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Tris(*N*-salicylideneanilines) [TSANs] exhibiting a room temperature columnar mesophase: synthesis and characterization

C. V. Yelamaggad* and A. S. Achalkumar

Centre for Liquid Crystal Research, Jalahalli, Bangalore 560013, India

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Abstract—Tris(*N*-salicylideneaniline) derivatives with peripheral branched alkyl chains, existing in their C_{3h} and C_s symmetric keto-enamine tautomeric forms, synthesized by condensing alkoxyanilines with 1,3,5-triformylphloroglucinol, display a technologically important columnar liquid crystal phase over a wide thermal interval (~160 °C) well below and above room temperature, as established by optical and calorimetric studies.

Liquid crystal (LC) phases are intermediate between the anisotropic solid and isotropic liquid states. They are liquid in their facile mobility, yet retain some of the intermolecular and intramolecular order of crystals. Conventionally, such LC phases consist of rod-like (calmitic) or disk-like (discotic) molecules comprising covalently bonded structurally incompatible entities namely, flexible aliphatic chains and a rigid anisometric core.[1] The parallel arrangement with long range orientational order of such molecules leads to the formation of the nematic (N) phase whereas microphase segregation of incompatible regions promotes a smectic (Sm) or columnar (Col) phase.[2]

In particular, Col phases, characterized by indefinitely long molecular columns aggregating into two-dimensional (2D) lattices with different symmetries, are of great significance. This is because they allow the possibility of combining several physical properties with the orientational control of the molecular order, self-healing of structural defects and ease of processability when compared to the inorganic semiconductors or zone refined single crystals currently used in electronic applications. The central aromatic core of a disc-like molecule acts as a conducting unit, while surrounding paraffinic tails serve as a mantle (insulator). Thus the organization of such molecules in one-dimensional Col stacks facilitates smooth charge-transport. This anisotropy in conduction can be well exploited in molecular electronic devices such as one-dimensional conductors,[3] photoconductors,[4] molecular wires and fibers,[5] light emitting diodes,[6] field-effect transistors, and photovoltaic cells.[7] The performance of such electronic devices depends critically on the high charge-carrier mobility.

The vast majority of disc-like mesogens, comprising electron-rich (donor) aromatic cores such as triphenylene, dibenzopyrene, and hexabenzocoronene, etc.; are good hole transporters, that is, the p-type materials. However, examples of n-type discotics derived from electron-deficient aromatic systems with electron-accepting character are rather scarce. Examples include coronene derivatives peripherally substituted with electron withdrawing carboximide groups or aromatic systems with electronegative nitrogen in the core such as triazines or quinoxalines.[8] Recently, electron deficient heterocycles like hexaazatriphenylene[9] and hexaazatrinaphthylene[10] have been reported as new n-type discogens.

Tris(*N*-salicylideneanilines) [TSANs], existing exclusively in keto-enamine forms with C_{3h} and C_s symmetries, undergo the multiple proton transfer process.[11] From the point of view of applications, especially in electronic devices involving n-type discogens, such an inherent property of TSANs is highly promising. In fact, we have recently demonstrated that the TSANs with appropriate molecular design self-assemble to form

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* Corresponding author. Tel.: +91 8028381119; fax: +91 9028382044; e-mail: yelamaggad@yahoo.com

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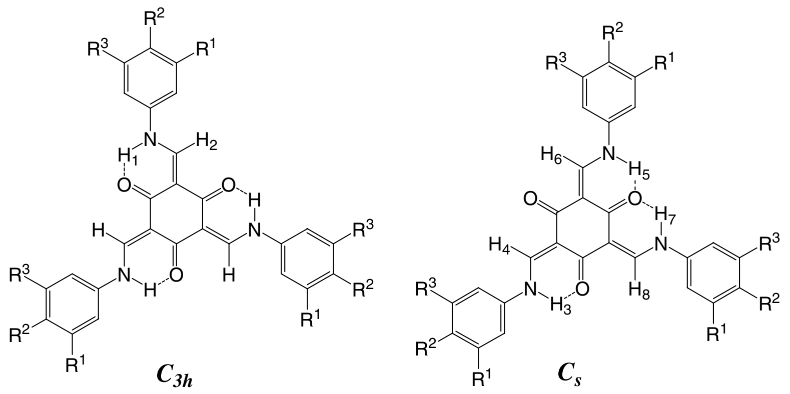


