

Nematic and Smectic Mesophase Formation by a Novel Triphenylene-Azobenzene Hybride Molecule

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A novel liquid crystal whose molecular structure consists of a disc-like triphenylene unit as central core and six rod-like azobenzenes as the peripheral units is reported. This molecule, 2,3,6,7,10,11-hexakis{[4-(4-acetylphenylazo)phenoxy]hexyloxy}triphenylene, was prepared by ferric chloride oxidative trimerisation of 1,2-bis{[4-(4-acetylphenylazo)phenoxy]hexyloxy}benzene. The mesomorphic properties were investigated by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. The existence of a nematic and a smectic A phase was confirmed by textures and X-ray diffraction. UV-Vis spectra show a significant absorption of the azobenzene mesogens at 392 and 460 nm, which would allow the use of this and related materials for photoinduced isomerization and reorientation of the azobenzene groups by using light sources in the visible range.

I. Introduction

Discotic liquid crystals have found wide spread attention in the last two decades. Extensive studies have been performed on the preparation and properties of discotic liquid crystals based on the triphenylene molecule and most of the compounds form columnar mesophases [1-3]. However, currently some efforts have been directed towards designing novel molecules in terms of combining the features of rod and disk-like molecules having photoactive properties. Photoactive liquid crystals have found special interest due to the possibility of potential applications such as high density optical data storage, optical image processing, dynamic holography, optical computing, parallel optical logic and pattern recognition [4-6]. Recently, an incompatible combination of two or three calamitic mesogens and a disc-shaped mesogen was reported, whose molecular topology induces the formation of a smectic phase, with alternating layers of discs and rod-shaped mesogens [7], while a compatible combination of calamitic and discotic mesogens resulted a nematic phase [8]. Shimizu et al. [9] described a disc-shaped triphenylene molecule linked with six alkoxy-substituted rod-shaped azobenzene moieties via rather short (C₃) alkylene chains and ester linkages. This compound shows kinetically controlled bimesomorphism with a metastable smectic A and a stable hexagonal columnar phase, due to a change of the average molecular shape from rod-like to disc-like. In this report a new molecule is described, in which six rod-shaped azobenzene moieties, each carrying a short electron withdrawing acetyl group at the terminus, are attached to a disc-shaped triphenylene unit via longer alkylene spacers (C₆) and ether linkages.

II. Experimental

2.1 Materials

4-Aminoacetophenone (Fluka), sodium nitrite (BDH), urea (BDH), phenol (Merck), 1,6-dibromohexane (Fluka), potassium carbonate (Fluka) and catechol (BDH) were used as received. Dry acetone and dry dichloromethane were obtained from distilling over phosphorus pentoxide (Merck). Other solvents and chemicals were used without further purification.

2.2 4-(4-Hydroxyphenylazo)acetophenone **2**

4-Aminoacetophenone (10 g, 0.074 mol) was dissolved in acetone (250 ml). Dilute hydrochloric acid [water (50 ml), conc. hydrochloric acid (27 ml)] was added and the mixture was cooled to 2 °C. Sodium nitrite (6.50 g, 0.094 mol), dissolved in water (20 ml) was added drop-wise to the cooled mixture and stirred for 1 h. Exactly, 5 ml of urea (1.21 g, 0.020 mol) solution was added for decomposing the excess of sodium nitrite for 10 min. Then, phenol (6.96 g, 0.074 mol), dissolved in an acetone/water mixture (200 ml/100 ml) was added to the diazotated mixture and the reaction mixture was maintained at pH 8-9 by adding sodium hydroxide solution (about 25 ml of 50%), stirring was continued for 2 h. The resulting mixture was made slightly acidic (pH <5) with dilute hydrochloric acid (ca. 80 ml, 10%) and 300 ml of water for precipitation of the product and the precipitate was collected by filtration. The product was crystallized twice from methanol and ethanol, respectively. Yield: 12.11 g (68.1%) as bright red crystals and m.p. 192 °C. IR (KBr, cm^{-1}): 3323 (OH, ν), 1665 (C=O, ν), 1591, 1500, 1468 (aromatic ν), 1398 (C-H, δ), 1362 (OH, δ), 1245, 1140 (C-O, ν), 845 (aromatic δ). ^1H NMR (600 MHz, acetone- d_6) δ : 9.25 (H, s, ArOH), 8.16 (2H, d, $J = 8.5$ Hz, ArH), 7.92 (4H, d, $J = 8.6$ Hz, d, $J = 5.9$ Hz, ArH), 7.04 (2H, d, $J = 8.8$ Hz, ArH), 2.64 (3H, s, CH_3).

