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V-shaped nematogens with the "magic bent angle"[†]

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V-shaped nematogens 1a-c and 2a-b with benzodithiophene bending units have been synthesised. The derivatives 1a-c comprise a flat core with a bending angle of 109° , which is almost the tetrahedral angle proposed to be optimal in the realization of mesogens forming a biaxial nematic thermotropic mesophase.

V-shaped mesogens are one principal target structure thought to be successful in order to find a real thermotropic biaxial nematic phase (N_b) for low molecular mass compounds at lower temperature. Such mesophases are highly interesting with respect to theory and application, however, whether they exist or not is strongly debated. So far there have been only few examples, for which a number of different techniques provide evidence for this elusive phase at relatively high temperatures.^{1–3} Theory predicts an optimum angle for V-shaped mesogens without dipoles to form the N_b phase at a critical point (Landau point). This special angle is proposed to be the tetrahedral angle (109.4°) ,^{4,5} to which we will refer as a "magic bent angle". A recent publication,⁶ however, shows that such a point can broaden to a line if dipoles along the bisector are introduced. The tetrahedral angle may apparently be achieved by using a diphenylmethane bending unit. However, early X-ray studies of a 4,4'-diiodo derivative demonstrated a much larger angle of about 118°.7 Moreover, in our approach towards V-shaped nematogens with shapepersistent oligophenyleneethynylene scaffolds, the diphenylmethane core did not generate liquid crystalline materials, presumably because of the non-planarity originating from the steric congestion of the ortho-hydrogens.8 Benzophenone or diphenylether bending units are close to the tetrahedral angle but do not allow for a planar conformation of the mesogen obviously needed for mesomorphic behaviour. Rarely, non-shapepersistent banana mesogens form nematic phases from molecules with an angle close to the tetrahedral value, but only at relatively high temperatures.^{9–11} Moreover, banana molecules tend to form lamellar phases and show a strong tendency for biaxial clustering in the temperature range of the nematic phases.^{9,12}

Therefore, we were seeking for heterocyclic cores with the ideal angle between coupling sites which guarantee planarity.

Additionally, heteroatoms may generate dipole moments along the bisector of the bending unit which can be favourable for direct formation of the N_b from the isotropic liquid (I). We succeeded to identify a potential candidate among the benzodithiophenes. Whereas AM1 and DFT (B3-LYP/TZVPP with TURBOMOLE package)¹³ energy minimised bending unit **B2** revealed a bending angle of 134°, the structure of derivative **B1** showed an angle of 108.9° which is extremely close to the desired value (Fig. 1).

The synthesis of the V-shaped mesogens 1 and 2 (Fig. 1) starting from benzodithiophene cores^{14,15} and the terminal alkynes^{8,16–18} is outlined in Schemes S1,S2. All compounds 1 and 2 were thoroughly purified and characterised with NMR techniques, elemental analysis and mass spectrometry (ESI†).

The thermotropic properties of all compounds were investigated by polarised optical microscopy (POM) and differential scanning calorimetry (DSC) and are collected in Table 1. Schlieren textures (Fig. S1, ESI⁺) of highly fluid phases revealed the exclusive formation of nematic liquid crystals with the present molecular design as stressed earlier for other bending units.^{14,17} The phases are monotropic but kinetically, extremely stable in the liquid crystal temperature range. This stability can be enhanced by the position of cyano-substituents on the terminal aromatic unit and the type of aliphatic lateral chains.^{17,19} Thus compound 1c with meta-CN substituents and a mixture of lateral pentyl and heptyl chains revealed the most kinetically stable monotropic nematic phase in the series, which could be annealed close to the clearing point (T_{NI}) for more than 24 hours without any sign of crystallisation. The transition enthalpies ΔH and entropies ΔS at $T_{\rm NI}$ are small pointing to a weak first order transition (Table 1).²⁰ This observation does not exclude a possible direct I-N_b transition.⁶



Fig. 1 Calculated (DFT) angles $\theta/^{\circ}$ and dipole moments μ/D and structure of V-shaped mesogens **1a–c** and **2a–b**.

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second cooling (I-N)^a Rate 10 °C min⁻¹ (onset [°C]/ ΔH [kJ mol⁻¹]) Compound Cr 128.1/37.3 (N 104.4/-0.3) I 1a 0.8 Cr 145^b (N 80.0/-0.3) I 1b 1.4 Cr 129.9/45.0^a (N 66.8/-0.4) I 1.2 1c 2a Cr 150.0/69.3 (N 118.2/-0.3) I 0.8 Cr 113.0/45.1 (N 86.1/-0.4) I 2h 1.1

^{*a*} Cr: crystal, N: nematic, I: isotropic phase. ^{*b*} Determined by POM.

