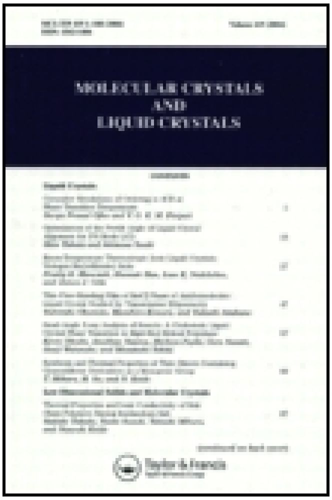

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Self-assembled Columnar Mesophase from a New Disclike Polar Mesogen Based on a 3,5-Dicyano-2,4,6-Tristyrylpyridine Core

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To cite this article: André-Jean Attias , Chantal Cavalli , Bertrand Donnio , Daniel Guillon , Philippe Hapiot & Jacques Malthête (2004) Self-assembled Columnar Mesophase from a New Disclike Polar Mesogen Based on a 3,5-Dicyano-2,4,6-Tristyrylpyridine Core, Molecular Crystals and Liquid Crystals, 415:1, 169-177, DOI: 10.1080/15421400490478803

To link to this article: http://dx.doi.org/10.1080/15421400490478803

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Mol. Cryst. Liq. Cryst., Vol. 415, pp. 169–177, 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490478803

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SELF-ASSEMBLED COLUMNAR MESOPHASE FROM A NEW DISCLIKE POLAR MESOGEN BASED ON A 3,5-DICYANO-2,4,6-TRISTYRYLPYRIDINE CORE

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We report on the design and synthesis of a new disc-like liquid crystal based on a 3,5-dicyano-2,4,6-tristyrylpyridine core. The mesogenic behavior was investigated by differential scanning calorimetry, polarized-light optical microscopy, and X-ray diffraction. The disc-like structure self-assembles into

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a hexagonal columnar mesophase and, due to the permanent dipole exhibited by the isolated molecule, the stacking along the columnar axis is antiparallel. Besides two-dimensional charge transfer and fluorescence, the disk-like molecule exhibits a high electron affinity due to the strong acceptor character of the 3,5-dicyanopyridine core.

Keywords: columnar mesophase; discotic liquid crystals; polar mesogen; 3,5-dicyano-2,4,6-tristyrylpyridine

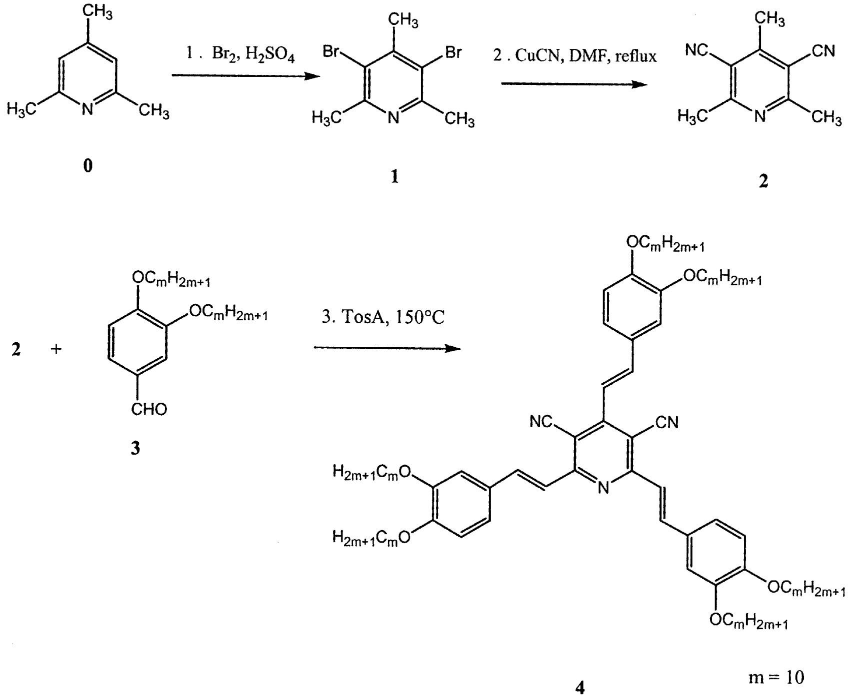
INTRODUCTION

Columnar mesophases of disk-like mesogens with an extended flat, aromatic, central core have attracted increasing interest as potential one-dimensional conducting systems [1]. Typically, the aromatic cores are stacked one upon another to build columns which are arranged in varied two-dimensional lattices. Very recently, it has been reported that derivatives of hexabenzocoronene [2] exhibit extremely high charge carrier mobilities (up to $1\,\mathrm{cm}^2/\mathrm{vs}$) as a consequence of a long-range order in a room-temperature hexagonal columnar mesophase. These high electronic properties associated with long-range columnar order make discotic liquid crystals promising as organic semi-conductors for applications in the domain of molecular electronics and optoelectronics [2–5], more particularly in the area of photoconductivity [3], for photovoltaic [4], and electro-luminescent devices [5].