2.3 1-Bromo[4-(4-acetylphenylazo)phenoxy]hexane **3**

A mixture consisting of a solution of compound **2** (2.00 g, 8.33 mmol) in dry acetone (150 ml), potassium carbonate (8.40 g, 62 mmol), a catalytic amount of potassium iodide (100 mg) and a ten-fold excess of 1,6-dibromohexane (20.3 g, 83.3 mmol) was refluxed for 24 h under argon atmosphere. The reaction mixture was filtered hot and the acetone was removed under reduced pressure. Sufficient amount of hexane was added to the product for removing unreacted 1,6-dibromohexane. The insoluble material was collected by filtration and product was dissolved in dichloromethane and water. The organic phase was washed with dilute hydrochloric acid, sodium carbonate solution and water successively. The solvent was removed under reduced pressure. The product was recrystallized from ethanol with hot filtration to ensure the removal of the dimeric side-product. Yield: 2.40 g (71.4%) and m.p. 120 °C. IR (KBr, cm^{-1}): 2938, 2862 (C-H, ν), 1672 (C=O, ν), 1590, 1484, 1435 (aromatic ν), 1398 (C-H, δ), 1354 (OH, δ), 1248, 1137 (C-O, ν), 848 (aromatic δ). ^1H NMR (600 MHz, CDCl_3) δ : 8.08 (2H, d, $J = 8.2$ Hz, ArH), 7.93 (4H, d, $J = 8.7$ Hz, d, $J = 5.8$ Hz, Ar-H), 7.02 (2H, d, $J = 8.9$ Hz, ArH), 4.06 (2H, t, $J = 6.4$ Hz, OCH_2), 3.44 (2H, t, $J = 5.2$ Hz, CH_2Br), 2.66 (3H, s, CH_3), 1.93-1.84 (4H, m, CH_2), 1.55-1.53 (4H, m, CH_2).

2.4 1,2-Bis[[4-(4-acetylphenylazo)phenoxy]hexyloxy]benzene **4**

A mixture consisting of a solution of compound **3** (2.24 g, 5.55 mmol) and catechol (0.305 g, 2.77 mmol) in dry acetone (150 ml), potassium carbonate (0.76 g, 5.54 mmol) and a catalytic amount of potassium iodide (100 mg) was refluxed for 40 h under argon atmosphere. The mixture was poured into ice-cold water and acidified with dilute hydrochloric acid. The precipitate was filtered off and dissolved in dichloromethane and water. The organic phase was

washed with sodium carbonate solution and water successively. Afterwards, the solution was dried by sodium sulfate and the solvent was evaporated under reduced pressure. The product was recrystallized from ethanol : ethyl acetate (2 : 1). Yield: 1.37g (32.6 %) and m.p. 125°C. IR (KBr, cm^{-1}): 2935, 2862 (C-H, ν), 1672 (C=O, ν), 1594, 1480, 1431 (aromatic ν), 1398 (C-H, δ), 1354 (OH, δ), 1260, 1133, 1105 (C-O, ν), 840 (aromatic δ). ^1H NMR (600 MHz, CDCl_3) δ : 8.08 (4H, d, $J = 8.2$ Hz, ArH), 7.93 (8H, d, $J = 7.6$ Hz, d, $J = 6.1$ Hz, ArH), 7.01 (4H, d, $J = 8.9$ Hz, ArH), 6.95-6.82 (4H, m, Ar-H), 4.08 (8H, m OCH_2), 2.66 (6H, s, CH_3), 1.89-1.84 (8H, m, OCH_2CH_2), 1.55-1.53 (8H, m, CH_2).

