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Biaxial Nematic Mesophases from Shape-Persistent Mesogens with a Fluorenone Bending Unit

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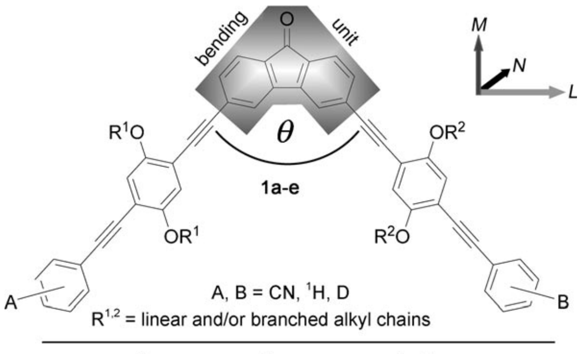
Nematic phases, applied in almost all commercial liquid-crystal (LC) displays, are LC phases with mesogens isotropically distributed and exhibiting orientational long-range order of one preferred molecular axis along a common direction defined by the so-called director. These are the phases with the lowest viscosity and besides the anisotropic properties, are most similar to isotropic liquids. Biaxial nematics should realise a long-range orientational order of all three molecular axes along three mutually perpendicular directors, but maintain the isotropic distribution of the molecular centres of gravity and their molecular mobility. Such phases are not only appealing from the viewpoint of basic research and theoretical modelling, but are also of technological interest to speed up the switching of LC displays.[1,2,3]

After the prediction by Freiser,[4] Saupe and Yu were the first to discover such mesophases in a narrow region of the phase diagram of a lyotropic LC.[5] The much-pursued synthesis of molecules for board-shaped mesogens, though suitable for forming thermotropic biaxial nematic phases, did not, however, reveal a widely accepted biaxial mesophase.[6] Only recently, biaxial nematic phases of multipodes[7] and polymers[8] with side-on attached nematogens, the rotation of which about the long axis is hindered, could be confirmed. In the area of low-molecular-weight mesogens, theory predicted V-shaped mesogens[1,9] and mixtures of rod- and disc-shaped molecules[1,10] as potential candidates for biaxial nematic phases. Indeed, the biaxial nematic phase at high temperatures, above 100 °C, was found in a series of oxadiazole derivatives,[11] the results of which were most widely accepted and confirmed.[12]

We were interested in parameters controlling biaxiality in such phases and focused therefore on shape-persistent molecules **1** with a well-defined bending angle (Scheme 1),[12–14] which is supposed to be a principal parameter in theoretical predictions.[1,9] They were designed to self-assemble exclusively in nematic phases owing to the substitution pattern of alkoxy chains.[13] However, only planar bending units with a dipole along the bisector revealed nematic phases.[15]



A, B = CN, ^1H, D
$R^{1,2}$ = linear and/or branched alkyl chains

	A	B	R^1, R^2
1a	*p*-D	*p*-CN	C_6H_{13}
1b	*p*-CN	*p*-CN	C_6H_{13}
1c	*m*-CN	*m*-CN	C_6H_{13}
1d	*m*-CN	*m*-CN	C_6H_{13}, 2-ethylhexyl
1e	*m*-CN	*m*-CN	2-ethylhexyl

Scheme 1. General structure of V-shaped, shape-persistent fluorenone nematogens and definition of molecular axes *N*, *M* and *L*.

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Among these derivatives, mesogens with a fluorenone bending unit have shown low-temperature monotropic nematic phases. At room temperature they transform to a nematic glass.[13] Results from earlier optical and X-ray studies pointed to a transition from a uniaxial to a biaxial nematic phase and eventually to a biaxial nematic glass although the bend angle of 90° was far from the proposed ideal angle of 109.5°. A selectively deuterated sample, **1a**, at the terminus of one arm was synthesised and investigated by X-ray, ^{2}H and ^{13}C solid-state NMR spectroscopy. All experiments reveal clear evidence for a high-temperature uniaxial and a low-temperature biaxial nematic order. Further synthetic effort proves to stabilise the nematic phases by molecular engineering, resulting in a material **1d** with a relatively large enantiotropic, uniaxial nematic mesophase range.

