A Circular Dichroism Approach to the Conformation of 1-Arylethylamino-Substituted 1,3,5-Triazine Derivatives

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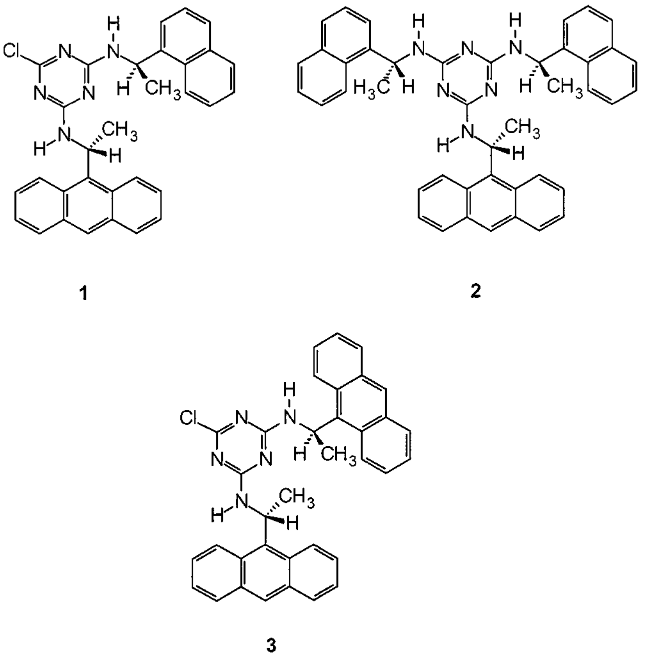
CD data of the optically pure 2-[(*R*)-1-(9-anthryl)ethylamino]-4-chloro-6-[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine, 2-[(*R*)-1-(9-anthryl)ethylamino]-4,6-bis[(*R*)-1-(1-naphthyl)-ethylamino]-1,3,5-triazine, 2,4-bis[(*R*)-1-(9-anthryl)ethylamino]-6-chloro-1,3,5-triazine are presented. The analysis of the CD spectra by means of the nonempirical DeVoe approach has afforded the complete conformational characterisation of the three *s*-triazine derivatives, allowing us to establish how the conformation of these derivatives depends on the nature of the substituent 1-arylethylamino groups.

Introduction

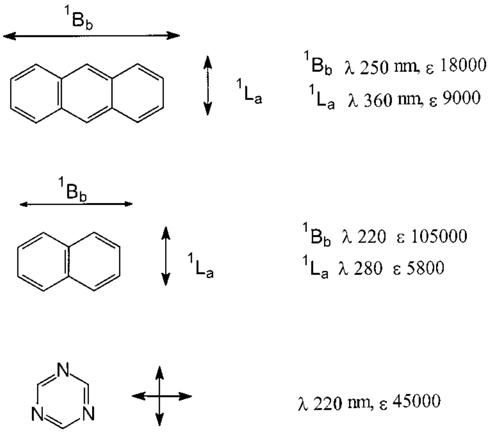
Circular dichroism (CD) spectroscopy has recently proven to be a powerful technique for determining the prevailing conformation assumed in solution by optically active bis- and tris[1-(1-naphthyl)ethylamino]-substituted *s*-triazine derivatives,[1] an attractive class of chiral solvating agents for NMR spectroscopy.[2] The CD spectra of these derivatives are dominated by the exciton coupling of the ^1B_b transition of the naphthalene chromophores with the electrically allowed transition of the *s*-triazine chromophore; the contribution of each moiety to the CD absorption is additive, the trisubstituted derivative showing a threefold amplitude of the triazine-naphthalene exciton couplet with respect to the monosubstituted derivative.[1] On the basis of the analysis of the CD spectra by the nonempirical DeVoe approach it was possible to establish that each 1-(1-naphthyl)ethylamino moiety assumes the same closed conformation with respect to the *s*-triazine aromatic ring (dihedral angle naphthalene-triazine $< 90°$) independently of the number or absolute configuration of the other 1-(1-naphthyl)ethylamino groups linked to the *s*-triazine moiety.[1]

In order to check how the conformation of the 1-arylethylamino-substituted *s*-triazine derivatives depends on the steric hindrance exerted by the 1-arylethylamino groups we have prepared the *s*-triazine derivatives **1**, **2** and **3** (Scheme 1) which possess the 1-(9-anthryl)ethylamino moiety, the aryl group of which has a different size than the 1-naphthyl one.