2.5 2,3,6,7,10,11-Hexakis{[4-(4-acetylphenylazo)phenoxy]hexyloxy}triphenylene 5

According to literature [10], compound **4** (0.50 g, 0.662 mmol) was added to a stirred suspension of iron (III) chloride (0.322 g, 1.98 mmol) in dichloromethane (25 ml) with 2 drops sulfuric acid. The mixture was stirred for 2 h and excess iron (III) chloride was removed by filtration. Methanol (60 ml) was added to the filtrate to quench the reaction and the precipitate was washed several times with methanol. The product was purified by column chromatography on silica gel with chloroform as eluent. The solid was crystallized from methanol : chloroform (10:1). Yield: 0.110 g, 22.0%. IR (KBr, cm^{-1}): 2939, 2862 (C-H, ν), 1680 (C=O, ν), 1594, 1492, 1435, (aromatic ν), 1390 (C-H, δ), 1358 (OH, δ), 1256, 1133, 1109 (C-O, ν), 844 (aromatic δ). ^1H NMR (600 MHz, CDCl_3) δ : 8.06 (12H, d, $J = 8.5$ Hz, ArH), 7.90 (24H, d, $J = 8.7$ Hz, d, $J = 5.4$ Hz, ArH), 6.97 (12H, d, $J = 9.1$ Hz, ArH), 6.88 (6H, s, Ar-H), 4.03 (24H, t, $J = 6.5$ Hz, t, $J = 5.4$ Hz, OCH_2), 2.62 (18H, s, CH_3), 1.87-1.82 (24H, m, OCH_2CH_2), 1.55-1.52 (24H, m, CH_2). ^{13}C NMR (400 MHz, CDCl_3) δ : 25.91, 25.99, 26.82, 29.25, 29.39, 68.31, 69.13, 114.25, 114.73, 121.11, 122.48, 125.13, 129.23, 137.75, 146.83, 149.12, 155.19, 162.16, 197.19. Elemental Analysis Calc. for $\text{C}_{138}\text{H}_{144}\text{N}_{12}\text{O}_{18}$ (2258.69): C, 73.38; H, 6.43; N, 7.44%. Found: C, 73.11; H, 6.25; N, 7.62%

2.6 Techniques

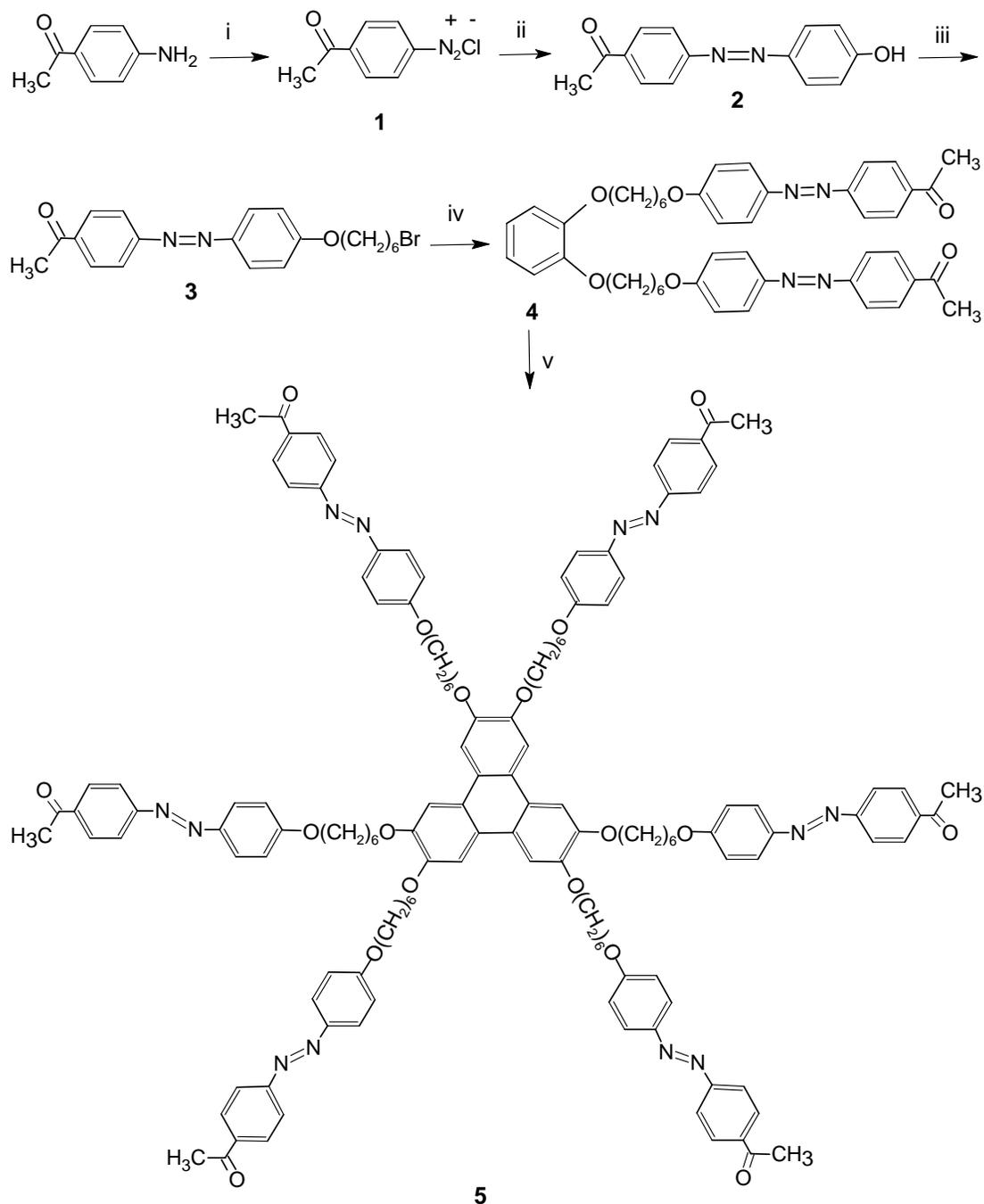
The structures of the intermediates and product were confirmed by spectroscopic methods: FT-IR spectra were recorded with a Perkin Elmer (BX 20) spectrometer. ^1H NMR spectra were recorded with a Joel BX50 (600 MHz) and ^{13}C NMR were recorded with a Varian (400 MHz) spectrometer. The transition temperatures and their enthalpies were measured by differential scanning calorimetry (Mettler Toledo Star, SW 7.01), heating and cooling rates were $10\text{ }^\circ\text{C min}^{-1}$. Optical textures were determined by using a Mettler FP 82 hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing optical microscope. UV-Vis spectra were recorded with a Perkin-Elmer Lambda EZ-210 spectrometer. The substances were dissolved in chloroform, about 1×10^{-6} mol L^{-1} were used to obtain the absorption spectra. The X-Ray investigations on non-oriented samples in capillary tubes (diameter: 1 mm) were carried out using a Guinier film camera (HUBER Diffraktionstechnik, Germany) and a home made small angle device with a position sensitive detector (PSD, MBBRAUN, Germany).

