The first examples of optically active tris(*N*-salicylideneaniline)s: manifestation of chirality from molecules to fluid columnar phases[†]

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Tris(*N*-salicylideneaniline)s comprising chiral tails in varying numbers self-organize into a room temperature helical columnar mesophase resulting from the chiral stacking of the constituent molecules differing in their rotational symmetry and ratio as evidenced by optical, chiroptical, calorimetric and X-ray studies.

Introduction

The thorough understanding and/or mimicking Nature's art of expressing and augmenting chirality from microscopic to mesoscopic levels remains elusive. However, the ubiquitous bio-molecular self-assembly into helical structures has inspired chemists to generate novel materials not only to reveal the structure-property correlation but also to explore their usage in diverse applications such as biosensors, lithography and drug delivery.¹ The foremost objective of such studies has been the design and synthesis of chiral molecular systems capable of yielding complex large-scale helical structures originating from the manifestation of chirality of the constituent molecules through noncovalent interactions such as hydrogen (H)bonding, π - π stacking and van der Waals forces.² Such investigations are becoming increasingly fascinating given the fact that many chiral molecules do not generate helical aggregates implying that the intramolecular rigidity (the distinct shape of molecules) and intermolecular interactions, although not directly related to molecular chirality, are also imperative.¹⁻³ This is especially noteworthy in the case of chiral discotic liquid crystals (LCs) exhibiting columnar (Col) phases characterized by indefinitely long molecular columns aggregating into two-dimensional (2D) lattices having different symmetries.³ For instance, the interactions among peripheral chiral tails of a discotic core are generally ineffective in inducing helical order at the mesoscopic level and thus the majority of the self-assembled fluid columns do not possess handedness. Nonetheless, few chiral columns are known to be formed if the discotic core³⁻⁵ or metallomesogen⁶ features an intrinsic shape that favors packing with a preferred rotation.

Recently, tris(*N*-salicylideneaniline)s [TSANs] have been demonstrated to be versatile compounds in which both electronic as well as novel molecular material features like self-organizing ability, molecular recognition *etc.* can be imbued.^{7–9} For example, we have discovered that novel discotics derived from TSANs existing in an inseparable

mixture of two keto-enamine forms with C_{3h} and C_{s} rotational symmetries (Fig. 1: I-IV), display Col phases.⁸ These discogens are rather unique as their central core is a flat electronaccepting (n-type) entity featuring multiple strong intramolecular H-bondings. Lee and co-workers^{9c} have shown that sterically hindered TSANs could be used as mechanically coupled biconcave molecules, which can release the clathrated guest molecules. Subsequently, MacLachlan and co-workers^{7a} revealed that, upon appending with additional functional groups, TSANs may form H-bonded capsules, clefts and chains. Apparently, the induction of molecular chirality in TSANs and the consequent effects on their self-assembly have not been reported hitherto. In continuation of our investigation on LC TSANs we became interested in realizing their optically active analogues. Since Col phases of TSANs comprise two keto-enamine forms in varying proportions, it may be reasoned that the presence of chiral tails at the peripheral region influence their self-assembly. Here we report on the synthesis and thermal behavior of the first examples of chiral TSANs exhibiting helical Col phases via the transfer of the exterior-chain chirality into supramolecular structure. Thus, another remarkable feature of TSANs has been disclosed.

Results and discussion

Synthesis

The molecular structures of different chiral TSANs prepared (Schemes 1 to 3) in the present investigation are shown in Fig. 1. For a comparative study, the central cyclohexane-1,3,5-trione core has been appended with either 1,2-bis(alkoxy) benzenes (where both alkoxy tails are chiral: 1) or 1,2,3-tris(alkoxy)benzenes [wherein one tail (**2a**) or two tails (**2b**) or all the three tails (**2c**) are chiral]. The literature reports^{3,5} and our earlier investigation^{8b} directed us to employ the (3*S*)-3,7-dimethyloctyloxy entity as a chiral tail. The target chiral TSANs 1 and **2a**-**c** were obtained by a 3-fold reaction of chiral 3,4-dialkoxyaniline **6a** and 3,4,5-trialkoxyanilines **6b**, **13a**, **13b** with 1,3,5-triformylphloroglucinol, respectively (Scheme 3). In turn, anilines were prepared, starting from catechol and pyrogallol.¹⁰ Catechol or pyrogallol upon *O*-alkylation with (*S*)-(+)-citronellyl bromide following

