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Synthesis and structural study of the enantiomers of α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol as a chiral solvating agent

Marta Sánchez-Aris, Carla Estivill and Albert Virgili*

Departament de Química Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

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Abstract—We describe the synthesis, the structure, and the behavior as a chiral solvating agent of the enantiomers of α,α′-bis(trifluoromethyl)-10,10′-(9,9′-biantryl)dimethanol. The thermodynamics of several associations are presented. We conclude that the association needs the approximation of the aromatic systems and that the geometry of complexation is the main factor that defines the enantiodiscrimination.

1. Introduction

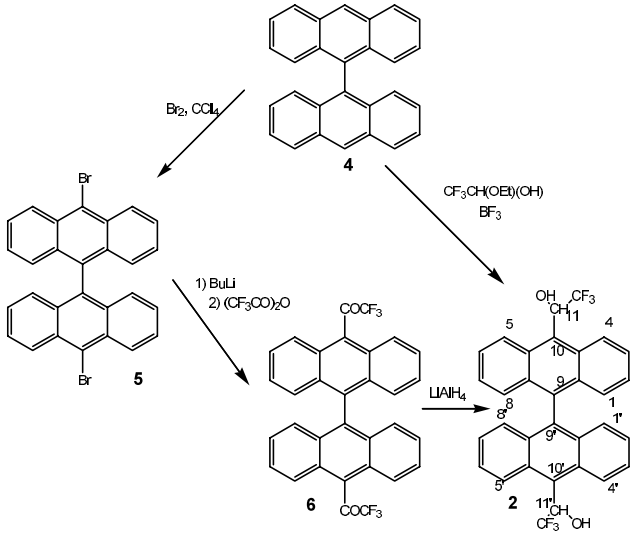
Recently, we described[1] the preparation and structural study of the enantiomers of α,α′-bis(trifluoromethyl)-9,10-anthracenedimethanol[2] **1** and their perdeuterated isotopomers, which are compounds with an excellent capacity to behave as chiral solvating agents (CSA).

Appropriately substituted biaryl compounds have been used as chiral auxiliaries[3] in the study of several enantioselective reactions and also in the study of structural chirality. BINOL and derivatives have been shown to be very important reagents in several reactions when enantioselectivity has been sought.[4]

Target compound **2** presents the same substituted aromatic ring as Pirkle's alcohol[5] **3**, and the arrangement between two aromatic rings is similar to the binaphthol. Moreover, as we show with compound **1**, the double functionality increases the capacity of enantiodifferentiation. The α,α′-bis(trifluoromethyl)-10,10′-(9,9-bianthryl)-dimethanol **2** is also a doubly functionalized compound that will be capable to associate, in a bidentate way, with compounds that present a complementary structure. The distance between these chemical functions will mean that the choice of the substrates should be crucial in the behavior of this chiral auxiliary. The present work analyzes the behavior of **2** as a CSA in front of several simple and small racemic compounds.

2. Results and discussion

As the bianthracenyl **4** is a well-known system, we start the synthesis (Scheme 1) by preparing this compound by reductive coupling of the anthraquinone using Zn in acidic medium[6]. Dibromination of **4** in the 10 and 10′ positions has also been described[7] and we obtained the 10,10′-dibromo-9,9′-bianthracenyl **5** in a 60% yield. By extension of the previously applied methodology,[1] the generation of the di-lithium derivative by using



Scheme 1. Synthesis of compound **2**.

* Corresponding author. E-mail: albert.virgili@uab.es

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butylithium and the subsequent reaction with trifluoracetic anhydride yields 10,10′-bis(trifluoroacetyl)-9,9-bianthracenyl **6**. This intermediate product was isolated and characterized by NMR. Reduction of the diketone **6** with $LiAlH_4$ give us the mixture of the isomers of α,α′-bis(trifluoromethyl)-10,10′-(9,9′-biantryl)dimethanol **2**.

A more direct way to obtain **2** uses a double Friedel–Crafts reaction with trifluoroacetaldehyde. Although this compound is in the gas phase under normal conditions, we substitute it with the more easily manipulated trifluoroacetaldehyde ethyl hemiacetal[8] whose use as an electrophilic reactant in front of aromatic compounds has only been described a few times.[9] We therefore first tested this reaction using the anthracene as substrate. When the anthracene ring was treated with trifluoroacetaldehyde ethyl hemiacetal in the presence of a Lewis acid as a catalyst (BF_3), we obtained, in high yield (90%), 1-(9-anthryl)-2,2,2-trifluorethanol. Although the conditions of the reaction were adapted to the double reaction, the di-reaction product was not detected. Possibly the presence of the first group decreases the reactivity of the anthracene towards a second electrophilic attack. In the case of bianthracenyl **4**, when it was treated with trifluoroacetaldehyde ethyl hemiacetal under the conditions for the double reaction, we obtained α,α′-bis(trifluoromethyl)-10,10′-(9,9′-biantryl)-dimethanol **2** in a 81% yield. The disconnection of the aromatic rings was demonstrated.