III. Results and discussion

3.1 Synthesis

The synthetic approach used to prepare the intermediates and compound **5** is outlined in scheme 1. The peripheral rod-like cores were prepared from 4-aminoacetophenone in which the amino group is diazotated by sodium nitrite in the presence of 3 equivalents of diluted hydrochloric acid and the obtained diazonium salt **1** was coupled with phenol to yield 4-(4-

hydroxyphenylazo)acetophenone **2**. The flexible spacer was introduced by alkylation of **2** with excess 1,6-dibromohexane in the presence of potassium carbonate as base to give 1-bromo[4-(4-acetylphenylazo)phenoxy]hexane **3**. Compound **3** was used for the alkylation of catechol with potassium carbonate to yield 1,2-bis[[4-(4-acetylphenylazo)phenoxy]hexyloxy]benzene **4**. The target molecule 2,3,6,7,10,11-hexakis[[4-(4-acetylphenylazo)phenoxy]hexyloxy]triphenylene **5** was prepared by oxidative cyclotrimerisation of **4** with ferric chloride as oxidant [10].



Scheme 1: Synthesis of triphenylene based liquid crystal. Reagents and conditions: i, NaNO_2 , HCl , $2\text{ }^\circ\text{C}$; ii, NaOH , $\text{C}_6\text{H}_5\text{OH}$; iii K_2CO_3 , KI , $\text{Br}(\text{CH}_2)_6\text{Br}$; iv, $\text{C}_6\text{H}_6\text{O}_2$ catechol, K_2CO_3 , KI ; v. FeCl_3 , CH_2Cl_2 , H_2SO_4 .

