Rigid Phenylene Ethynylene Units Linked by A V-shaped Centre. An Approach to Biaxial Nematogens?

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RIGID PHENYLENE ETHYNYLENE UNITS LINKED BY A V-SHAPED CENTRE. AN APPROACH TO BIAXIAL NEMATOGENS?

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Encouraged by theoretical predictions that nematic phases formed from V-shaped compounds could be biaxial, shape-persistent phenylene ethynylene arms linked by 1,3-phenylene, 4,4'-diphenylenemethane and 3,6-fluorenone units have been synthesised. Crystallisation and micro-segregation is prevented by 2,5-alkoxy substitution on the middle benzene ring of the arms. The specific molecular engineering, i.e. variation of peripheral substituents (H, CN) and different lengths of lateral alkoxy chains, lead to enantiotropic nematic liquid crystals over a wide temperature range for fluorenone containing materials II3d and mixtures of II3d with non-mesogenic II3b. These mesophases solidify at ambient temperature and form nematic glasses.

Keywords: biaxial nematics; phenylene ethynylene scaffold; shape persistent compounds; thermotropic liquid crystals; V-shaped molecules

INTRODUCTION

Thermotropic, biaxial nematic mesogens are of great theoretical and practical interest. Since the prediction of Freiser, there have been various concepts to restrict the rotation around the long axis of nematic mesogens which should lead to biaxiality of nematic liquid crystal phases [1]. However, although biaxial nematic systems are known for lyotropics [2] and side chain polymers [3], the low molar mass biaxial nematics claimed so far have been shown by ^{2}H NMR to have uniaxial symmetry [4a]. Attempts have been made to force lad like molecules into biaxial order by charge transfer interactions [5]. This lead to biaxial SmA_b phases. A monotropic nematic

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phase of highly biaxial molecules, where a rod is linked to a disc by a flexible spacer has been reported [6]. Recently, V-shaped molecules have been proposed to be possible biaxial nematogens [4]. A unit linking two arms by an angle between $\theta = 108.5-110°$ should be most promising [4a]. Limiting cases are linear molecules ($\theta = 180°$) and compounds with $\theta = 90°$, for which only uniaxial phases are proposed. The influence of various linking units on the supramolecular order of banana-shaped molecules has been studied, but only smectic phases were found [7]. Biaxial SmA phases for neat banana-shaped compounds has been proofed by conoscopy [8]. First evidence for a biaxial nematic in a small range at high temperature was mentioned for a compound bearing a oxadiazole center [9]. Nematic phases are rather rare for the family of V-shaped molecules and were mainly obtained with lateral substituents [10]. 2,5-Alkoxy substitution of stilbenoid, V-shaped molecules **I** (Chart 1) lead exclusively to nematic phases [11]. But, these compounds with a 1,3-phenylene centre, can possess various conformations leading to different linking angles θ. Shape persistent molecules can be envisaged by establishment of a rigid phenylene ethynylene scaffold, thus the effect of the linking unit can be studied independently from conformational influence. In the present contribution, structures **II** (Chart 1) were synthesised with two rigid arms linked by different centres, i.e. 1,3-phenylene, 4,4′-diphenylenemethane and 3,6-fluorenone, thus establishing angles from $120°$, $109.47°$ and $85°$. Analogous to **I**,
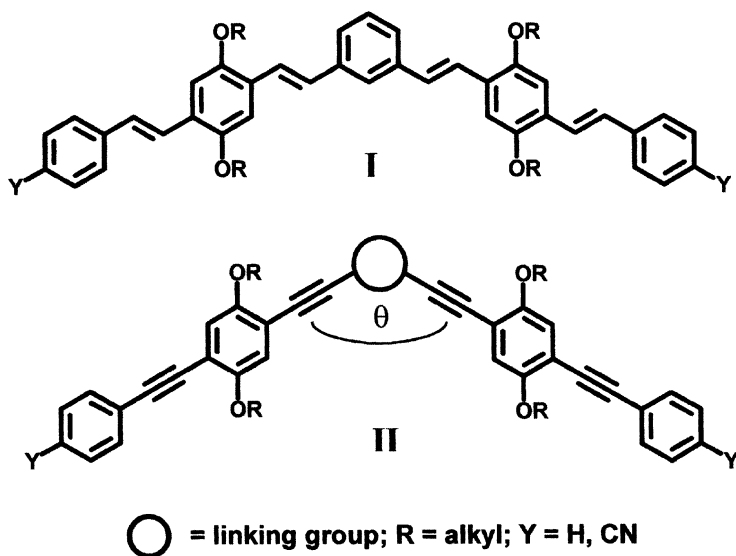

CHART 1 V-shaped molecules: stilbenoid system **I** and shape persistent phenylene ethynylene structure **II**.

lateral alkoxy side chains are attached to V-shaped molecules **II**, which should prevent the molecules from crystallisation and from micro-segregation. As stressed by Luckhurst, normal nematic phases tend to crystallise before reaching the temperature region where a second order transition to a biaxial nematic could theoretically occur [4a]. Peripheral substituents Y were introduced for mesophase stabilisation by specific interactions.