Mesogens **1a–d** (Scheme 1) were prepared by following previously published procedures.[13,14] The materials were carefully purified and their identity analysed by NMR spectroscopy, mass spectrometry and elemental analyses. Differential scanning calorimetry and polarised optical microscopy (POM) data confirmed the analogous thermotropic behaviour of compound **1a** compared with the non-deuterated derivative (Table 1). Optical studies of a 20 μm thick film in a commercial LC cell with planar alignment layer were performed to prove the biaxial nature of the low-temperature nematic phase. Conoscopy on the spontaneously homeotropic aligning sample exhibits a transition from a uniaxial to biaxial nematic phase between 50–60 °C by the typical splitting of isogyres and two optical axes when an additional circular polariser is adjusted in the optical path (see the Supporting Information). The same observations have been described earlier for the non-deuterated derivative on a thinner LC cell.[13] Wide-angle X-ray scattering on magnetic-field-aligned deuterated compound **1a** reveals a typical pattern observed for fluorenone derivatives in their nematic phase in a geometry in which the X-ray beam passed the sample perpendicular to the oriented direction (Figure 1 A). Since the scattered intensity at small angles on the equator can be attributed to distances along the bisector of the molecule and the intense diffraction on the meridian is related to the π stacking, at least a fraction of the material aligned with the molecular axes N, M along two directors $\hat{n}$, $\hat{m}$ as illustrated in Figure 1 D.[13] Consequently, also the third molecular axis L should be aligned along director $\hat{l}$. Assuming real long-range order, the result might confirm a biaxial phase. However, there is a further scenario related to the recently published theory that small clusters might be responsible for the formation of biaxial nematic phases.[17] The diamagnetic susceptibility of the aromatic units force the molecular planes to be parallel to the B field as displayed in Figure 1 D and E. The director $\hat{n}$ of a cluster or a domain, however, can be distributed about the B field vector as illustrated in Figure 1 F. In the case of a true biaxial monodomain, the X-ray pattern should reveal only the π stacking at a particular direction of the X-ray pattern when probed with the X-ray beam along the B vector.[18] In the second extreme case of the isotropic distribution of small biaxial aggregates about the B vector, the X-ray pattern should show only a halo in place of the distinct diffraction intensities for the π stacking and the phase would be uniaxial, denoted with

Table 1. Thermotropic properties of fluorenone nematogens **1**.

Compound	Heating rate 10 °C min^{-1} (onset [C°]/ΔH [kJ mol^{-1}])^{a}
1a	Cr 146[b] (g 39 N 117[c]/−0.3) I
1b	Cr 162/45 (g 34) N 178/0.7 I[d]
1c	Cr 118/48 N 146/0.4 I
1d	Cr 99[b] (g 31) N 126/0.6) I
1e	Cr 141[b] (N 108/0.7) I

[a] Cr crystal, g glass, N nematic LC phase, I isotropic phase. [b] POM data [c] broad signal with peak at 117 °C and onset at 110 °C. [d] from reference [13].