In this context we were interested in designing and synthesizing a new class of columnar disc-like liquid crystal molecule (i) with high electron affinity to favor electrons injection and (ii) based on a core having a permanent electric dipole perpendicular to the column axis to favor strong dipolar interactions and consequently long-range intra-columnar order. We report here on the synthesis and characterization of a new disk-like molecule, the 3,5-dicyano-2,4,6-tris(3,4-didecyloxystyryl)pyridine (**4**) (Scheme 1). 3,5-Dicyano-2,4,6-trimethyl-pyridine (**2**) has been chosen as starting material, the 3,5-dicyanopyridine structure acting as an acceptor core. Moreover, **2** has a permanent dipole because the two cyanide groups are at the 3 and 5 positions of the pyridine ring. According to the synthetic strategy described, **2** results, when reacting with aromatic aldehydes bearing electron-donor groups (**3**), in a highly π-conjugated molecule, **4**, which possesses also a permanent dipole.

SYNTHESIS

The general aspects of the synthetic routes are shown in Scheme 1. (**4**) was synthesized in 3 steps from collidine (**0**). Bromation of collidine with a



SCHEME 1

slight excess of elemental bromine afforded the 2,4,6-tristyryl-3,5-dibromopyridine (**1**), which was converted into the 3,5-dicyano derivative (**2**) in the presence of copper cyanide. The overall yield for the conversion of **0** to **2** was ca. 65%. Toluenesulfonic acid-catalyzed Knoevenagel type condensation of **2** with 3 equiv. of **3** afforded the resulting 3′,4′ -didecyloxy-2,4,6-tristyryl-3,5-dicyanopyridine, which was isolated in 42% yield as a yellow-orange powder.

The structure and purity of all the compounds were confirmed by using ^{1}H NMR, ^{13}C NMR, and elemental analyses. The ^{1}H and ^{13}C NMR spectra of **1, 2,** and **4** were consistent with the proposed structure. As example, concerning the ^{1}H NMR spectrum of **4**, (i) there is a complete disappearance of the methyl protons present in **2**, (ii) two doublets appear at 8.15 and 7.87 ppm with a three bond coupling constant $^3J_{H,H} = 15.55$ and 16.12 Hz respectively, indicative of a *trans* carbon-carbon double bond. These resonances are assigned to the two kinds of trans vinylene units at the 2 (6) and 4 positions of the pyridine ring respectively. In addition, the ratio of the integrated aromatic resonances versus the aliphatic ones is equal to 15/44 as expected.

Moreover, the elemental analysis data of **1, 2**, and **4** show good agreement with the proposed structures.

RESULTS AND DISCUSSION

Mesomorphic Behavior

The thermal behavior of compound **4** was examined by DSC (10°C/min) and phase assignments were based on powder X-ray diffraction (XRD) and polarized-light optical microscopy (POM). The transition temperatures, phase sequence and some thermodynamic data are listed in Table 1. Placed between glass and coverslide, **4** displays a beautiful fan-shaped texture, characteristic of a hexagonal columnar mesophase. Temperature- dependent X-ray diffraction (XRD) measurements were carried out every 10°C starting in the solid state at 30 up to 160°C in the isotropic liquid. A good agreement was found between the transition temperatures derived from both POM and DSC techniques with those determined by XRD. Figure 1 shows a representative X-ray diffractogram of the mesophase recorded at 100°C. The pattern consists of (i) a broad diffuse scattering halo (**II**) in the wide angle region, corresponding to the liquid-like disorder of the aliphatic chains, at *ca* 4.5 Å, (ii) another broad diffuse band (**III**) at *ca* 3.5 Å, which is a characteristic distance usually found between flat aromatic cores (and corresponding to the stacking period in a column [6]), (iii) a third less intense broad band at ca 7.1 Å which may be an indication of some "dimerisation", resulting from an antiparallel stacking of the molecules [7] (the double of **III**), and finally (iv) a single sharp and intense reflection (27.1 Å) in the small angle region. Identical X-ray patterns were obtained at all other temperatures of the mesomorphic range, with no change of position of the fundamental reflection. The disc-like structure of the molecules must lead preferably to the formation of columns, and thus of columnar phases, by their long range order stacking rather than to layered structures or nematic arrangements. Such stacking is also facilitated by the antiparallel arrangement of the molecular dipoles (estimated

TABLE 1 Thermodynamic Data and Phase Sequence of **4**

Transition temperatures (°C) – [Enthalpy Changes ΔH (kJ.mol^{-1})]^{a}	
1st Heating	1st Cooling
$\mathbf{M_1}$ 60[36] X 70.5[–4] $\mathbf{M_2}$ 74[19] $\mathbf{Col_H}$ 133.5[2.2]**I**	**I** 133.5 [–1.5]$\mathbf{Col_H}$61 [–6.3]$\mathbf{M_3}$

^{a}Determined by DSC. M_1, M_2 and M_3: Intermediate phases; Col_H = hexagonal columnar mesophase; X: exothermic peak; I = isotropic phase.