All compounds 1 and 2 aligned homeotropically spontaneously in an optically negative nematic phase, *i.e.* with the director **n** orthogonal to the aromatic planes and normal to the substrate (see Fig. S7 (ESI⁺) and discussion below), between two glass plates and in LC cells for homogenous alignment.[‡] Therefore, the materials could be studied by conoscopy²¹ in high quality LC cells (1) with a 23 μ m and (2) with a 50 μ m gap and planar antiparallely rubbed alignment layers (Nissan 130). Fig. 2 shows representative results for magic bent angle compound 1c in the 50 µm cell (2). After cooling the sample to the nematic LC at $T_{\rm NI} - T = 1.5$ °C, a strongly birefringent texture with randomly oriented domains appeared (A, B). After seven hours annealing, this phase transformed to a birefringent uniformly aligned film (D).²² The large and almost symmetric splitting of the optical axes in conoscopic investigations points to phase biaxiality (E). However, further annealing for 14 h afforded a multidomain texture visualised by the different colours when the λ -compensation plate was inserted (F, see also Fig. S7, ESI[†]). These areas of the LC cell with disordered biaxial microdomains give in sum a uniaxial response when investigated by conoscopy, which is evidenced by a slightly tilted conoscopic cross and only one optical axis. However, at the sample edge the material appears to be still uniformly oriented and exhibits biaxiality. Fig. 2F shows a multidomain structure which was uniaxial at 60 °C. Upon cooling this area aligned macroscopically and at room temperature (rt) the sample revealed maximum biaxiality (Fig. 2H). The director n was uniformly oriented but tilted by approximately 6° from the normal position with the substrate and oblique (azimuthal angle approx. 75°) with respect to the splitting of the optical axes: sample tilt by 6° along the rubbing direction centred the images (Fig. S2, ESI[†]). Various isochromes are visible at rt, which is a consequence of the sample thickness and the increasing density of the material with decreasing temperature. The transition from the uniaxial multidomain structure to the biaxial domain is reversible. Interestingly, in most of the well oriented areas the large refractive index is oriented parallel to the air-LC interface. This may be rationalised with the orientation of the lateral aliphatic chains towards the air interface which is favourable for most liquid crystals.²³ Thus the molecular long axes should be aligned parallel with the sample edge, which is in perfect agreement with the experimental observations. Conoscopy reveals also the optical negative anisotropy for all materials 1 and 2. Thus in the homeotropically aligned samples the aromatic planes are oriented parallel with the surfaces (Fig. S7, ESI⁺). However, we have no evidence whether the rubbing direction has any effect on the domain orientation. Consequently, the observed slow formation of N_b at the I–N transition is transient, not thermodynamically stable and breaks down in small biaxial domains, since the rubbed

Table 1 DSC data of 1a-c, 2a-b for the first heating (Cr-I) and the $\Delta S_{\rm NI}/{\rm JK}^{-1}~{\rm mol}^{-1}$

Fig. 2 (A–E) POM of 1c at $T_{NI}-T = 1.5$ °C in cell (2) between crossed polarisers (P, A). Texture after transition to the nematic phase at t = 0 (A) and t = 3 h (B). (C and D) Texture at normal (0°) and diagonal position (45°) after 7 h annealing. (E) Conoscopic images at 0° and 45° and optical axes visualised using a circular polariser at 45°. F: multi-microdomain structure observed applying the λ compensation plate at 60 °C. In the green part the largest refractive index of the sample adds on the largest refractive index of the λ plate (white arrow), indicating that the molecular long axes are oriented parallel with the same direction. G: same area uniformly oriented. H: conoscopic images at 0° (left) and 45° (right) and optical axes visualised with a circular polariser at 0° (middle).

polyimide layer does obviously not orient the second director of the nematic phase at a large (millimetre) scale. Upon cooling the anchoring to the interfaces becomes stronger which is presumably the driving force to the uniformly aligned areas at the sample edge. In principle these observations are in agreement with the generic cluster theory which predicts that molecules form biaxial clusters or small biaxial domains in the nematic phase which can be subsequently oriented by external forces such as electric, magnetic fields or surface anchoring.9 Note, however, that in the present case the small biaxial domains are already macroscopic (Fig. 2F).

