

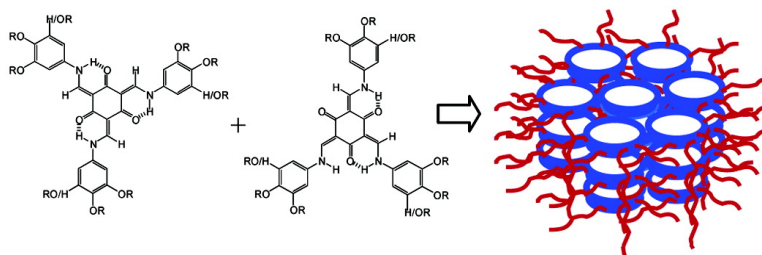
Communication

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## Self-Assembly of $C_{3h}$ and $C_s$ Symmetric Keto-enamine Forms of Tris(*N*-salicylideneanilines) into Columnar Phases: A New Family of Discotic Liquid Crystals

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Supramolecular chemistry, the noncovalent interactions between the molecules and their consequent self-assembly lead to the formation of a variety of superstructures.<sup>1</sup> Columnar (Col) liquid crystal (LC) phases formed by disc-shaped (discotic) compounds discovered by Chandrasekhar<sup>2</sup> et al. are well-known examples of supramolecular assemblies based on self-organization. These are fluid anisotropic phases in which disc-shaped molecules self-assemble such that they stack one on top of the other to form Col structures and are promising for potential applications<sup>3</sup> such as one-dimensional conductors,<sup>4</sup> photoconductors,<sup>5</sup> molecular wires and fibers,<sup>6</sup> light emitting diodes,<sup>7</sup> and photovoltaic cells.<sup>8</sup> A large number of polynuclear aromatic cores have been employed to tailor the charge mobility (transport) that occurs through overlapping intermolecular  $\pi$ -orbitals in a fluid media initiated either by making a charge-transfer complex or by photolysis.<sup>3</sup> In crystalline organic materials in which molecules are stacked so that charge migrates with a smooth periodic potential is well-known.<sup>9</sup> If such a crystalline system is associated with proton transfer and a simultaneous rearrangement of the  $\pi$ -orbitals occurs then a coupling between motions of the proton and the conduction electron might be produced, which is a key phenomenon for many proposed molecular electronic devices.<sup>10</sup> However, molecular systems with such a property are difficult to realize and also expensive to process because for an effective charge transport single crystals are required. On the other hand, Col LC phases have been regarded as suitable and inexpensive substitutes for single crystalline molecular systems. To our knowledge, there have been no attempts to form Col LC phases in conjunction with the unique property of proton-transfer accompanied by a configurational change of  $\pi$ -electrons.

*N*-Salicylideneanilines **1** (Figure 1) are an interesting class of compounds possessing intramolecular H-bonding. Although the two geometric forms of these systems, viz. enol-imine **1** (OH) and keto-enamine **2** (NH), are expected to be in equilibrium with each other, it is the enol-imine (**1**) form that is commonly encountered and well-characterized. The interest in these materials has been triggered because reversible proton transfer (tautomerism) between the two forms occurs, leading to properties such as thermo-<sup>11</sup> and photochromism.<sup>12</sup> Recently, Chong et al. have reported the first structural characterization of exclusive keto-enamine forms with  $C_{3h}$  (**4**) and  $C_s$  (**5**) symmetries of tris(*N*-salicylideneanilines) (TSANs) (**3**) by X-ray and NMR studies.<sup>13</sup> For TSANs the multiple proton transfer process leads to four tautomeric forms. From the point of view of applications, especially for electronic devices, such an inherent property of these molecules is highly promising. Here we demonstrate that the TSAN core with appropriate molecular design self-assembles to form Col LC phases in which the proton and electron interact with each other through the H-bonding<sup>14</sup> environment to furnish unique materials which, in our opinion, will exhibit high charge carrier mobility.<sup>15</sup>