Compound **7**, the diacetate derivative of **2**, was prepared quantitatively by treatment with acetyl chloride and was used to isolate pure enantiomers by HPLC on a semi-preparative Whelk-O1 (and preparative Whelk-O2) column using hexane/isopropyl alcohol (95/5) as the elution solvent (2 ml/min). The first eluted compound was assigned to (−)-(*R*,*R*)-**7**, the second to the *meso*-**7**, and the third to the (+)-(*S*,*S*)-**7**. These assignations were made with the help of (i) the analysis of the integration of the peaks (ii) the comparison with the elution order in the same conditions of the Pirkle's alcohol acetate[10] and of the α,α′-bis(trifluoromethyl)-9,10-anthracenedimethanol diacetate[1] and (iii) the coincidence of the chromophores with the cited acetates or with the alcohols suggesting a similar sign of the optical activity. Treatment of each isolated ester with K_2CO_3 (1 M) gave the stereoisomers (−)-(*R*,*R*)-**2**, *meso*-**2** and (+)-(*S*,*S*)-**2**, respectively. The parallelism of the experiments of enantiodiscrimination using **2** or the other chiral solvating agents **1** and **3**, giving a similar sense of the change of chemical shift in the same nucleus, reinforces the above assignation and configuration of the three isomers.

At room temperature, the ^1H NMR spectrum of each isomer of **2** shows broad resonances for several protons by the slow rotation of each C_{10}–C_{11} bond. Figures 1 and 2 show the ^1H NMR spectra of *meso*-**2** and (*R*,*R*)-**2** at several temperatures. At low temperatures, the internal rotation is frozen and the peaks of the pairs of protons H_4, $H_{4'}$ (those that are near H_{11}) and H_5, $H_{5'}$

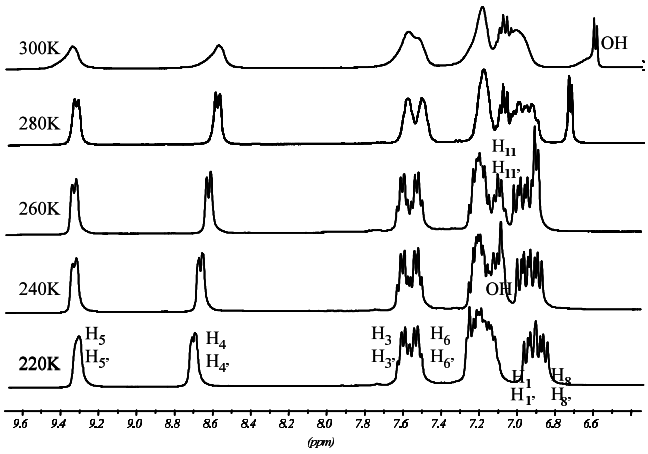


Figure 1. ^1H NMR spectra of *meso*-**2** at several temperatures.

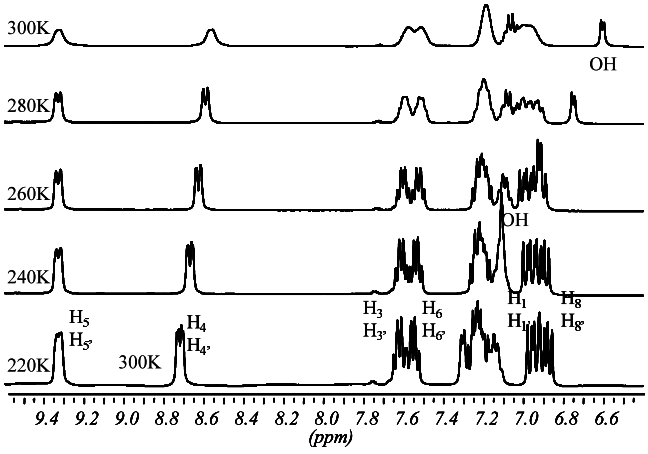


Figure 2. ^1H NMR spectra of (*R*,*R*)-**2** at several temperatures.

(those that are near the OH) become broad doublets. The rest of signals are only partially resolved.

To explain this behavior we must look to the corresponding conformational equilibrium. The more stable conformation corresponds to the perpendicular position of the CF_3 groups to the anthracene rings.[11] Figure 3 shows the two stabilized conformations of *meso*-**2** coming from the rotation of 180° of the C_{10}–C_{11} bond.

Neither structure has a symmetry element that converts one anthracene ring into the other anthracene ring, each proton being anisochronous to each *prima* proton. Thus, there is a slight difference between analogous protons of two anthracene rings broadening the corresponding absorption. The presence of two stereogenic centers and the rigidity of the bond between the anthracenes afford two distributions of the substituents of C_{11} and $C_{11'}$, a *Minus* and a *Plus*. These two conformers (*S*,*M*,*R* and *S*,*P*,*R*) are enantiomers, and consequently, their hydrogen atoms are isochronous.

For the other diastereoisomer [for example the enantiomer (*R*,*R*)-**2**] we find a different behavior but a similar result.

