



The first examples of supramolecular discotic C_{3h} tris(*N*-salicylideneamine)s featuring inter- and intra-molecular H-bonding: synthesis and characterization

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ABSTRACT

Supramolecular liquid crystalline tris(*N*-salicylideneamine)s (TSANs) featuring both inter- and intra-molecular hydrogen bonding have been synthesized and characterized for the first time. These TSANs formed by condensing 3 equiv of 3,4,5-trialkoxybenzoylhydrazine with 1,3,5-triformylphloroglucinol exist as the single C_{3h} -symmetric keto-enamine product solely, unlike the previously reported TSANs. Their self-assembly into supramolecular fluid hexagonal columnar phase over a wide thermal range is evidenced with the aid of optical microscopic, calorimetric, and powder X-ray diffraction techniques.

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Over the past two decades or so, the field of molecular engineering and the synthesis of advanced molecular materials which are promising from a variety of perspectives ranging from electrical conductivity,^{1a,b} electro- and photo-luminescence,^{1c} liquid crystal behavior (mesomorphism),^{1d,e} biotechnology^{1f} etc. has emerged as an exciting area of intense research. Within the field, the organic materials possessing modifiable (tunable) molecular sub-units, which enable to draw some structure–property correlations, and thus facilitate to incorporate several of the above-mentioned functional characteristics, are of immense interest. Tris(*N*-salicylideneamine)s (TSANs, **I**) where three aromatic cores in the form of arms are appended to the central C_3 symmetric cyclohexane-1,3,5-trione core (Fig. 1) are one among the wide variety of such tunable organic systems that are obtainable in a few steps starting from simple precursors.^{2–6} They have recently evoked considerable curiosity not only because of their technological potential^{3–6} but also on a more fundamental level given the experimental observation that they exist either as a mixture of two inseparable C_{3h} (**1a**) and C_s (**1b**) symmetric keto-enamine (NH) tautomers^{2,3,6} or only in the form of a former C_{3h} isomer^{4,5} instead of the more expected enol-imine (**1c**) (OH) product. These mixtures are generally formed when 1,3,5-tri-formylphloroglucinol (**4**, see Scheme 1) is condensed with three equivalents of amines,^{3,6} whereas, the C_{3h} isomers (**1a**) are obtained solely if the bulky^{4,5}/supramolecular^{2b} amines are used. However, both forms of TSANs are proven to be fascinating functional molecular and supramolecular materials;

they exhibit fluorescence and generate numerous supramolecular assemblies.^{2–6}

Of particular interest is their ability to self-assemble into a columnar (Col) liquid crystal (LC) phase where the individual fluid columns comprise co-facially stacked C_{3h} and C_s isomers featuring intramolecular H-bonding.³ Notably, regardless of the nature of the three arms, these LC TSANs exhibit fluorescence in both solution and Col states. These discotics stand strikingly apart from the others owing to their ability to undergo a contiguous multiple proton transfer with the concomitant rearrangement of the π -orbitals which might facilitate the coupling between motions of the proton and the conduction electrons. Such a process is expected to modulate the periodic potential within the fluid one-dimensional array.⁷

On the other hand, in recent times the supramolecular hydrogen (H)-bonded LCs have become a subject of major research.^{8–11} This is because H-bonds with an inherent moderate bonding