The study of the conformation of these derivatives can be undertaken by means of CD spectroscopy, because the anthracene moiety, as well as the naphthalene and the *s*-triazine groups, possesses electrically allowed electronic transitions[3,4] (Scheme 2). These transitions can give rise in



Scheme 1



Scheme 2

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the CD spectrum of **1**, **2** and **3** to exciton couplets,[5] the sign and intensity of which can be related, as in the case of the 1-(1-naphthyl)ethylamino-substituted *s*-triazine derivatives, to the orientation of the transition dipole moments of the interacting chromophores and, therefore, to the relative disposition of the aryl moieties in the molecular structure.[5]

Results and Discussion

The synthesis of the *s*-triazine derivatives **1**, **2** and **3** was performed by means of the nucleophilic displacement of the chlorine atoms of *s*-trichlorotriazine using optically pure (*R*)-1-(9-anthryl)ethylamine[6] and (*R*)-1-(1-naphthyl)ethylamine. All the nucleophilic displacements were carried out under solid-liquid phase-transfer conditions, with Na_2CO_3 as a base and 18-crown-6 as the phase-transfer catalyst.[7] According to this method the disubstituted derivative **1** was obtained by treating *s*-trichlorotriazine with an equimolar amount of (*R*)-1-(1-naphthyl)ethylamine and Na_2CO_3 in the presence of a catalytic amount of 18-crown-6 at 0 °C until complete conversion into the monosubstituted derivative was obtained; successive addition, to the same reaction mixture, of an equimolar amount of (*R*)-1-(9-anthryl)ethylamine and Na_2CO_3 gave, after four days reaction at room temperature, the derivative **1** in nearly quantitative yield. The disubstituted derivative **3** was prepared by treating *s*-trichlorotriazine with a twofold excess of (*R*)-1-(9-anthryl)ethylamine and Na_2CO_3 in the presence of a catalytic amount of 18-crown-6 at room temperature. The trisubstituted derivative **2** was synthesised by adding an equimolar amount of (*R*)-1-(9-anthryl)ethylamine and Na_2CO_3 in the presence of 18-crown-6 to the reaction mixture containing the bis[1-(1-naphthyl)ethylamino]-substituted *s*-triazine derivative, prepared in the same way as **3**, and heating to reflux in acetonitrile. All the compounds were purified by column chromatography or recrystallization; structural assignments were carried out by NMR spectroscopy and mass spectrometry.

The UV spectrum of **1** (Figure 1) shows two medium intensity absorption bands at 360 nm and 280 nm endowed with a complex vibrational structure, attributable to the ^1L_a transition of the anthracene chromophore[3] and to the ^1L_a transition of the naphthalene chromophore, respectively.[3] Two more intense bands are recorded at shorter wavelengths, the first one at 250 nm ($\varepsilon = 100000$), assignable to the ^1B_b transition of the anthracene chromophore[3] and a second one at 220 nm ($\varepsilon = 90000$), due to the sum of the ^1B_b transition of the naphthalene chromophore and the electrically allowed transition of the *s*-triazine chromophore.[4] The CD spectrum exhibits two positive Cotton effects at 360 ($\Delta\varepsilon = 5$) and 280 nm ($\Delta\varepsilon = 20$), a strong negative Cotton effect at 250 nm ($\Delta\varepsilon = -60$), a negative band at 230 nm ($\Delta\varepsilon = -5$) and an intense positive Cotton effect at 220 nm ($\Delta\varepsilon = 80$).

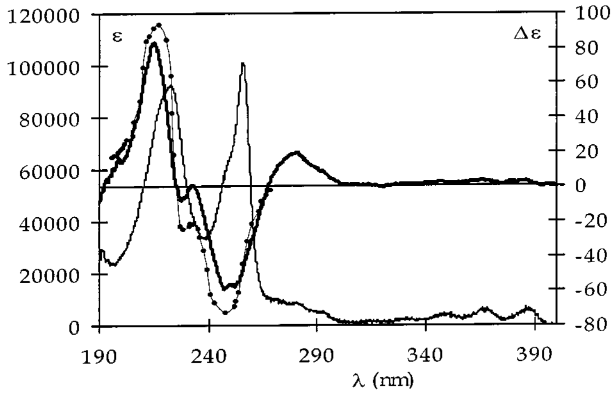

Figure 1. Absorption (solid line), experimental (bold line) and calculated (• • •) CD spectra of 2-[(*R*)-1-(9-anthryl)ethylamino]-4-chloro-6-[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (**1**); experimental spectra were recorded in acetonitrile solution