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I: $R_1 = H$; $R_2 = R_3 = n$ -OC_n H_{2n+1} ; II: $R_1 = R_2 = R_3 = n$ -OC_n H_{2n+1} III: $R_1 = H$; $R_2 = R_3 = 3$,7-Dimethyloctyloxy; IV: $R_1 = R_2 = R_3 = 3$,7-Dimethyloctyloxy

1 : $R_1 = R_2 = (3S)$ -3,7-Dimethyloctyloxy, $R_3 = H$ **2a**: $R_1 = (3S)$ -3,7-Dimethyloctyloxy, $R_2 = R_3 = n$ -OC₈H₁₇ **2b**: $R_1 = R_2 = (3S)$ -3,7-Dimethyloctyloxy, $R_3 = n$ -OC₈H₁₇ **2c**: $R_1 = R_2 = R_3 = (3S)$ -3,7-Dimethyloctyloxy

Fig. 1 Molecular structures of achiral and chiral TSANs, pertaining to the previous and present studies.

Williamson's ether synthesis protocol yielded alkoxybenzenes **3a** and **3b**. These compounds on catalytic hydrogenation furnished the intermediates **4a** and **4b**, in which the olefinic bond is reduced. The alkoxybenzenes **4a** and **4b** obtained were subjected to the two-phase nitration using an aqueous solution of nitric acid (70%) and sodium nitrite in dichloromethane to achieve the corresponding 3,4-dialkoxynitrobenzene **5a** and 3,4,5-trialkoxynitrobenzene **5b**. The catalytic hydrogenation of these nitro derivatives furnished the key 3,4-dialkoxyaniline **6a**



 \begin{cases} **6a** $: R_1 = R_2 = (3S)-3,7-Dimethy locty loxy, R_3 = H, X = NH_2 \\$ **6b** $: R_1 = R_2 = R_3 = (3S)-3,7-Dimethy locty loxy, X = NH_2 \end{cases}$

Scheme 1 Synthetic route for the compounds **6a–b**. Experimental conditions: (i) (*S*)-(+)-citronellyl bromide, anhyd. K_2CO_3 , DMF, 80 °C, 12 h (**3a**: 78%; **3b**: 74%); (ii) H₂ (1 atm, balloon), 10% PdC, THF, 12 h; (iii) 70% HNO₃, NaNO₂, CH₂Cl₂, rt, 1 h (**5a**: 56%; **5b**: 70%); (iv) H₂ (1 atm, balloon), 10% PdC, THF, 12 h (**6a**: 90%; **5b**: 88%).

and 3,4,5-trialkoxyanline 6b in almost quantitative yields. As shown in Scheme 3, by treating 1,3,5-triformylphloroglucinol with **6a** and **6b** in refluxing ethanol furnished target molecules 1 and 2c respectively. Similarly, the target compounds 2a and 2b were prepared starting from pyrogallol. To begin with, two vicinal hydroxyl groups of pyrogallol were protected using triethylorthoformate in the presence of 4 Å molecular sieves (as a water scavenger). The ethoxymethylene acetal 7 was then O-alkylated with either (S)-(+)-citronellyl bromide or n-octylbromide using Williamson's ether synthesis protocol to obtain intermediates 8a and 8b. These mono alkylated compounds were subjected to deprotection under mild acidic conditions to give dihydroxy compounds 9a and 9b. These products were O-alkylated with either *n*-octylbromide or (S)-(+)-citronellyl bromide using a mild base. The double bonds of the tails of trialkoxybenzenes 10a and 10b were reduced by catalytic hydrogenation to give 11a and 11b respectively. The abovementioned two-phase nitration of these trialkoxybenzenes followed by reduction yielded nitro compounds 12a-b and anilines 13a-b respectively. The anilines 13a and 13b thus obtained were condensed with 1,3,5-triformylphloroglucinol to obtain the target molecules 2a and 2b respectively. The molecular structures of all the target compounds and intermediates were confirmed by standard spectroscopic methods (see Experimental section) and elemental analysis. All the target molecules existed as a mixture of keto-enamine tautomers of C_{3h} and C_s symmetry as evidenced by ¹H (see Table 1) and ¹H-¹H COSY NMR spectra.¹⁰

Thermal behavior

The mesomorphism of optically active TSANs was probed with the help of polarized optical microscope (POM), differential scanning calorimeter (DSC), and X-ray diffraction (XRD) studies. Table 1 summarizes the phase behavior of these compounds as determined by these investigations. As can be seen, all the TSANs show enantiotropic Col mesophases.





