Structure studies of the nematic phase formed by bent-core molecules

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In recent years there are several reports showing that bent-core mesogenic molecules are able to form biaxial nematic phase in which molecular rotation around the long molecular axis is strongly hindered. The x-ray pattern with azimuthally split signals at low angle region of diffraction is usually given as evidence for the biaxial nematic phase. We show experimentally and theoretically that such x-ray pattern is due to the local smectic-C fluctuations ("cybotactic" groups) in the uniaxial nematic phase.

In recent years there are many reports showing that bent-core molecules can form not only uniaxial nematic phases, exhibiting orientational order of long molecular axes but also biaxial nematics with additional orientational order of short molecular axes [1]. Authors of these reports often relay on the x-ray diffraction data, in which azimuthal splitting of the low angle diffraction signal is observed. The splitting is explained to result from combination of the form factor for bent mesogenic core and structure factor from short-range positional correlation function [2]. However, all examples of such a "biaxial nematic phase" were found for the materials with the phase sequence either nematic (N)–smectic-C (SmC) [1,3] or N–smectic-X (SmX), where the undefined SmX phase is probably tilted smectic phase [1]. We found no reports on the biaxial nematic phase in material exhibiting N–smectic-A (SmA) phase sequence. This suggests that the splitting of the x-ray signals in the nematic phase might arise from the SmC-like fluctuations. In this Rapid Communication we present an experimental and theoretical study of several bent-core materials and their mixtures which show that the x-ray pattern of the nematic phase with split signals is in

fact related to the SmC-like fluctuations present in the nematic phase when the lower-temperature phase is SmC. Uniaxial properties of nematic materials formed by bent-core molecules are also confirmed by the ESR (electron spin resonance) spin probe method.

The investigated compounds (Fig. 1) exhibit either Iso-N-SmC (compound 1) or Iso-N-SmA (compound 2) phase sequence. The molecular modeling (HYPERCHEM software) shows that the bending angle of the mesogenic core is approximately 140° for compound 1, in agreement with crystallographic data [4] and approximately 115° for compound 2, the ratio of the length of the mosogenic core to the whole molecular length is approximately 1:2. The x-ray measurements were performed on the samples placed in Lidemann capillaries and aligned in magnetic field ($\sim$1 T). The Bruker NanoStar system with crossed Goebel mirrors and Vantec 2000 area detector was used for x-ray measurements. The system resolution in the measured angles range is 0.005 A^{-1}.

For compound 1 the low angle pattern of the aligned nematic phase is characterized by the azimuthal splitting of signals by $\sim$30° (Fig. 2). The splitting angle coincides with