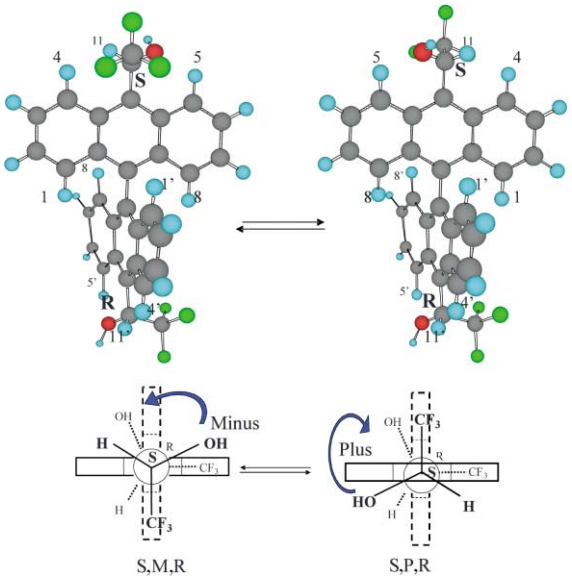


Figure 3. Frontal and vertical views of the conformational equilibrium of *meso*-**2**.

Figure 4 shows the two stabilized conformations of (*R*,*R*)-**2** resulting from the rotation of 180° of the C_{10}–C_{11} bond. Each structure has C_2 symmetry that converts one anthracene ring into the other anthracene ring. Each proton is isochronous of the corresponding *prima* proton. The two components of the conformational equilibrium (*R*,*P*,*R*)-**2** and (*R*,*M*,*R*)-**2** are diastereoisomers and each rotamer shows 10 different protons, each slightly different from the other. This also results in a lack of the resolution for the NMR spectrum.

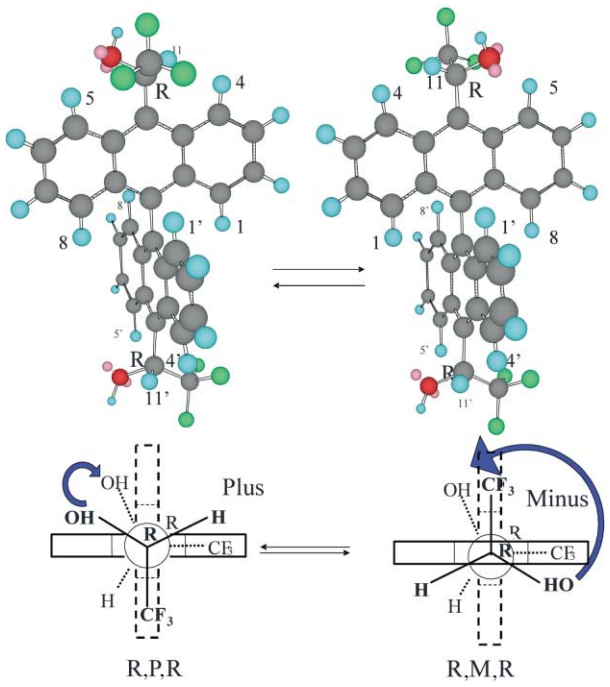
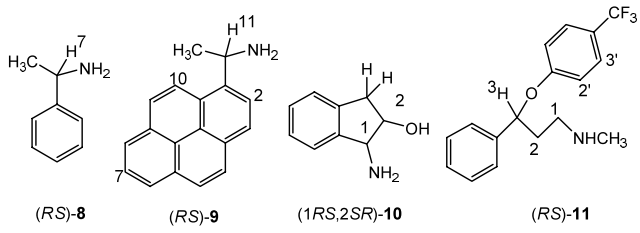


Figure 4. Frontal and vertical views of the conformational equilibrium of (*R*,*R*)-**2**.



Scheme 2. Chiral substrates analyzed in the tests of the behavior of **2** as CSA.

3. Enantiorecognition activity

The behavior of **2** as a chiral solvating agent was tested with the compounds described in Scheme 2. The following racemic substrates were used: 1-phenylethylamine **8**, 1-(1-pyrenyl)ethylamine **9**, *cis*-1-amino-2-indanol **10** and fluoxetine **11**. In all cases, the presence of a basic point and an aromatic ring allows the formation of an intermolecular hydrogen bond and a π/π stacking stabilization interaction.

Although both enantiomers of **2** are used, as the behaviors are symmetrical against the same racemic mixture, the results are always referred to those obtained when the (*S*,*S*)-**2** enantiomer is used. Given its structural relation, parallel experiments were obtained using Pirkle's alcohol[5] **3** that is a very useful CSA. The experiments were carried out in $CDCl_3$, adding portions of the CSA to a solution (0.04–0.05M) of racemic substrate until a maximum differentiation of the corresponding enantiomer's signals was obtained. The identification of signals of each enantiomer was reached using mixtures enriched in one of the enantiomers with a known composition. The integration of the separated signals affords the enantiomeric identity.

