpha_i(\tilde{\nu}) = R_i(\tilde{\nu}) + iI_i(\tilde{\nu})$. $I_i(\tilde{\nu})$, is obtainable from the experiment, i.e. from the absorption spectra of compounds that can be considered as good models for the subsystem [in fact $\alpha(\tilde{\nu})$ and $\varepsilon(\tilde{\nu})$ are related through a simple relationship[14a]]. $R_i(\tilde{\nu})$ can be calculated from $I_i(\tilde{\nu})$ by means of a Kronig−Kramers transform.[14a] From the general formulation of the DeVoe model, considering the case of two equal chromophores having only one electrically allowed transition, and retaining only the terms of first order in G_{12} (physically, this means considering that the electric dipole on the chromophore is caused by the external e.m. field plus the dipolar fields of the other dipole polarized by the external field only) the following expression can be deduced[14b] and provides CD as a frequency function:

$$\Delta\varepsilon(\tilde{\nu}) = 0.028\pi^2 N \mathbf{e}_1 X \mathbf{e}_2 R_{12} G_{12}\, \nu^2 I_1(\tilde{\nu}) R_1(\tilde{\nu})$$

$$G_{12} = (1/r_{12})^3[\mathbf{e}_1.\mathbf{e}_2 - 3(\mathbf{e}_1\mathbf{e}_{12})(\mathbf{e}_2\mathbf{e}_{12})]$$

Here $\mathbf{e}_1$ and $\mathbf{e}_2$ are the unit direction vectors of the transition dipole moments of the first and second chromophore, respectively, R_{12} is the distance between them, G_{12} is the point-dipole-point-dipole interaction term, and $\tilde{\nu}$ is expressed in cm^{-1}. This expression gives rise to a couplet feature.[14b]

The important parameters for the calculations were the following: the ^1B transition of the 2-naphthol chromophore has been described by a single oscillator (polarized along the long axis, placed in the center of the naphthalene ring, carrying a polarizability of 44 D^2, located at 224 nm) in order to reproduce the absorption feature of the 2-naphthol chromophore. The geometrical parameters, i.e. the atomic coordinates of the various structures of a binaphthyl at different θ angles, were obtained by the MMX routine.[15] With these parameters the CD spectra in the 200−250 spectral range were calculated for several θ angles between 0 and 180°. The curve in Figure 5 was then obtained by plotting the calculated maximum value of the intensity of the low-energy component of the couplet at 230 nm ca. versus the angle θ.