Compound **1**
Cry 113.7 SmC 128.0 N 161.0 Iso

Compound **2**
Cry 124.9 SmA 146.9 N 165.0 Iso

Compound **3, R** = OC$_{12}$H$_{25}$
Cry 67.5 [SmC 47.4] N 73.9 Iso

Compound **4, R** = O(CH$_2$)$_8$C$_4$F$_9$
Cry 76.1 SmA 104.1 Iso
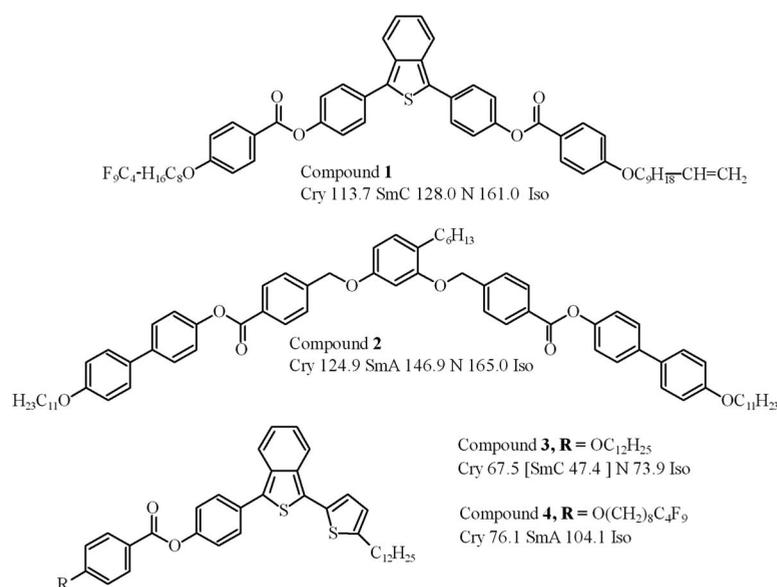
FIG. 1. Molecular structure of the studied compounds with phase sequence and phase-transition temperatures.
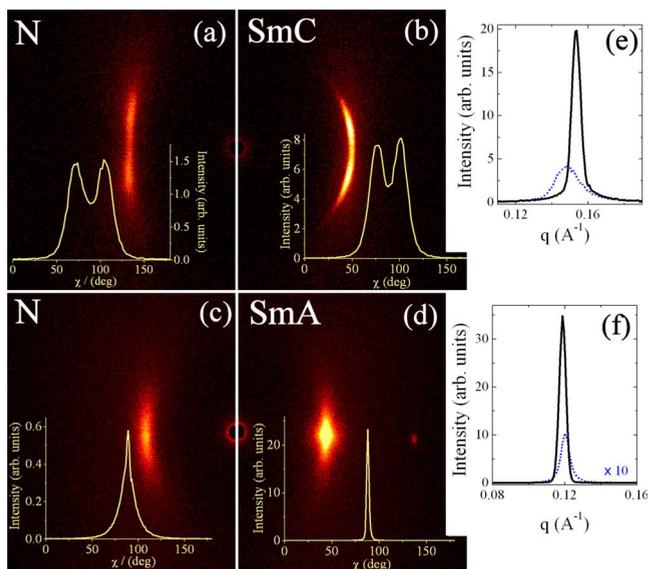
FIG. 2. (Color online) Low angle x-ray pattern for compound 1 in the (a) nematic and (b) SmC phase and compound 2 in the (c) nematic and (d) SmA phase. On each pattern the azimuthal dependence of the signal intensity is shown. Intensity of the signals in the nematic (dotted blue line) and smectic (solid black line) phases vs wave vector q for compounds (e) 1 and (f) 2.

FIG. 3. Experimental and simulated ESR spectra of paramagnetically doped compound 1 in nematic phase, T=142 °C. Sample is aligned with the director parallel to the external magnetic field.

those observed in the SmC phase (Fig. 2). In the SmC phase such a pattern is obtained if domains with different orientation of layer normal with respect to the aligning magnetic field direction are present. The position of the signals in q space corresponds roughly to the molecular length, both in the nematic and SmC phases.

In bent-core material 2, which exhibits the N-SmA phase transition, no azimuthal splitting is observed (Fig. 2), neither in the nematic nor in the smectic-A phase. Correlation between the type of the pattern, with or without splitting, and the phase sequence was further confirmed by studying the mixture of compounds 3 and 4, both being structurally similar to compound 1. Compound 3 exhibits the iso-N-SmC phase sequence and gives splitting of low angle diffraction signal in the nematic phase. The phase sequence changes to the iso-N-SmA-SmC upon adding small amount of compound 4 having the iso-SmA phase sequence. The mixture of materials shows no splitting of the low angle x-ray signal in the nematic phase. It cannot be expected that the ordering of the nematic phase, uniaxial or biaxial, is drastically changed by doping a small amount of compound with very similar molecular structure. However, it is very likely that the type of the smectic-like fluctuations in the nematic phase will depend on the type of the smectic phase formed below the nematic phase. This shows that the type of the x-ray pattern is related to the phase sequence and pretransitional fluctuation character, not to the potential "biaxiality" of the nematic phase made of bent-core molecules.