Enantiodifferentiation of **8** is observed for H_7, appearing as two quartets, one for each enantiomer [(*R*)-**8** at lower frequency]. Figure 5 shows the chemical shift variation of H-7 in **8** when several portions of (*S*,*S*)-**2** or (*S*)-**3** were added. Figure 6 shows the graphic difference between the enantiomers. As can be seen, comparing the results of both CSA's, the use of **2** affords lower shifting of signals for each enantiomer if alcohol **3** is used. However, a similar distinction exists between the signals of the two enantiomers using both chiral agents **2** and **3**. Moreover, while the effect of **3** seems to reach a plateau, the addition of **2** further increases the difference after the addition of 2.4 equiv. For similar equilibrium constants, it means that the two diastereoisomeric complexes of association show greater differences in the case of the use of the new compound **2**.

The distinction of enantiomers of 1-(1-pyrenyl)-ethylamine **9** was principally produced in the aromatic protons H_2, H_7, H_9, H_{10}, in H_{11} and in the methyl group. As most of the aromatic part of the spectrum

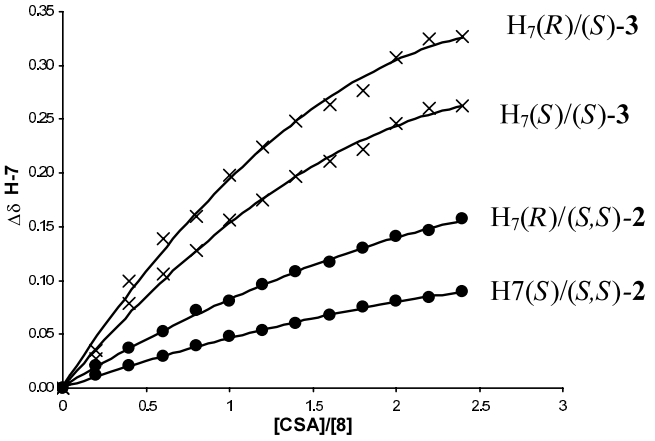


Figure 5. Evolution of the chemical shift of H_7 of enantiomers of 1-phenylethylamine **8** when portions of α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol [(*S*,*S*)-**2**] or Pirkle's alcohol (*S*)-**3** were added.

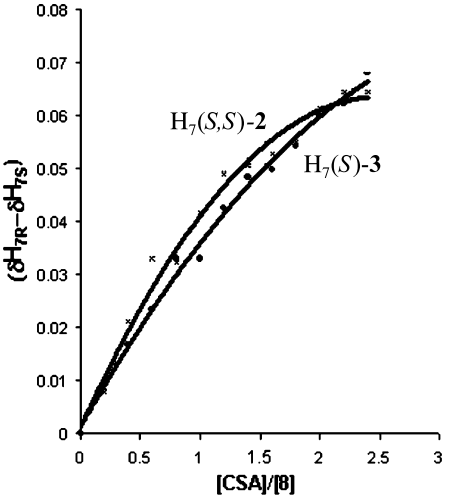


Figure 6. Evolution of the difference of the chemical shift of H_7 [$\delta H_7(R) - \delta H_7(S)$] of enantiomers of 1-phenylethylamine **8** when portions of (*S*,*S*)-α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol (*S*,*S*)-**2** or Pirkle's alcohol (*S*)-**3** were added.

becomes a complex broad signal, only the evolution of last three signals could be quantified. The maximum separation obtained was observed after the addition of 2 equiv. of **2** and was 0.023 ppm for H_{10}, 0.009 ppm for CH_3 and 0.016 ppm for H_{11}. The differentiation of the bencilic protons of two enantiomers is much greater in the case of 1-phenylethylamine **8**. Possibly, the perpendicular disposition of two anthracene groups of α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol **2**, avoids the approximation of the extended and rigid coplanar distribution of four aromatic rings of the pyrenyl group of subtract **9**. That is, if an hydrogen bond is formed between the hydroxy and the amine groups of **2** and **9**, respectively, the second anthracene group (perpendicular to the first one) keeps shuns the parallelism of aromatic parts eluding the π,π-stacking interaction.

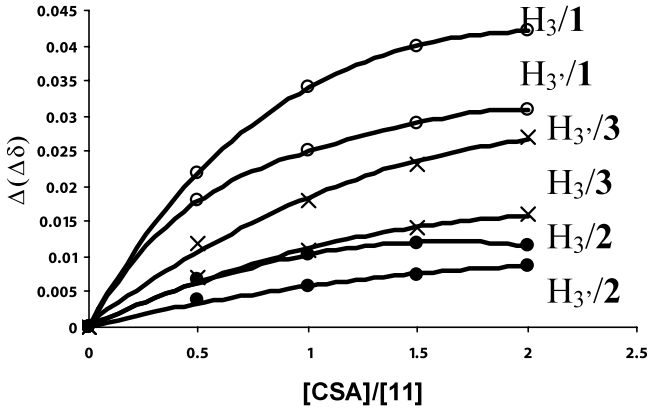


Figure 7. Evolution of the enantiodifferentiation of H_3 and $H_{3'}$ of fluoxetine **11** when (*S*,*S*)-**2**, (*S*)-**3** or (*S*,*S*)-**1** were added.

