

Synthesis and properties of oxadiazole based V-shaped, shape persistent nematogens†

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A series of biaxial V-shaped, shape-persistent molecules has been synthesised by stepwise coupling of phenylene ethynylene arms to an oxadiazole bending unit. Studies of their thermotropic nematic phases point to phase biaxiality.

V-shaped molecules are in the focus of liquid crystal research not only for their intriguing properties in banana phases,¹ but also owing to their potential to form the so elusive thermotropic biaxial nematic phase.² After the theoretical predictions,^{2a,3} many V-shaped mesogens have been proposed to possess a biaxial nematic mesophase (N_b).^{4–6} Theory predicts that the formation of this phase depends on the angle θ between the two wings of the molecule. Without a permanent molecular dipole, the optimum angle θ is expected to be tetrahedral,^{2a} however, this might vary if dipoles are introduced.⁷ The biaxial character of the nematic phase in a series of oxadiazole derivatives has been evidenced by ²H solid-state NMR and X-ray diffraction and, therefore, the compounds are widely recognised as the first low molecular thermotropic biaxial nematic materials.⁴ Recently, it has been claimed that switching about their molecular bisect is about 100 times faster than that about their long axis.⁸ Most of the molecular structures suggested to form N_b phases possess rather flexible backbones, without a well-defined bending angle θ , which prompted us to synthesise shape persistent mesogens based on a phenylene ethynylene scaffold **1** (Fig. 1). A shape-persistent fluorenone derivative has been shown to exhibit a uniaxial–biaxial nematic phase transition about 40 °C below the clearing temperature.⁶ These findings are in agreement with theoretical phase diagrams, where biaxial nematic phases are almost always predicted at low temperature if crystallisation or transitions to high ordered liquid crystal phases can be prevented. The latter processes can be hindered by laterally attached aliphatic chains (*cf.* Fig. 1). For these reasons it is highly attractive to combine the oxadiazole bending unit, as a leading structure, with shape persistent phenylene ethynylene arms containing lateral alkyl chains.

The synthesis† of the target molecules was performed by two consecutive Sonogashira–Hagihara cross-coupling reac-

tions of arms **2**^{6b} with oxadiazole derivative **3**⁹ (Scheme 1). The different reactivities of the iodo and bromo functionalities of compound **3** provide the possibility of the stepwise linkage of two different arms to obtain non C_2 -symmetric molecules **1a** and **1b**.

The phase behaviour of all the materials investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) is summarized in Table 1. Compounds **1a–c** show nematic phases; the only exception is **1d** which lacks a peripheral CN functionality. All these nematic phases are monotropic. The most stable liquid crystal phase is formed from **1a**, which can be supercooled into a nematic glass.¹⁰ We attribute this behaviour to the *meta*-cyano group which introduces additional attractive intermolecular interactions, but the rotation of the peripheral aromatic ring also results in a variation of the molecular dipole moment, which might be the origin of the low crystallisation tendency compared to **1b**.

The nematic phases of **1a–c** are characterized by schlieren textures at the I–N transition (Fig. 2a) and very low transition enthalpies (0.10–0.56 kJ mol⁻¹) and entropies (0.16–1.34 J K⁻¹ mol⁻¹). Such small values and the almost exclusive observation of two brushed disclinations in Fig. 2a have been reported to indicate a possible transition to a biaxial phase.¹¹ Only compound **1a** could be aligned between two glass plates with polyimide alignment layers by cooling from the isotropic liquid to the nematic phase (Fig. 2b) without crystallisation of the material.⁹ Rotation of the sample gives maximum birefringence with the rubbing direction at 45° to the polariser or analyser (Fig. 2c). The low birefringence can be explained by a small film thickness of approximately 7.5 μm.¹² Investigation in the conoscopy mode reveals separation of isogyres and two optical axes (Fig. 2d and 2e). Only annealing at room temperature (rt) for several days discloses a beginning crystallisation.