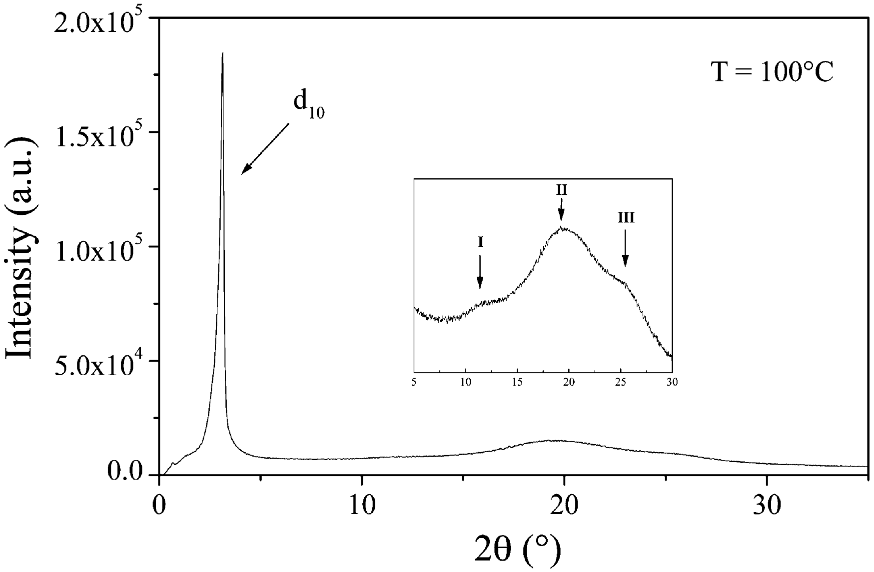


FIGURE 1 X-ray diffraction patterns of **4** in the mesophase at 100°C.

at 3.9 D by means of a calculation on the AM1-optimized geometry) as sketched in Figure 2a and confirmed by the presence of the diffuse halos **I** and **III** [7]. These facts suggest that the mesophase is columnar hexagonal (Col_H). The structural parameters of the Col_H mesophase (Fig. 2b), i.e. The columnar repeat distance h and the first-order spacing d_{10}, are equal to 3.5 (estimated from the center position of the halo **III**) and 27.1 Å respectively. The molecular diameter of the hard dis-like core ϕ_{Ar} (without the aliphatic chains) has been estimated at 18.7 Å by means of a calculation on the AM1-optimized geometry.

Electrochemical Study

In view of the potential application of such molecules in optoelectronics, it is important to consider the relative ionization potential (IP) and electron affinity (EA), parameters which indicate the facility to inject holes and electrons respectively in the material. These values can be estimated from the first oxidation and first reduction potentials in solution which are associated with the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO energy levels respectively) [8]. For this purpose, the electrochemical behaviors of **4** was investigated by cyclic voltammetry (CV), to measure the redox potentials, and thus to estimate