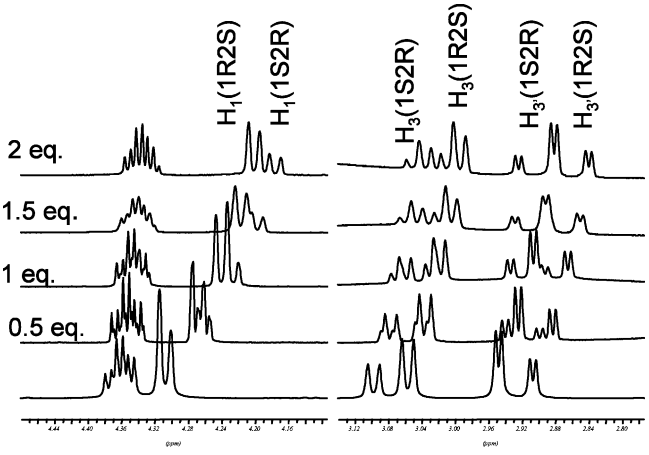


Figure 8. Aliphatic part of ^1H NMR spectrum of the enantiodiscrimination process of a mixture 3/1 of (1*R*,2*S*)- and (1*S*,2*R*)-*cis*-1-amino-2-indanol **10** by the addition of portions of 0.5 equiv. of (*S*,*S*)-α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol **2**.

Although most of the fluoxetine protons **11** are differentiated, only H_3, $H_{3'}$ and the methyl group could be measured. Figure 7 shows the ability of compound **2** to separate by NMR the H_3 and $H_{3'}$ of enantiomers of fluoxetine **11** and is compared with the always improved separation using bis(trifluoromethyl)-9,10-anthracenedimethanol **1**. The use of Pirkle's alcohol **3** allows a better separation of H_3 and the action on $H_{3'}$ is similar. The methyl group is not moved by **3** while, after the addition of two equivalents of **2**, the methyl group signals of each enantiomer could be easily integrated since are separated 0.01 ppm.

Figure 8 shows the aliphatic part of the ^1H NMR spectra of a mixture of the enantiomers of *cis*-1-amino-2-indanol **10** in a molar relation (1*R*,2*S*)/(1*S*,2*R*) of 3/1 when portions of entitled compound **2** were added. We can observe the doubling of all signals with a good resolution that also would allow a good integration

Table 1. Values of the enantiodiscrimination observed on several protons of *cis*-1-amino-2-indanol **10** when parts of 0.5 equiv. of (*S*)-**3** or (*S*,*S*)-**2** were added

Proton	CSA (subtract)	(*S*)-**3** Δ(Δδ) (ppm)	(*S*,*S*)-**2** Δ(Δδ) (ppm)
$H_{3'}$	0.5	0.015	0.016
	1	0.027	0.027
	1.5	0.037	0.037
	2	0.042	0.042
H_3	0.5	0.006	0.005
	1	0.013	0.010
	1.5	0.013	0.013
	2	0.013	0.015
H_1	0.5	0	0.07
	1	0.010	0.014
	1.5	0.015	0.020
	2	0.018	0.026

The comparison with the results obtained using Pirkle's alcohol are shown in Table 1 where the difference obtained after the addition of portions of 0.5 equivalents is reproduced for the two chiral agents (*S*,*S*)-**2** and (*S*)-**3**. In his case the behavior of both agents is very similar.

The stoichiometry of the complex was measured using Job[12] methodology obtaining in all cases a molar relation 1:1.

NMR is one of the most widely used techniques[13] for measuring Ka in the chemistry of associated compounds. In our case, the equimolar method[14] was applied to measure the binding constant of the association[15] of the CSA **2** with compounds **8** and **10**. In all cases, the degree of association[16] was kept at between 40 and 70% and, to avoid the presence of competitive processes, the pure enantiomers were used. Several solutions of identical concentration of substrate and solvating agent were analyzed at several temperatures. Plotting (Fig. 9) the variation of the ^{1}H NMR chemical shift ($\Delta\delta$) of H_7 of **8** in front of the square root of the relation between the changes of chemical shift versus concentration ($(\Delta\delta/S)^{0.5}$), yielded straight lines. These lines converge and intercept the abscissa where we obtained the chemical shift of the H_7 in the complex (4.335 and 4.225 for H_7(R) and H_7(S), respectively, from 4.100 of free molecule). From the scope we found the equilibrium constant value at several temperatures.

Table 2 shows the equilibrium constants (and the standard error) obtained for the association of the (*R*)- and (*S*)-1-phenylethylamine **8** with (*S*,*S*)-α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol **2** at three temperatures. It is obtained by measuring the variation of chemical shift of H_7 protons of each enantiomer. The similarity of the measured constants implies a very near thermodynamic behavior. This could be interpreted as the occurrence of the enantiodifferentiation thanks to the differential magnetic properties of each associate species. Therefore, the geometry of two diastereomeric