X-Ray diffraction patterns on an aligned sample of **1a** were recorded at rt (Fig. 3). The nematic phase shows an equatorial diffuse arc (iii) at wide angles ($d = 3.7$ Å), attributed to

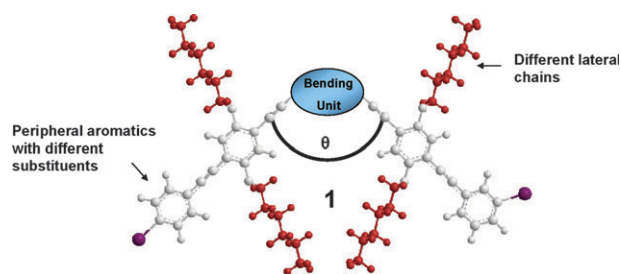


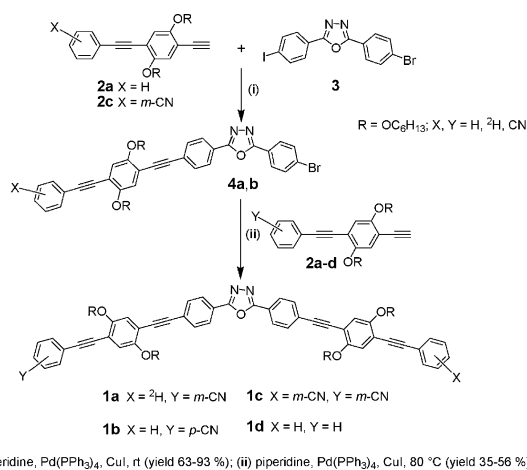
Fig. 1 Design of V-shaped, shape persistent nematogens.

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Scheme 1 Synthesis of oxadiazole based molecules.

π - π -interactions, a halo (iv) at 4.9 Å, corresponding to the liquid-like aliphatic chains and two broad reflections centred on the meridian at (i) 14.9 Å and (ii) 10.7 Å. The latter are assigned to periodical structures along the bisect of the molecule, as shown in the model of Fig. 3b. The molecular arrangement compares well with the one of fluorenone derivatives;^{6b} however, the distances along the bisect have decreased due to the larger angle θ of approximately 140°. The X-ray experiment shows the alignment of two molecular axes along directors and, thus, confirms the biaxial nature of the thermotropic nematic phase.

In order to study the molecular motion of **1a** with a strong dipole along the CN group and the oxadiazole unit, we performed dielectric spectroscopy¹⁵ on a sample aligned in a magnetic field. Dielectric data measured parallel and perpendicular to the director are presented in Fig. 4a and 4b. Two processes, a low frequency and a high frequency process overlapping each other, can be distinguished. The first is attributed to the reorientation of the molecular long axis and appears in both measurements, but is lower in intensity when measured perpendicular to the director. Consequently, the substance was not completely oriented, because, according to the classical experiments and the model by Maier and Meier,¹⁶ the low frequency relaxation mode should be seen only in the parallel direction. The second process at higher frequency is very broad and pronounced when measured perpendicular to the director. The shape of the absorption and its frequency, which is smaller than the frequency typically attributed to intramolecular motions or rotations of typical calamitic mesogens about their long axis,¹⁷ point to a complex process involving most probably the rotation of the bisect, *i.e.*

Table 1 Mesomorphic properties of **1a-1d**

Compound	Rate 10 °C min ⁻¹ (Onset [°C]/ ΔH [kJ mol ⁻¹])	$\Delta S_N/J K^{-1} mol^{-1}$
1a	Cr 130.1/18.4 ^b (g 25.0 ^a N 73.5/0.15) I 0.43	
1b	Cr 123.7/36.2 (N 104.0/-0.06) I 0.16	
1c	Cr 144.9/47.2 (N 127.0/-0.56) I 1.34	
1d	Cr 120 I ^c	—

^a Glass transition temperature. ^b Several overlapping melting transitions between 130–140 °C. ^c Determined by POM.