By comparing this spectrum with the CD spectra of the mono[(*R*)-1-(9-anthryl)ethylamino] derivative[6b] and the mono[(*R*)-1-(1-naphthyl)ethylamino] derivative,[1] shown in Figure 2, we can see that the CD spectrum of **1** is the sum of the CD spectra of the two different monosubstituted derivatives. In fact, the Cotton effects at 280 and 360 nm in the spectrum of **1** correspond perfectly to those found in the CD spectra of the two mono derivatives: the negative Cotton effect at 250 nm corresponds to the first component of the exciton couplet present in the spectrum of the mono[1-(9-anthryl)ethylamino]-substituted *s*-triazine derivative, due to the exciton couplet of the ^1B_b transition of the anthracene chromophore with the electrically allowed transition of the *s*-triazine chromophore,[6b] and the positive band at 210 nm corresponds to the second component of the exciton couplet naphthalene–triazine present in the CD spectrum of the mono-1-(1-naphthyl)ethylamino-substituted *s*-triazine derivative.[1]

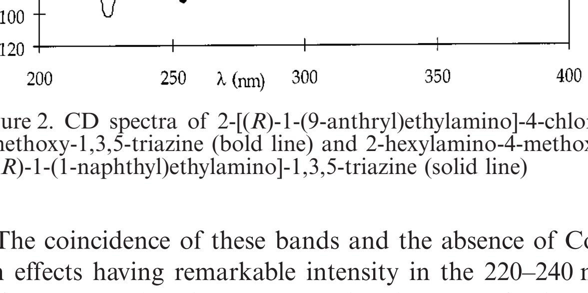

Figure 2. CD spectra of 2-[(*R*)-1-(9-anthryl)ethylamino]-4-chloro-6-methoxy-1,3,5-triazine (bold line) and 2-hexylamino-4-methoxy-6-[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (solid line)

The coincidence of these bands and the absence of Cotton effects having remarkable intensity in the 220–240 nm region suggest that the two strong bands present in the CD spectrum of **1** are the visible components of two exciton couplets, the first one due to a coupling between the ^1B_b

transition of the anthracene chromophore with the electrically allowed transition of the *s*-triazine aromatic ring, and the second one due to a similar naphthalene–*s*-triazine coupling. The second component of the first couplet and the first Cotton effect of the second couplet are not detectable because they have the same position in the CD spectrum (as clearly seen in the CD spectra of the two different monosubstituted derivatives) and opposite sign: therefore they are mutually cancelled, the weak negative Cotton effect at 230 nm being the only trace of their presence. The observation that the CD spectrum of **1** is, in practice, the sum of the CD spectra of the two different monoarylethylamino derivatives suggests that the ^1B_b transitions of the anthracene and naphthalene chromophores are not coupled between each other and the dichroic absorptions are only due to pairwise interactions between each substituent aryl chromophore and the *s*-triazine chromophore. Furthermore, given that the amplitude of the split-type Cotton effects depends on the dihedral angle between the transition dipole moments of the interacting chromophores,[5] the reciprocal orientation of each aryl moiety with respect to the *s*-triazine ring in derivative **1** must be very similar to the conformation assumed by the same aryl group in the corresponding monosubstituted derivative. This also means that each 1-arylethylamino moiety of compound **1** assumes a conformation very similar to that of the same substituent in the corresponding monosubstituted derivative.

Similar conclusions can also be drawn for compound **2**. The UV spectrum of this derivative (Figure 3) shows the typical absorption pattern of anthracene and naphthalene chromophores; in fact, two bands endowed with a complex vibrational structure are present at 360 nm ($\varepsilon = 10000$) and at 280 nm ($\varepsilon = 10000$), attributable to the ^1L_a transitions of the anthracene and naphthalene chromophores,[3] respectively, and two intense bands at 250 nm ($\varepsilon = 100000$) and at 220 nm ($\varepsilon = 140000$), the first one due to the ^1B_b transition of the anthracene chromophore[3] and the second one to the sum of the ^1B_b transition of the naphthalene chromophore[3] and the electrically allowed transition of the *s*-triazine ring.[4] The CD spectrum (Figure 3) shows a positive Cotton effect at 280 nm ($\Delta\varepsilon = +20$), a negative one at 255 nm ($\Delta\varepsilon = -50$) and two more intense Cotton effects having opposite sign at 230 nm ($\Delta\varepsilon = -150$) and at 210 nm ($\Delta\varepsilon = +140$).