I: $R^1 = H$; $R^2 = R^3 = O\text{-}n\text{-}C_nH_{2n+1}$
II : $R^1 = R^2 = R^3 = R = O\text{-}n\text{-}C_nH_{2n+1}$

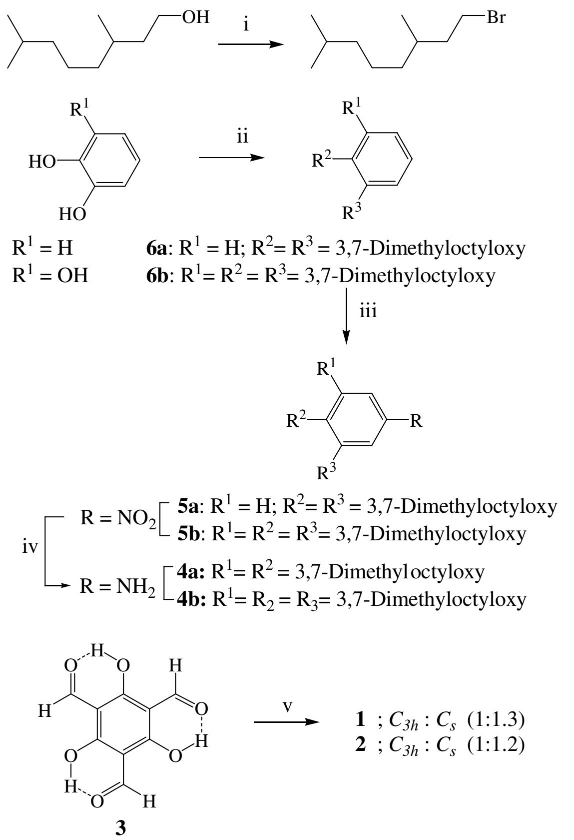
1 : $R^1 = H$; $R^2 = R^3$ = 3,7-Dimethyloctyloxy
2 : $R^1 = R^2 = R^3$ = 3,7-Dimethyloctyloxy

Figure 1. The molecular structure of tris(*N*-salicylideneanilines) [TSANs] existing in keto-enamine forms with C_{3h} and C_s from previous (**I** and **II**)[12] and present (**1** and **2**) investigations.

Col LC phases in which the proton and electron interact with each other through the H-bonding environment.[12] The central core of a TSAN, formed by strong intramolecular hydrogen bonding between the enamine proton and oxygen of the cyclohexanetrione, is almost the size as triphenylene. The core–core separation observed in the Col phase of these molecules is 3.29 Å. Remarkably, the magnitude of core–core separation further decreases to 3.26 Å on freezing the Col structure. This value is close to the shortest core–core separation observed hitherto.[9a] Small core–core separation leads to a better π–π* overlap; the formation of a glassy columnar phase ensures a defect-free alignment. These features make them promising materials for a rapid intracolumnar charge migration. However, ideal materials should have a wide mesophase range with low melting and clearing points to circumvent the difficulties involved in experimental investigations.

These features motivated us to design and synthesize TSANs exhibiting a room temperature columnar mesophase (Fig. 1). A number of research groups have recently shown that when branched alkyl chains are introduced at the peripheral region of discotic molecules, the liquid-like disorder is enhanced. This leads to a widening of the mesophase thermal range and lowering of melting points without altering the type of the mesophase.[13] Following this strategy, we have designed the first examples of TSANs that display a room temperature Col fluid phase. The molecular structures of the two TSANs, **1** and **2** existing in keto-enamine forms with C_{3h} and C_s symmetries, synthesized in the present investigation are shown in Figure 1. As can be seen, in these materials a 3,7-dimethyloctyloxy chain was used as the branched peripheral tail.

