A mix of molecules: Banana and rod-formation of a new SmA_{2b} phase in liquid crystals

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'Banana mania' is an active area of research being pursued worldwide in liquid crystals. Liquid crystals are more structured than liquids, but less structured than organic crystals[1]. They show several transitions that involve new phases whose properties are between those of the solid and liquid phases. Liquid crystals have 'liquid-like flow' but possess 'orientational order'. In both smectic and nematic type of liquid crystals, the molecules are 'strongly elongated'. The point of interest here is the smectic-A (SmA)-phase. All smectics are layered structures with a well-defined interlayer spacing. The arrangement of rod-like molecules in a SmA liquid crystal is shown in Figure 1. They possess a layer thickness (*d*) proportional to the length of the molecule itself and are optically anisotropic in nature.

In recent times, banana-shaped compounds have evolved as a new sub-field of liquid crystals[2]. These organic molecules, because of their bent-core or V-shape, are called 'bananas'. Sterically-induced packing defines new types of smectic phases. Some of these phases show unusual physical characteristics such as ferro- and antiferroelectricity, together with second harmonic generation (SHG), making interesting possibilities for all kinds of applications. A recent paper[3] describes the design and synthesis of a ferroelectric liquid crystal composed of racemic molecules. The molecular packing of bent-core molecules exhibits polarity in the arrangement within the smectic layers even though the individual molecules themselves are achiral. This produces a spontaneous transverse polarization.

Bent-core molecules basically consist of a V-shaped core and alkyl tags at the two ends of the V-bend. Bent-core mesogens which have between 5 and 7 aromatic or heterocyclic rings in the central core are being studied. Several types of bent-core molecules have been synthesized and the liquid crystalline phases they exhibit have been classified as B_1 to B_7 (B_3 and B_4 are now known to be crystalline phases). The structure and properties of some of these B_1–B_7 phases have been characterized using X-ray, NMR, dielectric and electrooptical measurements[2].

The chiral liquid structures formed by bananas have been studied theoretically[4]. This study investigated the stable molecular configurations within the layers that are associated with achiral bent-shaped molecules and worked out their phase diagrams. Different structures arise as a result of chirality of the layers, the polarization vectors and their tilting directions[5].

Breakthroughs in liquid crystal research are obtained when new molecules are synthesized with an aim to produce new phases with interesting properties. Indian researchers with single-minded focus and working as a 'hands-on' experimental team have come up with a research paper recently[6]. Their ingenious experiment actually produces a mixing of two types of new low molecular weight organic molecules synthesized by them, demonstrating some clever liquid crystal chemistry. The mixed system comprising bent-core (banana) and biphilic rod-like molecules, produced at certain concentrations, a new biaxial bilayer smectic-A_b phase. The 'mixing' that is experimentally established is itself novel. This is only the second known example of such a phase. The other was seen in a polymeric system[7].

The molecules synthesized for the above experiment at the Liquid Crystal Laboratory of Raman Research Institute, Bangalore are the V-shaped molecule (with a bend angle of ~ 120°) and the rod-like molecule without a highly polar end group as shown in Figure 2 *a* and *b*, respectively[6]. The bent-core molecule is 1,3-phenylene-*bis*[4-(3-methyl benzoyloxy]-4′-*n*-dodecylbiphenyl-4′-carboxylate ($R = C_nH_{2n} + 1$ where $n = 4, 5...12$). The molecule where $n = 12$ is (A). Rod-like molecule (B) is 4-biphenylyl-4″-*n*-undecyloxybenzoate. The synthesis and thermodynamic properties of biphenyl benzoates of type (B) have been discussed by Sadashiva[8]. The formation of mixtures of (A) and (B) is made possible because the researchers have matched the aromatic and alkyl groups such that in the SmA_{2b} phase,

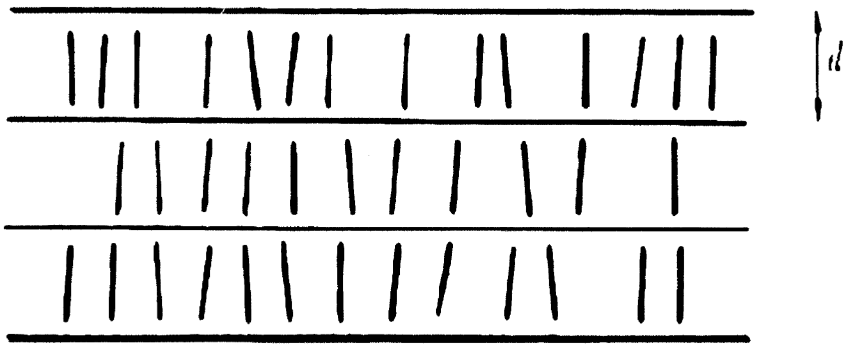

Figure 1. Arrangement of rod-like molecules in a smectic-A liquid crystal (from ref. 1a).

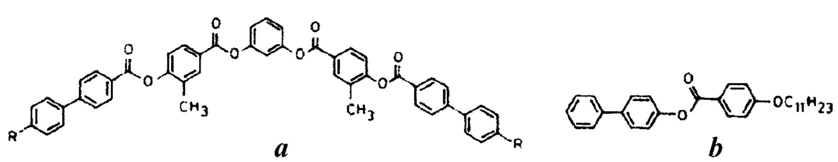

Figure 2. ***a***, Bent-core molecule; ***b***, rod-like molecule (both from ref. 6).