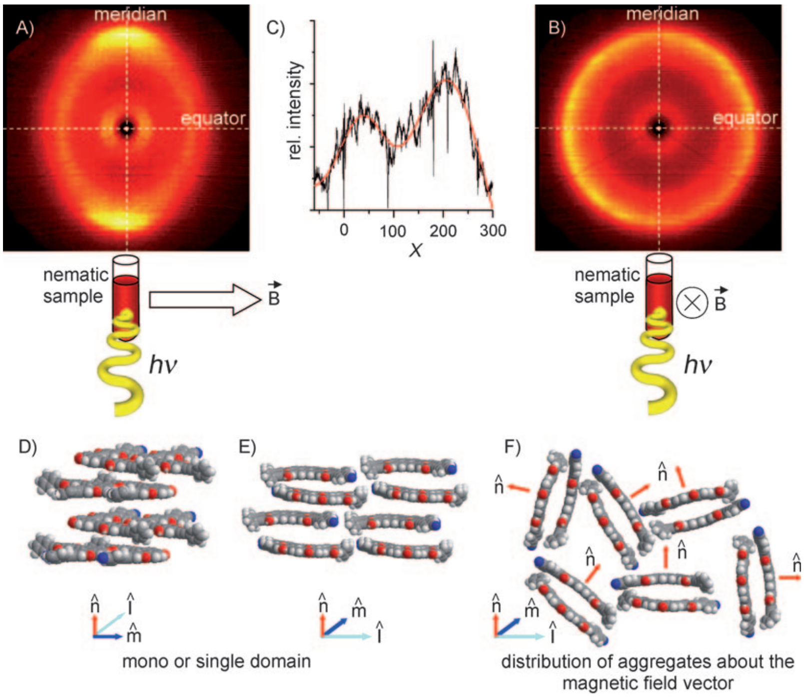

Figure 1. X-ray diffraction patterns of **1a** obtained at 30 °C in a sample previously aligned in the **B** field using an X-ray beam perpendicular (A) and parallel (B) to alignment direction. C) Integration of the halo in pattern shown in (B) along the azimuth angle χ from −60 to 300°. Model of the order of an ensemble of molecules in a monodomain viewed perpendicular (D) and parallel (E) to the alignment direction. F) Biaxial aggregates or domains viewed parallel to the alignment direction in the **B** field.

$N_u^{(bc)}$ according to Vanakaras and Photinos.[17] The experimentally recorded X-ray pattern with the X-ray beam along the oriented direction by the previously applied B field is shown in Figure 1B. At small angles, the signal reduces to almost only the background intensity, which confirms the alignment of the bisect along the B field. The signal attributed to π stacking is not confined to the meridian as seen in Figure 1A; however, the distribution is clearly anisotropic, as demonstrated by integration of the halo about the azimuthal angle χ (Figure 1C). Consequently, the experimental pattern can be rationalised with the scattering of several anisotropically distributed biaxial domains about the B direction.

In the search for the biaxial nematic phase, optical evidence has often been doubted owing to possible surface effects and X-ray evidence was distrusted because even if it shows the average correlation of mesogens along two directors, domains or aggregates may be still isotropically distributed about the direction of the B field. In the present study, the influence of surface effects was reduced by using a relatively thick oriented film and X-ray evidence was based on the results viewing perpendicular and parallel to the B field, thereby confirming two macroscopically oriented molecular axes. Techniques thought to determine, without doubt, the biaxial order of molecules in the bulk are ^{2}H and ^{13}C solid-state NMR spectroscopy.[1,19] The former can be performed either with selectively deuterated samples or with conveniently deuterated NMR probes.[1] The latter can be used on non-enriched samples. The current sample did not produce well-resolved ^{13}C NMR spectra in the nematic phase because the directors $\hat{n}$ were perpendicular to the external B field. However, a well-resolved isotropic spectrum was easily obtained by means of magic-angle spinning (MAS). In particular, we used a simple rotor-synchronised, 2D ^{13}C experiment to distinguish between uniaxial and non-uniaxial phase symmetry. For a sample with some sort of orientational order, as long as it does not possess a cylindrical symmetry about the rotor axis, the MAS sideband spectrum depends on the phase angle of the rotor at the start of the signal detection.[20] Hence, the sample alignment in the rotor is important. Figure 2 shows some typical sideband spectra [central band ($m=0$) corresponds to signals collected at the start of each rotor period (rotor phase is zero), and is the same as that seen in a 1D MAS CP experiment]. When a sample has transverse isotropy (uniaxial symmetry) or is an isotropic powder, the spinning sideband should be real and absorptive, whereas a dispersive sideband[21] with a broad shoulder could be seen when signals were collected with a non-zero rotor phase in single (and biaxial) crystals.[22] The uniaxial phase at 95 °C (Figure 2B) reveals exclusively absorptive sidebands for all m slices as expected. In the nematic glass at 25 °C (Figure 2A), however, the sidebands in $m=\pm1$ show clear dispersive character, which can only be rationalised with a biaxial order. The sample crystallised outside (or inside) the magnet shows almost purely absorptive sidebands, indicating its crystalline powder nature (see the Supporting Information).