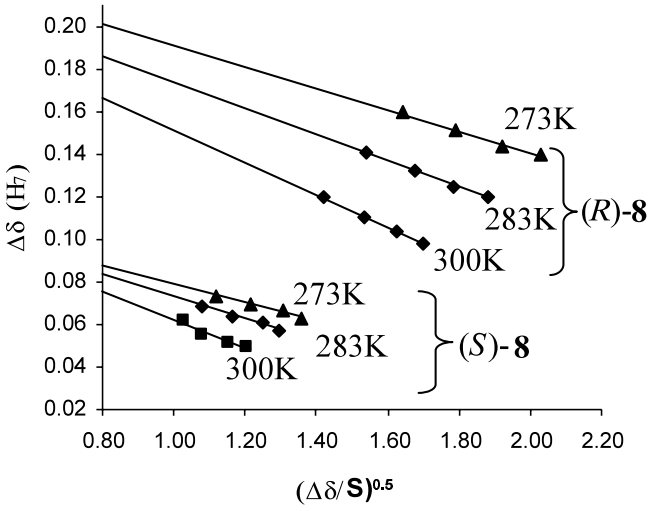


Figure 9. Measurement of the binding constant of the association of (*R*)- and (*S*)-1-phenylethylamine **8** with (*S*,*S*)-α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol **2** by the equimolar method at three temperatures.

Table 2. Binding constant (and the standard error) of the complex formation between each enantiomer of 1-phenylethylamine **8** and (*S*,*S*)-α,α′-bis(trifluoromethyl)-10,10′-(9,9′-bianthryl)dimethanol **2**

T (K)	(*R*)-**8**+(*S*,*S*)-**2**		(*S*)-**8**+(*S*,*S*)-**2**	
	K (M^{-1})	Δ*G*° (kJ/mol)	K (M^{-1})	Δ*G*° (kJ/mol)
298	39.2±20.8	−9.1±1.4	28.6±12.0	−8.4±1.1
283	61.8±6.9	−9.7±0.3	45.9±6.0	−9.0±0.3
268	95.1±12.85	−10.1±0.3	66.3±15.2	−9.3±0.5

complexes is enough different to distinguish the two enantiomers. Only when the temperature decreases the difference between binding constants increase. A significant difference in the proportions of the complex could be responsible for the increment in the value of the enantiodiscrimination.

In the case of the aminoindanol **10**, we obtained the constants measuring the chemical shifts on protons H_1, H_3 and $H_{3'}$ obtaining (the mean value) lower values and quite similar for two isomers: $K_{RS}=6.9$ and $K_{SR}=4.4$. Considering that the enantiodiscrimination is so good, newly, the different geometry of the approximation of the two components is the responsible for the enantiodistinction phenomenon.

We can conclude that compound **2** is an active chiral solvating agent, with a similar behavior to the Pirkle's alcohol **3**. Possibly, the distance between the two stereogenic and active centers of association is too high for a common action. Moreover, in some cases, the relative position of two anthracene rings obstructs a correct approximation of two components of complex. Possibly, the use of compound **2** will improve the separation of enantiomers with a complementary three-dimensional structure.

4. Experimental

NMR spectra were recorded at 400.13 and 500.13 MHz for ^{1}H. The temperature was controlled to 0.1°C. Chemical shifts are reported in parts per million relative to internal TMS. The complete identification of the NMR signals was carried out with the aid of several 1D (NOE) and 2D (COSY, HMQC and HMBC) spectra.

The NMR titration method was carried out with 0.4–0.5 ml of a solution 0.03–0.05 M of the compound **8** to **11**. After addition (at constant volume) of several portions of 0.2–0.5 equiv. of CSA **2**, NMR spectra were measured and the variations of the chemicals shifts calculated for each addition. The measures were continued until a maximum enantiodiscrimination (1.5–2.5 equiv.). The comparative experiments were carried out in identical conditions.

Binding constants were determined (equimolar method) by measuring chemical shifts of an equimolar solution in $CDCl_3$ of each compound **8** or **10** and the corresponding chiral solvating agent **2**. From 0.5 ml of an initial concentration of 0.06 M of each and after four additions of 0.1 ml of solvent we obtained four values of chemical shift correlated to the corresponding concentration. In the case of compound **8**, the measures were carried out at three temperatures after each dilution. Chiral semipreparative HPLC was carried out using a (*R*,*R*)-Whelk-O1 (250 mm×10 mm) column and a preparative HPLC using a (*R*,*R*)-Whelk-O2 (250 mm×25 mm) column.

4.1. 1-(9-Anthryl)-2,2,2-trifluoroethanol

To a solution of anthracene (1.50 g, 8.4 mmol) in anhydrous CH_2Cl_2 (75 ml) and in a stream of N_2, $BF_3{\cdot}Et_2O$ (5.0 ml, 40 mmol) and trifluoroacetaldehyde ethyl hemiacetal (3.0 ml, 26 mmol) were added. The mixture was stirred at rt for 3.5 h. The mixture was treated with ice cold water and diluted sulfuric acid and extracted with CH_2Cl_2 The organic layer was washed with water and dried with anhydrous Na_2SO_4. After evaporation of the solvent under vacuum, the residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 8/2) giving 1-(9-anthryl)-2,2,2-trifluoroethanol (2.10 g, 90%).

