A mix of molecules: Banana and rod-formation of a new SmA\textsubscript{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. 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\(^1\). 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\(^2\) 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\(^3\).

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\(_n\) 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 \(\sim 120\degree\)) and the rod-like molecule without a highly polar end group as shown in Figure 2 \(a\) and \(b\), respectively\(^8\). The bent-core molecule is 1,3-phenylene-\(h\)-bis\{4-(3-methylbenzoyloxy)-4′-\(n\)-dodecylbenzoyl\}-4′-carboxylate \((R = \text{C}_{n}\text{H}_{2n+1})\) where \(n = 4, 5, 12\). The molecule where \(n = 12\) is \((A)\). Rod-like molecule \((B)\) is 4-hydroxybenzoate. The synthesis and thermodynamic properties of biphenyl benzoates of type \((B)\) have been discussed by Sadashiva\(^9\). 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.
in which the symmetry axes point along (mol%), a structural change takes place 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 SmA₂ 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 A₂ (SmA₂b) phase.

For the composition range of about 8 mol% of the bent-core molecule (A) for the binary mixture, Pratibha et al. using glass plates treated with a polymer such as octadecyl triethoxysilane have obtained at a temperature lower than the N (nematic)-SmA₂ 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. 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 that ‘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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