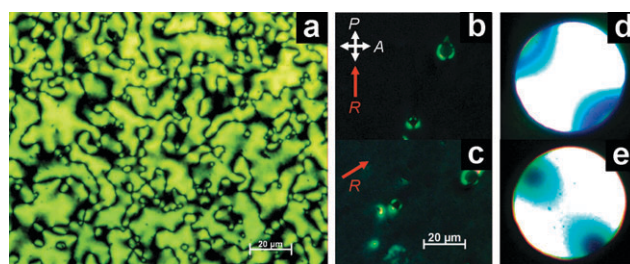


Fig. 2 POM investigations of **1a**. (a) Schlieren texture near the I–N transition at 68.5 °C during cooling. (b) Aligned sample with rubbing direction *R* parallel and (c) at 45° to polariser *P* and analyser *A* in the nematic phase at 64 °C. (d) Splitted isogyres in the conoscopic mode. (e) Two optical axes by using the circular polariser.

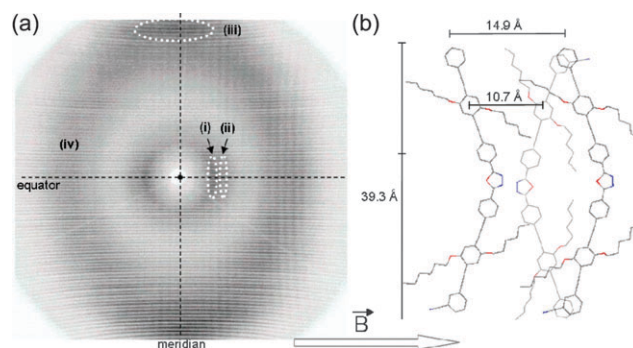


Fig. 3 (a) X-Ray diffractogram of an in the magnetic field oriented sample **1a** at 25 °C (the white arrow indicates the direction of the magnetic field). (b) Possible model rationalising reflections (i) and (ii) with short range order along the bisect of the molecules. The anti-parallel aligned mesogen is placed approximately 3.7 Å below the reference plane. Correlation lengths estimated by the Scherrer formula¹³ amounts to 3–6 molecules.¹⁴

the V-shaped molecule turns about the molecular long axis. The observation of both processes with different intensities at altered molecular orientations demonstrates that, in principal,

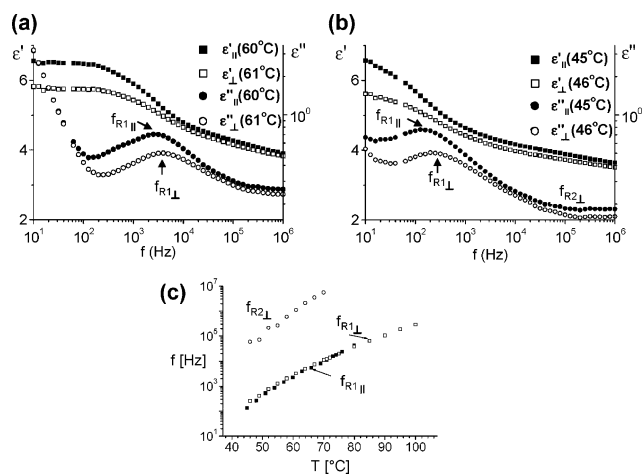


Fig. 4 Raw data of the complex dielectric permittivity of **1a** measured in the nematic phase (a) at 60 °C and (b) at 45 °C parallel or perpendicular to the director. (c) Relaxation frequencies. The stronger decreasing frequencies with decreasing temperature for process one can be rationalised by the approaching glass transition at 25 °C.[†]

the V-shaped molecules can be reoriented about their two different principal molecular axes when perfectly aligned.

In summary, new shape-persistent V-shaped compounds with an oxadiazole core have been synthesised. The molecular design, 2,5-alkoxy substitution at the middle benzene ring and peripheral cyano substituents, leads to low temperature, monotropic nematic mesophases. Indications for phase biaxiality of the nematic mesophase of **1a** were found in POM and X-ray investigations. Two processes are detected in dielectric studies, which are attributed to the rotations about the molecular short and long axes. Work is in progress to substantiate these findings by ^2H solid-state NMR techniques and to synthesise low temperature enantiotropic nematic phases applying the presented design principle.

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