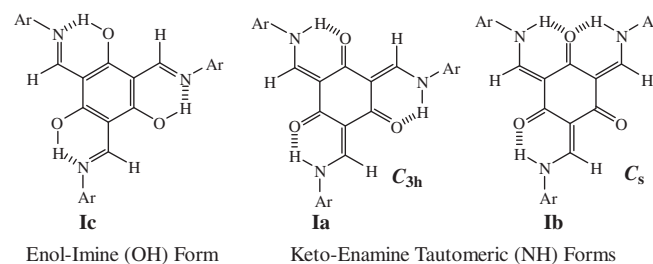
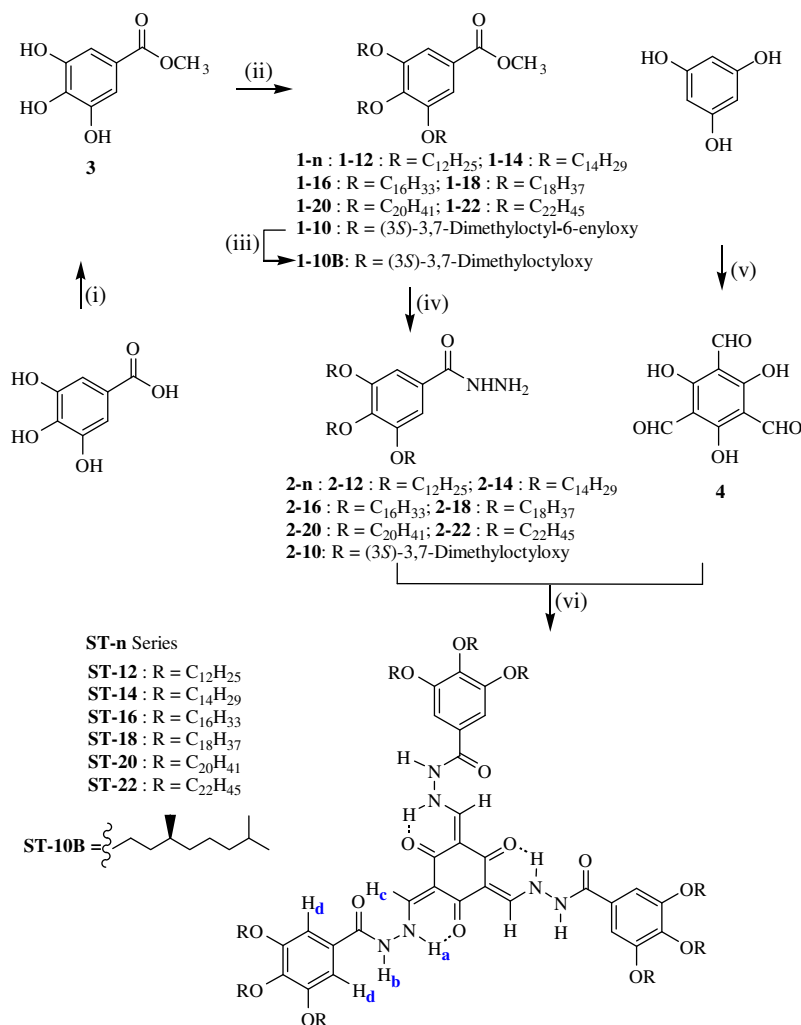


Figure 1. Molecular structures of three isomeric forms of TSANs (**I**).

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Scheme 1. Reagents and conditions: (i) methanol, H₂SO₄ (cat.), reflux 3 h (95%); (ii) bromoalkane or (*S*)-(+)-citronellyl bromide, anhyd K₂CO₃, DMF, 80 °C, 17 h (85–90%); (iii) H₂, (1 atm, balloon), 10% Pd-C, THF, 12 h (90%); (iv) hydrazine hydrate, ethanol, reflux 5 h (80–85%); (v) hexamine, CF₃COOH, 100 °C, 5 h, 3 N HCl, 100 °C, 1 h (22%); (vi) ethanol, reflux, 4 h (70–80%).

energy not only enforce strongly the self-assembly of supramolecules into LC phases but also provide them the added features such as directionality, selectivity, reversibility, and dynamic functions. It is especially noteworthy in the case of supramolecules that self-organize to yield hierarchical fluid Col networks that are promising from the point of view of both material^{1e,8} and biological sciences.⁹ These observations prompted us to introduce the self-complementing (H-bond donor and acceptor) moieties into TSANs to realize novel supramolecular discotics possessing both inter- and intra-molecular H-bonds that are scarcely reported.¹⁰ In fact, this particular theme originated partly because of a recent report that intermolecular H-bonded TSANs occur in a C_{3h} symmetric form.^{2b} As a first step in this direction, we present here the synthesis and thermal behavior of new TSANs where the central cyclohexane-1,3,5-trione core is linked to three supramolecular arms derived from 3,4,5-trialkoxybenzoylhydrazine.