We also attempted to detect biaxiality of the nematic phase using the spin probe ESR spectroscopy which is a well-known tool for the investigation of molecular order [5]. The advantage of the method is that the detection of hindered rotation, leading to phase biaxiality can be performed even
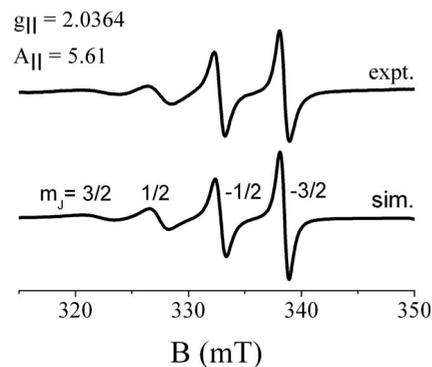
for powder samples since the method measures the individual molecular motions averaged in time. For ESR measurements X-band Bruker spectrometer ELEXYS-500, equipped by a nitrogen flow temperature controller was used. The method is based on the principle that the probe molecule behavior reflects molecular order of the matrix, i.e., in the isotropic phase the g factor and hyperfine coupling parameter A of the probe are isotropic, if the host molecule freeze rotation the probe should have biaxial magnetic g and A tensors. For both materials (1 and 2) bis(dimethyldithiocarbamato)copper(II) was used as a paramagnetic probe. Its paramagnetic properties are related to the unpaired electron of the copper(II) ion occupying $d_{x^2-y^2}$ orbital, being in highly anisotropic ligand environment. The magnetic g and A tensors eigenvalues of an isotropic glassy state, in which the molecules are randomly distributed and their motion is completely frozen, are $g_{xx}=2.0253$, $g_{yy}=2.0203$, $g_{zz}=2.0891$, $A_{xx}=4.1$ mT, $A_{yy}=3.7$ mT, and $A_{zz}=16.2$ mT, providing averaged values $g_{av}=2.045$ and $A_{av}=8.0$ mT that are slightly different from $g_0=2.0496$ and $A_0=7.9$ mT in isotropic liquid because of their small temperature dependence. In the nematic phase of both materials, 1 and 2, the registered spectrum is typical for uniaxial phase with the director aligned along the magnetic field (Fig. 3). Fast rotation of the molecules along long axis makes the g and A tensors axially symmetric with diagonal elements $g_\perp$, $A_\perp$ and $g_\parallel$, $A_\parallel$ perpendicular and parallel to the rotation axis, respectively. The parameters fulfill the relation: $a_\parallel - a_{iso}=(a_{yy}-a_{iso})\langle P_2^0\rangle$, where a_{iso} for g or A factors are calculated as $3a_{iso}=a_{xx}+a_{yy}+a_{zz}=2a_\perp+a_\parallel=3a_0$, $\langle P_2^0\rangle$ is the order parameter reflecting the orientation of long molecular axis. For both compounds nearly identical $g_\parallel=2.036-2.038$ and $A_\parallel=5.3-5.9$ mT parameters are obtained, giving order parameter $\langle P_2^0\rangle=0.5-0.6$. Moreover the splitting of the ESR signals expected for the biaxial phase (that should be visible at high-field region of the spectrum with $m_J=-3/2$ [6]) is not observed in the whole temperature range of the nematic phase. Thus we conclude that the nematic phase for both compounds is unambiguously uniaxial although the x-ray patterns registered in the nematic phase are much different.

The origin of the x-ray pattern was also studied theoretically by calculating the molecular form factor and the structure factor of the nematic phase using the appropriate pair-

correlation function. The structure factor is a sum of two contributions [7], the first one arises from very short-range fluidlike correlations with the correlation length of the order of molecular breadth. This corresponds to large scattering vectors q (large angle scattering). The second contribution arises from smectic-like fluctuations with the correlation length of the order of molecular length (low angle scattering). In the experiment the splitting of the scattering pattern is observed at low angles, and thus it cannot be determined by the short-range fluidlike correlations but it should be related to the smectic-like fluctuations.