Scheme 2 Synthetic route for the compounds 13a–b. Experimental conditions: (i) triethylorthoformate, toluene, 4 Å molecular sieves, 100 °C, 1 h; (ii) (*S*)-(+)-citronellyl bromide or *n*-bromooctane, anhyd. K_2CO_3 , butanone, reflux, 17 h; (iii) PTSA, methanol–water (9 : 1), rt, 2 h (9a: 68%; 9b: 70%); (iv) *n*-bromooctane or (*S*)-(+)-citronellyl bromide, anhyd. K_2CO_3 , DMF, 80 °C, 12 h (10a: 74%; 10b: 76%); (v) H₂ (1 atm, balloon), 10% PdC, THF, rt, 12 h; (vi) 70% HNO₃, NaNO₂, CH₂Cl₂, rt, 1 h (12a: 70%; 12b: 72%); (vii) H₂ (1 atm, balloon), 10% PdC, THF, rt, 6 h (13a: 74%; 13b: 76%).

The optical textures showed fan-shaped defects, homeotropic digitated stars, fernlike domains, a pattern with tiny needles

Scheme 3 Synthetic route for the chiral TSANs. Experimental conditions: (i) 6a, ethanol, reflux, 6 h (60%); (ii) 13a, ethanol, reflux, 6 h (72%); (iii) 13b, ethanol, reflux, 6 h (74%); (iv) 6b, ethanol, reflux, 6 h (72%).

and a grainy pattern (Fig. 2).¹⁰ Some of these textures are unusual, while their XRD patterns originate from Col phases. DSC thermograms showed first-order transitions at the phase transition temperatures in compliance with the optical observations. In general, the powder X-ray diffractograms obtained for Col phases (Table 2) showed a broad diffuse scattering centered around 4.6–4.9 Å at wide angles ($2\theta \approx 20^{\circ}$) which relates to the liquid like order of the peripheral tails. In some cases, another relatively sharp reflection corresponding to a distance of ~3.5 Å can be attributed to the stacking distance of the discs within the same column (core-core separation). In the small-angle region, sharp Bragg reflections observed could be indexed to hexagonal¹¹ or rectangular 2D lattices of the Col phases. Thus, analysis of the results of these

Table 1 Phase transition temperatures^a (°C) and correspondingenthalpies (J g⁻¹) of optically active TSANs. Cr: crystalline state; Col_r , Col_{r1} , Col_{r2} : rectangular columnar phase; Col_h : hexagonalcolumnar phase; I: isotropic liquid state

Compound $(C_{3h}: C_s)$	Phase sequence Heating/Cooling
1 (1 : 2.3)	Col _h 117.2 [2.9] I
2a (1 : 2.5)	1 113.4 [1.2] ⁶ Col _h Cr 64.3 [5.9] Col _r 136 ^c Col _h 160.8 [4.8] I
2b (1 : 1.3)	1 158.7 [4.9] Col _h 133.5 ^c Col _r -21.6 [1.6] Cr Col _r 133.3 ^c Col _h 144.4 [4.1] I
2c (1 : 1.1)	$1 142.3 [4.4] Col_h 129.1 Col_r Col_r Col_r Col_{r2} 53.9 [2.1] Col_{r1} 108.2 [2.8] I 102.7 [3.0] Col_r 44.1 [2.9]b Col_r$
	$1 102.7 [5.0] C01_{r1} + 1 [2.7] C01_{r2}$

^{*a*} Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at 5 °C min⁻¹. ^{*b*} The mesophase did not crystallize up to -60 °C as evidenced by DSC. ^{*c*} The phase transition observed with a POM was too weak to be detected by DSC.