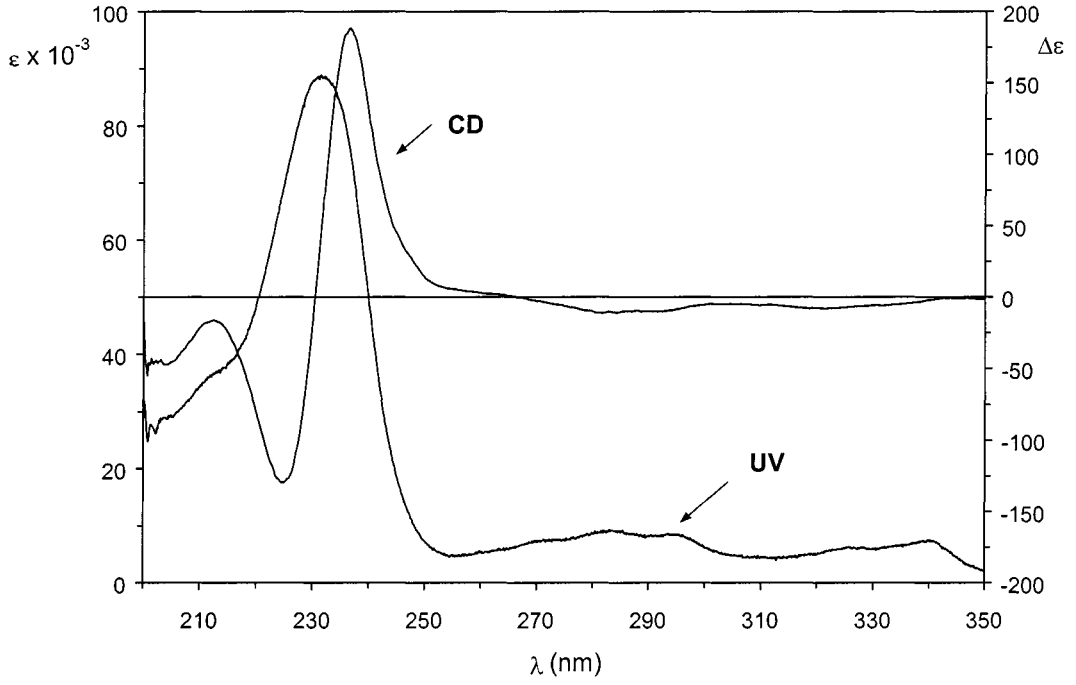


Figure 1. Absorption and CD spectra of compound (*S*)-**1**

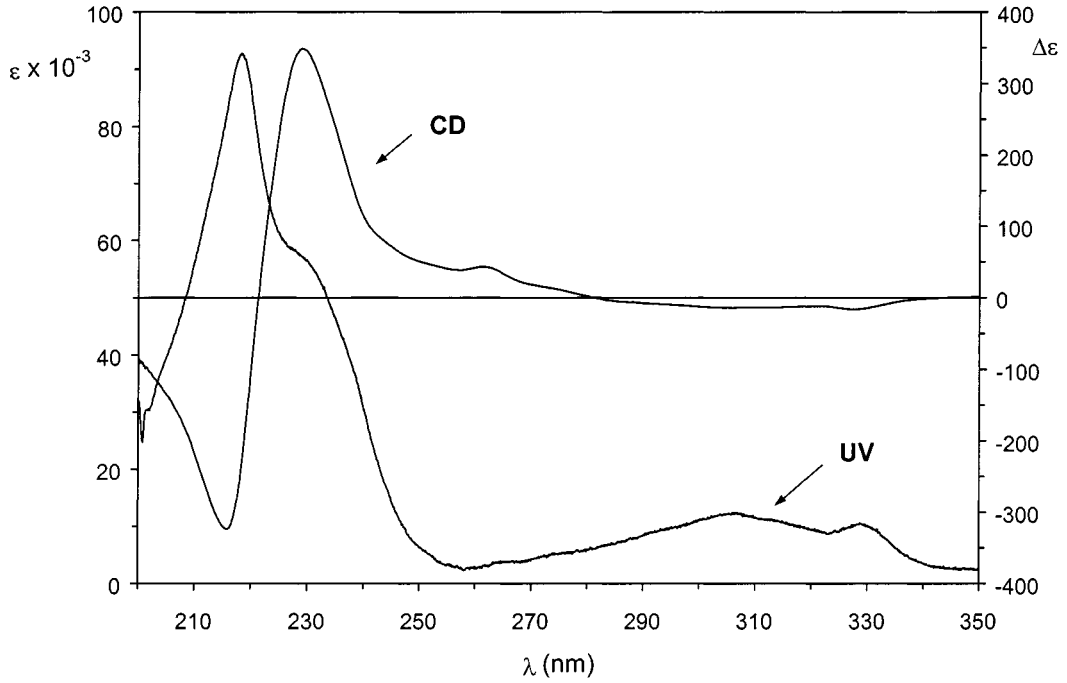


Figure 2. Absorption and CD spectra of compound (*S*)-**3**

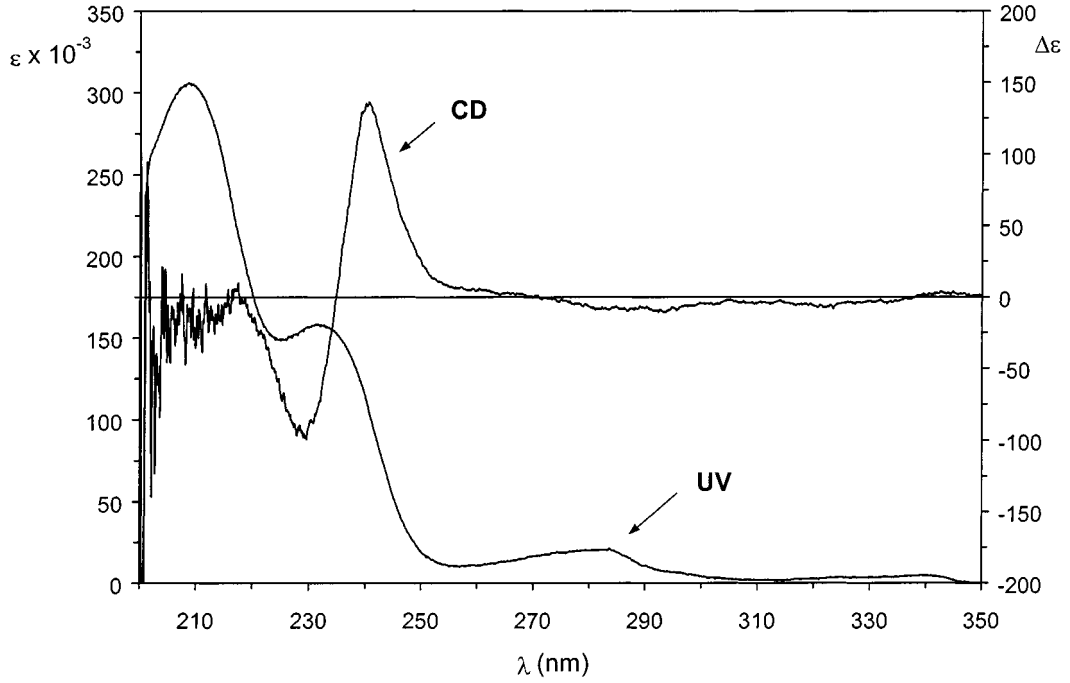


Figure 3. Absorption and CD spectra of compound (*S*)-**8**

This curve is similar in shape to the curve reported by Mason and, in fact, for the (*S*) absolute configuration it is positive for $0° < \theta < 110°$ and negative for $110° < \theta < 180°$, with positive and negative maxima at 60° and 140°, respectively. The reliability of the curve plotted in Figure 5 has been tested using the compounds belonging to classes A and B, which are conformationally defined. For compounds **1** and **2** (class A) the measured value of Δε of 200 indicates, from the curve in Figure 5, a θ angle of 90°, which is in agreement with the dihedral angle experimentally found for open chain derivatives.[13] Furthermore, the Δε values of 300−350 that were measured for compounds of class B[16] correspond (Figure 5) to small dihedral angles, in the range 60−75°, which are in satisfactory agreement