RESULTS AND DISCUSSION

Synthesis

The synthesis of the phenylene ethynylene scaffold was performed by a convergent strategy on the basis of Hagihara coupling [12]. The preparation of the arms is outlined in Scheme 1. The key compound **6** was obtained according to established reaction procedures [13]. 2,5-Dialkoxy-4-bromoiodobenzenes **5** were obtained by oxidative iodination of 2,5-dialkoxybromobenzenes **4** [14]. The different reactivity of the iodo and the bromo side in **5** allowed to couple triisopropylsilylacetylene followed by trimethylsilylacetylene without intermediate purification. The selective cleavage of the trimetylsilyl group under basic conditions led to mono deprotected **6** in high overall yields for the three steps. The different arms **7a-d** were obtained by Hagihara coupling of **6** with various arylhalogens and
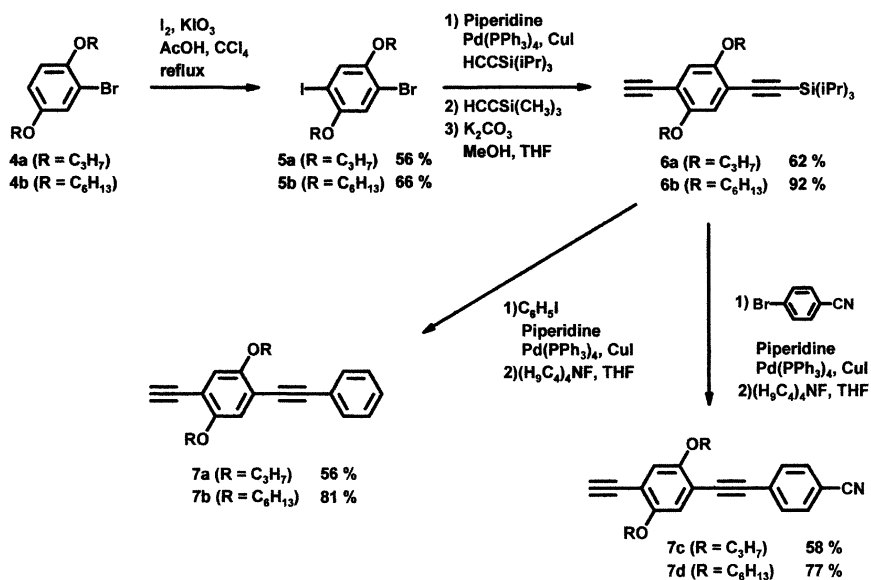
SCHEME 1 Synthesis of shape-persistent phenylene ethynylene arms.

succeeding cleavage of the triisopropylsilyl group using tetrabutyl-ammonium fluoride. In a final twofold reaction, arms **7** were linked to 1,3-diiodobenzene (**1**), 4, 4′-dibromodiphenylmethane (**2**) [15] and 3,6-dibromofluorenone (**3**)(Scheme 2) [16]. The yields of the obtained V-shaped molecules **II** are summarised in Table 1. Generally, the more reactive diiodo derivative **1** and the fluorenone **3** gave high yields, whereas the slow coupling with the less activated central unit **2** had to compete with the homocoupling of two arm segments, thus resulted in low amounts and pretentious purification of the target molecules **II2**.
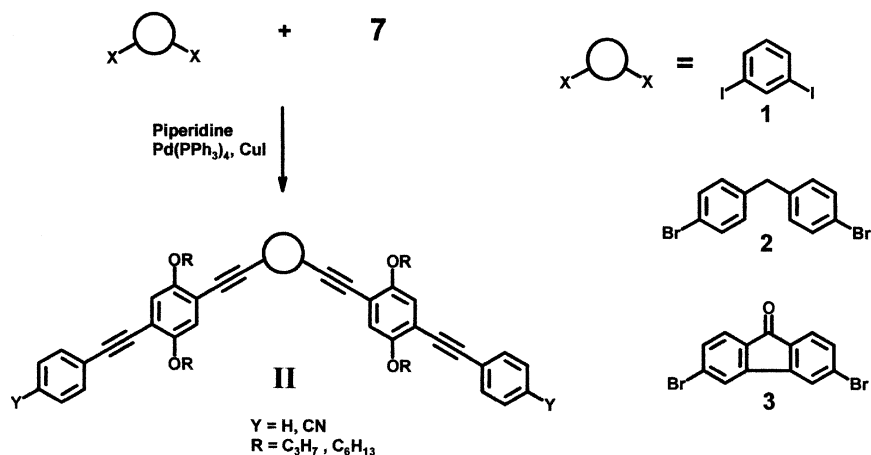
SCHEME 2 Synthesis of V-shaped phenylene ethynylene derivatives.