Spectroscopic analysis confirmed the structures of the intermediates and the final compound. The ^{13}C -NMR spectrum of compound **5** (figure 1) shows all peaks corresponding to the carbon atoms of **5** (only one peripheral azobenzene unit is shown in the chemical structure of **5** and R represent the others five azobenzene moieties with alkyl spacers and acetyl groups). There are in total 18 carbon atoms in the triphenylene core, found at 3 distinct positions (x, y, z). Each of the x, y and z positions correspond to 6 carbon atoms. All other peaks are due to the six rod-shaped azobenzene moieties with the alkyl chains and acetyl groups, as assigned in Figure 1.

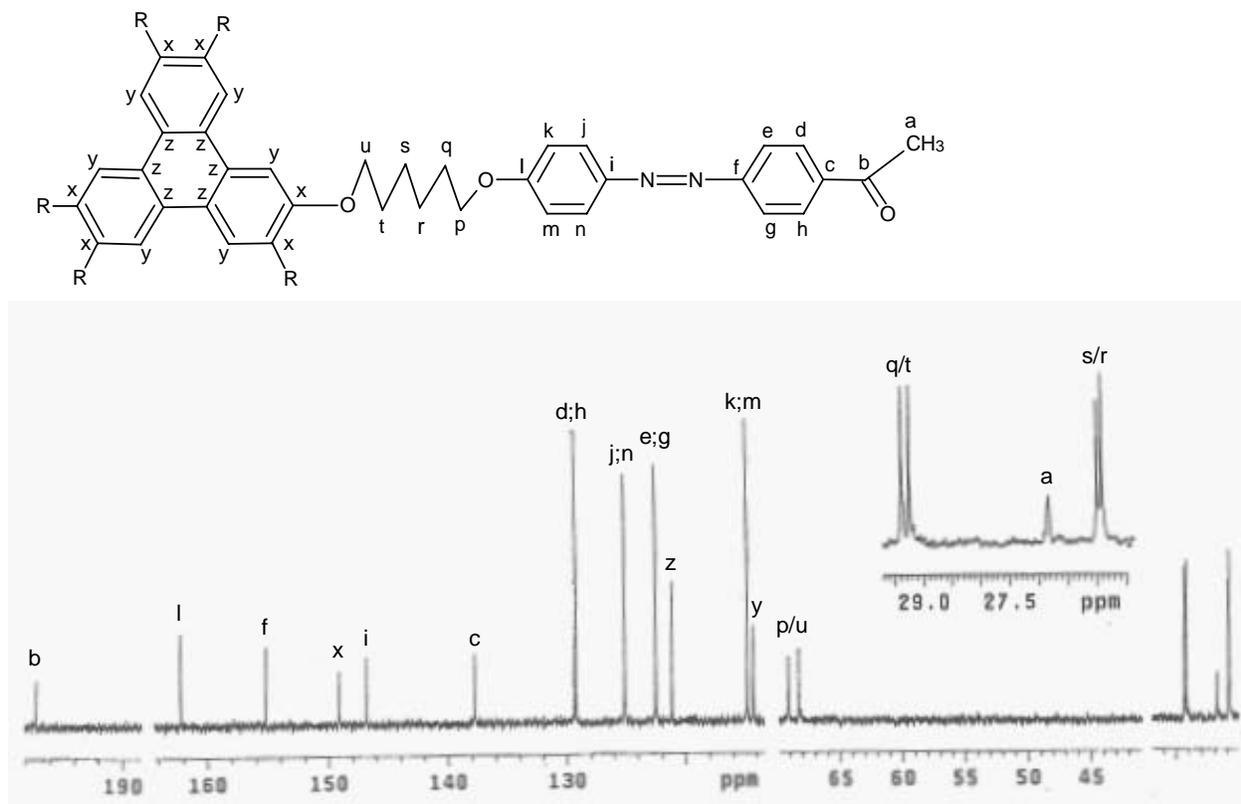


Figure 1: ^{13}C NMR spectra of compound **5**. Only one azobenzene with alkyl chain is shown in the chemical structure while R represents to others five azobenzene moieties with alkyl chains and acetyl groups.

3.2 Mesomorphic properties

The phase transition temperatures as well as the phase transition enthalpy changes were determined by differential scanning calorimetry (DSC) and the results of the second heating and cooling scans are summarized in Table 1.