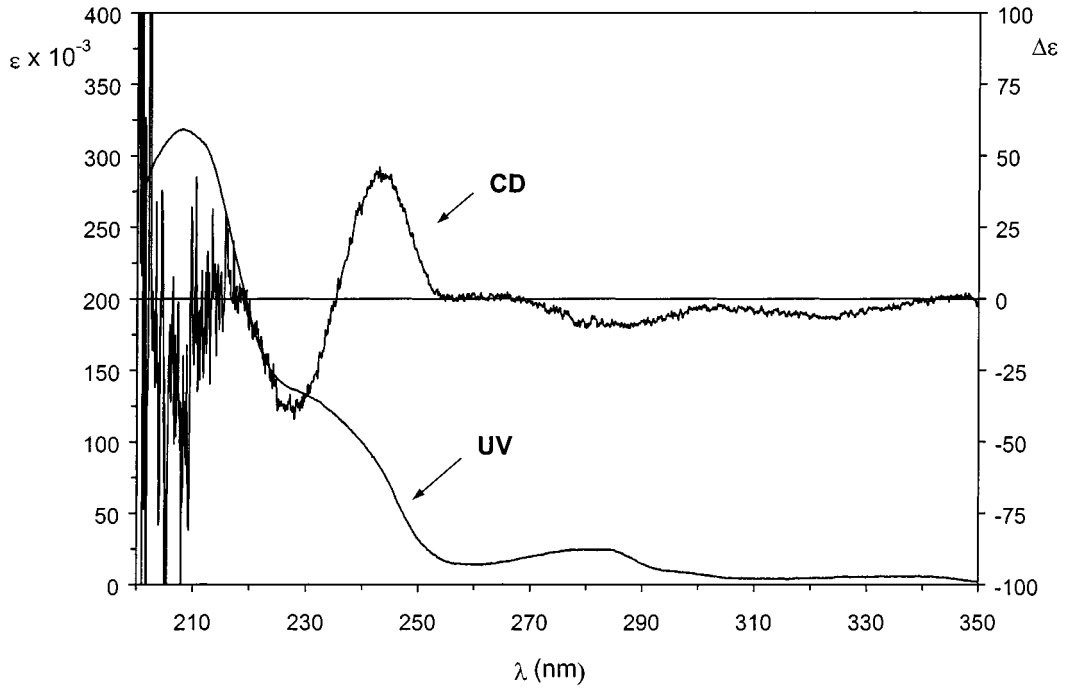


Figure 4. Absorption and CD spectra of compound (*S*)-**12**

with the values obtained[17] by MMX calculations. Such calculations revealed that, for compounds **3**−**6**, the angle θ ranges between 52° and 66°.[17] It is also interesting to note that compounds **3**−**6**, when dissolved in nematic liquid crystals (such as the biphenyl LCs K15 and E7), show very similar twisting powers, indicating similar conformations.[13] Moreover, the absorption spectrum can be used to evaluate θ values, confirming the results found from the CD data. For instance, in the case of compound **3** the absorption spectrum shows an absorption at 230 nm as a shoulder preceding a more intense absorption at 220 nm (Figure 2). This shape is typical of a dimer of two equal transition dipoles, forming a small angle between them.[13e,18] As can be seen in Chart 2, when the θ angle between the dipoles is small (i.e. say ≈ 60°) the high-energy exciton component carries an overall transition dipole moment that is significantly larger than that corresponding to the low-energy component. An absorption maximum having a less pronounced shoulder on its low-energy side results.

The exciton treatment[6a] allows the evaluation of the angle between the dipoles (which, in the present case, corresponds to the dihedral angle between the naphthalene rings) by the formula:

$$D(\mathrm{A})/D(\mathrm{B}) = (1 + \cos\theta)/(1 - \cos\theta) = R$$

Where D(A) and D(B) are the dipolar strengths allied to the transition to the symmetric (A) and antisymmetric (B) exciton excited states. An analysis of the absorption in this region in two Gaussian components allows an *R* value of 2.99 to be calculated, which corresponds to a θ angle of ca. 60°. X-ray analysis[2] of analogs of **3** as well as MMX calculations[17] provide an angle of ca. 55°, i.e. a value that is in more than satisfactory agreement with the one predicted by means of spectral data alone. When a similar analysis is carried out on compound **5** a dihedral angle θ of 65° is evaluated, indicating that the lengthening of the bridge opens the angle θ. Therefore it should be expected that on going from **3** to **4** to **5** to **6**, the angle θ will increase from a minimum value of 50−60° (as evaluated by the spectroscopic techniques based on the analysis of the absorption and CD spectra employed above) but, judging from Figure 5, it should not exceed 80°.

The decreasing molar rotation is then a consequence of the opening of θ, which reduces the positive intensity of the 235 nm Cotton effect and, in turn, determines the sign of the optical rotation at the sodium D line. In fact, in the specific case of **3**, the contribution of such a Cotton effect to the rotation at 589 nm can be calculated by employing formulae derived from[19] Krönig−Kramers transforms. Its value is 14355, which is reduced to +1781 by the negative Cotton effects at 310 and 216 nm. The calculated value is in satisfactory agreement with that experimentally found (+2337).

Once the reliability of the curve in Figure 5 has been demonstrated, it can be used to evaluate the dihedral angle for the dendrimers of classes C and D.

All the Fréchet[11] dendrimers, **7**−**10**, have been collected in class C and the Δε values as measured for **7**, **8**, and **9** are around 140 and that for **10** is around 110. From the curve in Figure 5, one can say that **7**, **8** and **9** are characterized by a θ angle of around 95°, while the smaller intensity of

Table 2. Main features of the absorption and CD spectra (THF) of compounds **1**−**12**

Class	compd	Absorption, $\varepsilon \cdot 10^{-3}$ (λ)			CD, $\Delta\varepsilon$ (λ)		
		^1L_b	^1L_a	$^1B_{a,b}$	^1L_b	^1L_a	$^1B_{a,b}$
A	**1**	5.8 (340) 4.5 (325)	6.7 (294) 7.2 (282) 5.8 (270)	88.8 (231)	-7.3 (321)	-8.7 (293) -10.1 (282)	+188.4 (236) -129.6 (225)
	2	7.2 (339) 5.9 (326)	9.8 (295) 12.1 (282) 12.7 (270)	160.3 (234)	+2.0 (342) -7.2 (321)	-11.8 (292) -12.9 (284)	+206.2 (238) -157.7 (226)
B	**3**	8.8 (329) 11.2 (306)	4.8 (264)	57.9 sh (228) 92.6 (218)	-16.6 (327) -14.5 (306)	+38.7 (261)	+348.6 (229) -323.3 (216)
	4	5.1 (326) 10.6 (298)	-	95.1 (221)	-9.4 (325) -14.7 (297)	-	+167.9 (242) +241.3 (230) -239.8 (216)
	5	4.7 (330)	7.7 (294) 6.7sh (269)	83.3 (226) 57.9sh (214)	-6.2 (327)	-15.3 (295) +13.1 (263)	+180.6sh (242) +314.6 (234) -232.7 (219)
	6	5.7 (332)	8.8 (291) 9.2 (281) 8.4 sh (270)	115.9 (233) 55.0 sh (212)	-7.7 (329)	-8.8 (291) +8.4 sh (270)	+359.4 (236) -252.7 (222)
C	**7**	6.3 (339) 5.0 (325)	8.0 (294) 13.3 (283) 11.8 sh (275)	126.3 (234) 140.1 (208)	+2.5 (341) -2.9 sh (330) -6.0 (320)	-8.8 (291) +1.7 sh (265) -9.0 (284)	+124.9 (239) -97.2 (227) +11.8 (214)
	8	6.2 (339) 5.0 (327)	8.4 sh (296) 23.0 (283) 21.9 sh (277)	157.5 (231) 304.4 (209)	+2.0 (342) -3.6 sh (330) -6.5 (322)	-9.7 (292) -9.2 (284) +2.4 sh (265)	+135.2 (240) -98.0 (229)
	9	6.6 (340) 5.2 (326)	41.6 (283) 41.5 (278)	261.8 sh (230) 496.1 (209)	+1.8 (343) -3.5 sh (335) -7.7 (322)	-11.1 (295)	+137.0 (241) -93.1 (230)
	10	6.2 (340) 5.1 (327)	49.0 (283) 49.2 (274)	412.6 sh (230) 523 (219) 535.1 (210)	+1.4 (343) -3.6 sh (335) -7.1 (322)	-10.1 (293)	+109.4 (241)
D	**11**	4.0 (340) 4.2 (328)	7.7 sh (296) 14.5 (283)	109.9 (238) 154.9 (206)	+1.0 (344) -4.1 (323)	-9.6 (286)	+71.2 (241) -44.5 (227)
	12	5.0 (340) 4.7 (327)	8.5 sh (296) 23.8 (283) 23.2 (277)	128.4 sh (240) 318.8 (208)	+2.3 (344) -4.6 (324)	-8.2 (283)	+43.6 (242) -39.1 (225)

the CD of **10** suggests a larger angle for this compound: the use of the same curve provides a value of about 100°. The steric hindrance exerted by the large substituents at the 2- and 2′-positions of these compounds opens the binaphthyl derivatives, reducing the intensity of the positive Cotton effect at 235 nm. In this way its positive contribution to the optical rotation at 589 nm is progressively reduced so that the molar rotation becomes more negative.