4.2. 10,10′-Bis(trifluoroacetyl)-9,9′-bianthracenyl 6

10,10′-Dibromo-9,9′-bianthracenyl **5** (0.38 g, 0.75 mmol) was dissolved in dried diethyl ether (20 ml) under inert conditions. At rt, butyllithium (1.26 ml, 1.6 M in hexane) was slowly added. At −78°C The mixture was stirred for 1.5 h and a solution of trifluoroacetic anhydride (0.85 ml, 7.50 mmol in 10 ml of diethyl ether) was added. After 2 h, the reaction was quenched and the resultant brown liquid was washed with a saturated solution of NH_4Cl (2×50 ml), a solution of 10% NaOH (2×50 ml), and finally water (2×50 ml). After dried and evaporated, the solid residue was purified by column chromatography on silica gel (hexane/dichloromethane 90/10) giving 0.14 g (0.26 mmol, 30%) of a yellow 10,10′-bis(trifluoroacetyl)-9,9′-bianthracenyl **6**. Mp: decompose. EM *m*/*z* (%): 546 (M, 27), 477 (100), 450 (17), 380 (52), 350 (43),204 (33), 175 (52). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.86 (d, $J_{4,5/3,6}=8.52$ Hz, 4H, H_4, $H_{4'}$, H_5 and $H_{5'}$), 7.57 (m, 4H, H_3, $H_{3'}$, H_6 and $H_{6'}$), 7.24 (m, 4H, H_2, $H_{2'}$, H_7 and $H_{7'}$), 7.10 (d, $J_{1,8/2,7}=8.80$ Hz, 4H, H_1, $H_{1'}$, H_8 and $H_{8'}$)

4.3. α,α′-Bis(trifluoromethyl)-10,10′-(9,9′-bianthracenyl)-dimethanol 2

4.3.1. Method A. A diethyl ether solution (20 ml) of 10,10′-bis(trifluoroacetyl)-9,9′-bianthracenyl **6** (0.60 g, 1.10 mmol) was slowly added to a diethyl ether slurry (10 ml) of $LiAlH_4$ (60 mg, 1.65 mmol) and kept under N_2 with continuous stirring at rt. After 2 h, reduction was completed. The reaction was quenched with water and the organic layer was separated, dried, and concentrated. The solid residue was purified by column chromatography on silica gel (hexane/dichloromethane 1/1 v/v) to give a white product **2** (0.42 g, 69% yield).

4.3.2. Method B. At rt and under inert conditions 1.43 ml (11.28 mmol) of $BF_3{\cdot}Et_2O$ was slowly added to a solution of 9,9′-bianthracenyl **4** (0.208 g, 0.59 mmol) in 15 ml of CH_2Cl_2 containing 0.26 ml (2.26 mmol) of trifluoroacetaldehyde ethyl hemiacetal. After 72 h, the reaction was quenched with ice/HCl, treated with CH_2Cl_2 and the organic phase was dried and evaporated. The yellow crude was purified by column chromatography on silica-gel (hexane/CH_2Cl_2 1:1) yielding 0.262 g (0.47 mmol, 81%) of **2**. Mp: decompose. IR (KBr) cm^{-1}: 3370 (O–H, broad), 1447 (m), 1262 (s), 1165 (s), 1127 (s), 1097 (s), 1036 (m), 877 (w), 768 (s). UV λ_{max} (nm) (CH_2Cl_2): 240, 340, 358. EM *m*/*z* (%): 550 (M,100), 481 (78), 463 (38), 435 (22), 354 (36), 206 (82), 175 (46). ^{1}H NMR ($CDCl_3$, $T=300$ K, 400 MHz) δ (ppm): 9.31 (broad, 2H, H_5 and $H_{5'}$), 8.58 (broad, 2H, H_4 and $H_{4'}$), 7.52 (broad, 4H, H_3, $H_{3'}$, H_6 and $H_{6'}$), 7.20 (broad, 4H, H_2, $H_{2'}$, H_7, $H_{7'}$), 7.05 (q, $J_{11/F}=7.92$ Hz, 2H, H_{11}, $H_{11'}$), 7.00 (broad, 4H, H_1, $H_{1'}$, H_8 and $H_{8'}$), 6.60 (d, $J_{OH/H11}=4.72$ Hz, 2H, OH and OH′). ^{1}H NMR (CD_3COCD_3, $T=270$ K, 400 MHz) δ (ppm): 9.33 (d, $J_{5/6}=J_{5'/6'}=9.08$ Hz, 2H, H_5 and $H_{5'}$), 8.61 (d, $J_{4/3}=J_{4'/3'}=9.40$ Hz, 2H, H_4 and $H_{4'}$), 7.60 (m, 2H, H_3 and $H_{3'}$) 7,52 (m, 2H, H_6 and $H_{6'}$), 7.21 (m, 4H, H_2, $H_{2'}$, H_7 and $H_{7'}$), 7.08 (q, $J_{11/F}=8.20$ Hz, 2H, H_{11} and $H_{11'}$), 7.00 (m, 2H, H_1 and $H_{1'}$), 6.93 (m, 2H, H_8 and $H_{8'}$), 6.88 (d, $J_{OH/H11}=5.88$ Hz, 2H, OH and OH′). ^{13}C NMR (CD_3COCD_3, $T=270$ K, 100 MHz) δ (ppm): 70.44 (C_{11} and $C_{11'}$), 125.23 (C_4 and $C_{4'}$), 126.47, 129.29 (C_9 and $C_{9'}$), 126.69, 126.75 (C_6 and $C_{6'}$), 127.02, 127.38 (C_2 and $C_{2'}$), 127.18 and 127.22 (C_7 and $C_{7'}$), 128.03, 128.09 (C_8 and $C_{8'}$), 128.41, 128.48 (C_3 and $C_{3'}$), 128.71, 128.77 (C_1 and $C_{1'}$), 130.11 (C_5 and $C_{5'}$), 132.02, 132.06, 132.11, 132.15 (C_{4a}, $C_{4a'}$, C_{10a} and $C_{10a'}$), 132.27, 132.32 (C_{9a} and $C_{9a'}$), 132.99, 133.04 (C_{8a} and $C_{8a'}$), 137.53 (C_{10} and $C_{10'}$).