The results indicate biaxiality of the phase, which cannot originate solely from surface effects as sometimes suggested. However, certain director field distributions were proposed to exhibit signs of biaxiality similar to a real biaxial phase (see Fig. S3, ESI[†]).^{24,25} In the present case, the director **n** is tilted by 6° oblique to the direction of the separation of the effective optical axes. To explain this effect other than by biaxiality we would need a special director field with opposite tilt of the molecules at the substrate. This is highly unlikely, because the cell was assembled to achieve a constant pretilt across the bulk of the liquid crystal (see ESI[†]). Moreover, the sign of biaxiality does not vanish in very thick LC cells (2), in which the uniformly aligned uniaxial bulk should dominate. Therefore, the results point to a real biaxial nature of the nematic phase already at the I-N transition. In subsequent POM studies of the mesogen 2b with the 134° angle we did expect to find only a uniaxial phase. However, the sample revealed the same properties in cell (1) than compounds 1 (Fig. S4, ESI[†]). This points to a direct I-N_b transition also in the series of large angle derivatives 2.

Magnetic field aligned samples were investigated by temperature-dependent wide angle X-ray scattering (WAXS) to get more detailed structural information. A typical diffraction pattern when probed with X-ray radiation perpendicular to the





Fig. 3 (A) WAXS pattern of **1b** at 50 °C recorded with the X-ray beam orthogonal to the direction of the previously applied magnetic field. (B) Model of the short range order in the N phase. The vectors N, M and L show the direction of the different molecular axes. (C) Integration along the equator. (D) Orientation of biaxial domains with directors **n**, **m** and **l** consistent with the diffraction pattern.

previously applied magnetic field B is shown in Fig. 3A. Three very diffuse signals, (i) at small angles at the equator d(i) =14.0 Å, (ii) at wide angles at the meridian d(ii) = 3.7 Å and (iii) the halo d(iii) = 4.4 Å, correspond to the mean distance along the bisect, between the π -faces and the liquid-like aliphatic chains. There are two additional diffuse peaks (iv) and (v), which are only apparent when integrating the WAXS pattern along the equator (see Fig. 3C and Fig. S5, ESI[†]). The origin of these two signals at d(iv) = 6.6 Å, d(v) = 5.2 Å is not yet known, but may be rationalised by intra- and intermolecular sulfur separations (Fig. 3B). All signals possess very low scattering intensities and are broad, with liquid-like correlation lengths ξ/d in the range of a few molecules, pointing clearly to nematic liquid crystalline nature of the phases. Analogous to the microscopical studies, a multidomain structure was expected to be formed in the magnetic field treated samples. Possible orientations of the domains are shown in Fig. 3D. Biaxial domains are rotationally distributed about the director **m** or **n**, thus the diamagnetic anisotropy forces the aromatic scaffold to align parallel with the magnetic field. More detailed analysis reveals that the molecular axis M orients preferentially along the magnetic field (see Fig. S6, ESI⁺). Therefore the π - π -distance reveals only at the meridian, whereas the distances along the bisector are visible exclusively at the equator of the diffraction pattern. Similar results have been recently obtained for other biaxial optically negative nematics.^{16,17} Interestingly, there is no important influence of the angle on the mean separation of the molecules along the bisector, when mesogens with the same length of lateral chains are compared.^{16,17,19} This becomes also apparent for derivatives **1b** (d(i) = 13.9 Å) and **2b** (d(i) = 14.4 Å) which reveal almost no difference with the change of the bending angle from 109° to 134° . Note that these X-ray results do not prove the macroscopic biaxiality of the nematic phase. They show only the alignment of two directors in small biaxial microdomains.

In conclusion, the two series of newly prepared benzodithiophene shape-persistent V-shaped nematogens with the "magic bent angle" **1** and the larger 134° angle **2** exhibit optical biaxial areas and multi-microsized domain areas in LC cells of various thicknesses close to the phase transition N–I. The optical negative phases align uniformly (**n** almost normal to the substrate). The second director is aligned in some areas at the air–LC interface and POM indicates a biaxial nature of the nematic phases. WAXS studies confirm the biaxiality of the microdomains. These results indicate that the angle is not important for this mesogen family to form a biaxial phase directly from the isotropic phase. Further studies are in progress to confirm and substantiate the phase biaxiality and the structure–property relationship.

Notes and references

[‡] Homeotropic orientation is defined for uniaxial phases, when the director **n** and consequently the optical axis is normal to the substrate and light becomes extinct in POM. In a biaxial phase the same alignment appears to be birefringent, see P. Collings, M. Hird, *Introduction to Liquid Crystals—Chemistry and Physics*, Taylor and Francis, London 1997.

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