The backfolding dendrimers **11** and **12**, comprising class D, show very small Cotton effects at 235 nm, with the $\Delta\varepsilon$ values being 71 and 44, respectively. Following the previous procedure, θ values of 104° and 107° were evaluated. These results show that the effect of the different substitution patterns of the dendrimeric wedges (2,6 versus 3,5) produce, as expected, greater steric hindrance: in fact at the 2nd generation we have θ values that are significantly larger than those obtained for the 4th generation of the Fréchet dendrimers!

It is informative that the large variation in the CD intensity (for instance from $\Delta\varepsilon$ = 125 for **7** to $\Delta\varepsilon$ = 44 for **12**) is actually associated with a relatively small variation in θ (from 95° to 107°). This is because in this range of angles

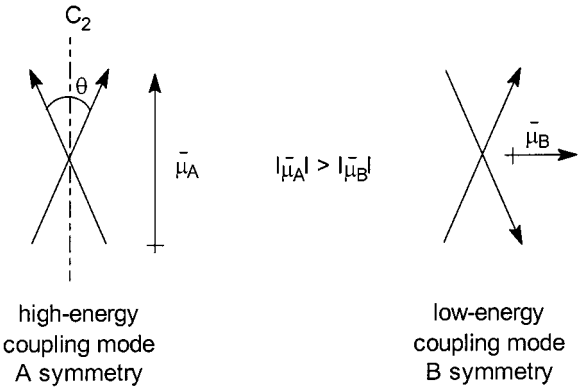


Chart 2. The two possible coupling modes of two transition dipoles, defining a small θ angle

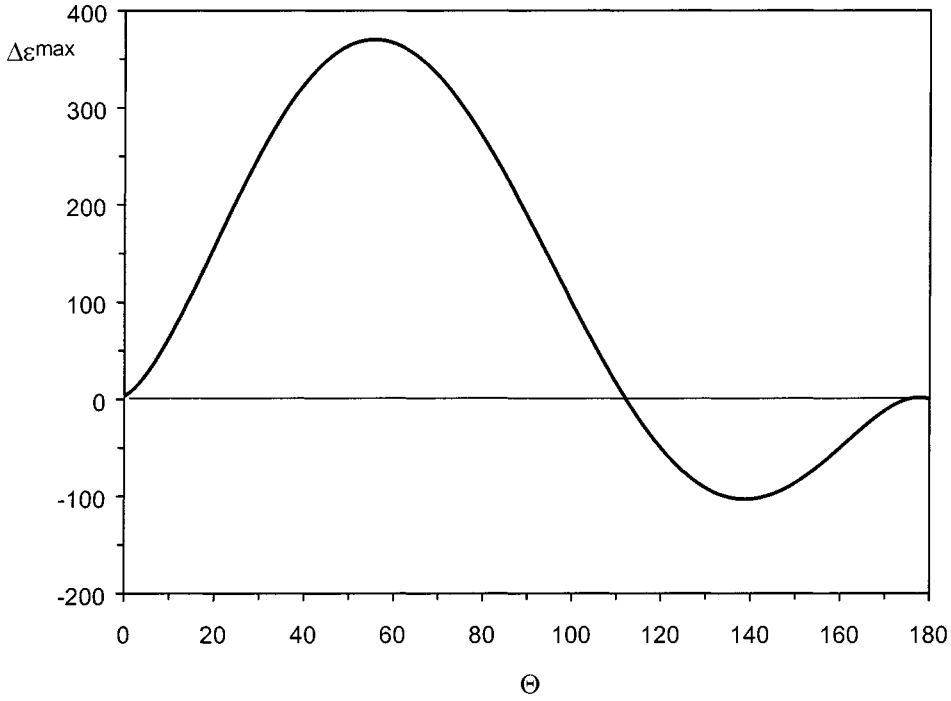


Figure 5. Intensity of the calculated low-energy component at 230 nm versus the dihedral angle θ

the curve in Figure 5 is particularly steep. For this reason CD spectroscopy can be considered as the technique *par excellence* for studying this kind of structural problem in that it allows the discovery of relatively small structural changes.

Conclusion

The CD investigation carried out within this work has shown that the binaphthyl moiety can open the dihedral angle θ up to a value of 110°. It is interesting to note that θ never exceeds (or even reaches) this critical value, even if the steric hindrance at the 2- and 2′-positions becomes particularly large (note that θ ranges from 50−60° for bridged binaphthyl ethers to 105−110° for dendrimers). From a more general point of view, it is clear that this work has shown that a careful, quantitative analysis of the CD data provides information about subtle changes in the conformation of the 1,1′-binaphthyl moiety in complex structures.

As Nakanishi has recently pointed out,[20] CD spectroscopy is still underused in spite of its great potential, mainly because the interpretation of CD data is often complicated. However, this investigation has confirmed the wide utility of this spectroscopic technique, which provides geometrical information that cannot be obtained by other types of structural analyses. For instance, several of the compounds from **1**−**12** are foams, meaning that X-ray analysis cannot be used for their structural investigation. Hence, a detailed quantitative analysis of the Circular Dichroism data is unprecedented as a means of acquiring information about the supramolecular and/or conformational arrangement of complex organic and macromolecular structures.

Experimental Section

General Remarks: All solvents were of c.p. quality, except those used as reaction solvents, which were of p.a. quality. THF was distilled over sodium/benzophenone prior to use. − Column chromatography was performed with Merck silica gel 60 (particle size 0.063−0.200 mm). − Melting points are uncorrected and were determined with a Jeneval microscope equipped with a Linkam hot-stage. − NMR spectra were run on a Bruker AM-400 spectrometer at frequencies of 400.1 MHz and 100.6 MHz for ^{1}H and ^{13}C nuclei, respectively. TMS was used as an internal standard and δ values are given in ppm. The following abbreviations are used in the peak assignment: Ar refers to aromatic rings derived from 2,6-dihydroxybenzyl alcohol or bromide at the reactive center and Ar′ refers to the aromatic rings derived from 3,5-dihydroxybenzyl alcohol one generation remote from the reaction center. Ph refers to aromatic rings derived from benzyl bromide. BN refers to resonances of the bisnaphthol core. − IR spectra were recorded on a Perkin−Elmer 1600 series FT-IR and data are given in cm^{-1}. − Optical rotation data were measured on a Jasco DIP-370 digital polarimeter. − LSI-MS spectra were recorded at the University of Birmingham using a VG ZabSpec mass spectrometer, using a p-nitrobenzyl alcohol matrix. MALDI-TOF-MS measurements were performed on a Voyager-DE machine at the University of Berkeley using an α-cyano-4-hydroxycinnamic acid matrix. − Elemental analyses were performed on a Perkin−Elmer 2400 series II machine.