The synthetic route to target molecules **1** and **2** is depicted in Scheme 1. The pure liquid crystalline yellowish products were characterized by ^1H NMR, ^{13}C NMR, IR, UV–vis spectroscopy, FAB mass spectrometry and elemental analysis.[14]



Scheme 1. Synthesis of **1** and **2**. Reagents and conditions: (i) 48% HBr, H_2SO_4, (80%); (ii) 1-bromo-3,7-dimethyloctane, anhyd K_2CO_3, DMF, 80 °C, 17 h, (**6a**: 82%; **6b**: 85%); (iii) 70% HNO_3, $NaNO_2$, CH_2Cl_2, 1 h, (**5a**: 75%; **5b**: 80%); (iv) 10% Pd/C, H_2, THF, 12 h, (**4a**: 80%; **4b**: 85%) and (v) **4a** or **4b**, EtOH, 80 °C, 5 h, (**1**: 70%; **2**: 75%).

^1H NMR and ^1H–^1H COSY NMR spectra provided proof of the existence of **1** and **2** in their C_{3h} and C_s symmetric keto-enamine tautomeric forms in the ratio of 1:1.3 and 1:1.2, respectively. The coupling between the enamine protons and vinylic protons was clearly

Table 1. Mesomorphic behaviour of tris(*N*-salicylideneanilines) **1** and **2**

TSANs (C_{3h}:C_s)[a]	Phase sequence[b]	
	Heating (°C)	Cooling (°C)
1 (1:1.3)	Col 109.9 (5.8) I	I 105.5 (1.9) Col[c]
2 (1:1.2)	Col_2 68[d] Col_1 109.9 (4.1) I	I 106.3 (20.7) Col_1 64[d] Col_2[c]

Col = Columnar phase (Col_1 and Col_2 are different columnar phases); Iso = Isotropic phase.

[a] Ratio obtained from ^{1}H NMR.

[b] Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles.

[c] No crystallization was observed till −60 °C.

[d] The phase transition observed with a microscope was too weak to be detected by DSC.

elucidated from ^{1}H–^{1}H COSY NMR. These NMR spectral data are in agreement with earlier reports.[11,12]

The mesomorphic behaviour of the two TSANs was examined by observing optical textures as well as ascertaining the transition temperatures using polarizing optical microscope (POM) (Leitz DMRXP) equipped with a programmable hot stage (Mettler FP90). The transition temperatures and associated enthalpies were obtained from thermograms recorded on a differential scanning calorimeter (DSC) (Perkin–Elmer DSC7) that was calibrated previously using pure indium as the standard. The results obtained are shown in Table 1. These compounds, placed between an ordinary glass slide and cover slip, could be readily spread around the slide at room temperature by mechanical shearing. The spread-over samples showed a highly birefringent texture, clearly indicating that both compounds were already in the LC state. On cooling at a rate of 5 °C/min from their isotropic phase, compound **1** showed a mesophase at 105 °C; the corresponding optical texture consisted of pseudo-focal conic fan-shaped defects, a typical feature for the columnar phase.[15] Interestingly, the optical texture remained unchanged till room temperature as shown in Figure 2a and no sign of crystallization was noticed even after maintaining the samples at low temperature or even when sheared.

Upon cooling from the isotropic phase, sample **2** showed a mesophase (at 106 °C) with a texture having pseudo-focal conic fan-shaped defects and homeotropic digitated stars (Fig. 2b), which is typical of the Col phase (Col_1). On further cooling, the texture of the Col_1 phase sharply transformed to another pattern comprising tiny needles (Fig. 2c) that coalesces to a grainy texture. This indicates the presence of another Col phase, which we abbreviate as Col_2.[12]

In this case also, the Col phase was found to be stable at room temperature. The DSC thermograms of both compounds corroborated the microscopic observations. For example, the DSC trace obtained during the first heating cycle of TSAN **2** from −60 °C showed only one endothermic peak at 110 °C corresponding to the Col–Iso transition (Fig. 3h_1). In the subsequent cooling scan (down to −60 °C), as expected, a sharp exothermic peak due to an Iso–Col transition was seen (Fig. 3c_1). As shown in Fig. 3h2 and c2, identical DSC profiles were obtained for the second (or any number of subsequent) heating–cooling runs. These results clearly demonstrate that the phase transitions are highly reproducible and thus the TSANs are quite stable.