Table 1: Phase transition temperatures and enthalpies obtained from the DSC scans of **5**.^a

	Transition temperature ($T/^\circ\text{C}$) and associated transition enthalpy values ($\Delta H/\text{Jg}^{-1}$)
Heating	Cr 138.6 (67.2) SmA 141.1 (2.5) N 152 (1.6) I
Cooling	I 151.7 (2.1) N 140.6 (5.1) SmA 84.2 (43.9) Cr

^a Abbreviations: Cr = crystal, SmA = smectic A, N = nematic and I = isotropic phase

In figure 2, the DSC thermogram of compound **5** is shown. On cooling, three exothermic peaks were found. The enthalpy change at the SmA-N transition is higher than at the N-Iso transition, as usually observed. An additional broad exotherm is found for the crystallization of the SmA phase at ca. 84 °C.

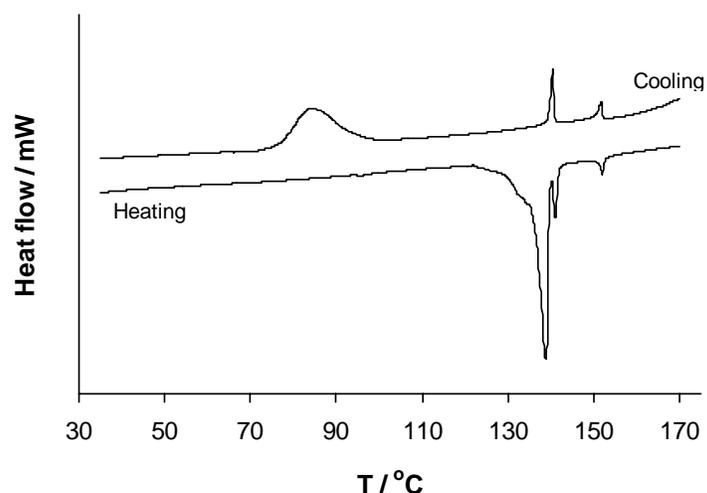


Figure 2: DSC heating and cooling traces of compound **5** (10 °C min⁻¹)

The mesophase structures were evaluated by means of polarizing optical microscopy. The micrographs of the two mesophases of compound **5** as observed upon cooling are shown in Figure 3. A schlieren texture, as typical for nematic phases, was observed at 151 °C upon cooling from the isotropic phase (figure 3a). This nematic phase is highly fluid. Upon further cooling a fan-like texture develops at 140 °C (figure 3.b). This texture is characteristic for smectic A phases. Shearing leads to a homeotropic alignment, which appears optically isotropic. There is no further phase transition on further cooling, except crystallization.

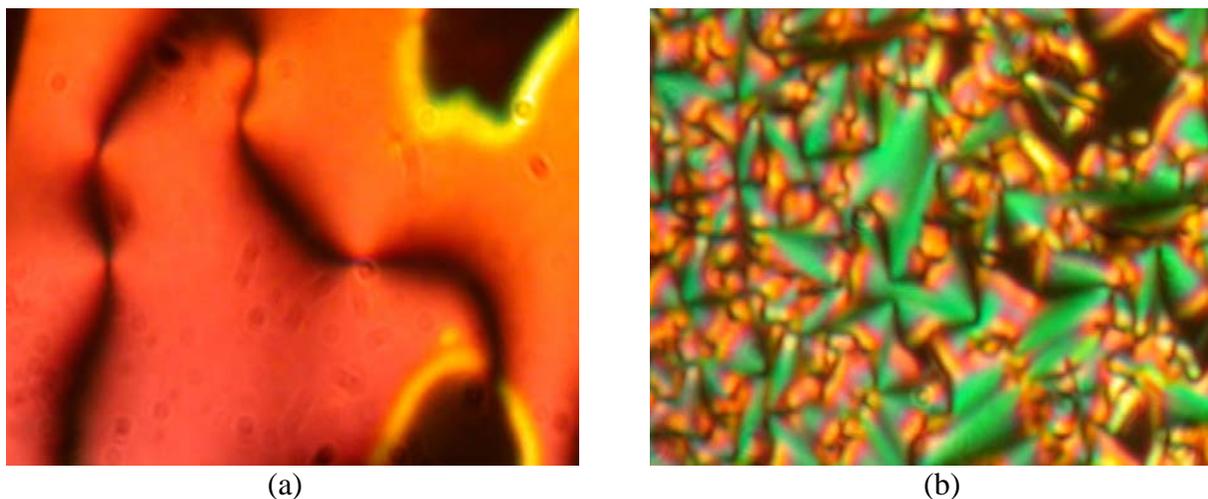


Figure 3: (a) Optical texture of **5** at 151.2 °C in the nematic phase and (b) smectic A phase at 140.1 °C.