Spectra: Absorption and CD spectra of compounds **1**−**12** were recorded on a JASCO J600 spectropolarimeter at room temperature, in THF, using 0.1 mm cells and concentrations of about 1×10^{-3} M. During the measurement, the instrument was thoroughly purged with nitrogen.

Calculations: CD calculations were performed by means of a program written by W. Hug et al.[21]

2,6-Dibenzyloxybenzyl Alcohol (14): A mixture of 2,6-dihydroxybenzoic acid (15.4 g, 100 mmol), benzyl bromide (53 g, 0.31 mol), potassium carbonate (43.5 g, 0.31 mol) and 18-crown-6 (0.26 g, 1.0 mmol) in acetone (100 mL) was heated under reflux overnight with vigorous stirring. The reaction mixture was allowed to cool to room temperature and the salts were removed by filtration. The filtrate was concentrated in vacuo yielding crude benzyl 2,6-dibenzyloxybenzoate (**13**) as a yellow syrup, which was dissolved in anhydrous diethyl ether (200 mL). This solution was added dropwise to an argon-blanketed suspension of $LiAlH_4$ (5.0 g, 0.13 mol) in diethyl ether (200 mL) at a suitable rate to ensure gentle reflux. The reaction mixture was heated under reflux for 1 h. After allowing the reaction mixture to cool down to room temperature it was subsequently neutralized by the addition of ethyl acetate (10 mL) and aqueous sodium hydroxide (10% w/v, 10 mL). After removal of the salts by filtration and evaporation of the solvent, the residue was subjected to crystallization (toluene/hexane = 1:4, 300 mL), yielding **14** (20.72 g, 65%) as a white crystalline solid, m.p. 80−81°C. − ^{1}H NMR ($CDCl_3$): δ = 2.55 (t, *J* = 6.9 Hz, 1 H, OH), 4.90 (d, *J* = 6.9 Hz, 2 H, C*H*$_2$OH), 5.09 (s, 4 H, C*H*$_2$Ph), 6.62 (d, *J* = 8.4 Hz, 2 H, ArH-3,5), 7.17 (t, *J* = 8.3 Hz, 1 H, ArH-4), 7.32 (t, *J* = 6.9 Hz, 2 H, PhH-*para*), 7.38 (t, *J* = 7.7 Hz, 4 H, PhH-*meta*), 7.42 (d, *J* = 6.9 Hz, 4 H, PhH-*ortho*). − ^{13}C NMR ($CDCl_3$): δ = 55.0 (CH_2OH), 70.4 (*C*H$_2$Ph), 105.5 (ArC-3,5), 118.0 (ArC-1), 127.2, 128.0, 128.6 (PhCH), 129.1 (ArC-4), 136.8 (PhC-*ipso*), 157.6 (ArC-2,6). − IR (KBr): $\tilde{\nu}$ = 3572 (OH stretch), 2942 and 2882 (CH_2 stretch), 1596 and 1496 (C=C stretch), 1451 (CH_2 deformation) cm^{-1}.

2,6-Dibenzyloxybenzyl Bromide (15): To a stirred and cooled (ice/salt bath) solution of **14** (8.02 g, 25.0 mmol) in diethyl ether (75 mL) was added dropwise a solution of phosphorus tribromide (2.5 g, 9.2 mmol) in diethyl ether (10 mL). After completion of the addition, the solution was stirred for a further 30 min. The reaction mixture was poured into ice-cold water and the layers were separated. The organic layer was extracted with saturated aqueous sodium bicarbonate (1 × 25 mL). The organic layer was dried (Na_2SO_4) and the solvent evaporated in vacuo, yielding **15** (9.22 g, 96%) as a white solid, which became slightly purple upon standing. − ^{1}H NMR ($CDCl_3$): δ = 4.80 (s, 2 H, CH_2Br), 5.15 (s, 4 H, CH_2Ph), 6.58 (d, *J* = 8.4 Hz, 2 H, ArH-3,5), 7.18 (t, *J* = 8.3 Hz, 1 H, ArH-4), 7.32 (t, *J* = 7.3 Hz, 2 H, PhH-*para*), 7.39 (dd, *J* = 7.1 and 1.6 Hz, 4 H, PhH-*meta*), 7.49 (d, *J* = 7.1 Hz, 4 H, PhH-*ortho*). − ^{13}C NMR ($CDCl_3$): δ = 23.6 (CH_2Br), 70.3 (CH_2Ph), 105.3 (ArC-3,5), 115.4 (ArC-1), 127.1, 127.9, 128.6 (PhCH), 130.0 (ArC-4), 136.9 (PhC-*ipso*), 157.6 (ArC-2,6). − IR (KBr): $\tilde{\nu}$ = 3060 and 3027 (=C−H stretch), 2901 and 2861 (CH_2 stretch), 1598 and 1497 (C=C stretch), 1447 (CH_2 deformation) cm^{-1}.

Methyl 2,6-Dihydroxybenzoate (16): To a stirred mixture of 2,6-dihydroxybenzoic acid (7.73 g, 50.0 mmol) in DMF (50 mL) were added sodium bicarbonate (12.8 g, 152 mmol) and methyl iodide (4.8 mL, 77 mmol). After one night another portion of methyl iodide (4.8 mL, 77 mmol) was added and stirring was continued for another 4 d at room temperature. The mixture was filtered, the solvent evaporated in vacuo, the residue subsequently taken up in CH_2Cl_2 and the suspension extracted with aqueous HCl (3 × 50 mL, 0.5 M) and saturated aqueous sodium bicarbonate (4 × 50 mL). The organic layer was dried, the solvent evaporated, and the solid residue sublimated at 0.2 mbar, yielding **16** (6.50 g, 77%) as a slightly yellow crystalline solid, m.p. 60−61°C. − ^{1}H NMR ($CDCl_3$): δ = 4.08 (s, 3 H, CH_3), 6.49 (d, *J* = 8.2 Hz, 2 H, ArH-3,5), 7.31 (t, *J* = 8.3 Hz, 1 H, ArH-4), 9.66 (br s, 2 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 52.0 (CH_3), 99.8 (ArC-1), 108.1 (ArC-3,5), 136.5 (ArC-4), 160.7 (ArC-2,6), 169.9 (C=O). − IR (KBr): $\tilde{\nu}$ = 3416 (OH stretch), 1575 and 1475 (C=C stretch), 1325 (OH deformation, phenol), 1196 (COH stretch, phenol) cm^{-1}.