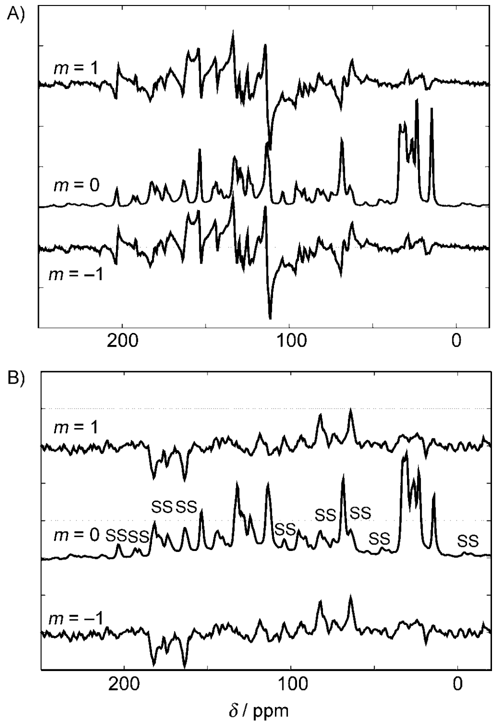

Figure 2. ^{13}C MAS slices for $m=0$ (central band) and $m=\pm1$ for the biaxial glass at 25 °C (A), and uniaxial phase at 95 °C (B). Only the $m=\pm1$ slices are shown here and have been scaled up for clarity. ss denotes spinning sideband in the 1D spectrum.

^{2}H NMR were performed on the selectively deuterated sample **1a** in order not to lose its sensitive biaxial nematic phase by adding a deuterated solute. Spectra of **1a** were collected as a function of temperature. 2D powder patterns were obtained at low temperatures to probe the presence of biaxial order without the necessity for more-demanding methods generally used for this task, including continuous rotation of the NMR sample around one axis perpendicular to the B field or repeated 90° sample tilting.[1,7a,11b,23] As the sample progressively crystallised upon slow cooling in the B field (7.05 T) , the sample was heated to the isotropic phase and then slowly cooled to 2 K below the clearing temperature T_c, stabilised for 10 min and rapidly cooled to 300 or 250 K; temperatures close to and well below the glass transition. By this procedure crystallisation was prevented, which would otherwise result in the loss of the ^{2}H NMR signal.

Figure 3A shows the typical NMR spectrum for the motional averaged isotropic liquid. In the nematic phase close to T_c, the NMR pattern reveals a doublet with a small quadrupole splitting of 15.8 kHz, indicating fast rotating molecules around the main director direction. The nematic order parameter S is calculated to be 0.23 at T_C-1 K. At low temperatures, close to the glass transition at 300 K and well within the nematic glass at 250 K, the obtained powder spectra disclose a 2D powder line shape, which can be related to a distribution of bisector orientations in the plane containing the external B field, which peaks at the field direction in agreement with the X-ray results. The rotation of molecules is frozen and only librational motions remain. The biaxiality