TABLE I Yields of V-shaped Phenylene Ethynylene Derivatives **II**

Compound	Y	R	Yield [%]
II1a	H	C_3H_7	10
II1b	H	C_6H_{13}	93
II1c	CN	C_3H_7	72
II1d	CN	C_6H_{13}	62
II2a	H	C_3H_7	14
II2b	H	C_6H_{13}	7
II2c	CN	C_3H_7	5
II2d	CN	C_6H_{13}	28
II3a	H	C_3H_7	77
II3b	H	C_6H_{13}	44
II3c	CN	C_3H_7	80
II3d	CN	C_6H_{13}	77

The analytical data is consistent with the structural pure compounds **II** [17].

Thermotropic Properties

The thermotropic properties of compounds **II** were studied by differential scanning calorimetry (DSC) and polarised optical microscopy (POM). Results are summarised in Table II.

Generally, as proposed, the 2,5-alkoxy substitution prevent the molecules from crystallisation. Compounds **II1a** to **II3b** are isotropic liquids or pass into a liquid phase after a glass transition during the second heating of the sample (entry 1–9, Table II). Some molecules (**II1a**, **II2a**, **II2d**, **II3a**) eventually show a cold crystallisation before they melt again to form an isotropic liquid. Comparison of the melting temperatures of the compounds, including the melting transitions of the first heating trace for molecules, which are not crystallising, shows that with shorter alkoxy chains or with CN groups transition temperatures to the isotropic phase are increased as expected.

Only two exceptions from these observations were found. Molecule **II3c**, which crystallises upon cooling from the isotropic phase, and **II3d** which

TABLE II Thermotropic Properties of **II**. Results of DSC and POM Investigations

Compound[†]	DSC results of the second heating, rate 10°C/min (Onset [°C]/ΔH [kJ/mol])
II1a	**I**86.9/ $-$ 33.8 **Cr** 153.9/37.0 **I**
II1b	**g** $-$ 10.2(Tg) **I** (m.p. 64.9°C first heating)
II1c	**g** 51.0 (T_g) **I** (m.p. 130.2°C first heating)
II1d	no transition[#] (m.p. 83.7°C first heating)
II2a[‡]	**g** 34.7 (T_g) **I** 103.7/ $-$5.4 **Cr** 166.5/5.9 **I**
II2b	no transition[#] (m.p. 86.4°C first heating)
II2d	**g** 20.9 (T_g) **I** 69.7/ $-$45.5 **Cr** 131.6/54.8 **I**
II3a	**g** 52.9 (T_g) **I** 95.9/* $-$ 22.5 **Cr$_1$** 132.3/ $-$ 2.1 **Cr$_2$** 156.0/36.5 **I**
II3b	**g** 29.7 (T_g)**I** (m.p. 104.3°C first heating)
II3c	**Cr** 213.5/20.8 **I**
II3d	**g**3 4.4 (T_g) **N** 178.0/0.7 **I**
II3b:II3d = 1:1	**g** 22.0 (T_g) **N** 118.0/0.3 **I**

†all compounds except **II2a**, **II3c** and **d** show no crystallisation or formation of a mesophase in the cooling process.

‡partial cold crystallisation.

#no transition down to $-$ 10°C. **Cr** crystal, **g** glass, **N** nematic phase, **I** isotropic phase.