complementary studies indicate that TSANs 1, 2b and 2c bearing multiple chiral tails, stabilize hexagonal Col (Col_h) or rectangular Col (Col_r) phases over a wide thermal range well below and above room temperature (RT). Of special significance, 2c shows a transition from one rectangular (Col_{r1}) phase to another (Col_{r2}) which must originate from the increase in the intercolumnar distance but a closer packing of the discs within the same column (Fig. 3, Table 2). Compound 2a, with one chiral and two achiral tails, which is crystalline at

Fig. 2 Photomicrographs of the textures obtained for (a) Col_h phase of **2a** at 135 °C; (b) Col_r phase of **2a** at 129 °C; (c) Col_h phase of **2b** at 135 °C; (d) Col_r phase of **2b** at 123 °C; (e) Col_{r1} phase of **2c** at 101 °C; (f) Col_{r2} phase of **2c** at 42 °C.

Table 2	The results	of indexation	of XRD	profiles	of chiral	TSANs
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TSANs (D/Å) ^a	Phase $(T/^{\circ}C)$	d₀₀₅/ Å	$\overset{d_{\mathrm{cal}}}{\mathrm{\AA}}$	Lattice parameters/Å	Miller indices hki
1 (27.6)	Col _h (50)	26.66 4.8	26.66	<i>a</i> : 30.78 <i>c</i> : 3.46	100
		3.46			001
2a (31.6)	Col _h (144)	24.79 4.7	24.79	<i>a</i> : 28.63	100
	$\operatorname{Col}_{r}(30)$	27.5	27.5	a: 44.5	110
	,	22.25	22.25	b: 34.97	200
		13.73 4.6	13.75		220
2b (31.7)	Col _h (136)	24.87 4 8	24.87	<i>a</i> : 28.72	100
	Col. (50)	27.64	27.62	<i>a</i> : 45.86	110
	004 _r (00)	22.93	22.93	h: 34.6	200
		13 78	13.81	01 0 110	220
		9.3 4.7	9.21		330
2c (29.2)	Col_{s1} (90)	25.82	25.82	a: 46.62	110
		23.31	23.31	<i>b</i> : 31.04	200
		4.9		c: 3.65	
		3.65	3.65		001
	$Col_{r_2}(30)$	28.34	28.34	a: 43.37	110
	12 ()	18.72	18.72	b: 37.44	020
		12.29	12.48	c: 3.42	030
		11.44	11.44		320
		10.69 4.7	10.82		230
		3.42	3.42		001
^{<i>a</i>} The dia	meter (D) of	the disk	(estimat	ted from Chem3	D Ultra 90

[&]quot;The diameter (D) of the disk (estimated from Chem3D Ultra 9.0 molecular model software).

RT, stabilizes Col_r and Col_h phases, among which Col_r phase supercools well below ambient temperature.

Circular dichroism studies

In view of the fact that TSANs 1 and 2a-c possess chromophores and molecular chirality, their fluid columnar as well as isotropic states were probed for electronic absorption and chiroptical properties. UV-Vis spectroscopy was used to measure the wavelength and intensity of ordinary light absorption by the chromophores of the constituent TSANs of the two states. On the other hand, the circular dichroism (CD) spectroscopic technique was employed to know if the molecular chirality has facilitated molecular organization in a helical fashion in the LC and isotropic phases. The substances held between two quartz plates were heated to their isotropic phase and cooled slowly. To have a uniform sample the plates were mechanical sheared repeatedly while maintaining the material in the isotropic state and subsequently cooled slowly. Owing to the small thickness of the sample required to keep the sample within the upper limit of measurement, no prefabricated cells were used and thus the thickness was not fixed. Hence, the optical (absorption and CD) experiments performed using such cells are rather qualitative.