X-ray diffraction (non-aligned sample, Guinier method) confirms the phase assignment. The diffraction pattern of the SmA phase is characterized by a diffuse scattering in the wide angle region and only one sharp reflection in the small angle region, corresponding to $d = 2.6$ nm (140 °C). As confirmed by small angle X-ray diffraction experiments no additional reflection can be seen at smaller angles. The layer distance is a bit less than one half of the molecular length in a conformation as shown in Figure 4.

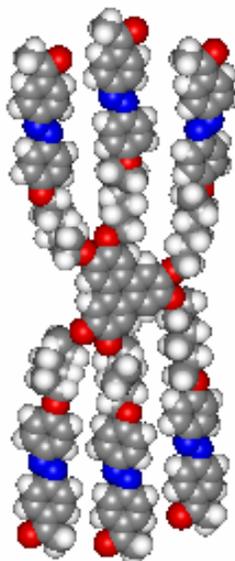


Figure 4: Molecular model of compound 5 whose triphenylene central core is linked to six azobenzene moieties as peripheral units

Therefore it can be deduced, that the rod-like azobenzene units determine the mesophase structure, i.e., the smectic layers should be formed by these rod-like units and the triphenylene units act only as linking unit interconnecting the rods. It is assumed that the aromatic rod-like cores are organized in common layers together with the disc-like triphenylene cores as shown in Figure 5. The spacer units are located between these aromatic sublayers and form sublayers with a reduced concentration of the azobenzene segments. In such an arrangement, the layer spacing amounts to a value between $1/3$ and $1/2$ of the total molecular length L , depending on the degree of intercalation of the azobenzene moieties.

Considering the fact that the hexamethylene spacers and the azobenzene units have a similar cross sectional area and that the layer distance is close to $1/2 L$, there should be only a weak partial intercalation of the acetylazobenzene units. As this intercalation gives rise to a lateral expansion of the azobenzene sublayers the molecules are shifted by $1/2 L$ with respect to each other, that the intercalated parts of the azobenzene rods can be located between the triphenylene units of adjacent molecules, where additional space is available. Hence, common layers composed mainly of azobenzene units and triphenylene units are formed, which are separated by sublayers composed mainly of the alkylene spacers and parts of the azobenzene units. Because the azobenzene segments are incorporated in both sublayers, the interlayer interfaces are very diffuse and increasing the temperature leads to an easy transition from the SmA phase to a nematic phase where the segregation is lost.

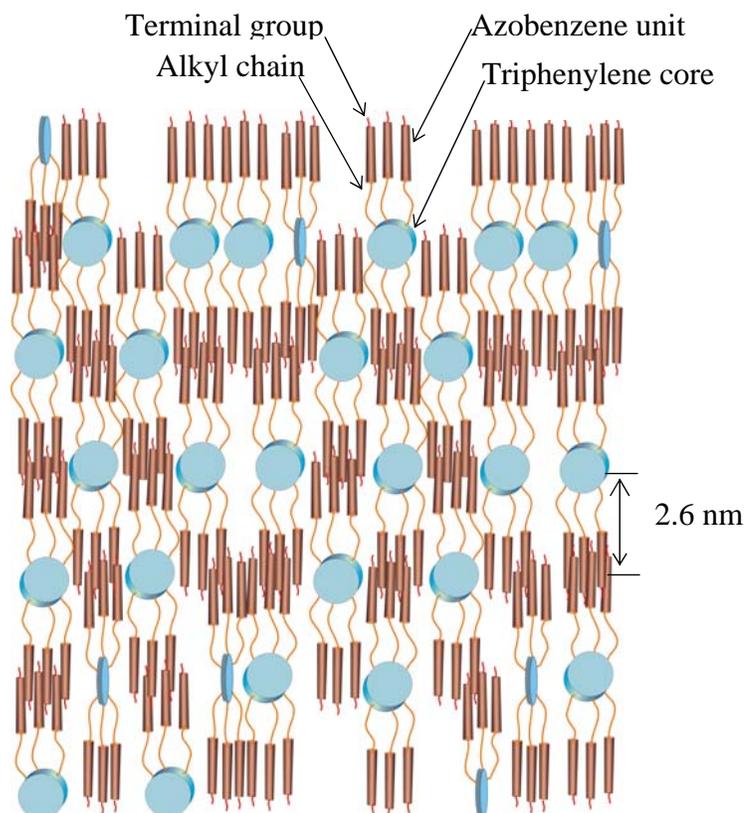


Figure 5: Model of the intercalated layer structure of the smectic A phase of compound 5.