indeed forms an enantiotropic liquid crystalline phase. The enthalpy related to the transition from the mesophase to the isotropic liquid amounts to 0.7 kJ/mol ($\triangle$S/R = 0.47), which is a typical value found for nematic phases. Two- and four-brushed disclinations are observed in the Schlieren texture of droplets below the clearing temperature (Fig. 1). The LC phase shows a high fluidity and spontaneous homeotropic alignment is observed between two glass slides (Fig. 2, right hand side). Thus **II3d** forms an uniaxial nematic liquid crystalline phase. Uniaxiality of V-shaped molecules with an angle θ around 90°, which is close to the angle realised with the fluorenone centre ($\theta \cong 85°$), was predicted theoretically [4]. It is worth noting, that the temperature range extends to 144°C, although slow crystallisation is observed when the sample is cooled slowly or annealed above the glass transition temperature. These crystals melt again at 140 °C to form the nematic phase. In order to prevent the nematic phase from crystallisation, mixtures of **II3b** and **II3d** were investigated by means of contact method and by DSC measurements of a 1:1 mixture. The interface of the contact sample of **II3b** and **II3d** is presented in Figure 2. On the right hand side, the spontaneous homeotropically aligned nematic phase of **II3d** (black region) can be seen. On the lower left hand side, the isotropic liquid phase of **II3b** is exposed. In the interface a new liquid crystal phase can be observed. POM studies for the 1:1 mixture reveal typical Schlieren tex-
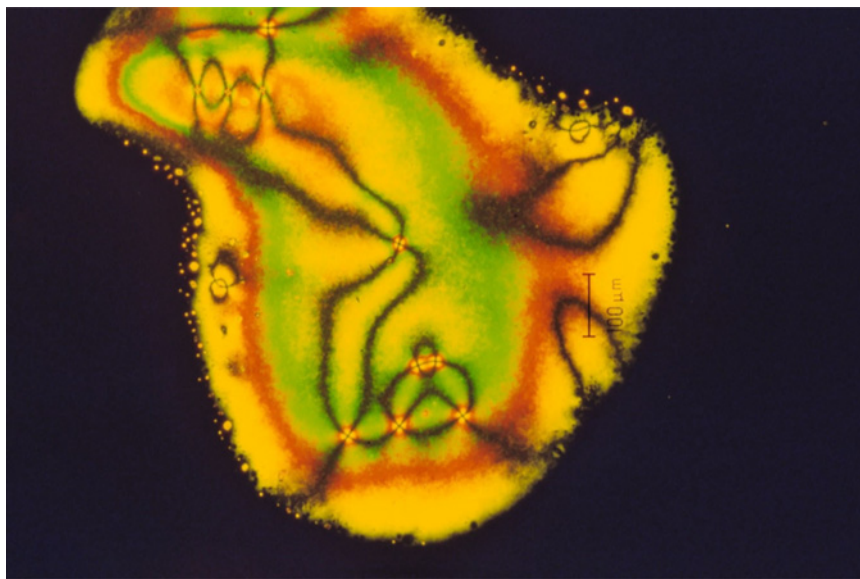

FIGURE 1 Schlieren texture of a nematic droplet obtained from **II3d** at 178.3°C between crossed polarizers. (See COLOR PLATE IV)
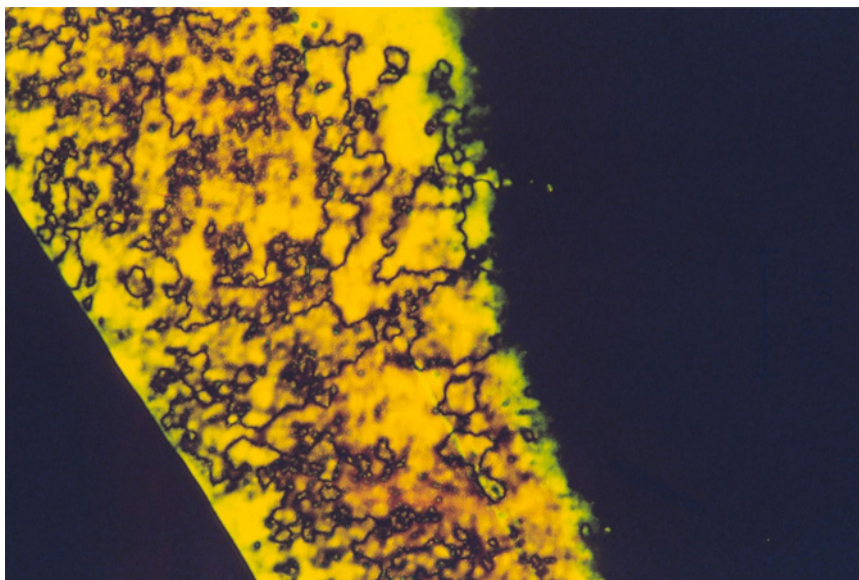
FIGURE 2 Interface of a contact sample obtained from **II3b** and **II3d** at 155.0°C between crossed polarizers. Left hand side: isotropic phase of **II3b**. Right hand side: homeotropic aligned nematic phase of **II3d**. (See COLOR PLATE V)