The proposed TSANs, denoted as **ST-n** series (where **S** signifies supramolecular and **T** stands for TSAN, **n** indicate the number of carbon atoms in the alkoxy tails), were synthesized in five simple steps as depicted in Scheme 1. Methyl gallate (**3**) was alkylated with different bromoalkanes in the presence of K₂CO₃ in hot DMF to get methyl 3,4,5-tris(alkoxy)benzoates (**1-n**), which were reacted with hydrazine hydrate in refluxing absolute ethanol to yield 3,4,5-tris(alkoxy)benzohydrazides (**2-n**) as white compounds. Finally,

three molar amounts of each of benzohydrazides **2-n** and 1,3,5-triformylphloroglucinol (**4**, itself prepared by subjecting phloroglucinol to Duff reaction) were heated to reflux in absolute ethanol to obtain the target TSANs (**ST-n** series of compounds) in 70–80% yield.¹²

All the compounds were probed for their molecular structure by spectroscopic and microanalytical techniques. The FTIR spectra of all the solid TSANs (KBr pallet) appeared alike, and importantly, indicated the H-bond molecular interactions. The occurrence of a characteristic N–H stretching vibration ($\nu_{\text{N-H}}$) band at 3220 cm⁻¹ and the strong absorption of amide I ($\nu_{\text{C=O}}$) at 1648 cm⁻¹ clearly revealed the interaction of N–H groups with the C=O groups through H-bonds (C=O...H–N). This assignment is supported by the fact that a non H-bonded (free) N–H stretching band appears at about 3400 cm⁻¹. Owing to their partial solubility in common organic solvents, especially in CDCl₃, the ¹H NMR spectra were acquired in a 1:1 mixture of CDCl₃ and CCl₄ at room temperature (except for **ST-12**). The spectra showed the expected signals, and the peaks appearing downfield from δ 3.5 ppm were found to be relatively broad (see Fig. 2A) suggesting the intermolecular co-facial interactions of TSANs through H-bonding. Two broad singlets at δ 13.2 and 8.5 ppm corresponding to the resonance of 2°-amine (H_a) and enamine (H_c) protons, respectively, clearly indicate their occurrence in a C_{3h} keto-enamine isomeric form which is in agreement with the recent observation that TSANs with self-comple-

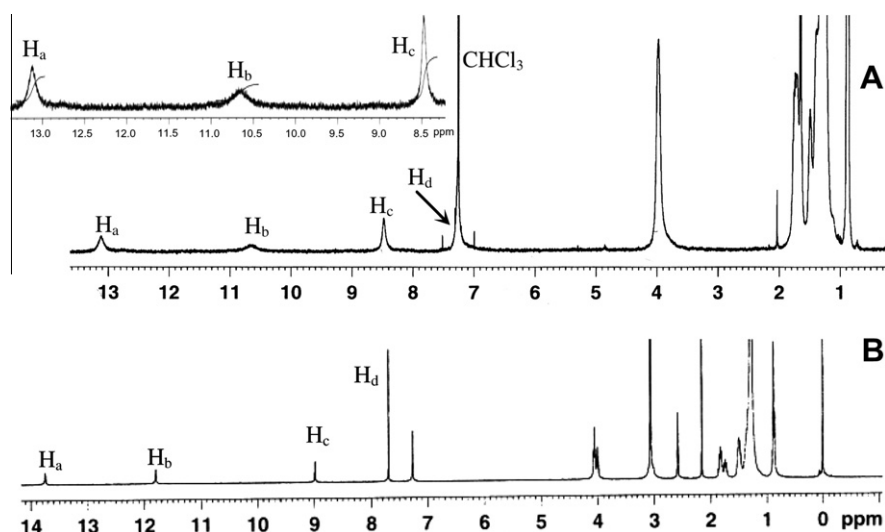


Figure 2. ^1H NMR spectra of **ST-12** in CDCl_3 (A) and $\text{CDCl}_3 + \text{DMSO-}d_6$ (B); in spectrum A the proton signals are broad suggesting aggregation of C_{3h} keto-enamine isomers through H-bond network; these signals resolve by adding a few drops DMSO that breaks the H-bonds (see spectrum B).

