Liquid Crystals

A Low-Molar-Mass, Monodispersive, Bent-Rod Dimer Exhibiting Biaxial Nematic and Smectic A Phases

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In memory of V. N. Raja

Liquid crystal (LC) phases are a unique state of matter. Apart from their importance in life sciences, they have been used as novel media in many practical applications.[1,2] Of the variety of thermotropic LC phases known, the simplest but most exploited phase in display device technology is the optically uniaxial nematic (N_u) phase, in which the constituent rodlike molecules, on average, orient about a common axis called the director **n** (Figure 1 a). In contrast, one of the most sought after phases in thermotropic LCs is the biaxial nematic (N_b) phase, in which there is, additionally, a correlation of the molecules in a direction **m** perpendicular to the prime director **n** (Figure 1 b). Chandrasekhar et al.[3] were the first to observe this phase, which is yet to be universally accepted.[4] Designing a molecular structure for realizing a N_b phase is not a trivial task, necessitating careful molecular engineering. Nonetheless, several different classes of LCs have been realized[4–8] in which the shape biaxiality[9] of the rodlike or disclike entity is optimized by breaking the shape symmetry. Another phase, the smectic A (SmA) phase, generally has a uniaxial character (Figure 1 c), although the possibility of a biaxial smectic A (SmA_b) phase in which the molecules are along the layer normal, but have an additional director **m** in the plane of the layers, was pointed out.[10] Brand et al.[11] developed this idea and proposed a SmA_b phase whose symmetry depends on the type of constituent molecules: D_{2h} if the molecules are boardlike (Figure 1 d) and C_{2v} if they are bent-core or banana-shaped molecules (Figure 1 e, f). The phase will be SmA_{AP} if the bent-core molecules are randomly oriented within the smectic layer (Figure 1 g) The SmA_b phase was first observed in a polymeric system[12] and

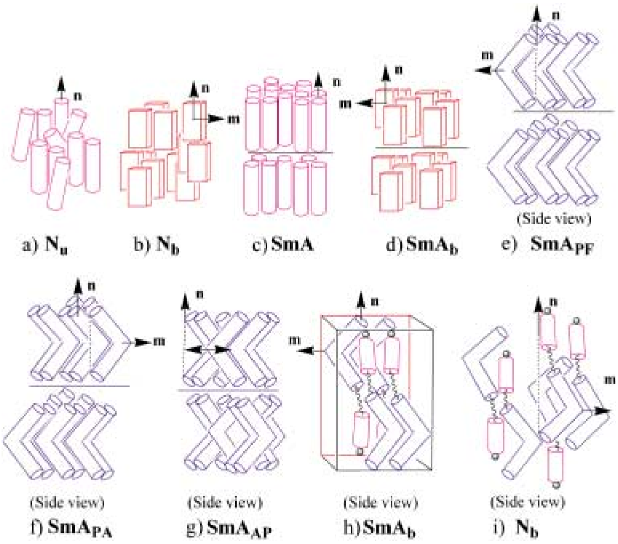

Figure 1. Structural representation of a) the N_u phase formed by conventional rodlike mesogens; b) the N_b phase in which the constituent molecules are boardlike; c) the SmA phase with $D_{8\infty}$ symmetry formed by rodlike molecules; d) the SmA_b phase with the local D_{2h} symmetry built up by boardlike mesogens; e) the SmA_{PF} phase (C_{2v} symmetry) formed by bent-core molecules having a common bent direction; f) the SmA_{PA} phase in which the bent direction of molecules in the neighboring layer alternates; g) the SmA_{AP} phase formed by bent-core molecules with a random orientation of molecules; h) a quartet structure for the SmA_b phase with D_{2h} symmetry, in which a pair of nonsymmetric dimeric molecules in the plane of the paper have their **m** director antiparallel to the pair below that plane; and i) the dimeric molecules in the N_b phase, which is based on ideas of the frustrated spin gas model.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