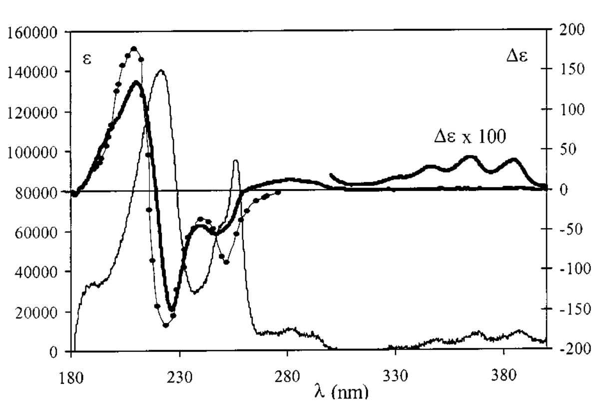

Figure 3. Absorption (solid line), experimental (bold line) and calculated (• • •) CD spectra of 2-[(*R*)-1-(9-anthryl)ethylamino]-4,6-bis[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (**2**); experimental spectra were recorded in acetonitrile solution

These CD data can be interpreted on the basis of a comparison with the CD spectra of the mono (*R*)-1-(9-anthryl)ethylamino derivative[6b] and the bis[(*R*)-1-(1-naphthyl)ethylamino] derivative.[1] This last compound showed an exciton couplet centred at 220 nm due to pairwise interaction between each naphthalene chromophore and the *s*-triazine chromophore; a naphthalene–naphthalene coupling was not observed in this spectrum.[1] The curve obtained by summing the CD spectra of the mono[1-(9-anthryl)ethylamino] and the bis[1-(1-naphthyl)ethylamino] derivatives is reported in Figure 4, along with the experimental CD spectrum of **2**.

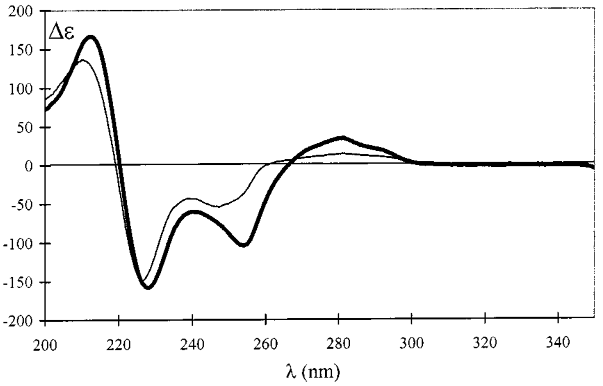

Figure 4. CD spectrum of **2** (solid line), and sum of the CD spectra of 2-[(*R*)-1-(9-anthryl)ethylamino]-4-chloro-6-methoxy-1,3,5-triazine and 2-chloro-4,6-bis[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (bold line)

The high similarity of the curves indicates the CD spectrum of **2** is due to a superimposition of two exciton couplets, the first one between the ^1B_b transition of the anthracene chromophore and the electrically allowed transition of the *s*-triazine ring, and the second one between the ^1B_b transition of each naphthalene group and the electrically allowed transition of the *s*-triazine chromophore. The additivity of the contributions of each group to the CD spectrum of **2** suggests that the substituent aryl chromophores do not interact between themselves, and that only pairwise interactions between the ^1B_b transition of the aromatic chromophores and the electrically allowed transition of the *s*-triazine ring are present. Of course, the conformation assumed by each substituent with respect the *s*-triazine ring in **2** must be very similar to the conformation assumed by the corresponding substituents in the mono[1-(9-anthryl)-ethylamino] derivative and bis[1-(1-naphthyl)ethylamino] derivative.

The additivity of the contributions of each 1-arylethylamino substituent to the CD spectrum of **1** and **2** suggests that a prevailing closed conformation of the substituent moieties with respect to the *s*-triazine ring must also be assumed in these cases, as was the case for the mono[1-(9-anthryl)ethylamino] and mono[1-(1-naphthyl)ethylamino] derivatives. Therefore, in order to obtain the prevailing conformation of **1** and **2** it would be sufficient to place their 1-arylethylamino moieties so that they have the same conformation as assumed in the corresponding mono[1-(9-anthryl)ethylamino] and mono[1-(1-naphthyl)ethylamino] derivatives, and in the bis[1-(1-naphthyl)ethylamino] derivative: it is worthy of note that although two conformations were present at room temperature for the mono[1-(9-anthryl)ethylamino] and the bis[1-(1-naphthyl)ethylamino] derivatives, the ^{1}H-NMR spectra of **1** and **2** show the presence of a single set of signals for each proton, indicating that a highly prevalent conformation is present, at room temperature, for these compounds.

In order to support the conclusions drawn from the qualitative analysis of the CD data, DeVoe calculations of the CD spectra were performed.[8] Molecular mechanics calculations[9] were carried out to obtain the minimum energy conformations which were used as starting geometries for the DeVoe calculations.[10] The molecular mechanics calculations performed placing the 1-(9-anthryl)ethylamino moiety in the conformation assumed in the most populated conformer of the mono[1-(9-anthryl)ethylamino] derivative, and the two 1-(1-naphthyl)ethylamino moieties of **2** in the conformation assumed in the most populated conformer of the bis[1-(1-naphthyl)ethylamino] derivative, afforded the minimum energy conformations depicted in Figure 5.