Methyl 2,6-Bis(3,5-dibenzyloxy-benzyloxy)benzoate (17): A mixture of **16** (1.68 g, 10 mmol), 3,5-dibenzyloxybenzyl bromide ([G-1]Br, 8.05 g, 21.0 mmol), potassium carbonate (4.15 g, 30 mmol) and 18-crown-6 (0.26 g, 1.0 mmol) in acetone (50 mL) was heated under reflux for 2 d with vigorous stirring. The mixture was allowed to cool to room temperature and the salts were filtered off. The solvent was evaporated and the residue was subjected to column chromatography (250 g SiO_2, toluene/CH_2Cl_2 = 1:1, R_f = 0.15) yielding **17** (5.14 g, 67%) as a slightly yellow viscous syrup. − ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 3 H, CH_3), 5.02 (s, 8 H, CH_2Ph), 5.06 (s, 4 H, CH_2Ar'), 6.54 (m, 4 H, ArH-3,5, Ar′H-4), 6.66 (d, *J* = 1.9 Hz, 4 H, Ar′H-2,6), 7.17 (t, *J* = 8.2 Hz, 1 H, ArH-4), 7.20−7.45 (m, 20 H, PhH). − ^{13}C NMR ($CDCl_3$): δ = 52.3 (CH_3), 70.0 (CH_2Ph), 70.3 (CH_2Ar'), 101.5 (Ar′C-4), 105.6 (Ar′C-2,6), 105.9 (ArC-3,5), 114.3 (ArC-1), 127.5, 128.0, 128.5 (PhCH), 131.0 (ArC-4), 136.8 (PhC-*ipso*), 139.3 (Ar′C-1), 156.3 (ArC-2,6), 160.1 (Ar′C-3,5), 166.6 (C=O). − IR (KBr): $\tilde{\nu}$ = 3088 and 3031 (=C−H stretch), 2946 and 2874 (CH_2 stretch), 1732 (C=O stretch, ester), 1595 and 1497 (C=C stretch), 1451 (CH_2 deformation) cm^{-1}.

2,6-Bis(3,5-dibenzyloxy-benzyloxy)benzyl Alcohol (18): A solution of **17** (3.63 g, 4.70 mmol) in anhydrous THF (30 mL) was added dropwise to an argon-blanketed suspension of $LiAlH_4$ (0.3 g, 8 mmol) in anhydrous THF (30 mL) at a suitable rate to ensure mild reflux. The mixture was stirred overnight at room temperature and was subsequently neutralized with ethyl acetate (10 mL) and aqueous sodium hydroxide (10% w/v, 2 mL). The salts were filtered off and the solvent was removed in vacuo to yield **18** (2.62 g, 75%) as a viscous oil that crystallized slowly, m.p. 85−87°C. − ^{1}H NMR ($CDCl_3$): δ = 2.55 (t, *J* = 4.3 Hz, 1 H, OH), 4.87 (d, *J* = 4.3 Hz, 2 H, C*H*$_2$OH), 5.01 (s, 12 H, CH_2Ph and CH_2Ar'), 6.56 (d, *J* = 8.3 Hz, 2 H, ArH-3,5 and t, *J* = 2.2 Hz, 2 H, Ar′H-4), 6.66 (d, *J* = 2.2 Hz, 4 H, Ar′H-2,6), 7.12 (t, *J* = 8.4 Hz, 1 H, ArH-4), 7.25−7.50 (m, 20 H, PhH). − ^{13}C NMR ($CDCl_3$): δ = 54.9 (CH_2OH), 70.0 (CH_2Ph), 70.3 (CH_2Ar), 101.5 (Ar′C-4), 105.5 (ArC-3,5), 106.0 (Ar′C-2,6), 117.9 (ArC-1), 127.5, 127.9, 128.5 (PhCH), 129.1 (ArC-4), 136.5 (PhC-*ipso*), 139.2 (Ar′C-1), 157.4 (ArC-2,6), 160.1 (Ar′C-3,5). − IR (KBr): $\tilde{\nu}$ = 3581 (OH stretch), 3031 (=C−H stretch), 2927 and 2874 (CH_2 stretch), 1595 and 1497 (C=C stretch), 1448 (CH_2 deformation), 1048 (CO stretch, primary OH) cm^{-1}.

2,6-Bis(3,5-dibenzyloxy-benzyloxy)benzyl Bromide (19): To a stirred and cooled (ice/salt bath) suspension of **18** (0.74 g, 1.00 mmol) in dry diethyl ether/THF (3:1 v/v, 12 mL) was added dropwise phosphorus tribromide (0.25 g, 0.92 mmol) in diethyl ether (4 mL). Stirring of the cooled solution was continued for 2 h and then methanol (70 mL) was added. Subsequent filtration of the white precipitate gave **19** (0.60 g, 0.74 mmol, 74%). − ^{1}H NMR ($CDCl_3$): δ = 4.80 (s, 2 H, CH_2Br), 5.05 (s, 8 H, CH_2Ph), 5.08 (s, 4 H, CH_2Ar'), 6.52 (d, *J* = 8.4 Hz, 2 H, ArH-3,5), 6.57 (t, *J* = 2.2 Hz, 2 H, Ar′H-4), 6.75 (d, *J* = 2.2 Hz, 4 H, ArH′-2,6), 7.23 (t, *J* = 8.3 Hz, 1 H, ArH-4), 7.30−7.55 (m, 20 H, PhH). − ^{13}C NMR ($CDCl_3$): δ = 24.0 (CH_2Br), 70.0 (CH_2Ar'), 70.1 (CH_2Ph), 101.8 (Ar′C-4), 105.2 (ArC-3,5), 105.8 (Ar′C-2,6), 127.5, 127.9, 128.6 (PhCH), 130.1 (ArC-4), 136.8 (PhC-*ipso*), 139.4 (Ar′C-1), 157.5 (ArC-2,6), 160.2 (Ar′C-3,5). − IR (KBr): $\tilde{\nu}$ = 3031 (=C−H stretch), 2927 and 2875 (CH_2 stretch), 1595 and 1497 (C=C stretch), 1450 (CH_2 deformation) cm^{-1}.