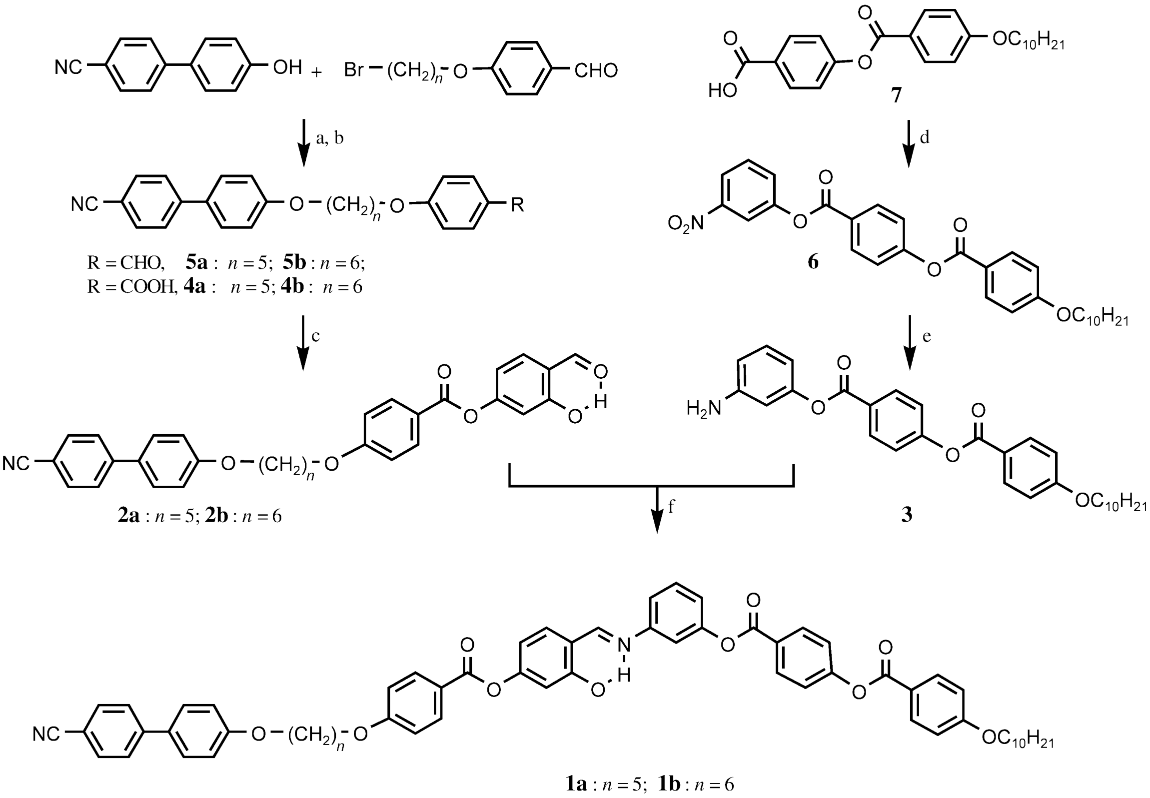
DOI: 10.1002/ange.200453908

subsequently in a mixture of rodlike and bent-core molecules,[13] pure bent-core molecules,[14] and a metallomesogen mixed with 2,4,7-trinitrofluorenone (TNF).[15] The nematic–smectic A transition (N–SmA) is perhaps the most exhaustively studied, but is still the least understood with quite a few open questions.[16] Investigations on the N_b–SmA_b transition that could answer some of these questions have thus far been limited to a report on a side chain LC polymer[12] in which the authors mentioned the difficulties of working with polymeric material. Thus the need arises to observe such a transition in a low-molecular-weight system. Here we report the first example of a low-molar-mass system displaying a N_b–SmA_b transition, as evidenced by textural pattern, in-plane birefringence, conoscopic, calorimetric, electro-optical switching, and X-ray studies.

In view of the fact that bent-core molecules have strong shape biaxiality,[17,18] we introduced a new molecular engineering concept in which the shape biaxiality of a rodlike mesogen is enhanced by covalently linking the mesogen linearly to a bent-core molecule through a flexible polymethylene spacer to form nonsymmetrical dimers.[19,20] Additional support for this idea came from the results of the frustrated spin-gas model.[21] Thus we produced linear dimers consisting of a cyanobiphenyl unit—that is, a rodlike molecule known to exhibit the nematic phase—covalently attached to a salicylaldimine-based, unsymmetrical, banana-shaped molecule that generally supports the formation of smectic phases through a central flexible spacer containing an odd or even number of methylene units.