As shown in the lower panels of Fig. 4(a–d), irrespective of the difference in the molecular structures and the temperatures at which measurements were carried out, UV-Vis spectra of all the TSANs showed two absorption maxima centered around 335 nm and 416 nm due to π - π * and n- π * transitions,

Fig. 3 (a) DSC thermograms obtained during the first heating (red trace)–cooling (blue trace) cycles for TSAN **2c**; (b) and (c) show the X-ray 1D profiles obtained for the Col_{r1} (at 90 °C) and Col_{r2} (at 30 °C) phases of **2c**.

respectively. The CD spectra were recorded over the entire thermal range of Col phases¹⁰ at 10 °C temperature intervals. However, for comparison, the CD spectra at three temperatures, for which UV-Vis data are also available, are shown in the top panels of Fig. 4(a-d). It is important to mention here that the origin of these CD peaks in the mesophase of all the TSANs was authenticated by recording the spectra at three different temperatures by rotating (in-plane) the sample cells through 90° ; the spectra were found to be nearly identical to those obtained for the original orientation of the samples. This clearly indicated that the signal is not arising from the possible linear dichroism (LD) of the sample.^{3d} In fact, the instrument used is capable of detecting the LD signal directly; in the measurements performed no LD signal was found within the instrument limits.¹⁰ Notably, all the Col structures displayed intense peaks in the CD spectra signifying large chiral correlations in the molecular packing.³ For compounds 2a-c the optical (CD) activity was not observed in the isotropic state [see red traces of Fig. 4(b-d)] indicating that the chromophores are not influenced by the molecular chirality. Thus, the occurrence of CD bands in the mesophase corresponds to chromophores that are organized into a specific chiral orientation. That is, CD activity originates from intermolecular interactions between two or more electronic transition dipoles arranged in a helical order.

On the other hand, the CD spectrum of the isotropic phase of TSAN 1, unlike others, showed an intense negative signal implying the existence of helical aggregates made of chromophores (TSANs) due to the favorable stacking effects.^{11a} Obviously, CD activity was also observed in the Col phase. Thus, the molecular chirality of 1 is well expressed in the isotropic state and LC phase. It can bee seen that there are certain similarities in the CD spectral patterns¹⁰ of Col phases of 1 [Fig. 4a] and 2a [Fig. 4b], and 2b [Fig. 4c] and 2c [Fig. 4d]. Among these, the spectral pattern of 2a is much simpler exhibiting a strong negative Cotton effect ($\lambda_{max} = 496$ nm), where the CD signal increases on lowering the temperature. In the case of 1, the CD spectra of lower temperatures (25–60 $^{\circ}$ C) consisted of a positive first Cotton effect ($\lambda_{max} = 492$ nm), a negative second Cotton effect (475 nm) and a positive third Cotton effect (371 nm) [see blue trace in Fig. 4(a) and ref. 10]. At higher temperatures, the first positive band disappears. In contrast, the spectra of 2b obtained in the temperature interval of 20 °C to 120 °C showed a first negative (481 nm) followed by two positive (443 and 358 nm) Cotton effects. At higher temperatures (above 120 °C), the first negative Cotton effect almost merges with the base line and concomitantly the intensity of the two positive bands decreases. Whereas, for TSAN 2c the higher temperature (70 °C to 100 °C) CD spectra showed a negative band (491 nm), besides a positive (464 nm) and two negative (381 nm, 310 nm) Cotton effects. The intensity of all the CD signals subsides on lowering the temperature, which is opposite to the behavior of 2b. These results suggest the possibility of different chiral dispositions of the Col phase, which seem to be dependant on the temperature. Importantly, the bisignate nature of the CD bands indicates closer packing of TSANs within the column. Importantly, the manifestation of chirality seems to be independent of the number of chiral tails in the peripheral region of the TSANs.

Given the fact that chiral Col phases can be ferroelectric, electrical switching studies were performed on all of the abovementioned mesophases. For this purpose, samples contained between two indium tin oxide (ITO) coated glass plates were cooled slowly from the isotropic phase. After transition to the Col phase, a low frequency AC triangular wave electric field was applied and increased gradually. Surprisingly, even with quite large voltages, no switching was observed. Therefore, it may be assumed that the columns are upright. In fact, XRD data support the view that the molecular director is along the columnar axis. As is well known various helical structures have been suggested for the columnar phases in the literature.³ In particular, two different helices are reported 3e,f to exist along the column axis if the discotic core (with peripheral chiral tails) features an intrinsic shape that favors packing with a preferred rotation: (i) the spiral staircase-like helix where the flat cores are displaced perpendicular to the Col axis and (ii) the helix where the constituent discs are tilted along the columnar axis and rotate around the columnar axis. Thus, all the optically

Fig. 4 CD (top panels) and UV-Vis spectra (bottom panels) obtained in the isotropic and columnar phases for chiral TSANs 1 (a), 2a (b), 2b (c) and 2c (d).