Shimizu et al. [9] have reported a related azobenzene triphenylene couple. The main difference to compound **5** concerning the chemical structure is a shorter spacer unit (C_3) and the longer (C_{10}) end-chains at the periphery of the azobenzene units. With this material it was found that depending on the cooling rate either a smectic or a hexagonal columnar phase was formed. In this compound the coupling of the rod-like units to the central core is stronger (shorter spacers, semirigid ester groups) which gives rise to an increased importance of the disc-like shape of the triphenylene units for the self organization. In addition, the importance of the segregation is larger (long terminal alkyl chains) compared to compound **5**, disfavoring the formation of a nematic phase. Both effects seem to be responsible for the observed phase behavior.

In compound **5** the triphenylene core and peripheral azobenzenes are linked by more flexible spacers (longer, no semirigid COO group), which allows a more easy conformational change. Thus, the rod-shaped parts could easily align parallel and form a smectic layer structure. The molecular recognition among the disc-like central core is less important for the organization of the molecule as a whole. Furthermore, the short terminal acetyl groups do not contribute to segregation. Because in compound **5** layer formation is only based on the partial segregation of the rather short hexamethylene spacers from the aromatic parts, a nematic phase is the alternative organization at higher temperature.

3.3 Absorption spectra

The maximum absorption of compound **5** was found at 392 nm assigned to the π - π^* of the azobenzene trans-configuration and a weak shoulder at about 460 nm, which is related to the n - π^* of the azobenzene trans-configuration. In addition, two other absorption bands, centered at 334 and 380 nm are due to the π - π^* transitions of the triphenylene core. Some calamitic and dendrimers compounds containing azobenzene chromophores were reported and most of the mesogens exhibited the π - π^* transitions of the azobenzene trans-configuration at wave lengths ranging from 359 to 450 nm [11-13]. The UV-Vis spectra of the azobenzene groups shows that the maximum of absorbance is at 392 nm with a significant tailing beyond 460 nm, which would allow the use of laser in the visible range for photoinduced reorientation of the azobenzene moieties.

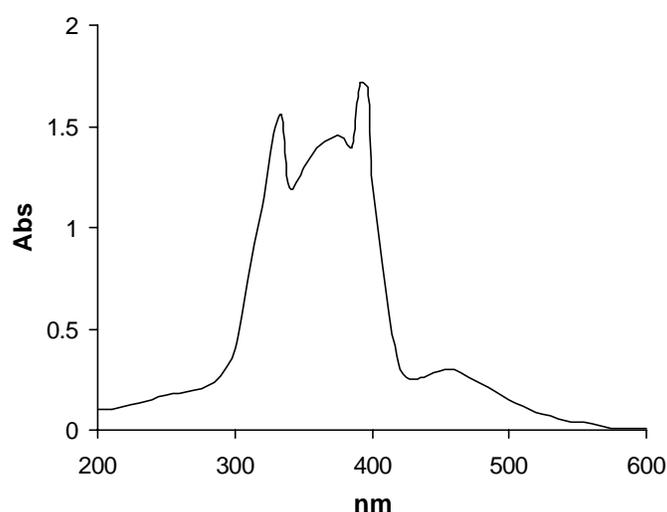


Figure 6: UV-vis absorption spectrum of **5**

IV. Conclusion

A hybrite molecule was prepared whose molecular architecture is composed of a disc-like triphenylene unit as central core and six rod-like azobenzenes as the peripheral units linked through alkyl spacers. A smectic A and a nematic phase were formed due to the assembly of the rod-shaped azobenzene parts. It seems that the triphenylene unit acts only as linking unit, interconnecting the rod-like units (oligomer effect) rather than as a disc-like unit, which would lead to a columnar organization. The absorption wave length of the azobenzene units of this mesogen is shifted into the visible region, compared to other azobenzene derived LC systems. Therefore such materials could be useful for photoinduced reorientation of azobenzenes for holographic grating with visible light.

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V. References

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