The synthesis of the unique dimers **1a** and **1b**, which contain a pentamethylene and a hexamethylene spacer, respectively, is depicted in Scheme 1 (see the Supporting Information for data on **1a** and **1b**). Owing to the presence of the terminal polar group and the asymmetric structure, the molecule can be regarded as a "peelable banana" in which the top (with the stalk) can be differentiated from the bottom. This new structural feature is the important factor in stabilizing the mesomorphic sequence observed for **1b** (see below).

Contrary to our expectations, dimer **1a** is non-liquid crystalline, perhaps due to the stiffer conformation of the spacer. On the other hand, three mesophases could be detected for **1b** by polarizing microscopy, calorimetry, and X-ray investigations. The lowest temperature mesophase (M) was found to be uniaxial with a layered structure but with some unusual textures. Detailed characterization is underway to establish the nature of this phase. From preliminary microscopic observations the other two phases could easily be identified as nematic (N) and smectic (Sm) phases, respectively. First, we will discuss the characterization of the Sm phase. The X-ray measurements were carried out by placing **1b** in a Lindemann capillary tube and aligning it in the



Scheme 1. Synthesis of the nonsymmetrical, bent-rod dimers **1a** and **1b**. a) K_2CO_3, DMF, 80°C, 12 h; b) **5a** or **5b**, Jones's reagent (CrO_3, H_2SO_4, H_2O); c) 2,4-dihydroxybenzaldehyde, DCC, DMAP, CH_2Cl_2, RT, 2 h; d) 3-nitrophenol, DCC, DMAP, CH_2Cl_2, RT, 4 h; e) H_2/Pd–C (10%), EtOH, 16 h; f) abs. EtOH, AcOH (one drop), reflux, 2 h. DCC = *N,N'*-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine. Phase transition temperatures and transition enthalpies: **1a**: Cr 141.7°C (35.8 J g^{-1}) I. **1b**: I 162.1°C (0.4 J g^{-1}) N_b 135.6°C (0.1 J g^{-1}) SmA_b 119.2°C M 105.5°C (49.6 J g^{-1}) Cr. (Cr crystalline, I isotropic, M uniaxial smectic, N nematic, Sm smectic).

presence of a magnetic field (≈2 T) by cooling it from the isotropic (I) phase through the N phase. The X-ray diffraction pattern collected using a two-dimensional imaging plate showed a pair of small-angle reflections and a pair of wide-angle diffuse arcs orthogonal to the small-angle ones (Figure 2 a). The extracted spacing of the low-angle reflection (see the Supporting Information) is comparable to the length of the molecule in its most extended configuration, showing that the phase is SmA.

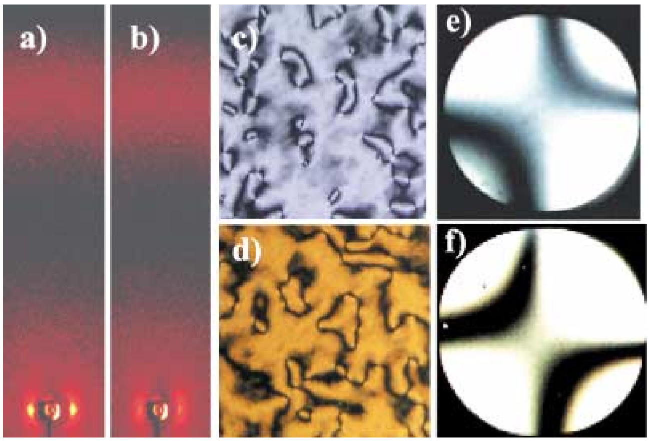


Figure 2. The X-ray (a, b), textural (c, d), and conoscopic (e, f) patterns obtained for the SmA_b (a, c, e) and N_b phases (b, d, f). The texture consists of only 1/2 strength disclinations and isogyres in the conoscopic pattern are well separated.