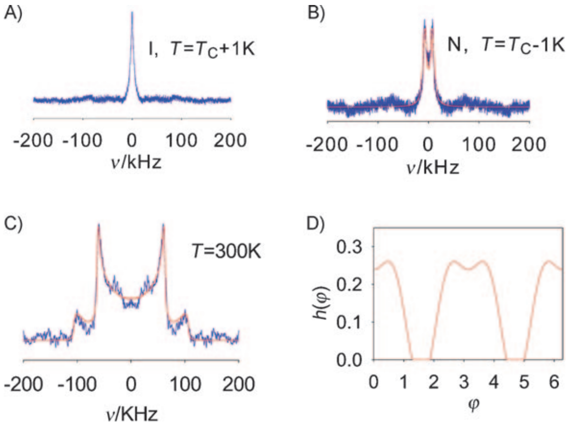

Figure 3. Spectra collected in the isotropic (A) and uniaxial nematic (B) phase. C) Spectrum collected at $T=300$ K (grey line) and simulation (black line). D) The ϕ (in radians) dependence of the domain distribution function obtained from the fit.

of the phase is shown by the finite asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$; $(|V_{xx}|<|V_{yy}|<|V_{zz}|)$, in which $V_{\alpha\beta}$ is the average electric field tensor (EFG). Simulations result in η values of 0.17 at 300 K and 0.18 at 250 K, and also show that the average EFG tensors from the two distinct molecular configurations in each domain do not share the same principal axis. The four order parameters usually used for biaxial nematics[24] with D_{2h} symmetry are S, D, P and C. Based on the simulation results, these are found to be 0.64, 0.0, 0.0 and 0.81 for C/3, respectively, at 300 K. Besides S, D, P and C, an additional order parameter is also finite, that is, $S^{X'Y'}_{Z''Z''}=0.17$ in the order supermatrix, indicating a lower than D_{2h} symmetry for the mesophase domains. The results are compatible with a C_{2h} or lower phase symmetry.

An important issue for biaxial nematic materials of low-molar-mass molecules is the thermodynamic stability of the nematic phase at low temperature. Compound **1a** forms crystal germs after several hours at RT, which grow slowly when the sample is reheated to the LC phase (Figure 4A). To prevent crystallisation, *meta*-cyano groups (**1c**), branched racemic chains (**1e**) or mixtures of branched and linear chains (**1d**) are introduced. *meta*-Cyano-substituted aryl groups can realise various conformers with cyano groups pointing in different directions in the nematic phase and considerably reduces the melting and clearing temperature compared with the *para*-cyano-substituted derivative (see Table 1, entries 2 and 3). Their combination with bulky 2-ethylhexyl chains in **1e** results in the destabilisation of the nematic phase and again an increased crystallisation tendency. If branched chains are attached only at one side of the molecule, as in **1d**, the nematic phase is significantly stabilised. During heating of the sample, which was annealed for four days at RT, no sign of crystal germs were observed (Figure 4B). Only after one month, small crystallites had formed which melted at 99 °C. Compound **1d** exhibits also an uniaxial to biaxial nematic phase transition between 50 and 60 °C in the same commercial LC cell used for the study of compound **1a** (Figure 4C–H). In the temperature range