To obtain TSANs, various amines were condensed with 1,3,5-tri-

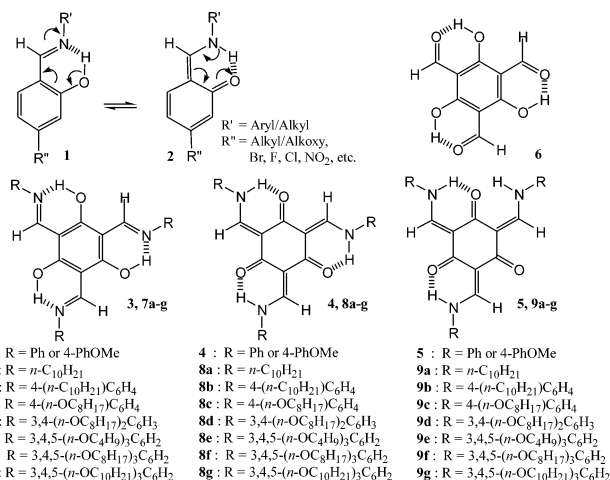


Figure 1. Structures of the compounds pertaining to the present study.

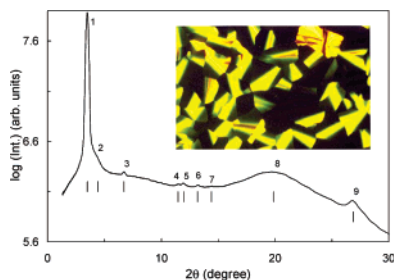
formylphloroglucinol (**6**).<sup>13</sup> With a view to realize a LC Col structure in these systems, we first softened the core by condensing decylamine or 4-*n*-decylaniline or 4-*n*-octyloxyaniline to obtain TSANs **7a–c**. As evidenced by <sup>1</sup>H NMR (see Supporting Information (SI)) studies, these compounds actually exist in their keto-enamine ( $C_{3h}$  (**8a–c**) and  $C_s$  (**9a–c**) tautomeric forms in the ratios mentioned in Table 1. Optical microscopic studies revealed that these derivatives are not mesomorphic (Table 1). However, it is well-known that Col phases can be stabilized by space-filling properties. We anticipated that the TSANs derived from di/trialkoxyanilines would perhaps fulfill the space-filling conditions and promote the formation of Col phases. Therefore, we synthesized a dialkoxo **7d** and three trialkoxo **7e–g** derivatives, which were again found to exist *exclusively* in their keto-enamine tautomeric forms. Interestingly, they were found to be LCs as discussed below.

On cooling from the isotropic phase, the tautomeric forms **8d** and **9d** show a mesophase with a mosaic texture (Figure 2, inset), which is characteristic of a Col phase. The pattern remains unaltered until room temperature (RT), although a strong peak is observed at  $\sim 57$  °C in the DSC run. The “1-D cut” (intensity vs  $2\theta$  profile) extracted from the X-ray diffraction (XRD) pattern obtained while cooling the sample from the isotropic (I) phase is shown in Figure 2. Several sharp peaks (labeled 1–7 in Figure 2) are seen in the low-angle region, features which are typical for a Col phase. While peak number 9 arises because of the stacking of the cores within a column, peak number 8 arises from the packing of floppy chains. The diffuse nature of these two reflections indicates that the ordering within the columns is not long-range. The spacings of the first three low-angle reflections are in the ratio of 1:0.76:0.5. These and other sharp reflections could be indexed to a rectangular lattice. All these features are characteristic of Col phase with a 2D rectangular lattice (Col<sub>r</sub>). On cooling the sample to RT, although the peak intensities changed, the pattern remained the same (see SI for XRD pattern).