active TSANs form the chiral Col phases where either the position of the molecules or the orientation of the molecular director may spiral within the column. In order to postulate which of these chiral organizations is favored in TSANs, the lattice parameter a and diameter of the disks (estimated from Chem3D Ultra 9) may be taken into account. As can be seen in Table 2, the lattice parameter is either comparable to or higher than the estimated diameter of the molecules. Therefore, we suggest that the helix could be of the form shown in Fig. 5, where the constituent discs are slightly tilted and rotate around the columnar axis.^{3d,g}

Absorbance and fluorescence studies

Tris(*N*-salicylideneaniline)s, owing to the presence of multiple chromophores and possible π -conjugation between the peripheral region and the central core, are expected to exhibit promising photophysical properties, which is evident from earlier reports.^{86,9} Thus, fluorescence as well as UV-Vis absorption spectra (for comparison) for a representative TSAN 2c were obtained in both solution and the mesophase states. Indeed, the THF solution absorption spectra were

Fig. 5 Schematic representation of the self-assembly of C_{3h} and C_s rotational isomers of TSANs into a helical Col phase where the constituent discs are slightly tilted and rotate around the columnar axis.

recorded for all the compounds and their patterns looked alike, as expected. For studying photophysical properies of the mesophase, a thin film was employed. As shown in the upper and lower panels of Fig. 6, the UV-Vis spectra (blue trace) of chiral TSAN 2c in solution and the mesophase, respectively. showed two absorption maxima centered around 333 nm and 413 nm. Upon irradiating the solution with one of the absorption maxima viz., 413 nm, a fluorescence maximum was observed at around 481 nm with a negligible shoulder (orange traces in the upper panel of Fig. 6). The Stokes shift, which is the difference between the spectral positions of the band maxima of absorption and florescence arising from the same electronic transition, was found to be 68 nm. The occurrence of luminescence at a longer wavelength than the absorption is in agreement with the general observations. As shown in the inset, the green light is visually perceivable in the emissive state. The lower panel of Fig. 6 shows the absorption and the emission spectra of the fluid Col phase. As can be seen, the Col structure of 2c shows two absorption bands analogous to the solution state. The apparent small red shift in the two absorption maxima of the Col structure is indicative of the intimate overlap of the fluorophores in such states. When excited at 413 nm, two broad bands with fluorescence maxima at around 540 and 610 nm (see red trace of the lower panel of Fig. 6) were observed.

Further, the fluorescence spectra of the thin film at different temperatures (above room temperature) for the above-mentioned excitation wavelength were measured and are shown in the right hand side of lower panel of Fig. 6. As can be seen, the intensity of the emission peak decreases progressively with the increase in the temperature, that can be attributed to the breaking of larger columnar stacks into smaller ones and

Fig. 6 Absorption and emission spectra in THF solution (upper panel) and in the thin film state at different temperature intervals (lower panel) of 2c. The inset in the upper panel shows emission in THF solution on irradiation with 365 nm light.

thermally activated radiationless processes.¹² Notably, when compared with the emission behavior of the solution, the films of neat Col phase exhibit a strong bathochromic (red) shift that can be attributed to the strong co-facial proximity of C_{3h} and C_s isomers within the Col structure as well as the formation of excimers/aggregates. In general, the excimers are considered as molecular dimers or stoichiometric complexes with associated excited electronic states, dissociative ground states, and structureless emission spectra.¹³ Thus, it is apparent that the TSANs realized in the present investigation are capable of generating light in both solution and mesophase states. This is especially remarkable in the latter situation wherein the 2D order with short inter-core distances facilitates motion of the charges with the concomitant freezing of the impurities¹⁴ with the preserved luminescence. ionic Nonetheless, detailed investigations involving the annealing of films, film morphology, fluorescence efficiency, solvent effects, etc. are required to further elucidate the photophysical properties of these molecules quantitatively.

Conclusion

In summary, novel optically active TSANs are synthesized and shown to self-assemble into room temperature helical fluid Col phases. The preferential rotation of the constituent shapepersistent C_{3h} and C_s keto-enamine tautomers enables the chirality present in the side-chains to be expressed into the helical conformation of the columns that is reflected by Cotton effects in the CD. Thus, another remarkable feature of TSANs is reported.

