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Ferroelectric Mesophase with Randomized Interlayer Structure

Damian Pociecha,[1,*] Mojca Čepič,[2,†] Ewa Gorecka,[1] and Jozef Mieczkowski[1]
[1]*Chemistry Department, Warsaw University, Zwirki i Wigury 101, 02-089 Warsaw, Poland*
[2]*Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

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We present the experimental and theoretical evidence that a new Sm *X* phase made of asymmetric bent-shaped molecules has a layered, nontilted, optically uniaxial and polarly ordered structure with random direction of the layer polarization. The randomness results from the sign degeneracy of the difference in polarization directions in neighboring layers, although the magnitude of the phase difference is constant. Lifting the degeneracy by external fields two additional structures of the Sm *X* phase are possible.

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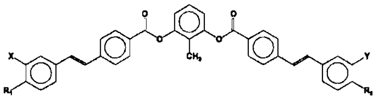
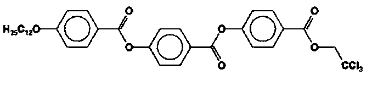
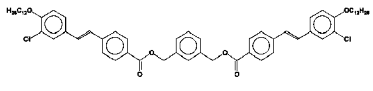
The synthesis of bent-shaped molecules that form a wide variety of new liquid-crystalline phases continues to attract the attention of soft matter chemists and physicists. As bent-shaped molecules possess C_{2v} rather than $D_{\infty h}$ symmetry, typical for a standard rodlike molecule, they form complex structures substantially different from the known rodlike systems. In this Letter we present experimental evidence and a theoretical model for three such structures. One of them has not been included in the almost complete set of predicted layered phases obtained by a systematic symmetry analysis [1], and represents a glassy-state analog in systems of bent-shaped molecules.

In addition to the smectic order, a layered system formed by bent-shaped molecules is described by the average molecular tilt which gives the direction of the line joining both ends of a bent-shaped molecule, and the average direction of the molecular bend. Since a standard bent-shaped molecule possesses an electric dipole in the direction of the bend, the order parameter that gives the magnitude and the direction of the dipolar order within the *j*th layer is called polarization p_j. The most studied phase consists of synclinically or anticlinically tilted layers with antiferroelectric polar order in neighboring layers [2]. For molecules with branched terminal chains similar structures with the ferroelectric polar order were observed [3,4]. Although in rodlike molecules nontilted phases are preferred to the tilted ones, nontilted phases of bent-shaped molecules are rarely seen. The only observed nontilted layered structure has the antiferroelectric polar order in neighboring layers [5], but ferroelectric nontilted systems have eluded experimentalists. In this Letter we report a peculiar phase of newly synthesized asymmetric bent-shaped molecules [6], which is nontilted, optically uniaxial, and has ferroelectric properties. Within the proposed theoretical model we have found a set of nontilted structures that have neither parallel nor antiparallel polarizations in neighboring layers and are either helicoidally modulated, have bilayer structure, or the direction of layer polarization changes randomly. The structures can be transformed one into another under the influence of very weak external fields.

The phase, tentatively labeled Sm *X*, was found in four newly obtained compounds [6], with asymmetric bent-shaped molecules (Table I). The phase transitions were determined by DSC (Perkin Elmer DSC 7) and optical methods (polarizing microscope Nikon OPTIPHOT-2POL). For materials 1 and 2 the Sm *X* phase is detected above the tilted layered phase with antiferroelectric properties and of yet unknown structure (here tentatively

TABLE I. Molecular structure and phase sequences, phase transition temperatures (in °C), and enthalpy changes (in parentheses, Jg^{-1}) of the studied compounds. The Sm *X* phase is uniaxial phase, the Sm *Y* is the birefringent phase with antiferroelectric properties and an unknown structure.