menting arms exist in such a form.^{2b} This is in stark contrast with the earlier observation that discotic TSANs show sharp multiple peaks in the above mentioned regions due to the co-existence of C_{3h} and C_s isomers in varying proportions³ where the intermolecular H-bond interactions are non-existent. As shown in Figure 2B, the signals of the protons were well resolved when the spectrum was recorded by adding few drops of a polar solvent (DMSO) that breaks the H-bonds. This strongly supports the aforesaid view that C_{3h} discotic TSANs interact with each other through the interamide H-bonds. When ^1H NMR spectra were recorded as a function of temperature for one of the samples viz., **ST-12** in CDCl_3 , the enamine and 2°-amine peaks turn relatively sharp and split; besides, the NH (attached to $\text{C}=\text{O}$) signal occurring as a broad singlet in the region 10.7–11.3 becomes sharp with splitting. These results imply that at a higher temperature, the aggregates of C_{3h} isomers dissociate to yield a mixture of C_{3h} and C_s isomers.

The thermal behavior of the **ST-*n*** series of compounds was evaluated with the aid of a polarizing optical microscope (POM) and a differential scanning calorimeter (DSC); the results are summarized in Table 1. The samples sandwiched between an untreated slide and a cover slip were employed for the microscopic study where the simultaneous occurrence of birefringence and fluidity was tested to establish their liquid crystallinity. Compound **ST-12** turned out to be a gummy material that could be spread around the slide when subjected to mechanical stress. The sheared sample

showed a non-specific birefringent texture which was found to be similar to the one seen, under identical conditions, for the known TSANs exhibiting Col phase at room temperature (rt).^{3b} However, the viscosity of the phase seems to be relatively high when compared with that of the Col phase of aforesaid known compounds. The texture of the phase (Fig. 3a) remains almost unaltered till the temperature (265 °C) at which the sample begins to thermally degrade slowly. Besides, the lack of signature due to the melting event in DSC supports the view that **ST-12** possibly exhibits an LC phase at rt. The structure of the LC phase was elucidated with the help of powder X-ray diffraction (XRD) study and the results are summarized in Table 2. The 2D pattern (Fig. 3b) and its extracted intensity versus diffraction angle (2θ) profile (Fig. 3c) obtained at rt supported the results of our optical study that **ST-12** is a Col LC. The diffractograms obtained at higher temperatures viz., 100 °C and 180 °C were also similar and thus, supported the assignment that **ST-12** exhibits a single Col phase over the entire thermal range. In these profiles, the occurrence of a sharp and intense peak at low angles as well as two diffused peaks at wider angles clearly points to a Col phase where the long columns aggregate into a 2D hexagonal lattice.^{3,13} Another diffuse peak seen at intermediate angles in the XRD patterns (see Fig. 3b and c) suggests that the cores of a few molecules within the column form loosely defined aggregates.

Table 1
Phase transition temperatures (in °C) of supramolecular TSANs (**ST-*n*** series) deduced from POM and/or DSC studies

ST-12	Col_h 270 ^{a,b}
ST-14	M 134 ^a Col_h 262 ^{a,b}
ST-16	M 129 ^a Col_h 260 ^{a,b}
ST-18	M 123 ^a Col_h 255 ^{a,b}
ST-20	Cr 72.7 [43.5] ^c Col_h 258 ^{a,b}
ST-22	Cr 63.6 [46.3] ^c Col_h 250 ^{a,b}
ST-10B	M 123 ^a Col_h 260 ^{a,b}

Cr = Crystal; M = unknown phase (soft solid or glassy state); Col_h = hexagonal columnar phase.

^a The phase transition temperature was deduced from the POM study since no peaks/signatures due to the transition was seen in the DSC thermograms.

^b At this temperature the compound decomposes completely.

^c Peak temperatures in the DSC thermograms obtained during the first heating cycles at a rate of 5 °C/min.

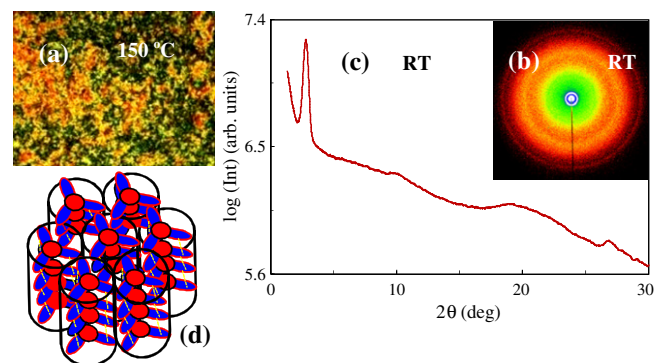


Figure 3. Microphotograph of the texture (a) XRD pattern; (b) and 1D-intensity versus 2θ profile; (c) obtained for the Col_h phase of **ST-12**; (d) schematic representation of the Col_h phase where the individual columns are formed by the self-assembly of C_{3h} TSANs through H-bonds (yellow lines).