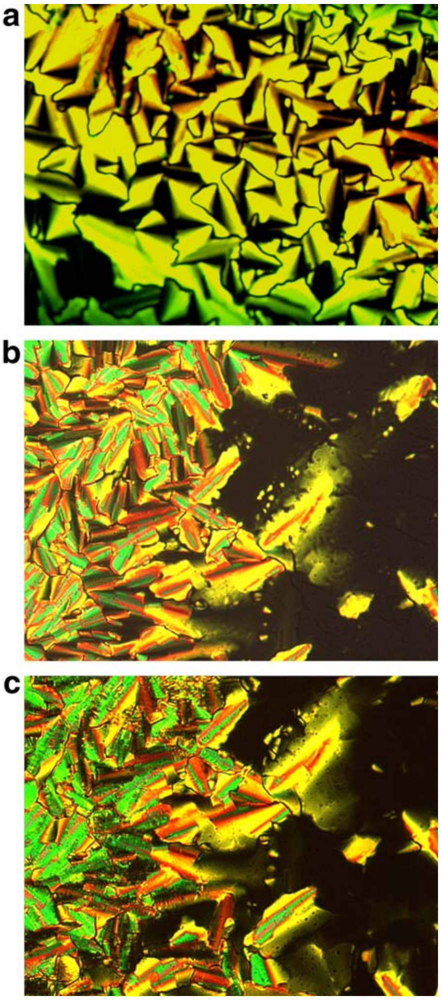


Figure 2. Optical microphotographs (cross polarizers) of the textures observed: (a) the Col phase of TSAN **1** at RT; (b) the Col_1 phase of TSAN **2** at 95 °C and (c) the Col_2 phase of TSAN **2** at 64 °C.

Furthermore, these mesogens exhibited fluorescent properties. In the UV–vis spectra, both compounds showed two absorption maxima at 329 nm (π–π*) and 416 nm (*n*–π*). Excitation at 420 nm for both the compounds, showed an emission spectrum with maximum of 482 nm. As a representative case, the absorption and emission spectra of compound **2** in THF solution are shown in Figure 4a and b, respectively. The difference

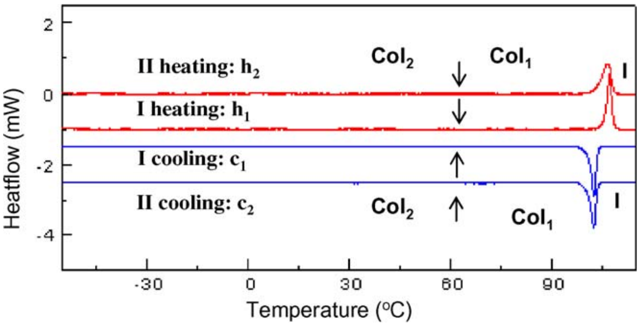


Figure 3. The DSC traces of TSAN **2** (at a rate of 5 °C/min).

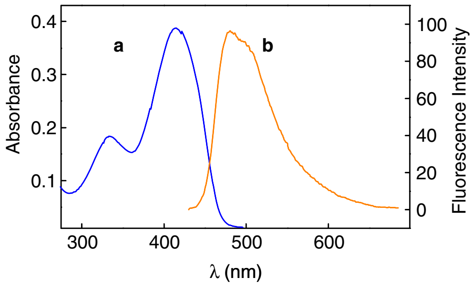


Figure 4. (a) UV absorption and (b) emission (for the excitation at 420 nm) spectra of TSAN **2** in THF.

in the number of peripheral alkoxy chains does not affect their absorption and emission characteristics noticeably, as both show identical patterns.

In conclusion, we have reported the synthesis and characterization of the first examples of TSANs (existing exclusively in their C_{3h} and C_s keto-enamine tautomeric forms) exhibiting a technologically important columnar mesophase over a large thermal range, well below and above ambient temperature. Seemingly, the branched alkyl tails at the peripheral region of the TSAN core, prevent crystallization and thus the molecules stay in a liquid crystalline state over a wide temperature range including room temperature. In our opinion, these Col LCs featuring proton and electron interaction through the H-bonding environment are ideal candidates for electronic device applications.