tures. The observed nematic phase does not align homeotropically between glass slides. The enthalpy at the I-N transition amounts to 0.3 kJ/mol ($\triangle S/R = 0.31$), which is a typical value found for I-N_u transitions of molecules organising in uniaxial nematic phases. For a material forming a biaxial nematic mesophase from the uniaxial nematic phase a second order transition has been theoretically predicted [18]. However, no second order transition besides the glass transition at 22°C has been detected. Crystallisation is slower for the mixture of **II3b** and **II3d** than for the neat **II3d** and could not be observed during DSC measurements, thus the material can be frozen to a nematic glass. The nature of the nematic phases have to be explored in future studies, by conoscopy and ^{2}H solid state NMR.

CONCLUSIONS

V-shaped, shape-persistent molecules **II**, with central units linking rigid arms, based on a phenylene ethynylene scaffold, by angles θ of approximately 120°, 109.47° and 85°, were synthesised in an efficient convergent strategy. Lateral 2,5-alkoxy substitution of the middle benzene ring prevents effectively the molecules from crystallisation. For compounds **II1** and **II2**, with linking units realizing angles θ for which biaxial nematic

phases are theoretically expected, no supramolecular liquid crystalline order is observed. In the series **II3**, where the central unit is formed by a larger fluorenone moiety, the tendency of crystallisation increases. An enantiotropic nematic phase is observed only for **II3d**. Interestingly, it extends over a large temperature range of 144°C and forms a nematic glass at room temperature. In accordance with theoretical predictions, the nematic phase of **II3d** was found to be uniaxial, since the linking angle is close to 90°. A 1:1 mixture of **II3b** and **II3d** forms a nematic phase which could not be homeotropically aligned. The nature of this phase has to be explored in future studies, which will include experiments applying electric fields, in order to establish eventually phase biaxiality.

In conclusion, the question raised in the title can not yet be positively answered. In the series of molecules **II** no biaxial nematogen was found, but molecular shape and substitution pattern can still be optimised.

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[17] Analytical data for **II3d** : ^{1}H NMR (300 MHz, CDCl$_3$) δ = 0.91 (m, 12H), 1.38 (m, 8H), 1.57 (m, 8H), 1.88 (m, 8H), 4.06 (m, 8H), 7.03, 7.04 (2s, 4H), 7.49 (dd, ABC, 2H), 7.60, 7.65 (AA′BB′, 8H), 7.67 (m, ABC, 4H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 14.0, 14.1, 22.6, 22.7, 25.7, 25.8, 29.2, 31.5, 31.6, 53.4, 69.5, 69.6, 89.7, 90.3, 93.4, 94.7, 111.5, 113.6, 114.1, 116.7, 118.5, 123.1, 124.3, 128.2, 129.8, 131.96, 132.0, 132.7, 133.7, 143.7, 153.8, 153.9, 191.8. FT-IR (KBr) ν [cm^{-1}] = 3055, 2926, 2855, 2224, 2206, 1708, 1601, 1510, 1217, 1027, 919, 880, 854, 783, 689, 553. MS (FD) m/z (%) = 1030.4 (100, M$^+$). EA (C$_{71}$H$_{70}$N$_2$O$_5$) calculated %C 82.69, %H 6.84, %N 2.72, found %C 82.59, %H 6.77, %N 2.63. Analytical data for **II3b** : ^{1}H NMR (300 MHz, CDCl$_3$) δ = 0.91 (m, 12H), 1.37 (m, 8H), 1.57 (m, 8H), 1.88 (m, 8H), 4.06 (m, 8H), 7.04, 7.05 (2 s, 4H), 7.36 (m, 6H), 7.49 (dd, ABC, 2H), 7.55 (m, 4H), 7.67 (m, ABC, 4H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 14.0, 14.1, 22.6, 22.7, 25.7, 25.8, 29.3, 31.6, 31.6, 53.4, 69.6, 69.7, 85.8, 90.1, 94.3, 95.3, 113.0, 115.0, 116.8, 117.0, 123.1, 123.3, 124.3, 128.3, 128.3, 130.0, 131.6, 132.7, 133.6, 143.7, 153.6, 153.9, 191.9. FT-IR (KBr) ν [cm^{-1}] = 3054, 2925, 2855, 2200, 1716, 1610, 1599, 1506, 1216, 1026, 917, 876, 851, 782, 753, 689, 668. MS (FD) m/z (%) = 980.6 (100, M$^+$). EA (C$_{69}$H$_{72}$O$_5$) calculated %C 84.45, %H 7.40, found %C 83.92, %H 7.99.

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