Table 2
The results of indexation of XRD profiles of TSANs

TSAN	Phase T (°C)	d ^a (Å)	Intensity	Lattice parameters (Å)	Miller indices <i>hkl</i>
ST-12	Col _h rt	31.7	s	a: 36.6	1 0 0
		4.48	d	c: 3.29	0 0 1
		3.29	d		
	Col _h 100	32.3	s	a: 37.3	1 0 0
		4.6	d		
		3.31	d	c: 3.31	0 0 1
	Col _h 180	32.9	s	a: 38	1 0 0
		4.78	d		
3.31		d	c: 3.31	0 0 1	
ST-16	Col _h rt	35.01	s	a: 40.43	1 0 0
		4.18	d	c: 3.27	0 0 1
		3.27	d		
	Col _h 150	36.61	s	a: 42.27	1 0 0
		4.68	d	c: 3.28	0 0 1
		3.28	d		
ST-10B	Col _h rt	29.42	s	a: 33.97	1 0 0
		4.73	d	c: 3.31	0 0 1
		3.31	d		
	Col _h 150	29.8	s	a: 34.4	1 0 0
		4.8	d	c: 3.3	0 0 1
		3.3	d		

Col_h, hexagonal columnar phase; s, strong, d, diffuse.

^a d = spacing.

The higher members namely, **ST-14**, **ST-16**, and **ST-18**, as well as the compound **ST-10B** with branched alkoxy tails, exhibit an identical behavior. Unlike the first member of the series, these were immobile materials at rt, although it was difficult to point out whether they were crystalline. In the thermal study by DSC, the endothermic peak due to melting transition was not observed implying that these samples are perhaps in the glassy or soft solid (M) state. On heating, they transformed into another phase at the temperatures shown in Table 1. In this state they became fluid and thus, could be moved around the glass slide by mechanical shearing. Indeed the sheared birefringent fluid pattern was analogous to that for the LC phase of **ST-12**. Further, the mesophase stabilized by these higher members and **ST-10B** could be very well mixed with the Col phase of **ST-12** in the contact mixture preparation. The other higher members namely **ST-20** and **ST-22** existed in crystalline solid state at rt and melted into a birefringent fluid (LC) state on heating at 73 °C and 64 °C, respectively; in the DSC traces of the first heating cycles the peak due to this process could be seen. Yet again, the texture of mechanically stressed mesophase of these compounds was identical to that of the Col phase stabilized by the other members of the series. In addition, owing to the thermal degradation of these members at elevated temperatures (>250 °C) a meaningful (an identifiable) texture of the ordered fluid phase could not be obtained on cooling the isotropic phase and thus, a precise identification of the phase by optical study was not possible. However, the molecular structure of these supramolecular TSANs, like the other members of the present series and the known discotic TSANs, is quite conducive to stabilize Col phase/s. To test this, both the samples (**ST-20** and **ST-22**) were subjected to contact mixture study using the present compounds (**ST-14**, **ST-16**, and **ST-10B**) or previous Col TSANs as standard samples. As expected, the mesophases of all the systems were found to be miscible in the contact region suggesting that **ST-20** and **ST-22** also display Col mesomorphism. This implies that the higher members of the **ST-n** series of TSANs, including **ST-12** and **ST-10B** exhibit an identical (monomesomorphic) Col behavior.