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14. The requisite branched chain alkyl bromide, 1-bromo-3,7-dimethyloctane was prepared by treating 3,7-dimethyloctanol with 48% hydrobromic acid in the presence of sulfuric acid. The O-alkylation of catechol or pyragallol with the alkylbromide was carried out by employing a Williamson's ether synthesis protocol to obtain dialkoxy or trialkoxy benzenes **6a** or **6b**, respectively. The nitration of **6a** or **6b** using an aqueous solution of nitric acid (70%) and catalytic amounts of sodium nitrite in dichloromethane generated the corresponding nitrobenzenes **5a** or **5b**, which upon catalytic hydrogenation furnished anilines **4a** and **4b**. 1,3,5-Triformylphloroglucinol **3** was prepared by the Duff formylation of phloroglucinol as described by Chong et al.[11] Finally, the amines (**4a** and **4b**, 0.57 mmol, 4 equiv) and **3** (0.14 mmol, 1 equiv) were taken in absolute ethanol and heated at 80 °C for 4 h.[12] The solvent was removed in vaccuo from the reaction mixture to give the target compounds as dull yellow gummy masses. These 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. Data for **1**: $R_f = 0.72$ (30% EtOAc–hexanes); A yellow liquid crystalline gummy mass; yield = 60%; UV–vis (THF): $\lambda_{max} = 416.09$ nm, $\varepsilon = 7.4044 \times 10^4$ L mol^{-1} cm^{-1}; IR (KBr pellet): ν_{max} in cm^{-1} 3450, 2924, 2853, 1621, 1592, 1458, 1018, and 829; ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 13.48 (d, $J = 13.0$ Hz, =CNH), 13.37 (d, $J = 13.3$ Hz, =CNH), 13.01 (d, $J = 13.2$ Hz, =CNH), 12.96 (d, $J = 13.4$ Hz, =CNH) (these three resonances are due to 3H), 8.63–8.77 (m, 3H, =CHN), 6.82–6.9 (m, 9H, Ar), 4.03–4.11 (m, 12H, $6 \times OCH_2$), 0.86–1.88 (m, 114H, $12 \times CH$, $24 \times CH_2$, $18 \times CH_3$); MS (FAB+): m/z for $C_{87}H_{142}N_3O_9$ (M+1), Calculated for $C_{87}H_{142}N_3O_9$: 1373.1, Found: 1373.3; Elemental analysis: calculated (found) (%): C 76.1 (75.75), H 10.35 (9.95), N 3.06 (2.96). **2**: $R_f = 0.73$ (30% EtOAc–hexanes); A yellow liquid crystalline gummy mass; yield: 72%; UV–vis (THF): $\lambda_{max} = 416.10$ nm, $\varepsilon = 5.605 \times 10^4$ L mol^{-1} cm^{-1}; IR (KBr pellet): ν_{max} in cm^{-1} 3448, 2923, 2852, 1627, 1591, 1459, 1308, 1120, 824; ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 13.48 (d, $J = 13.0$ Hz,

═CNH), 13.31 (d, $J = 13.2$ Hz, ═CNH), 13.01 (d, $J = 13.2$ Hz ═CNH), 12.89 (d, $J = 13.4$ Hz, ═CNH) (these four resonances are due to 3H), 8.63–8.8 (m, 3H, ═CHN), 6.49 (s, 6H, Ar), 3.99–4.05 (m, 18H, $9 \times OCH_2$), 0.86–1.90 (m, 171H, $18 \times CH$, $36 \times CH_2$, $27 \times CH_3$); MS (FAB+): *m*/*z* for $C_{117}H_{201}N_3O_{12}$ (M+), Calculated for $C_{117}H_{201}N_3O_{12}$: 1840.5, Found: 1840.3; Elemental analysis: calculated (found) (%): C 76.29 (75.70), H 10.99 (10.9), N 2.28 (2.76).

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