Experimental

General methods

Chemicals were obtained from Fluka, Aldrich, Lancaster and local chemical companies, and were used without any purification; solvents were dried following the standard procedures. Chromatography was performed using either silica gel (60-120, 100-200 and 230-400 mesh) or neutral aluminiun oxide. For thin layer chromatography, aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254) were employed. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. The spectral positions are given in wave number (cm⁻¹) units. NMR spectra were recorded using either a Bruker DRX-500 (500 MHz) or Bruker AMX-400 (400 MHz) spectrometer or Bruker Aveance series DPX-200 (200 MHz) spectrometer. For ¹H NMR spectra, the chemical shifts are reported in ppm relative to TMS as an standard. Coupling constants are in Hz. internal Microanalyses were performed using a Euro EA3000 elemental analyzer. Mass spectra were determined on a JEOL JMS-600H spectrometer in FAB⁺ mode using 3-nitrobenzyl alcohol as a liquid matrix. The molecular length is calculated from the energy minimized structure deduced from the CS Chem 3D version 9 programme. X-Ray diffraction studies were carried out on powder samples in Lindemann capillaries with Cu Ka radiation using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focusing optics. The compounds were investigated for their liquid crystalline behavior employing an optical polarizing microscope (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Mettler FP90) and differential scanning calorimeter (Perkin Elmer DSC7); these were also used to determine the melting points of non-mesomorphic compounds. Circular dichroism spectra were recorded using JASCO J-810 spectro-polarimeter. The specific rotation of the target molecules was measured using the same instrument. Emission spectra in solution were recorded with a luminescence spectrometer (Perkin Elmer LS 50B), while emission spectra as a function of temperature were obtained by using a Fluorolog spectro-fluorimeter (SPEX) in conjunction with a programmable hotstage (Linkam).

Materials

General procedure for the synthesis of 1, 2a, 2b and 2c. A mixture of triformylphloroglucinol (0.4 mmol, 1 equiv.) and alkoxy aniline (1.36 mmol, 3.4 equiv.) in absolute ethanol (15 ml) was heated to reflux under inert an atmosphere for 2 h with vigorous stirring. The solvent was removed *in vaccuo* from the reaction mixture to give the target molecules as a gummy mass. The crude products were purified by repeatedly dissolving them in dichloromethane and re-precipitating the LC mass by the addition of a large excess of ethanol at 10–15 °C.

1. Yield = 60%; $R_{\rm f}$ = 0.73 (30% EtOAc–hexanes); a brown gummy mass; $[\alpha]_{\rm D}$ = -17.7 (c = 1; CHCl₃, temperature = 22.6 °C); UV-Vis: $\lambda_{\rm max}$ = 416.84 nm, ε = 9.3157 × 10⁴ L mol⁻¹cm⁻¹; IR (KBr pellet): $v_{\rm max}$ in cm⁻¹ 3423, 2953, 2925, 2868, 1621, 1594, 1544, 1519, 1460, 1383, 1306, 1262, 1136, 1018, 828 and 756; ¹H NMR (CDCl₃, 400 MHz): δ 13.48 (d, J = 13.1 Hz, =CNH), 13.37 (d, J = 14.4 Hz, =CNH), 13.01 (d, J = 11.6 Hz, =CNH), 12.96 (d, J = 16.4 Hz, =CNH), 8.63–8.77 (m, 3H, =CHN), 6.82–6.9 (m, 9H, Ar), 4.29 (m, 12H, 6 × OCH₂), 0.86–1.88 (m, 114H, 12 × CH, 24 × CH₂, 18 × CH₃); MS (FAB+): m/z for C₈₇H₁₄₁N₃O₉, calculated: 1372.1, found: 1372.7; anal. calcd for C₈₇H₁₄₁N₃O₉: C, 76.1; H, 10.35; N, 3.06. Found: C, 76.3; H, 10.2; N, 3.2.