**Table 1.** Tautomers (**8a–g** and **9a–g**) and Optical and Thermal Properties of **7a–g**<sup>a</sup>

| comps (ratio) <sup>b</sup> | heating   | cooling   |
|----------------------------|---|---|
| <b>8a + 9a</b> (1:2.3)     | Cr 74 (107.1) I   |   |
| <b>8b + 9b</b> (1:2)       | liquid  |   |
| <b>8c + 9c</b> (1:1.5)     | gummy mass  |   |
| <b>8d + 9d</b> (1:1.8)     | Cr 75.6 (33.1) Col <sub>r</sub> 136.4 (4.4) I                                     | I 135 (4.3) Col <sub>r</sub> 57 (0.9) X <sup>c</sup>                                |
| <b>8e + 9e</b> (1:0.3)     | Cr 176.1 (6.1) Col <sub>k</sub> 219.1<br>(0.7) Col <sub>h</sub> 246 (7.5) I       | I 245 (7.2) Col <sub>h</sub> 218<br>(0.6) Col <sub>k</sub> 171.6 (6.1) Cr           |
| <b>8f + 9f</b> (1:0.9)     | Cr 57.2 (5.2) Col <sub>r</sub> 164.4<br>(0.1) Col <sub>h</sub> 186.2 (8.1) I      | I 185.1 (8) Col <sub>h</sub> 163<br>(0.2) Col <sub>r</sub> <sup>c</sup>             |
| <b>8g + 9g</b> (1:1.1)     | Cr 64.2 (4.5) Col <sub>r</sub> 158.5 <sup>d</sup><br>Col <sub>h</sub> 175.2 (8) I | I 173.6 (7.8) Col <sub>h</sub> 157.7 <sup>d</sup><br>Col <sub>r</sub> 62.9 (6.1) Cr |

<sup>a</sup> Transition temperatures (°C) and enthalpies (kJ mol<sup>-1</sup>) were determined by DSC (at a rate of 5 °C/min). <sup>b</sup> Based on <sup>1</sup>H NMR spectra (see Supporting Information for spectra of **8d** and **9d**). <sup>c</sup> This phase supercools until -60 °C. <sup>d</sup> Transition observed only under microscope.



**Figure 2.** XRD pattern and optical texture (inset) obtained for the Col<sub>r</sub> phase of the geometric forms **8d** and **9d** at 70 and 127 °C, respectively.

As mentioned above, the texture seen under the microscope also does not undergo any change, whereas a phase transition is observed in the DSC scans. Noting that while the sample can easily be sheared at temperatures above this transition, but not below, we feel that the low-temperature structure (X) is glassy in nature with the structure of the high-temperature Col<sub>r</sub> phase frozen in. In contrast, the trialkoxy derived geometric forms **8f** and **9f** show a different behavior. As the sample is cooled from the I phase, it displayed an optical texture that was a mixture of the low-birefringence dendritic pattern and linear high-birefringent defects, a feature also observed for the Col phases. A clear phase transition was observed at 163 °C, in agreement with the DSC scan, when a needlelike texture developed (see SI). The XRD profile taken in the high temperature (HT) phase showed five sharp reflections (see SI), the lowest-angle peak being very intense. The spacings of the first three reflections are in the ratio of 1:0.576:0.5, and together with the diffuse reflections in the wide-angle region confirm that the phase is the hexagonal columnar (Col<sub>h</sub>) phase. The pattern in the low-temperature (LT) phase (see SI) was that of the Col<sub>r</sub> phase with features mentioned for **8d** and **9d**. Decreasing the chain length (**8e** and **9e**) does not alter the scenario much, even retaining the transition between two Col phases with very similar textural changes as in **8f** and **9f**. However, the XRD pattern in the LT (Col<sub>k</sub>) phase, although similar to that for the LT phase of **8f** and **9f**, has additional peaks (see SI), which have to be indexed, a process that is in progress. The higher homologue with decyloxy tail forms **8g** and **9g** behaves similarly to **8f** and **9f**.