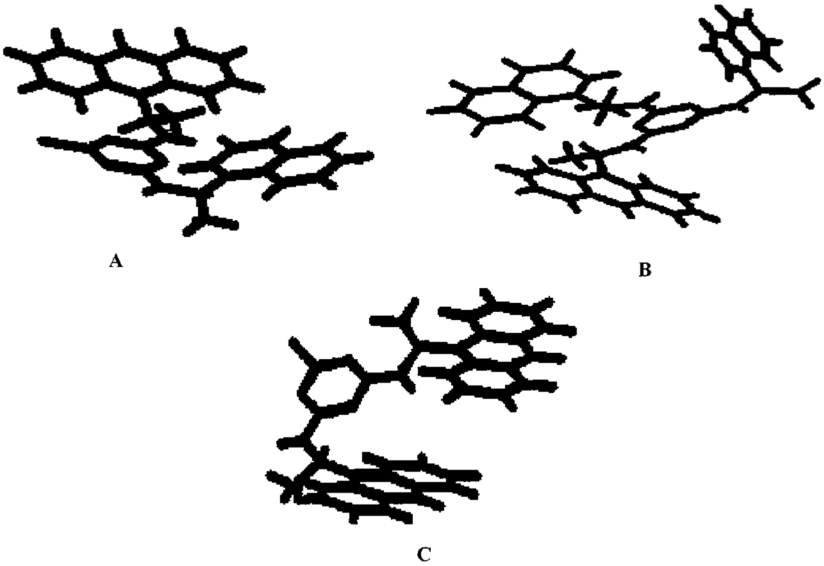

Figure 5. Minimum energy conformation of 2-chloro-4-[(*R*)-1-(9-anthryl)ethylamino]-6-[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (**1**) (A), 2-[(*R*)-1-(9-anthryl)ethylamino]-4,6-bis[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (**2**) (B) and 2,4-bis[(*R*)-1-(9-anthryl)ethylamino]-6-chloro-1,3,5-triazine (**3**) (C)

The calculated CD spectra for these conformations are in keeping with the experimental ones, as clearly shown in Figure 1 and Figure 2, indicating also that the 1-arylethylamino moieties of **1** and **2** assume a closed conformation with respect to the *s*-triazine ring. In order to confirm the lack of exciton couplings between the electronically allowed transitions of the substituent aryl chromophores, we performed DeVoe calculations on the minimum energy conformations of **1** and **2**, eliminating the *s*-triazine transition: CD-calculated spectra where any couplet-like feature was distinguishable were obtained in both cases, so confirming the above conclusions. On the basis of the minimum energy conformations obtained it is now clear why the electrically allowed transitions of the substituent aryl chromophores do not interact between themselves in compounds **1** and **2**. In fact, due to the conformation of the 1-arylethylamino moieties, the angles between the transition dipole moments of the aryl chromophores in **1** and **2** have values ranging between 87 and 92°, therefore the coupling between the substituent aryl chromophores is prevented.[5]

As far as derivative **3** is concerned, its UV spectrum (Figure 6) shows a medium intensity absorption band, endowed with a complex vibrational structure, centred at 360 nm ($\varepsilon = 20000$), attributable to the ^1L_a transition of the anthracene chromophores,[3] two more intense absorption bands at 260 nm ($\varepsilon = 170000$) and at 250 nm ($\varepsilon = 135000$) in the region of the absorption of the ^1B_b transition of the anthracene chromophores[3] and a less intense band at 225 nm ($\varepsilon = 45000$) attributable to the electrically allowed transition of the *s*-triazine chromophore.[4] Two intense Cotton effects are present in the CD spectrum of **3** (Figure 6), the first one at 260 nm ($\Delta\varepsilon = +290$) and the second one at 245 nm ($\Delta\varepsilon = -190$) together with a less intense positive Cotton effect at 220 nm ($\Delta\varepsilon = +50$).