In the optical studies, with the substrates treated for planar configuration of the molecules, a focal conic texture was observed. However, even glass plates treated with octadecyltriethoxysilane failed to produce a perfectly homeotropically aligned sample. Instead a low-birefringence schlieren texture consisting of exclusively two-brush disclinations (strength $S=\pm 1/2$, Figure 2 c) was seen, which has some important implications. Firstly, it rules out the phase being a SmC phase. The ±1/2 defects have been predicted[11] as well as observed for the SmA_b/SmA_p phase.[12–15] However, the ordering of the bent-core molecules in a layer such that their “arrow” directions are uniformly oriented would result in a polar layer (Figure 1 e) with an electric polarization parallel to the in-plane director **m**. Since **m** is polar, such a structure will not support the formation of ±1/2 defects. But if the direction of **m** alternates between adjacent layers (Figure 1 f), it can exhibit a two-brush schlieren pattern and the structure would be antiferroelectric in character. However, the absence of any switching upon the application of square-wave as well as triangular-wave, low-frequency (1–10 Hz) fields rules out the antiferroelectric structure. The optical biaxiality of the phase was evidenced by conoscopic studies on a homeotropically aligned sample in which the molecules are uniformly oriented with the director **n** normal to the substrate. Application of a 1-kHz sine wave, in-plane electric field (70 V magnitude) to this sample aligned the director **m**. The conoscopic pattern obtained shows clear separation of the isogyres (Figure 2 e), a characteristic feature of biaxial phases. Two other aspects that need to be mentioned are the strong intensity fluctuations and the formation of a striped texture (see the Supporting Information), both features being reported for the SmA_b/SmA_p phase.[14,15] All these points unambiguously prove that this phase is the SmA_b. Quantitative measurements of the in-plane birefringence (Δm) using a tilting plate compensator yielded a value of 0.013 at ≈10 °C away from the transition to the N phase.

When the sample was taken between either untreated or polyimide-coated, unrubbed plates, the N phase showed the typical schlieren texture, except that the pattern consisted entirely of two-brush disclinations (Figure 2 d), which is an indication of biaxiality.[6] This is supported by the topological considerations of Mermin[22] and recent computer simulations.[23] To ensure that the biaxiality was not introduced by the glass surfaces, we examined the textures formed in both the N and SmA_b phases in a free-standing film. Again only $S=\pm 1/2$ spontaneous defects were observed (see the Supporting Information). The conoscopic observations carried out in the N phase as described above showed clear separation of the isogyres (Figure 2 f), confirming the biaxiality of the phase, although Δm is only 0.005. The X-ray pattern (Figure 2 b) obtained in this phase was identical to that in the SmA_b phase, except that the width of the reflections was more indicative of a lack of positional order along any direction. Furthermore, samples taken between kapton sheets that were coated with a polyimide solution and unidirectionally rubbed also yielded essentially similar patterns in both the SmA_b and N_b phases.

As discussed earlier, two apparent forms of molecular packing for SmA_b having ferroelectric and antiferroelectric arrangements of the dimers are similar to the structures shown in Figures 1 e and 1 f. However, the observation of the $S=\pm 1/2$ defects and the absence of any antiferroelectric-like electric switching signal rules out these structures. (Even with moderately high fields we did not observe any switching. However, the presence of a cyano group adds a new dimension to the problem, namely, that higher fields result in Freedericksz transition. Therefore, measurements at higher fields were not possible.) Although a packing of the molecules such that the **m** director of the neighboring molecules lies in the molecular plane, but points randomly to the left or to the right (Figure 1 g), can explain the observed features, it is not efficient from the point of view of excluded volume. The quartet structure[14] (Figure 1 h) in which four dimers form a group is a possibility since this structure, as an entity, has D_{2h} symmetry and accounts for all the features observed for the SmA_b phase. The quartet model can also be used to explain a nonpolar N_b phase, in which the quartets are arranged in such a fashion as to loose the one-dimensional positional order of the smectic phase, leading to the appearance of the N_b phase. For the N_b phase, the problem of excluded volume mentioned above does not place any serious restrictions on the packing of the molecules. Hence, the structure shown in Figure 1 i is more probable than the quartet structure. Furthermore, from a molecular point of view, the appearance of the N_b phase in a system of bent-core molecule of the type we have synthesized can be explained on the basis of the quite successful frustrated spin gas model developed by Berker and Walker.[21]

In summary, we report the first occurrence of the N_b–SmA_b phase transition in a low-molecular-weight LC system. This was achieved by a careful design of the constituent molecules that incorporates covalently linking a bent-core molecule to a rodlike mesogen through a flexible spacer. Realization of a biaxial nematic phase in a low-molar-mass system is significant since it opens up the possibility of fabricating new types of liquid crystal display devices. A device employing such a material is attractive as the switching of the in-plane **m** director is expected to be much faster than the switching of the **n** director.

Received: February 3, 2004 [Z53908]

Keywords: biaxial phases · liquid crystals · mesogens · phase transitions

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