	X	R_1	*Y*	R_2
1	NO_2	$OC_{12}H_{25}$	OCH_3	$OC_{12}H_{25}$
Cr 98.8 (20.2) Sm *Y* 106.2 (0.9) Sm *X* 117.6 (10.3) Iso				
2	NO_2	$OC_{12}H_{25}$	Cl	$OC_{12}H_{25}$
Cr 121.7 (15.8) Sm *Y* 127.8 (0.9) Sm *X* 137.5 (11.2) Iso				
3	NO_2	$OC_{14}H_{29}$	Cl	$OC_{14}H_{29}$
Cr 116.5 (22.1) B_{1RT} 127.7 (1.0) Sm *X* 141.3 (9.1) Iso				
4	NO_2	$OC_{12}H_{25}$	I	$OC_{12}H_{25}$
Cr 89.5 (31.7) B_{1RT} 112.9 (1.0) Sm *X* 125.6 (8.6) Iso				
5				
Cr 96.3 (69.7) Sm *C* 104.6 (3.3) Sm *A* 168.4 (7.1) Iso				
6				
Cr 109.4 (65.4) Sm *A* 119.1 (8.8) Iso				

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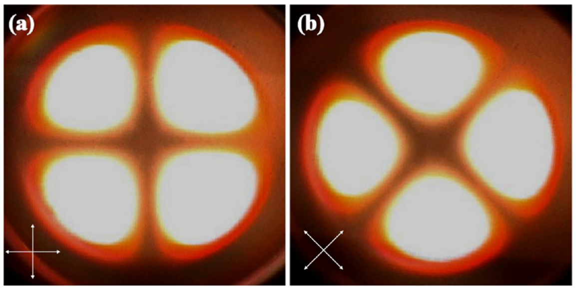


FIG. 1 (color online). The conoscopic cross obtained for the 100 μm film sample in Sm X phase of compound 3 showing that the phase is optically uniaxial. In (b) both polarizers are rotated by 45° from their positions in (a). Arrows indicate polarizer directions.

called Sm Y), while for materials 3 and 4 it appears above $B_{1,\mathrm{RT}}$ phase (symmetry $p11n$), which is tilted columnar phase with broken layers and the 2D density modulation in the plane perpendicular to the polarization direction [7]. The x-ray studies have shown that the Sm X phase has a simple layered structure with layer spacing close to molecular length and liquidlike in-plane order. In a film of the Sm X phase a uniform, nonbirefringent, uniaxial texture is observed (Fig. 1). No optical activity was detected. In a planar cell [2, 5, 10, 20 μm thick, with indium tin oxide (ITO) electrodes] the texture of the Sm X phase is reminiscent of the fan texture of the Sm A phase. Well-aligned samples can be easily obtained by applying an ac electric field. The light extinction directions are along the polarizers, the measured birefringence is $\Delta n \approx 0.11$–0.13. Applying an electric field does not change the extinction directions while the birefringence slightly increases. A single, rather broad current peak is detected during reversal of applied electric field (Fig. 2). The spontaneous electric polarization calculated from the switching current is 150–300 $\mathrm{nC\,cm^{-2}}$ for all studied compounds. It increases linearly with decreasing temperature (e.g., for material 2 from 200 to 300 $\mathrm{nC\,cm^{-2}}$). In the planar geometry, where an electric field is applied along the layers, a pronounced dielectric mode is detected (measured with WayneKerr impedance analyzer 6425) in Sm X phase [Fig. 3(a)]. The mode was analyzed using the Cole-Cole formula given by

$$\epsilon^* - \epsilon_\infty = \frac{\Delta\epsilon}{1 + (if/f_r)^{(1-\alpha)}} - i\frac{\sigma}{2\pi\epsilon_0 f}, \qquad (1)$$

where $\Delta\epsilon$, f_r, and α are mode strength, relaxation frequency, and the distribution parameter, respectively. For compound 2 the mode is characterized by $\Delta\epsilon$ reaching 140 and the relaxation frequency f_r which changes within 15 K temperature range from 1 kHz to 50 Hz. The activation energy of the corresponding process is therefore $\approx$ 270 $\mathrm{kJ\,mol^{-1}}$. The frequency of the mode does not depend on the cell thickness. The mode is inherent to the Sm X phase, it disappears upon entering the lower temperature Sm Y or $B_{1,\mathrm{RT}}$, as well as isotropic phase. For the ITO cells with homeotropic alignment, in which the electric field is applied along the layer normal, no low frequency modes were found. The Sm X phase seems to be miscible with the nontilted, nonpolar Sm A phase. The pure Sm X