This hypothesis was found to be consistent with the results (see Table 2) derived from the powder XRD experiments carried out in the frozen (at rt) and fluid (at 150 °C) LC states of compounds **ST-16** and **ST-10B**, as representative cases. Notably, the diffractograms of both the materials were found to be quite identical to the ones obtained for **ST-12** and thus, confirmed the Col structure of the mesophase. In particular, the patterns exhibited a strong maximum at the smaller scattering angles, which corresponds to the (1, 0) reflection from 2D hexagonal lattice. Of course, the presence of the only (1, 0) reflection rules out the unambiguous symmetry assignment but such a scenario is frequently encountered in the diffractograms of hexagonal Col phase stabilized by different discotics^{3,13} and it is ascribed to a minimum in the form factor. Besides, at high angles, two diffuse reflections corresponding to the liquid-like order of the peripheral tails and the stacking distance of cores within the column were seen. Thus, the **ST-n** series of supramolecules exhibit a hexagonal columnar phase where the individual indefinitely long fluid columns formed by the co-facial stacking of C_{3h} isomers through H-bond network self-assemble into a hexagonal lattice, with a possible intercalation of discs belonging to adjacent columns.

The absorption and emission characteristics of these compounds were examined using their dilute solutions in CHCl₃ (10⁻⁴ mol/L). The UV spectrum shows two bands at ~350 nm (weak) and ~270 nm (strong); the former absorption band can be ascribed to the imine π-π* transition and latter might have originated due to the strong intermolecular interactions. The absence of an absorption band at about 400 nm seen for other discotic TSANs³ due to n-π* transition is noteworthy. Besides, they did not show emissive characteristics under any condition suggesting the effective decrease in the π-conjugation area of the molecules. These findings imply that the three supramolecular arms in the form of trialkoxybenzoylhydrazine are not in conjugation with the central core and thus, the electronic delocalization of the system is suppressed significantly. Of course, the absence of emissive property due to non-radiative decay via low-energy excimeric states, or via double bond twisting or excited state proton transfer cannot be ruled out.

The preparation and characterization of supramolecular TSANs exhibiting columnar mesomorphism are reported for the first time. Their occurrence in a single C₃ keto-enamine tautomeric form is remarkable given the observation that the known discotic TSANs comprise C_s isomer additionally. The intermolecular H-bonding and π-stacking are the key factors that favor their self-assembly into fluid Col structure. The former feature is especially significant in improving the thermal range of the Col phase. The non-emissive nature of these materials indicates that the self-complementing arms present around the central C₃ core aid in suppressing π-conjugation effectively. This work therefore serves to support the emerging notion that the structural features and material properties of TSANs can be readily altered by subjecting them to a simple chemical transformation such as substituting the central core with appropriate functional wings.

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12. The target supramolecular LCs were synthesized following a synthetic procedure described below. The characterization data has been given for **ST-12** as a representative case. In a typical reaction, a mixture of 1,3,5-triformylphloroglucinol (0.4 mmol, 1 equiv) and 3,4,5-tris(alkoxy)benzohydrazides **2-n** (1.6 mmol, 4 equiv) in absolute ethanol (15 ml) was heated at reflux under nitrogen for 4 h. The pale yellow solid separated was collected by filtering the hot heterogeneous reaction mixture and repeatedly washed with hot ethanol and dried in vacuo. The crude product was repeatedly recrystallized in a mixture of ethanol–dichloromethane (9:1) to obtain pure pale yellow solids. Yield: 70%; a gummy mass [Found: C, 74.70, H, 10.63, N, 3.7. C₁₃₈H₂₄₀N₆O₁₅ requires C, 74.55, H, 10.88, N, 3.78]; UV–vis: $\lambda_{\text{max}} = 360.9$ nm, $\epsilon = 2.4 \times 10^2$ L mol⁻¹ cm⁻¹, 275.4 nm, $\epsilon = 6.3 \times 10^3$ L mol⁻¹ cm⁻¹; IR (KBr pellet): ν_{max} in cm⁻¹: 3221, 2920, 2851, 1648, 1581, 1468, 1227, 1117, and 721; ¹H NMR (CDCl₃, 400 MHz): δ 13.2 (br s, 3H, 3 × OH), 10.7 (br s, 3H, 3 × NH), 8.5 (br s, 3H, 3 × CH=N), 7.25 (s, 6H, Ar), 3.97 (br s, 18H, 9 × OCH₂), 1.75–0.85 (m, 207H, 90 × CH₂, 9 × CH₃); ¹³C NMR of this compound could not be obtained due to its low solubility in organic solvents.
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