(*S*)-2,2′-Bis(2,6-dibenzyloxy-benzyloxy)-1,1′-binaphthalene (11): A vigorously stirred mixture of (*S*)-(−)-2,2′-dihydroxy-1,1′-binaphthalene (143.4 mg, 0.501 mmol), **15** (383.8 mg, 1.001 mmol), 18-crown-6 (0.03 g, 0.1 mmol) and potassium carbonate (2.5 g, 18 mmol) in acetone (40 mL) was heated under reflux for 2 d. The reaction mixture was allowed to cool to room temperature and the salts were removed by filtration. The filtrate was concentrated in vacuo and the residue was subjected twice to column chromatography (30 g SiO_2, toluene, $R_f = 0.24$) to yield pure **11** (0.19 g, 43%) as a slightly yellow foam. − ^{1}H NMR ($CDCl_3$): δ = 4.55, 4.66 (2 × d, J = 12.1 Hz, 8 H, ArOCH_2Ph), 5.15, 5.24 (2 × d, J = 10.7 Hz, 4 H, CH_2Ar), 6.25 (d, J = 8.3 Hz, 4 H, ArH-3,5), 6.82−6.90 (m, 4 H, BNH), 6.93 (t, J = 8.3 Hz, 2 H, ArH-4), 7.21−7.37 (m, 22 H, PhH, BNH), 7.51 (s, 4 H, BNH), 7.63 (dd, J = 8.1 and 0.8 Hz, 2 H, BNH). − ^{13}C NMR ($CDCl_3$): δ = 61.6 (*C*H_2Ar), 70.1 (ArO*C*H_2Ph), 105.6 (ArC-3,5), 115.1 (ArC-1), 118.6 (BNCH), 122.0 (BNC), 123.0 (BNCH), 125.5 (BNCH), 125.7 (BNCH), 127.0, 127.3, 128.2 (PhCH, BNCH), 128.5 (BNCH), 129.4 (2 × C, ArC-4, BNC), 134.3 (BNC), 137.2 (PhC-*ipso*), 155.1 (BNC), 158.3 (ArC-2,6). − IR (KBr): $\tilde{\nu}$ = 3031 (=C−H stretch), 2927 and 2868 (CH_2 stretch), 1595 and 1507 (C=C stretch), 1452 (CH_2 deformation), 1264 (CO stretch, arylalkyl ether) cm^{-1}. − $[\alpha]_D^{20}$ = −53.3 (c = 0.90, CH_2Cl_2). − MALDI-TOF-MS: calcd. for $C_{62}H_{50}O_6$: 889.4; found: 915 $[M + Na]^+$, 931 $[M + K]^+$. − $C_{62}H_{50}O_6$: calcd. C 83.57, H 5.66; found C 83.53, H 5.69.

(*S*)-2,2′-Bis[2,6-bis(3,5-dibenzyloxy-benzyloxy)benzyloxy]-1,1′-binaphthalene (12): A vigorously stirred mixture of (*S*)-(−)-2,2′-dihydroxy-1,1′-binaphthalene (141.5 mg, 0.494 mmol), **19** (821.7 mg, 1.02 mmol), 18-crown-6 (0.03 g, 0.1 mmol) and potassium carbonate (2.5 g, 18 mmol) in acetone (50 mL) was heated under reflux for 2 d. The reaction mixture was allowed to cool to room temperature and the salts were removed by filtration. The filtrate was concentrated in vacuo and subjected to column chromatography (30 g SiO_2, toluene, $R_f = 0.2$), which furnished pure **12** (0.52 g, 60%) as a slightly yellow foam. − ^{1}H NMR ($CDCl_3$): δ = 4.38, 4.48 (2 × d, J = 12.6 Hz, 8 H, ArOCH_2Ar′), 4.78, 4.83 (2 × d, J = 11.6 Hz, 16 H, Ar′OCH_2Ph), 5.17, 5.19 (2 × d, J = 10.1 Hz, 4 H, CH_2Ar), 6.10 (d, J = 8.4 Hz, 4 H, ArH-3,5), 6.44 (d, J = 2.1 Hz, 8 H, Ar′H-2,6), 6.54 (t, J = 2.2 Hz, 4 H, Ar′H-4), 6.77 (m, 2 H, BNH), 6.81 (t, J = 8.3 Hz, 2 H, ArH-4), 6.91 (d, J = 8.5 Hz, 2 H, BNH), 7.02 (m, 2 H, BNH), 7.18−7.29 (m, 40 H, PhH), 7.41 (d, J = 8.1 Hz, 2 H, BNH), 7.48 (d, J = 9.0 Hz, 2 H, BNH), 7.55 (d, J = 9.1 Hz, 2 H, BNH). − ^{13}C NMR ($CDCl_3$): δ = 61.1 (*C*H_2Ar), 69.8 (ArO-*C*H_2Ar′, Ar′O*C*H_2Ph), 101.2 (Ar′C-4), 105.3 (Ar′C-2,6), 105.7 (ArC-3,5), 114.6 (ArC-1), 116.8 (BNCH), 121.1 (BNC), 122.9 (BNCH), 125.4 (BNCH), 125.6 (BNCH), 127.4, 127.7, 128.4 (PhCH, BNCH), 128.8 (BNCH), 129.2 (BNC), 129.6 (ArC-4), 134.2 (BNC), 136.8 (PhC-*ipso*), 140.0 (Ar′C-1), 155.0 (BNC), 158.1 (ArC-2,6), 159.9 (Ar′C-3,5). − IR (KBr): $\tilde{\nu}$ = 3061 and 3031 (=C−H stretch), 2927 and 2869 (CH_2 stretch), 1595 and 1497 (C=C stretch), 1451 (CH_2 deformation) cm^{-1}. − $[\alpha]_D^{20}$ = −23.2 (c = 1.74, CH_2Cl_2). − MALDI-TOF-MS: Calcd. for $C_{118}H_{98}O_{14}$: 1739.7. Found: 1763.6 $[M + Na]^+$, 1780.6 $[M + K]^+$. − $C_{118}H_{98}O_{14}$: calcd. C 81.45, H 5.68; found C 81.04; H 5.77.

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[1] [1a] C. Rosini, L. Franzini, A. Raffaelli, P. Salvadori, *Synthesis* **1992**, 503. − [1b] J. Bao, W. D. Wulff, J. B. Dominy, M. J. Fasno, E. B. Grant, A. C. Robb, M. C. Whitcomb, S. Yeung, R. L. Ostrander, A. L. Rheingold, *J. Am. Chem. Soc*. **1996**, *118*, 3392. − [1c] L. Pu, *Chem. Rev.* **1998**, *98*, 2405.