The two opposite-signed intense Cotton effects are likely the two components of the exciton couplet centred at 250 nm, due to the coupling of the ^1B_b transition of the anthracene chromophores; this coupling is also detectable in the UV spectrum, the two absorption maxima at 260 and 250 nm being the two components. The presence of an exciton coupling between the ^1B_b transition of the anthracene chromophores makes this CD spectrum very different from the CD spectra of **1** and **2**, where no coupling between the transitions of the substituent aryl chromophores was detectable. This feature suggests that the conformation that the two substituent moieties assume with respect to the *s*-triazine ring must be different from the conformation assumed by the substituent moieties in the derivatives **1** and

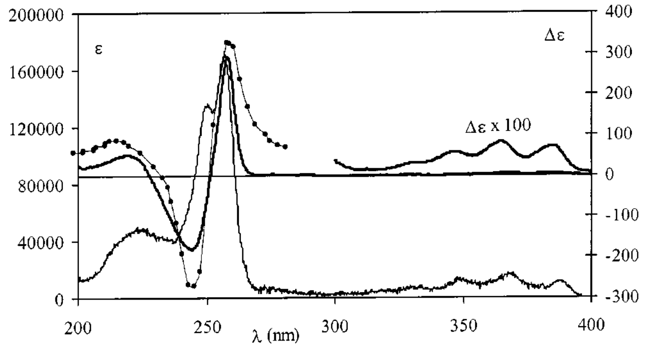

Figure 6. Absorption (solid line), experimental (bold line) and calculated (• • •) CD spectra of 2,4-bis[(*R*)-1-(9-anthryl)ethylamino]-6-chloro-1,3,5-triazine (**3**); experimental spectra were recorded in THF solution

2. Considering that the coupling of the anthracene chromophores produces a positive couplet, their relative disposition can be easily obtained taking into account the dipoles allied to the ^1B_b transitions which describe a right handed chirality.[5] Therefore, it would be sufficient to place the two 1-(9-anthryl)ethylamino moieties so that the ^1B_b transition dipole moments of the anthracene chromophores describe a right handed chirality. This interpretation of the experimental data can be confirmed, as was the case for **1** and **2**, by calculating the CD spectrum of **3** with the DeVoe model,[8,9] using as starting geometry a conformation in accordance with the above considerations, taking into account that the presence in the NMR spectrum of only one set of signals for each proton, at room temperature, indicates the existence of a highly prevalent conformation for this derivative. The minimum energy conformation of **3** was obtained by means of molecular mechanics calculations,[9] after placing the two 1-(9-anthryl)ethylamino moieties so that the anthracene chromophores describe a positive chirality, as previously discussed: the calculated CD spectrum, as shown in Figure 6, is in keeping with the experimental one indicating that the prevailing conformation assumed in solution by **3** is that one depicted in Figure 5. The two 1-(9-anthry)-ethylamino moieties do not assume the same conformation with respect to the *s*-triazine ring, whereas one of them has a closed conformation, the other one assumes an opened conformation (dihedral angle anthracene–triazine > 150°). Because of this molecular arrangement, the ^1B_b transition dipole moments of the anthracene chromophores are not perpendicular to each other and therefore they can give rise to an exciton couplet. In order to check if a triazine–anthracene coupling was present in the CD spectrum of **3**, we carried out DeVoe calculations on the minimum energy conformation of this derivative, eliminating the *s*-triazine transition: A calculated CD spectrum, identical to the experimental one, was obtained showing that no triazine–anthracene coupling is present in the CD spectrum of **3**. This looks very anomalous, as in the mono 1-(9-anthryl)ethylamino derivative a triazine–anthracene exciton couplet was present. In order to clarify this phenomenon DeVoe calculations were performed, initially on the *s*-triazine opened moiety and then on the *s*-triazine closed moiety. Two calculated CD spectra were obtained, showing the presence of a triazine–anthracene exciton couplet in both cases. These couplets have the same intensity, but they are opposite in sign, the *s*-triazine closed moiety affording a negative couplet and the *s*-triazine opened moiety a positive one. Therefore, the two anthracene chromophores are exciton coupled with the *s*-triazine chromophore, but these couplets are mutually cancelled and, hence, not detectable.

In conclusion, the study of the conformation of bis- and tris(1-arylethylamino)-substituted *s*-triazine derivatives by CD spectroscopy has allowed us to establish that the steric hindrance of the aryl moieties influences the conformation of this class of compounds. The 1-arylethylamino moieties assume a closed conformation as a general trend, unless this is prevented by the steric hindrance generated by bulky aryl groups. When only one 1-(9-anthryl)ethylamino moiety is present, even if together with other less bulky moieties, a closed conformation is highly prevalent; in contrast, the presence of two bulky moieties, which can sterically interact between themselves, gives rise to a different conformation of the *s*-triazine derivative.