The form factor is obtained as the Fourier transform of the electron density inside the molecule. The molecule is approximated by two rods connected at the proper bending angle [8]. The rod length was taken from the molecular modeling. In the calculation of the form factor we have used only the core of the molecule as the difference in the electron density between the core and the aliphatic tails is responsible for the diffraction signal. Orientational order of the long molecular axes was assumed to be saturated, molecular long axes being oriented along the z axis. As regards the rotation of the molecular plane around the z axis, two cases were considered: (i) free and (ii) frozen rotation. In case (i) the square of the form factor was averaged over all possible orientation of the molecular plane around the z axis. In case (ii) the average was taken over two possible molecular orientation of molecules positioned with their planes perpendicular to the incident x-ray beam propagating along the y direction. The form factor projection on the q_{xz} plane has off axis maxima [Fig. 4(a)], which do not completely merge even if the molecules are free to rotate along long axis because of the overall double conical shape of the rotating bent-core molecule [Fig. 4(b)].

The scattering intensity is obtained by combining the form factor and the structure factor resulting from the SmA or SmC-like fluctuations. The former are used when the response of the biaxial nematic and the latter when the response of the uniaxial nematic is modeled. The structure factor due to the SmA-like fluctuations is described by the Lorenz function:

$$S_A \propto [1 + \xi_\parallel^2 (q_z \pm q_0)^2 + \xi_{\perp 1}^2 q_x^2 + \xi_{\perp 2}^2 q_y^2]^{-1},$$

where $q_0 = 2\pi/l$, l is the length of the molecule (which is approximately twice the length of the molecular core), and $\xi_\parallel$ and $\xi_\perp$ are the correlation lengths along and perpendicular to layer normal; in the biaxial case there are in general two perpendicular correlation lengths, and in the uniaxial case there is only one perpendicular correlation length. The structure factor is a sum of two terms, one with the "+" and the other one with the "−" sign.

In the case of SmC-like fluctuations the structure factor is

$$S_C \propto [1 + \xi_\parallel^2 (q_z \pm q_0)^2 + \xi_\perp^2 (q_x \pm q_0 \tan \vartheta \cos \varphi)^2$$
$$+ \xi_\perp^2 (q_y \pm q_0 \tan \vartheta \sin \varphi)^2]^{-1},$$

where the direction of the smectic layer normal is defined as $(\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)$ and the smectic layer periodicity is given by $q_0/\cos \vartheta$ with ϑ being the average molecular tilt with respect to the smectic layer normal (the cone
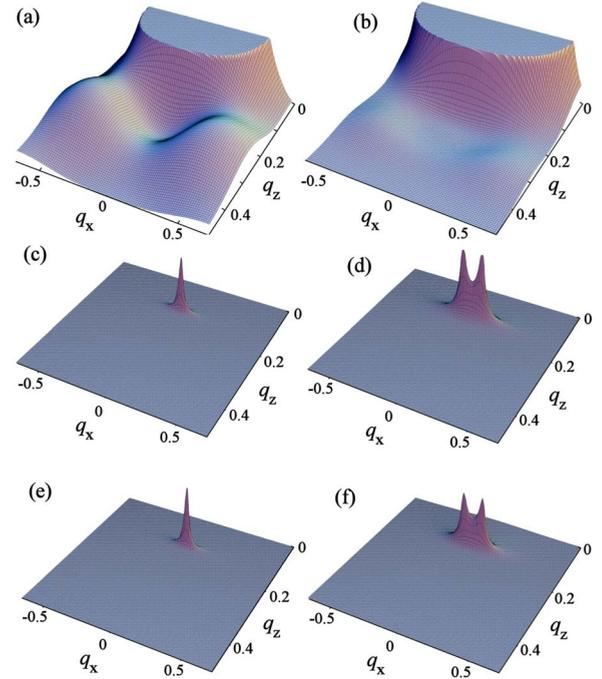
FIG. 4. (Color online) Simulated form factor for molecules with bent core shape if (a) molecular rotation is completely frozen and biaxial order is ideal and (b) molecules are free to rotate around the long molecular axis. Parameters: the core length is half of the whole molecule length, the bending angle is 120°. Structure factor for the nematic phase with (c) SmA-like fluctuations and (d) SmC-like fluctuations; $\xi_\parallel$ is 10 molecular lengths, $\xi_\perp$ is 10 molecular breadths. (e) Simulated x-ray pattern for the nematic phase obtained by combination of the form factor presented in (a) with the structure factor presented in (c). Despite the strong biaxial order no x-ray signal splitting is observed. (f) Simulated x-ray pattern for the nematic phase obtained by combination of the form factor presented in (b) with structure factor presented in (d). Despite the uniaxial order splitting of the x-ray signal is observed in the presence of SmC-like fluctuations.