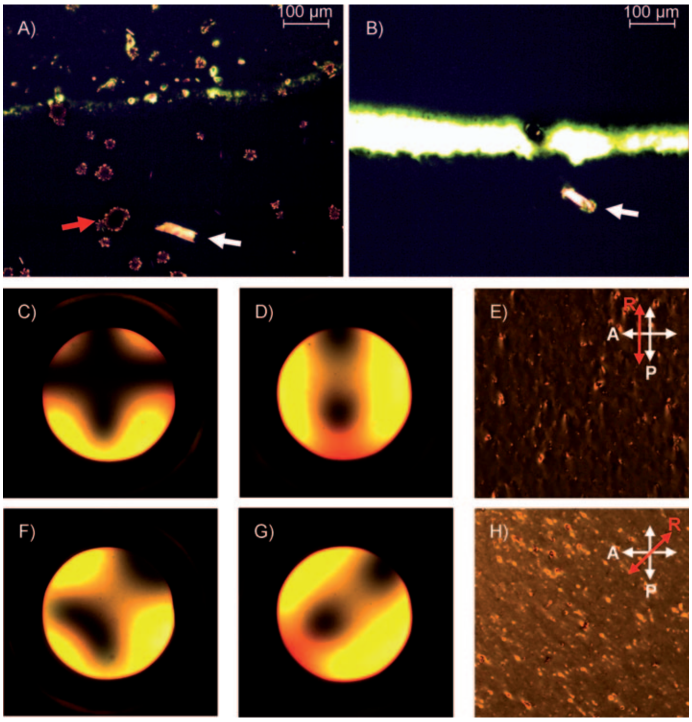

Figure 4. A) POM results of compound **1a** at 127 °C. Top: homeotropically aligned nematic uniaxial phase. Bottom: isotropic phase with crystallites (red arrow) and a dust particle (white arrow). B) Compound **1d** at the phase transition (133.2 °C). Top: isotropic phase. Bottom: homeotropically aligned uniaxial nematic mesophase with a dust particle (white arrow). Both materials were kept at RT for four days prior to the thermal treatment. C)–H) Conoscopy without and with circular polariser and orthoscopy of sample **1d** at 50 °C. Alignment direction parallel (C–E) and at 45° (F–H) with respect to the polariser. The low birefringence in (H) is related to the position of one optical axis, which is almost parallel to the propagation direction of light owing to the pre-tilt angle associated with the alignment layer of the LC cell.

of the uniaxial nematic phase, the material possesses a broad enantiotropic region. In the temperature interval in which the sample shows only monotropic properties, the biaxial nematic phase appears. This mesophase, however, is kinetically well stabilised.

In conclusion, the nematic phases of a deuterated fluorenone nematogen have been studied by POM, X-ray and solid-state NMR spectroscopy methods. All techniques show evidence for biaxial order in the phase close to the glass transition. Molecular engineering has afforded a nematic material that maintains the uniaxial to biaxial phase transition at low temperature, but with a wide enantiotropic uniaxial nematic range and a considerably stabilised biaxial nematic phase. Work is in progress towards a derivative forming a room temperature enantiotropic biaxial nematic mesophase.

Experimental Section

The synthesis of fluorenone derivatives **1** were performed by following previously published procedures.[13,14] POM was performed with a LC

Cells (SA100A200uG180) instrument from Instec. ^{2}H and ^{13}C NMR spectroscopy were carried out, respectively, at 46.1 MHz using the quadrupolar echo sequence and at 100.6 MHz by using a published method.[20] For ^{13}C NMR spectroscopy experiments, the sample in the rotor was heated to the isotropic liquid inside the NMR probe without spinning and cooled below the glass transition before doing the rotor-synchronised experiment. The sample was spun at 5 kHz in the B field of 9.4 T.

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Keywords: biaxial nematic phases · liquid crystals · shape persistence · solid-state NMR spectroscopy