Experimental Section

General: The ^{1}H- and ^{13}C-NMR spectra were recorded with a Varian Gemini 200 spectrometer operating at 200 MHz for ^{1}H and at 50 MHz for ^{13}C, using the TMS signal as internal standard; the temperature was controlled (± 0.1 °C) by means of the Varian control unity. The signal multiplicity is indicated as s (singlet), d (doublet), t (triplet), dd (double doublet), m (multiplet). – The ion spray mass spectra (IS-MS) were recorded with a triple quadrupole mass spectrometer Perkin–Elmer Sciex API III under the following experimental conditions: nebulizer potential 5.5KV, orifice potential 60 V, scan interval 200–800 Da, scan speed 32 ms/amu, resolution > 1 amu. The sample was dissolved in methanol (ca. 10^{-4} M) and the solution was analysed by means of Flow Injection Analysis, employing a Perkin–Elmer HPLC pump equipped with a Rheodyne 7125 injector and a 20 µL loop. – UV/Vis absorption spectra were recorded with a Perkin–Elmer Lambda 19 spectrophotometer with spectrophotometric-grade acetonitrile and THF and 0.1-mm path-length cells at 25 °C. – The circular dichroism spectra were recorded with a Jasco J-600 dichrograph with spectrophotometric-grade acetonitrile and THF and 0.1-mm path-length cells at 25 °C. Sample concentrations for UV and CD analysis were typically (6–9) × 10^{-4} M. – Melting points were measured with a Kofler–Reichert–Jung apparatus and are uncorrected. – Optical rotation measurements were performed with a Jasco DIP-360 digital polarimeter, using 1-dm path-length cells. – The CD calculations were performed by means of the program written by Hug et al.[11] whilst the molecular mechanics calculations were carried out by the MMX routine.[9] – THF was refluxed over Na/K alloy and distilled before use; acetonitrile was refluxed over CaH_2 and distilled before use. (*R*)-1-(9-Anthryl)ethylamine was prepared according to the Kuhn and Buddrus method[6a] and matched the reported characteristics. 2-Chloro-4,6-bis[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine was prepared as previously described[2] and matched the reported characteristics. Unless otherwise specified, the other chemicals were used without any purification.

2-[(*R*)-1-(9-Anthryl)ethylamino]-4-chloro-6-[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (1): To a solution of 2,4,6-trichloro-1,3,5-triazine (0.25 g, 1.35 mmol) in dry THF (5 mL) anhydrous K_2CO_3 (0.18 g, 1.356 mmol) and a catalytic amount of 18-crown-6 were added. The mixture was kept at 0 °C and a solution of (*R*)-1-(9-anthryl)ethylamine (0.3 g, 1.35 mmol) in dry THF (9 mL) was dropwise added. After 5 h at the same temperature, anhydrous K_2CO_3 (0.18 g, 1.356 mmol) and a solution of (*R*)-1-(1-naphthyl)-ethylamine (0.234 g, 1.356 mmol) in dry THF (5 mL) were added. The reaction mixture was stirred at room temperature for 7 d, then filtered through a pad of Celite. The crude product, obtained after evaporation of the solvent under reduced pressure, was recrystallized (ethyl acetate/hexane), affording chemically pure **1** (0.65 g, 1.29 mmol) in 95% yield. – M.p. 123–125 °C. – $[\alpha]_D^{30} = +138.3$ (*c* = 0.83, THF). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.30 (m, 2 H, aromatics), 8.05 (d, *J* = 8.3 Hz, 2 H, aromatics), 7.90 (d, *J* = 8.6 Hz, 2 H, aromatics), 7.70 (m, 4 H, aromatics), 7.35 (m, 6 H, aromatics), 6.35 (q, *J* = 6.7 Hz, 1 H, CH), 6.10 (d, *J* = 5.5 Hz, 1 H, NH), 5.55 (q, *J* = 6.7 Hz, 1 H, CH), 4.90 (d, *J* = 7.3 Hz, 1 H, NH), 1.32 (d, *J* = 7.3 Hz, 3 H, CH_3), 1.00 (d, *J* = 6.7 Hz, 3 H, CH_3). – ^{13}C NMR (50 MHz, DMSO): δ = 166.6, 163.5, 162.9 (triazine carbons), 136.9, 134.9, 132.4, 130.4, 129.8, 128.3, 127.6, 127.4, 126.6, 125.9, 125.3, 124.6, 124.5, 124.3, 123.8, 123.3, 122.5, 122.3 (aromatics), 45.8, 43.5 (stereogenic carbons), 19.8, 17.8 (methyl carbons). – IS-MS; *m*/*z* (%): 504 (100). – $C_{31}H_{26}ClN_5$ (504.03): calcd. C 75.87, H 5.09, Cl 6.40, N 12.64; found C 75.78, H 5.12, Cl 6.44, N 12.61.