angle). Such fluctuations are known in literature by the name *cybotactic groups* [9]. Axially distributed *cybotactic groups* appear in the nematic phase because keeping molecules with their long axes parallel to magnetic field imposes growing of the local smectic order with layer normal tilted to the magnetic field direction. The SmC structure factor has to be averaged over all possible directions of the smectic layer normal which lie on the cone around the z axis. The average gives

$$S_C^{\mathrm{av}} = \frac{1}{2\pi} \int_0^{2\pi} S_C d\varphi$$

$$\propto \{[1 + \xi_\parallel^2 (q_z \pm q_0)^2]^2 + 2\xi_\perp^2 [1 + \xi_\parallel^2 (q_z \pm q_0)^2] \times (q_\perp^2 + q_0^2 \tan^2 \vartheta) + \xi_\perp^4 (q_\perp^2 - q_0^2 \tan^2 \vartheta)^2\}^{-1/2},$$

where $q_\perp = \sqrt{q_x^2 + q_y^2}$. Quantitative information about correlation lengths was obtained by analyzing the x-ray signal broadening in $q_\parallel$ direction, at few temperatures few degrees above the transition to the smectic phase. The signal ob-

served in the nematic phase was fitted to Voigt function, which resolved the broadening coming from the machine resolution [Gauss function with half-width at half maximum (HWHM) 0.005 A^{-1}] and from limited correlation length of positional ordering of molecules (Lorentz function). By the deconvolution of the x-ray signal the range of the correlation length in the direction of long molecular axes was obtained to be ~20 nm (~5 molecular lengths) for all studied materials.

If the similar analysis is performed for signal broadening in $q_\perp$ direction the correlation length in the direction perpendicular to the long molecular axis can be obtained. For material 2 it is about 5–7 nm, i.e., few molecular breadths, which is in the range typical for uniaxial *rodlike* nematic material [10]. It should be pointed out that this is the lower limit of correlation length, as in this direction the signal broadening is additionally influenced by some sample mosaicity. The ratio $\xi_\parallel / \xi_\perp$ is close to the one reported for uniaxial nematics far from the critical region of smectic fluctuation [11].

The simulated x-ray patterns for the nematic phase show no splitting of low angle signal, neither in the uniaxial nor biaxial case, when SmA-like fluctuations are considered. The splitting reported in [1,2,7] was obtained because small correlation length $\xi_\perp$ of one molecular width was used and because it was assumed that the whole molecule contributes uniformly to the form factor, which is a rather unphysical assumption. The molecular core has higher electron density than tails and gives the main contribution to the form factor, while the whole molecular length is important when estimating the smectic layer thickness. However, it is possible to simulate the pattern with split signals as measured for compounds 1 and 3 using realistic correlation lengths (similar to those observed for the nematic phase of material 2) if the structure factor accounts for the existence of the SmC-type

fluctuations in the nematic phase. This type of fluctuations are usually discarded in the explanation of the split x-ray signals, with the argument that the splitting is observed in a wide temperature range of the nematic phase, while the SmC fluctuations could be observed only close to the phase-transition temperature [1]. However, SmC fluctuations, similarly as smectic-A fluctuations can exist in broad temperature range above the transition point [12], the difference is that the correlation length increases more rapidly near the nematic–SmA phase transition because it can be of second order.