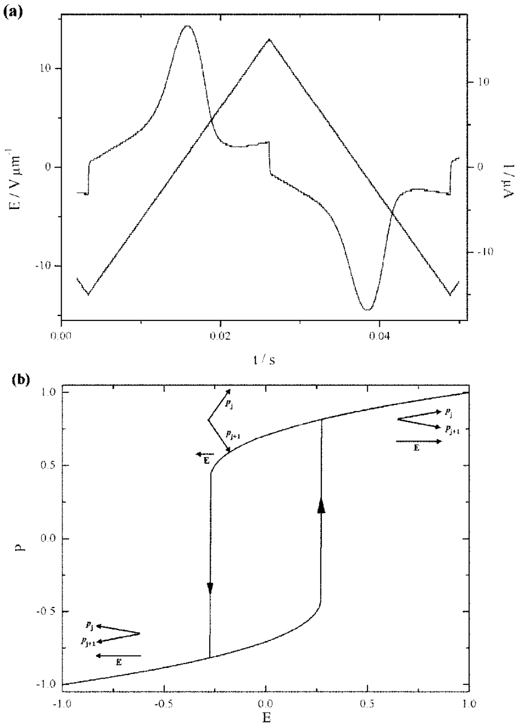


FIG. 2. (a) Single current peak observed during the spontaneous electric polarization reversal in the Sm X phase of compound 3; (b) theoretical dependence of the electric polarization on the applied voltage for the bilayer structure (Sm AP_2) of the Sm X phase. Arrows show the relative orientation of external electric field and the polarization vectors in neighboring smectic layers. Polarization and electric field are expressed in dimensionless units.

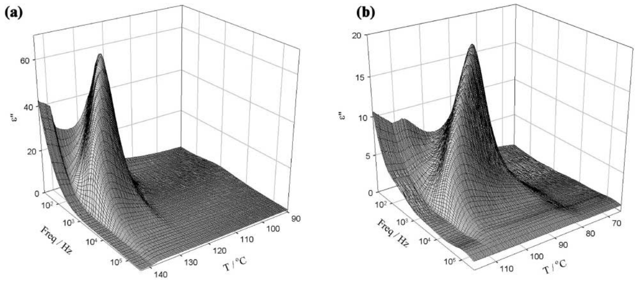


FIG. 3. 3D frequency-temperature dependence of the imaginary part of dielectric constant for (a) compound 2 and (b) for the mixture of compound 2 (34 wt.%) with material forming nonpolar Sm A phase. In the mixture the mode strength is significantly depressed, the relaxation frequency is increased, and the temperature range of the mode is wider than in the pure sample.

compound was mixed with two types of Sm A materials: made of typical rodlike molecules (compound 5) and resorcine derivatives (compound 6). Although similar to bent-shaped materials, molecules of 6 adopt a rodlike shape due to the more flexible joints between the central unit and the branches and even number of atoms in the joints. In both cases no phase boundary between Sm A and Sm X could be observed in the contact cells. The full phase diagram is presented for mixtures with compound 6 (Fig. 4). The spontaneous polarization in the mixtures decreases monotonically with increasing concentration of the non-bent-shaped component; however, even in a mixture with 0.8 wt. fraction of rodlike component the polarization current peak could still be detected. As the value of polarization P_s decreases also the dielectric mode strength diminishes and mode relaxation frequency rises [Fig. 3(b)]. The temperature range of Sm X phase increases with increasing concentration of the non-bent-shaped component in the mixture (Fig. 4). In none of the mixtures were we able to detect phase transition between nonpolar Sm A and polar Sm X phase.