2-[(*R*)-1-(9-Anthryl)ethylamino]-4,6-bis[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (2): To a solution of 2-chloro-4,6 bis[(*R*)-1-(1-naphthyl)ethylamino]-1,3,5-triazine (0.6 g, 1.35 mmol) in dry acetonitrile (20 mL) anhydrous K_2CO_3 (0.18 g, 1.35 mmol), a catalytic amount of 18-crown-6 and (*R*)-1-(9-anthryl)ethylamine (0.3 g, 1.35 mmol) were added. The reaction mixture was stirred under reflux for 6 d, then cooled to room temp. and filtered through a pad of Celite. After removing the solvent under vacuum, the crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane, 4:6), giving chemically pure **2** (0.39g, 0.61mmol) as a foaming solid in 45% yield. – M.p. 128–134 °C. – $[\alpha]_D^{30} = +23.8$ (*c* = 0.50, THF). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.50–7.30 (m, 23 H, aromatics), 6.55 (br. s, 1 H, CH), 5.80 (br. s, 3 H, NH), 5.15 (br. s, 2 H, CH), 1.90 (br. s, 3 H, CH_3), 1.50 (br. s, 3 H, CH_3), 1.15 (br. s, 3 H, CH_3). – ^{13}C NMR (50 MHz, DMSO): δ = 164.9, 164.7, 164.4 (triazine carbons), 140.6, 140.3, 133.8, 133.1, 131.1, 130.2, 128.6, 128.1, 127.9, 127.9, 126.4, 126.3, 126.2, 125.2, 124.8, 124.7, 124.0, 122.9, 122.8, 122.1 (aromatics), 45.1, 44.9, 44.7 (stereogenic carbons), 21.2, 20.9, 20.8 (methyl carbons). – IS-MS; *m*/*z* (%): 639 (100). – $C_{43}H_{38}N_6$ (638.81): calcd. C 80.85, H 6.00, N 13.16; found C 80.92, H 5.97, N 13.05.

2,4-Bis[(*R*)-1-(9-anthryl)ethylamino]-6-chloro-1,3,5-triazine (3): To a solution of 2,4,6-trichloro-1,3,5-triazine (0.17 g, 0.92 mmol) in dry THF (8 mL) anhydrous K_2CO_3 (0.25 g, 1.84 mmol) and a catalytic amount of 18-crown-6 were added. A solution of (*R*)-1-(9-anthryl)-ethylamine (0.4 g, 1.84 mmol) in dry THF (11 mL) was added dropwise and the mixture was stirred at room temp. for 7 d, then filtered through a pad of Celite. After removing the solvent under vacuum, the crude product was purified by column chromatography, affording chemically pure **3** (0.76 g, 1.38 mmol) in 76% yield. – M.p.210–213 °C. – $[\alpha]_D^{30} = +467.1$ (*c* = 0.70, THF). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 6.4 Hz, 4 H, aromatics), 8.38 (s, 2 H, aromatics), 8.00 (d, *J* = 7.4 Hz, 4 H, aromatics), 7.50 (m, 8 H, aromatics), 6.45 (q, *J* = 6.4 Hz, 2 H, CH), 6.20 (d, *J* = 5.8 Hz, 2 H, NH), 1.30 (d, *J* = 6.9 Hz, 6 H, CH_3). –^{13}C NMR (50 MHz, DMSO): δ = 166.4, 166.5 (triazinics), 133.6, 130.6, 128.2, 127.5, 126.3, 124.7, 123.8, 123.7 (aromatics), 44.8 (stereogenic carbons), 19.1 (methyl carbons). – IS-MS; *m*/*z* (%): 554 (100). – $C_{35}H_{28}ClN_5$ (554.09): calcd. C 75.87, H 5.09, Cl 6.40, N 12.64; found C 75.94, H 5.04, Cl 6.45, N 12.61.

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[10] The ^1B_b transition of the naphthalene chromophore was described by means of a single dipole located in the centre of the naphthalene system and directed along the molecular long axis; a dipolar strength of 47 D^2, centred at 220 nm, was attributed to it, according to the intensity of its transition.[3] In a similar way, the ^1B_b transition of the anthracene chromophore was described by means a single dipole located in the centre of the anthracene system and directed along the molecular long axis; a dipolar strength of 87 D^2, centred at 250 nm, was attributed to it, according to the intensity of its transition.[3] Two dipoles located in the centre of the triazine nucleus and directed perpendicularly to each other were used for describing the electrically allowed double degenerate transition of the triazine chromophore: it should be noted that "the degeneracy does not prevent the exciton approach since any choice of the polarization directions gives the same final results of calculations".[12] A dipolar strength of 25 D^2 centred at 220 nm was attributed to this transition on the basis of the UV spectrum of the 2,4,6-tris[(*S*)-1-cyclohexylethyl]-1,3,5-triazine[6b] used as a model compound.

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