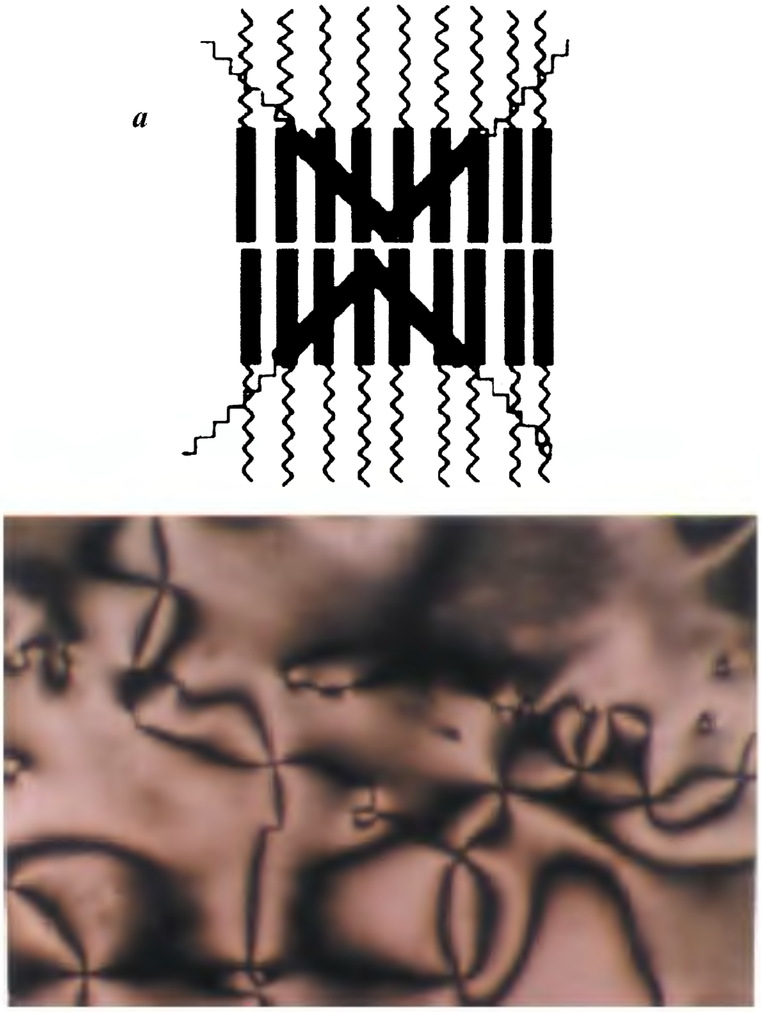

Figure 3. ***a***, Schematic diagram of the SmA_{2b} liquid crystal (from ref. 6); ***b***, SmA_{2b} phase showing the schlieren texture (photo credit Pratibha *et al.*[6]).

the aromatic core of the bent-core molecules match and sits on the aromatic groups of the (B) molecules; so do the alkyl groups of (A) and (B) (Figure 3 *a*).

Binary mixtures of liquid crystals are of considerable importance due to their practical applications. Such mixtures have properties more suitable for device applications than that of pure liquid crystals, especially in the area of display devices. The mean field theory of binary mixtures in nematic liquid crystals predicts temperature-composition phase diagrams[9]. The binary system reported by Pratibha *et al.*[6], shows a new type of orientational transition when the bent-core molecule (A) mixes in an anisotropic SmA matrix made up of rod-like molecules (B). At concentration of (A) below ~ 13 mole per cent (mol%), a structural change takes place in which the symmetry axes point along the layer normal of the SmA_2 structure formed by (B). For concentration of (A) between ~4 and 13 mol%, the molecules of (A) order themselves in the smectic layers with the director being orthogonal to the molecules of (B) displaying the biaxial smectic A_2 (SmA_{2b}) phase.

For the composition range of about 8 mol% of the bent-core molecule (A) for the binary mixture, Pratibha *et al.*[6] using glass plates treated with a polymer such as octadecyl triethoxysilane have obtained at a temperature lower than the N (nematic)-SmA_2 transition point, a schlieren texture using crossed polarizers (Figure 3 *b*). Defects in the schlieren texture obtained, have strength of ½ with two brushes. The projected length along the 'bow' of the bent-core has been found to be about 26 Å by the researchers. In the bilayer structure, one half of the bilayer has an 'up' and the other half a 'down' orientation of the bows of the bent-core molecule's aromatic core (Figure 3 *a*).

In the study, Pratibha *et al.*[6] have at the molecular level, successfully woven a strategy by suitably matching dimensions of banana and rod-like molecules and given a new twist to the area of liquid crystal chemistry by producing binary mixtures. According to one of the authors, N. V. Madhusudana, 'the new bilayer created has the potential for occurrence of 2D fluctuations. So far, there have been no reports of experimental systems where influence of fluctuations on orientational order in 2D have been noticed'. He further stated sult of impact in this area of liquid crystals has been made possible by focused collaborative work by the team involved beginning from materials preparation, techniques used, to the final analysis. Rods and discs do not mix. The very fact of mixing is itself interesting'. He stressed that it 'opens up immense possibilities, one of which is in the area of bio-membranes that could be tailored into 2D orientationally ordered structures'.

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