Summarizing, our results are in line with the recent optical studies in which the biaxiality of nematic phase for bent-core molecules was put in doubts [13]. For the materials studied in the present Rapid Communication, the type of the low angle x-ray pattern observed in the nematic phase is unambiguously related to the phase sequence and the type of the pretransitional fluctuations in the system not to the biaxiality of the nematic phase. We believe this is also the case for previously reported materials as these materials show apparent biaxial nematic above the tilted smectic phase. Moreover, the spin probe ESR method confirmed that despite different x-ray patterns, all studied here compounds are uniaxial. However, it should be also mentioned that even biaxial spectrum, which is sometimes observed by this method, cannot be taken as a definite proof of hindered molecular rotation and long-range biaxial order as it could be caused by molecular motions which are slow in the ESR time scale [14]. Although we cannot exclude that biaxial ordering can be found in the nematic phase of some exotic molecular system [15,16], in our opinion there is still a lack of solid evidence for biaxial order of bent-core molecules in the nematic phase, apart from the situation in which such an order is induced by external fields [17].

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[1] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004); V. Prasad *et al.*, J. Am. Chem. Soc. **127**, 17224 (2005); M. Lehmann *et al.*, J. Mater. Chem. **16**, 4326 (2006).

[2] B. R. Acharya, S.-W. Kang, and S. Kumar, Liq. Cryst. **35**, 109 (2008).

[3] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).

[4] A. K. Mohanakrishnan and P. Amaladass, Tetrahedron Lett. **46**, 4225 (2005).

[5] D. Kivelson, *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972); R. Wilson and D. Kivelson, J. Chem. Phys. **44**, 154 (1966); G. Luckhurst, M. Setaka, and C. Zannoni, Mol. Phys. **28**, 49 (1974); G. Luckhurst and C. Zannoni, Proc. R. Soc. London, Ser. A **353**, 87 (1977); F. Pusnik and M. Schara, Chem. Phys. Lett. **37**, 106 (1976); G. Luckhurst, M. Ptak, and A. Sanson, J. Chem. Soc., Faraday Trans. **69**, 1752 (1973); G. R. Luckhurst, Angew. Chem. **44**, 2834 (2005).

[6] I. Bikchantaev *et al.*, J. Chem. Phys. **107**, 9208 (1997); Mol. Cryst. Liq. Cryst. (Phila., PA) **303**, 121 (1997).

[7] M. A. Osipov and B. I. Ostrovskii, Crystallogr. Rev. **3**, 113 (1992).

[8] B. R. Acharya, S.-W. Kang, V. Prasad, and S. Kumar, J. Phys. Chem. B **113**, 3845 (2009).

[9] A. de Vries, Mol. Cryst. Liq. Cryst. (Phila., PA) **10**, 216 (1970).

[10] L. Chen, J. D. Brock, J. Huang, and S. Kumar, Phys. Rev. Lett. **67**, 2037 (1991); C. W. Garland, M. Meichle, B. M. Ocko, A. R. Kortan, C. R. Safinya, L. J. Yu, J. D. Litster, and R. J. Birgeneau, Phys. Rev. A **27**, 3234 (1983).

[11] R. Shashidhar, B. R. Ratna, and S. K. Prasad, Phys. Rev. Lett. **53**, 2141 (1984).

[12] A. G. Vanakaras and D. Photinos, J. Chem. Phys. **128**, 154512 (2008).

[13] K. Van Le *et al.*, Phys. Rev. E **79**, 030701(R) (2009).

[14] J. Matraszek, J. Mieczkowski, J. Szydlowska, and E. Gorecka, Liq. Cryst. **27**, 429 (2000).

[15] C. Cruz *et al.*, Phys. Rev. E **78**, 051702 (2008).

[16] P. K. Karahaliou *et al.*, J. Phys. Chem. B **112**, 6550 (2008).

[17] R. Stannarius, A. Eremin, M. G. Tamba, G. Pelzl, and W. Weissflog, Phys. Rev. E **76**, 061704 (2007).