Since the signals of the ^{1}H and ^{13}C NMR spectra are broad the spectrum corresponding to each isomer appears indistinguishable from those of the mixture.

The pure enantiomers are obtained after hydrolysis of the isolated acetate derivatives **7**
(*S*,*S*)-**2**: $[\alpha]_D^{25} = +7.3$ (*c* 2.2, CH_2Cl_2)
(*R*,*R*)-**2**: $[\alpha]_D^{25} = -7.3$ (*c* 2.2, CH_2Cl_2)
meso-**2**: $[\alpha]_D^{25} = 0.0$ (*c* 2.2, CH_2Cl_2)

4.4. α,α′-Bis(trifluoromethyl)-10,10′-(9,9′-bianthracenyl)-dimethyl diacetate 7

To a solution of **2** (0.59 g, 1.13 mmol) in dichloromethane (60 ml) was added 0.055 g of (dimethylamino)pyridine (DMAP) (0.45 mmol), 2.19 ml of triethylamine (15.83 mmol) and 0.80 ml of acetyl chloride (11.31 mmol). After 2 h, the reaction was finished and the mixture was washed with water (2×50 ml), HCl 1 M (2×50 ml), and a solution of 10% $NaHCO_3$ (2×50 ml). The organic layer was separated, dried and concentrated. The solid residue was purified by chromatography on silica gel (hexane/dichloromethane 1/1 v/v) to give a pale yellow product (71% yield). Mp: 311–314°C. Anal. calcd for $C_{36}H_{24}F_6O_4$: C, 68.14%; H, 3.81%. Found: C, 68.10%; H, 3.98%. IR (KBr) cm^{-1}: 2958 (w), 1758 (s), 1448 (w), 1370 (w), 1272 (m), 1217 (s), 1176 (s), 1133 (s), 1077 (m), 1040 (m), 943 (w), 765 (s). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.88 (d, $J_{5/6} = 8.80$ Hz, 2H, H_5 and $H_{5'}$), 8.50 (d, $J_{4/3} = 8.80$ Hz, 2H, H_4 and $H_{4'}$), 8.01 (q, $J_{11/F} = 7.92$ Hz, 2H, H_{11} and $H_{11'}$), 7.59 (broad, 2H, H_3 and $H_{3'}$), 7.52 (broad, 2H, H_6 and $H_{6'}$), 7.15 (broad, 4H, H_2, $H_{2'}$, H_7 and $H_{7'}$), 7.05 (m, 4H, H_1, $H_{1'}$, $H_{8,}$ and $H_{8'}$), 2.30 (s, 6H, CH_3 and $CH_{3'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 169.01 (C=O), 137.38 (C_9 and $C_{9'}$), 131.53, 131.16, 130.54 and 130.94 (C_{4a}, $C_{4a'}$, C_{8a}, $C_{8a'}$, C_{9a}, $C_{9a'}$, C_{10a} and $C_{10a'}$), 127.99 (C_3 and $C_{3'}$), 127.64 (C_1, $C_{1'}$, C_8 and $C_{8'}$), 126.64 (C_5 and $C_{5'}$), 126.29 (C_6 and $C_{6'}$), 125.67 (C_2, $C_{2'}$, C_7 and $C_{7'}$), 122.84 (C_{10} and $C_{10'}$), 122.28 (C_4 and $C_{4'}$), 69.08 (C_{11} and $C_{11'}$), 20.76 (CH_3 and CH_3').

Isomers (*R*,*R*)-**7**, *meso*-**7** and (*S*,*S*)-**7** were obtained by chiral HPLC (Welch-O1) using hexane/2-propanol 93/7. $\lambda = 290$ nm, flow 2.8 ml/min. $K_{RR} = 2.10$, $K_{meso} = 3{,}05$ and $K_{SS} = 4.80$
(*R*,*R*)-**5**: $[\alpha]_D^{25} = -50.5$ (*c* 1.9, CH_2Cl_2)
(*S*,*S*)-**5**: $[\alpha]_D^{25} = +50.5$ (*c* 1.9, CH_2Cl_2)

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