2a. Yield: 72%; $R_{\rm f} = 0.72$ (30% EtOAc–hexanes); a brown solid, $[\alpha]_{\rm D} = -3.6$ (c = 1; CHCl₃, temperature = 22.6 °C); UV-Vis: $\lambda_{\rm max} = 415.50$ nm, $\varepsilon = 7.4893 \times 10^4$ L mol⁻¹cm⁻¹; IR (KBr pellet): $v_{\rm max}$ in cm⁻¹ 2925, 2855, 1619, 1587, 1509, 1459, 1384, 1296, 1252, 1118, 1040, 991, 835, 758 and 624; ¹H NMR (CDCl₃, 400 MHz): δ 13.46 (d, J = 13.6 Hz, =CNH),13.27 (d, J = 13.2 Hz, =CNH), 12.99 (d, J = 13.0 Hz, =CNH), 12.87 (d, J = 13.3 Hz, =CNH), 8.62–8.77 (m, 3H, =CHN), 6.48 (s, 6H, Ar), 3.91–4.06 (m, 18H, 9 × OCH₂), 0.86–1.88 (m, 147H, 6 × CH, 48 × CH₂, 15 × CH₃); MS (FAB+): *m/z* for C₁₀₅H₁₇₈N₃O₁₂ (M+1), calculated: 1673.3, found: 1673.2; anal. calcd for C₁₀₅H₁₇₇N₃O₁₂: C, 75.36; H, 10.66; N, 2.51. Found: C, 75.7; H, 10.7; N, 2.6.

2b. Yield: 74%; $R_{\rm f} = 0.71$ (30% EtOAc–hexanes); a brown gummy solid, $[\alpha]_{\rm D} = -9.7$ (c = 1; CHCl₃, temperature = 22.6 °C); UV-Vis: $\lambda_{\rm max} = 416.74$ nm, $\varepsilon = 7.3582 \times 10^4$ L mol⁻¹cm⁻¹; IR (KBr pellet): $v_{\rm max}$ in cm⁻¹ 2956, 2362, 1620, 1588, 1509, 1459, 1384, 1295, 1232, 1117, 1050, 991, 834, 773, and 623; ¹H NMR (CDCl₃, 400 MHz): δ 13.5 (d, J = 12.0 Hz, =CNH), 13.3 (d, J = 12.0 Hz, =CNH), 13.0 (d, J = 13.3 Hz

=CNH), 12.87 (d, J = 12.9 Hz, =CNH), 8.66–8.7 (m, 3H, =CHN), 6.48 (s, 6H, Ar), 3.96–4.0 (m, 18H, 9 × OCH₂), 0.87– 1.92 (m, 159H, 12 × CH, 42 × CH₂, 21 × CH₃); MS(FAB+): m/z for C₁₁₁H₁₉₁N₃O₁₂ (M+2), calculated: 1758.4, found:1758.2; anal. calcd for C₁₁₁H₁₈₉N₃O₁₂: C, 75.85; H, 10.84; N, 2.39. Found: C, 75.6; H, 11; N, 2.4.

2c. Yield: 72%; $R_{\rm f} = 0.70$ (30% EtOAc–hexanes); a brown gummy solid, $[\alpha]_{\rm D} = -8.5$ (c = 1; CHCl₃, temperature = 22.6 °C); UV-Vis: $\lambda_{\rm max} = 413.08$ nm, $\varepsilon = 6.6967 \times 10^4$ L mol⁻¹cm⁻¹; IR (KBr pellet): $v_{\rm max}$ in cm⁻¹ 2953, 2926, 2869, 1618, 1585, 1550, 1509, 1459, 1383, 1293, 1233, 1308, 1118, 1050, 989, 835, 810, 754, 665, 624 and 436; ¹H NMR (CDCl₃, 400 MHz): δ 13.48 (d, J = 13.0 Hz, =CNH), 13.29 (d, J = 13.6 Hz, =CNH), 13.01 (d, J = 14.0 Hz =CNH), 12.87 (d, J = 14.4 Hz, =CNH), 8.63–8.8 (m, 3H, =CHN), 6.49 (s, 6H, Ar), 3.92–4.07 (m, 18H, 9 × OCH₂), 0.92–1.92 (m, 171H, 18 × CH, 36 × CH₂, 27 × CH₃); MS (FAB+): m/z for C₁₁₇H₂₀₁N₃O₁₂: c, 76.3; H, 10.99; N, 2.28. Found: C, 76.4; H, 10.7; N, 2.5.

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