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[1] G. R. Luckhurst, *Thin Solid Films* **2001**, *393*, 40.
[2] J.-H. Lee, T.-K. Lim, W.-T. Kim, J.-I. Jin, *J. Appl. Phys.* **2007**, *101*, 034105.
[3] R. Berardi, L. Muccioli, C. Zannoni, *J. Chem. Phys.* **2008**, *128*, 024905.
[4] M. J. Freiser, *Phys. Rev. Lett.* **1970**, *24*, 1041.
[5] L. J. Yu, A. Saupe, *Phys. Rev. Lett.* **1980**, *45*, 1000.
[6] K. Praefcke, D. Blunk, D. Singer, J. W. Goodby, K. J. Toyne, M. Hird, P. Styring, W. D. J. A. Norbert, *Mol. Cryst. Liq. Cryst.* **1998**, *323*, 231–259.
[7] a) J. L. Figueirinhas, C. Cruz, D. Filip, G. Feio, A. C. Ribeiro, Y. Frère, T. Meyer, G. H. Mehl, *Phys. Rev. Lett.* **2005**, *94*, 107802; b) C. Cruz, J. L. Figueirinhas, D. Filip, G. Feio, A. C. Ribeiro, Y. Frère, T. Meyer, G. H. Mehl, *Phys. Rev. E* **2008**, *78*, 051702.
[8] a) K. Severing, K. Saalwächter, *Phys. Rev. Lett.* **2004**, *92*, 125501; b) K. Severing, E. Stibal-Fischer, A. Hasenhindl, H. Finkelmann, K. Saalwächter, *J. Phys. Chem. B* **2006**, *110*, 15680.
[9] P. I. C. Teixeira, A. J. Masters, B. M. Mulder, *Mol. Cryst. Liq. Cryst.* **1998**, *323*, 167.
[10] R. Alben, *Phys. Rev. Lett.* **1973**, *30*, 778–781.
[11] a) B. R. Acharya, A. Primak, T. J. Dingemans, S. Kumar, *Pramana* **2003**, *61*, 231; b) L. A. Madsen, T. J. Dingemans, M. Kakata, E. T. Samulski, *Phys. Rev. Lett.* **2004**, *92*, 145505; c) B. R. Acharya, A. Primak, S. Kumar, *Phys. Rev. Lett.* **2004**, *92*, 145506.
[12] a) C. D. Southern, P. D. Brimicombe, S. D. Siemianowski, S. Jaradat, N. W. Roberts, V. Görtz, J. W. Goodby, H. F. Gleeson, *Europhys. Lett.* **2008**, *82*, 56001; b) Y. Xiang, J. W. Goodby, V. Görtz, H. F. Gleeson, *Appl. Phys. Lett.* **2009**, *94*, 193507; c) G. S. Lee, J. S. Cho, J. C. Kim, T.-H. Yoon, S. T. Shin, *J. Appl. Phys.* **2009**, *105*, 094509.
[13] M. Lehmann, S.-W. Kang, C. Köhn, S. Haseloh, U. Kolb, D. Schollmeyer, S. Kumar, *J. Mater. Chem.* **2006**, *16*, 4326.
[14] M. Lehmann, Ch. Köhn, H. Kresse, Z. Vakhovskaya, *Chem. Commun.* **2008**, 1768.
[15] a) M. Lehmann, J. Seltmann, A. A. Auer, E. Prochnow, U. Benedikt, *J. Mater. Chem.* **2009**, *19*, 1978–1988; b) M. Lehmann, J. Seltmann, *Beilstein J. Org. Chem.* **2009**, *5*, 73.
[16] M. Lehmann, J. Levin, *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 273–281.
[17] A. G. Vanakaras, D. J. Photinos, *J. Chem. Phys.* **2008**, *128*, 154512.
[18] In this case, the bisects orient parallel with the X-ray beam and will not contribute to the diffraction pattern. Scattering intensity related to the molecular long axes L has never been observed for the present material.
[19] R. Y. Dong, A. Marini, *J. Phys. Chem. B* **2009**, *113*, 14062.
[20] K. Schmidt-Rohr, H. W. Spiess, *Multidimensional Solid-State NMR and Polymers*, Academic Press, London **1994**, p. 372.
[21] The dispersive line shape has zero intensity at the centre of the line in contrast to a maximum in its corresponding absorption line.
[22] M. M. Maricq, J. S. Waugh, *J. Chem. Phys.* **1979**, *70*, 3300.
[23] G. R. Luckhurst, *Nature* **2004**, *430*, 413.
[24] D. A. Dunmur, K. Toriyama in *Physical Properties of Liquid Crystals* (Eds.: D. Demus, J. Goodby, H. W. Spiess, V. Vill), Wiley-VHC, Weinheim, **1999**.

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