To account for the structure of the Sm X phase we assume that smectic layers are present. The optical studies in planar cells show no rotations of the extinction direction when applying electric field. This might imply that the structure is either anticlinically tilted and ferroelectric or nontilted. But the uniaxiality in free standing film excludes the possibility of tilted layers. Uniaxial properties could be recovered only by anticlinic tilts very close to 35° where the dielectric tensor averaged over two adjacent layers [8] becomes uniaxial. Since uniaxial optical properties have been observed in four different materials over a wide temperature range, it is highly improbable that this criterion is met in all cases. Moreover, in the lower temperature liquid-crystalline phases measured tilts are much smaller (around 10°). Thus the nontilted structure of Sm X phase should be considered. The continuous miscibility with the Sm A phase supports this assumption. The magnitude of polar order in the Sm X phase decreases upon addition of rodlike molecules. The rotation of molecules along the long axis becomes less hindered and results in short-range polarization correlations that in Sm A phase extends only to the nearest intralayer neighbors.

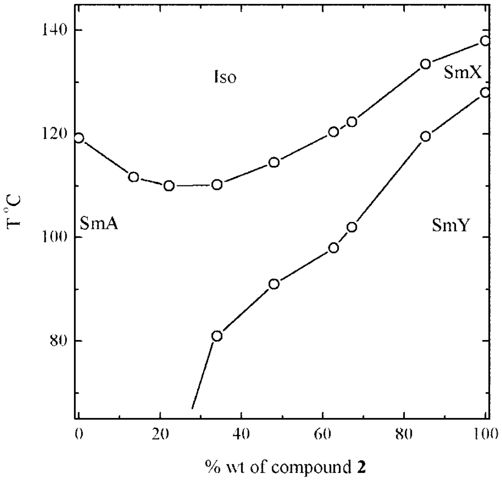


FIG. 4. (a) Phase diagram for mixtures of compounds 2 and 6 that shows miscibility of the Sm X phase with the Sm A phase.

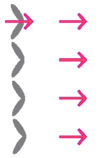
To account theoretically for the possible structures we analyze the free energy as a function of polarization. Since optically uniaxial structures can only result from nonuniform polarization orientation in neighboring layers, we keep the part of the free energy that accounts for interactions between neighboring layers [9]:

$$G_{\mathrm{NN}} = \sum_j \Big[\frac{1}{2} a_{1p} (p_j \cdot p_{j+1}) + \frac{1}{4} b_{1p} (p_j \cdot p_{j+1})^2 \Big], \qquad (2)$$

where NN stands for nearest neighbor interactions. For $a_{1p} < 0$ bilinear interlayer interactions favor ferroelectric order due to van der Waals attraction between parts of molecules from neighboring layers, whereas for $a_{1p} > 0$ antiferroelectric order is stabilized by electrostatic dipolar interlayer interactions. The introduction of biquadratic interlayer coupling with positive b_{1p} accounts for favorable nonparallel orientation of molecular branches due to the asymmetry of bent-shaped molecules.

We minimize the free energy using the constant amplitude approximation, $p_j = P(\cos\psi_j, \sin\psi_j)$, where P gives the magnitude of the layer polarization and ψ its azimuthal angle and we find five possible nontilted phases given in Table II. The names used give the phase structures in the following way: Sm A stands for nontilted and P for polarly ordered; subscript F stands for ferroelectric, A for antiferroelectric, α for helicoidally modulated polarization with the short pitch, reminiscent of the Sm C_α^*

TABLE II. Five possible arrangements of nontilted and polarly ordered layered systems with interactions between nearest layers, and their tentative structural names. The first subcolumn shows a side view where one schematic molecule presents molecular orientation in a single layer. In the second subcolumn the corresponding polarization vector as seen from above is given. The model parameters are described below.