[2] H. Deussen, C. Boutton, N. Thorup, T. Geisler, E. Hendrickx, K. Bechgaard, A. Persoons, T. Bjoernholm, *Chem. Eur. J.* **1998**, *4*, 240.

[3] [3a] H. W. I. Peerlings, E. W. Meijer, *Eur. J. Org. Chem.* **1998**, *1*, 573. − [3b] Y. Chen, C. Chen, F. Xi, *Chirality* **1998**, *10*, 661.

[4] [4a] R. Noyori, H. Takaya, *Chem. Scripta* **1985**, *25*, 83. − [4b] T. Harada, M. Takeuchi, M. Matsuda, S. Ueda, A. Oku, *Tetrahedron: Asymmetry* **1996**, *7*, 2479.

[5] [5a] H. Deussen, P. V. Shibaev, R. Vinokur, T. Bjoernholm, K. Schaumburg, K. Beechgaard, V. P. Shibaev, *Liq. Cryst*. **1996**, *21*, 327. − [5b] G. Solladiè, P. Hugelè, R. Bartsch, *J. Org. Chem*. **1998**, *63*, 3895.

[6] Treaments of exciton coupling and its application in organic stereochemistry: [6a] S. F. Mason, *Quart. Rev.* **1962**, *17*, 20. − [6b] S. F. Mason, Chapter 4, *Theory II*, in *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*, (Ed.: Snatzke, G.), Heyden and Son, London, UK, **1967**, p. 71. − [6c] G. Gottarelli, S. F. Mason, G. Torre, *J. Chem. Soc. (B)* **1971**, 1349. − [6d] N. Harada, K. Nakanishi, *Acc. Chem. Res.* **1972**, *5*, 257. − [6e] S. F. Mason, *Molecular Optical Activity and the Chiral Discriminations*, Cambridge University Press, Cambridge, **1982**. − [6f] N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*, University Science Books, Mill Valley, CA, U.S.A., **1983**.

[7] [7a] H. H. Jaffè, M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, J. Wiley, New York, **1962**, p. 303. − [7b] S. Suzuki, T. Fujii, H. Baba, *J. Mol. Spectroscopy* **1973**, *47*, 243.

[8] S. F. Mason, R. H. Seal, D. R. Roberts, *Tetrahedron* **1974**, *30*, 1671.

[9] J. J. G. S. van Es, H. A. M. Biemans, E. W. Meijer, *Tetrahedron: Asymmetry* **1997**, *8*, 1825. For more information see: J. E. Simpson, G. H. Daub, F. N. Hayes, *J. Org. Chem*. **1973**, *38*, 1771; C. Tétreau, D. Lavalette, D. Cabaret, N. Geraghty, Z. Welvart, *J. Phys. Chem.* **1983**, *87*, 3234.

[10] H. W. I. Peerlings, D. C. Trimbach, E. W. Meijer, *Chem. Commun.* **1998**, 497.

[11] [11a] C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.* **1990**, 1010. − [11b] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc*. **1990**, *112*, 7638. − [11c] K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc*. **1991**, *113*, 4252. − [11d] K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc., Perkin Trans. 1* **1991**, 1059. − [11e] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1992**, *114*, 8405. − [11f] J. M. J. Fréchet, C. J. Hawker, K. L. Wooley, *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1627. − [11g] K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *Angew. Chem.* **1994**, *106*, 123; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 82. − [11h] J. M. J. Fréchet, *Science* **1994**, *263*, 1710. − [11i] M. R. Leduc, W. Hayes, J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1. − [11j] K. W. Pollak, E. M. Sanford, J. M. J. Fréchet, *J. Mater. Chem.* **1998**, *8*, 519. For a linear analog of these dendrimers see: C. J. Hawker, E. E. Malmström, C. W. Frank, J. P. Kampf, *J. Am. Chem. Soc.* **1997**, *119*, 9903.

[12] W. Kauzmann, *Quantum Chemistry*, Academic Press, New York, **1957**.

[13] [13a] G. Gottarelli, M. Hibert, B. Samorì, G. Solladiè, G. P. Spada, R. Zimmermann, *J. Am. Chem. Soc*. **1983**, *105*, 7318. − [13b] G. Gottarelli, G. P. Spada, R. Bartsch, G. Solladiè, R. Zimmermann, *J. Org. Chem*. **1986**, *51*, 589. − [13c] G. Solladiè, G. Gottarelli, *Tetrahedron* **1987**, *43*, 1425. − [13d] C. Rosini, L. Franzini, P. Salvadori, G. P. Spada, *J. Org. Chem.* **1992**, *57*, 6820. − [13e] C. Rosini, I. Rosati, G. P. Spada, *Chirality* **1995**, *7*, 353.

[14] [14a] H. DeVoe, *J. Chem. Phys.* **1964**, *41*, 393; *J. Chem. Phys.* **1965**, *43*, 3199. − [14b] M. Zandomeneghi, C. Rosini, P. Salvadori, *Chem. Phys. Lett.* **1976**, *44*, 533. − [14c] For some applications of these calculations to structural problems see: C. Rosini, P. Salvadori, M. Zandomeneghi, *Tetrahedron: Asymmetry* **1993**, *4*, 545.

[15] MMX routine, Serena Software, Bloomington IN, USA.

[16] Actually, the low energy branch of the 230 nm exciton couplet in **3** shows a reduced intensity with respect to **2**, **5**, and **6**. In addition, only in this case is a clear maximum present at 242 nm

instead of a small inflection as seen in **5**. The reasons for this behavior are still unclear.
[17] M. Zhang, G. B. Schuster, *J. Phys. Chem.* **1992**, *96*, 3063.
[18] [18a] C. Rosini, R. Tanturli, P. Pertici, P. Salvadori, *Tetrahedron: Asymmetry* **1996**, *7*, 2971. – [18b] C. Rosini, R. Ruzziconi, S. Superchi, F. Fringuelli, O. Piermatti, *Tetrahedron: Asymmetry* **1998**, *9*, 55.
[19] A. Moscowitz, *Theory and Analysis of Rotatory Dispersion Curves* in C. Djerassi, *Optical Rotatory Dispersion* McGraw-Hill, New York, **1960**, chapter 12, p. 150.
[20] K. Nakanishi, N. Berova, in *Circular Dichroism: Principles and Applications*, (Eds.: K. Nakanishi, N. Berova, R. W. Woody), VCH Publishers, New York, **1994**, Preface.
[21] W. Hug, F. Ciardelli, I. Tinoco Jr., *J. Am. Chem. Soc*. **1974**, *96*, 3407.

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