A notable feature in all the XRD patterns is the presence of a peak (at  $2\theta \approx 25^\circ$ ) due to correlations between the molecular cores of disks within the same column. This peak is observed even at high temperatures and close to the isotropic phase also. For example, for the geometric forms **8e** and **9e**, the core–core peak is observed even at temperatures as high as 230 °C. Generally, thermal fluctuations drastically reduce such correlations, and therefore, the coherence length associated with them is strongly temperature-dependent. Further, the size (area) of the core also has a significant influence on the magnitude of the correlations. It may be recalled

that for the benzene hexanoates, the core–core peak is not observed at all as the core size is smaller,<sup>16</sup> whereas for the triphenylene (having a larger core) systems it is commonly observed. For the compounds studied here the central region is just a phenyl ring, and thus the observation of the core–core peak should have been surprising. However, the formation of strong intramolecular hydrogen bonding results in an effective larger molecular core. Consequently, the average stacking distance of the disks within the same column (core–core separation) is quite small, especially for **8d** and **9d**, showing a value of 3.29 Å in the HT mesophase. This value is near one of the lowest values observed in the Col phase of any nonmetallomesogen.<sup>17</sup> A further decrease is seen in the glassy phase and with a value of 3.26 Å is the same as that reported for the case of a complex with two phthalocyanine cores linked by a lutetium atom.<sup>18</sup> The significance of these numbers should be seen in light of the fact that the materials exhibiting a Col phase but show a small core–core separation which ensures the enhanced  $\pi$ – $\pi^*$  orbital overlapping are good candidates for rapid intracolumnar charge migration.

In conclusion, we have discovered a unique class of discotic LCs derived from TSANs existing *exclusively* in their C<sub>3h</sub> and C<sub>s</sub> keto-enamine tautomeric forms. These compounds display Col LC phases in which the proton and electron interact with each other through the H-bonding environment. Remarkably, the core–core separation is quite small, making them promising materials for many proposed electronic devices.

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**Supporting Information Available:** Synthetic procedure and characterization data for **8a–g** and **9a–g** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (a) Lehn, J.-M. *Supramolecular Chemistry*; Wiley-VCH: New York, 1995.
- (b) Ikkala, O.; ten Brinke, G. *Science* **2002**, *295*, 2407. (c) Tschierske, C. *Annu. Rep. Prog. Chem. Sect. C: Phys. Chem.* **2001**, *97*, 191.
- Bushby, R. J.; Lozman, O. R. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 343.
- Chandrasekhar, S.; Balagurusamy, V. S. K. *Proc. R. Soc. London, Ser. A* **2002**, *458*, 3.
- Adam, D.; Schuhamcher, P.; Simmerer, J.; Hayssling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141.
- Osburn, E. J.; Schmidt, A.; Chau, L. K.; Chen, S. Y.; Smolnyak, P.; Armstrong, N. R.; O'Brian, D. F. *Adv. Mater.* **1996**, *8*, 926.
- Christ, T.; Glusen, B.; Greiner, A.; Kettner, A.; Sander, R.; Stumpf, V.; Tsukruk, V.; Wendorff, J. H. *Adv. Mater.* **1997**, *9*, 48.
- Schmidt-Mende, L.; Fechtenkotter, A.; Mullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119.
- Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*; Oxford University Press: Oxford, 1999.
- Inabe, T. *New. J. Chem.* **1991**, *15*, 129.
- Ogawa, K.; Kasahara, Y.; Ohtani, Y.; Harada, J. *J. Am. Chem. Soc.* **1998**, *120*, 7107.
- Harada, J.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5809.
- Chong, J. H.; Sauer, M.; Patrick, B. O.; MacLachlan, M. J. *Org. Lett.* **2003**, *21*, 3823.
- Gearba, R. I.; Lehmann, M.; Levin, J.; Ivanov, D. A.; Koch, M. H. J.; Barbera, J.; Debije, M. G.; Piris, J.; Geerts, Y. H. *Adv. Mater.* **2003**, *15*, 1614. It is worth noting that in this system tautomerism does not exist.
- Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem Rev.* **2001**, *101*, 4071.
- Safinya, C. R.; Clark, N. A.; Liang, K. S.; Varady, W. A.; Chiang, L. Y. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 205.
- Kumar, S.; Rao, D. S. S.; Prasad, S. K. *J. Mater. Chem.* **1999**, *9*, 2751.
- van de Craats, A. M.; Warman, J. M.; Hasebe, H.; Naito, R.; Ohta, K. *J. Phys. Chem. B* **1997**, *101*, 9224.

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