Sm AP_F	Sm AP_A	Sm AP_α	Sm AP_2	Sm AP_R
				
$a_{1p} < 0$ $\lvert a_{1p}\rvert > b_{1p}P^2$	$a_{1p} > 0$ $a_{1p} > b_{1p}P^2$	$\lvert a_{1p}\rvert < b_{1p}P^2$ $\cos(\psi_{j+1} - \psi_j) = -(a_{1p}/b_{1p}P^2)$		

found in chiral rodlike systems [10,11], subscript 2 for a structure with a bilayer repetitive unit, and R for a randomly oriented polarizations. Except for the Sm AP_A structure [5], these phases have not been observed yet.

Interlayer organization of the last three phases is energetically equivalent. The azimuthal phase difference is, according to the free energy Eq. (2), doubly degenerated with respect to its sign. Differences between the last three structures arise solely due to this degeneracy.

The Sm AP_R should appear in systems where only interactions between neighboring layers are present. The magnitude of the azimuthal phase difference is constant but its sign varies randomly from one pair of neighboring layers to another, resulting in a random direction of the polarization p_j in a specific smectic layer. Such a structure is optically uniaxial and optically nonactive. It might be stable in free standing films, one surface free films and cells with homeotropic alignments.

In the bilayer structure of the Sm AP_2 the sign of the azimuthal phase difference between polarizations in neighboring layers alternates. The structure should be optically biaxial and should have distinct polar properties. Fluctuation of the noncompensated bilayer polarization should be observed as a strong relaxation mode in dielectric measurements. The electric field applied parallel to the noncompensated polarization changes the azimuthal phase difference and consequently polarization. Two (meta)stable minima are present in the free energy giving rise to the discontinuous change of the sample polarization that might be observed as typical ferroelectric switching [Fig. 2(b)]. The Sm AP_2 structure can be stabilized by interactions between polarizations from next-nearest neighboring layers, that favor parallel polarization orientation in the interacting layers. Even in the absence of such longer-range interactions, external influences as quadrupolar interactions with glass surface or an ac electric field might also lift the azimuthal difference degeneration.

In the Sm AP_α phase the signs of all azimuthal phase differences are the same, therefore the polarization is helicoidally modulated and the modulation pitch is short. The structure is uniaxial but probably behaves different in the electric field than Sm AP_R. Because of short pitch of the modulation we do not expect a measurable optical activity. The Sm AP_α can be stable in systems with competing next-nearest neighbors interactions between polarizations or in systems doped with chiral admixture.

To account for experimental observations, we suggest that all three structures appear in the same temperature window. In free standing films and homeotropic cells, the Sm X adopts the "glassylike" randomized Sm AP_R structure. Since the Sm AP_α structure is optically equivalent to Sm AP_R, it is also a candidate for Sm X phase in film samples. Unfortunately, we do not see a straightforward experimental method that would distinguish between Sm AP_R and Sm AP_α. Given that the expected helices are short, measurements of circular dichroism and optical rotatory power at optical wavelengths are not applicable, and strong enough electric fields along the layers could not be applied in films and homeotropic samples. Based on preliminary doping studies we still suggest that in pure samples the randomized Sm AP_R is stable, but in systems with even very small amounts of chiral dopant the degeneracy is lifted and Sm AP_α appears instead.

In planar cells, upon application of an ac field, we believe that the Sm X phase adopts the structure of the Sm AP_2, which is biaxial, does not change the extinction direction in reversed electric fields, is strongly polar, and exhibits the "ferroelectric" switching. Since interactions that would lift the azimuthal phase difference degeneration could be very weak, for the correct description of the Sm X phase we need the whole set of three (Sm AP_R, Sm AP_α and Sm AP_2) proposed structures.

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*Electronic address: pociecha@chem.uw.edu.pl
†Electronic address: mojca.cepic@ijs.si

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