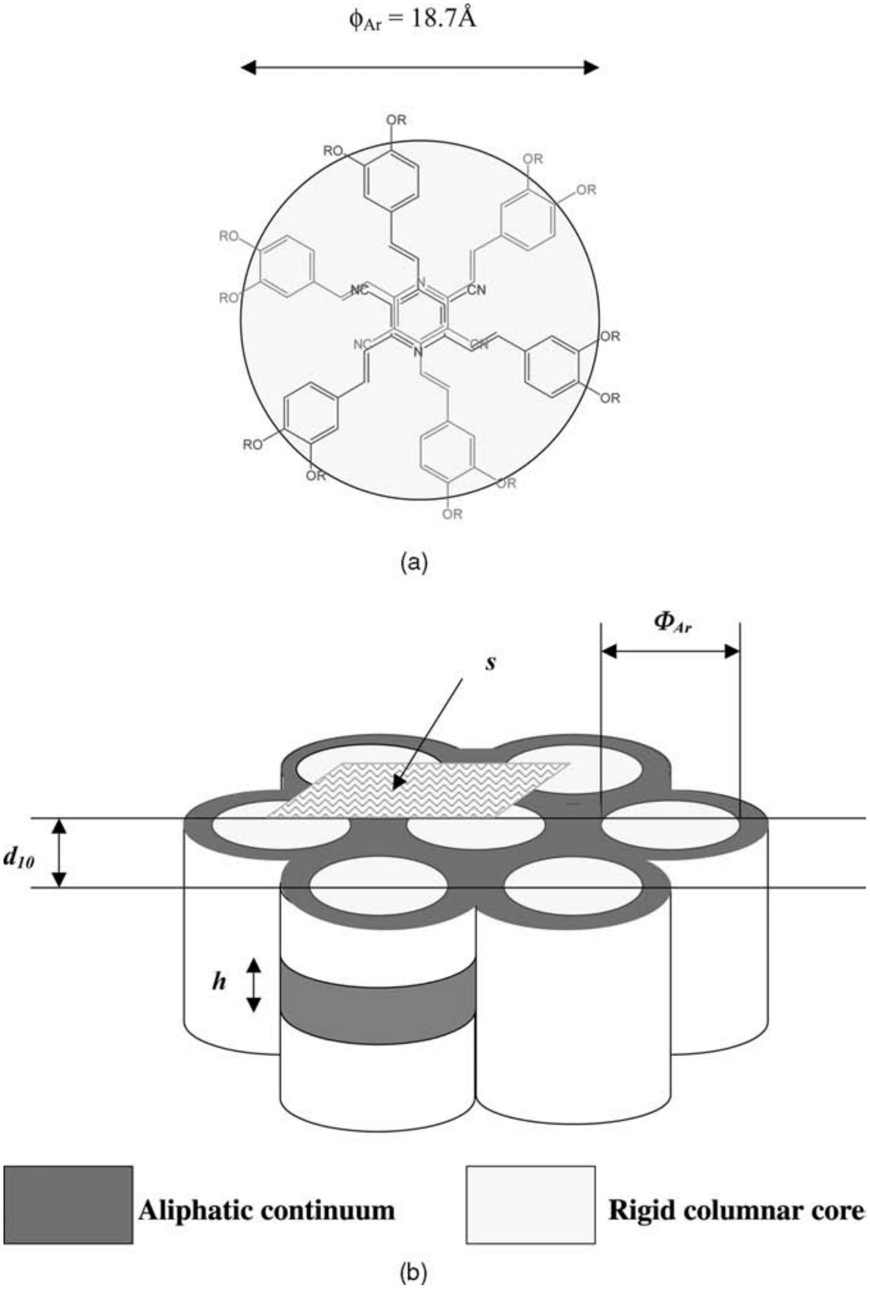


FIGURE 2 Schematic representation of (a) the disc-shaped structure formed with the dimer of **4**. ϕ_{Ar} is the diameter of the dimer's aromatic part. (b) the hexagonal columnar lattice. Structural parameters h, s, and d_{10} are discussed in the text.

IP and EA. In reduction, the studied compound presents a mono-electronic transfer. The reduction process was reversible at scan rates higher than $10\mathrm{V}s^{-1}$, showing a relatively good chemical stability of the radical-anion (life-time in the order of 1 s). From this reversible voltammogram, the formal potential E^0_{red} was immediately derived as the half-sum between the forward and the reverse scan peak potentials [9] ($E^0_{red} = 1.28$ V vs SCE). In oxidation, only one irreversible process has been observed, indicating that the life-time of the produced radical cation is shorter than 1ms in our experimental conditions. It is noticeable that the radical-cation has a much lower chemical stability than the corresponding radical-anion. In our determination, E°_{ox} value was approximated by the corresponding peak potential ($E_{ox} = -1.19$ V vs SCE). To a first approximation, the reduction potential can be related to the electron affinity and thus to the LUMO energy level [8], according to the following equation: $IP = (E_{ox} + 4.75)$. The estimated ionization potential ranges in the 6.0 eV.

Optical Properties in Solution

The photophysical properties of **4** in dichloromethane (i.e., absorption and emission maxima, Stokes shift, and quantum yield of fluorescence) are reported in Table 2. A single structureless and broad absorption peak is observed at 400 nm (3.10 eV). It is attributed to a $\pi - \pi^*$ transition due to the large molar coefficient absorption ($\varepsilon > 80000$ L mol^{-1} cm^{-1}) indicative of a highly π-conjugated system. The photoluminescence spectrum of **4** results in a broad peak at 550 nm (2.26 eV) with a shoulder around 620 nm (2.00 eV). Additionally, it should be noted that the Stokes shift is of the order of 150 nm. Since the Stokes shift is usually dependent on the structural relaxation of the excited molecule, such a large value (0.84 eV or 1580 cm^{-1}) results from a significant conformational change that occurs

TABLE 2 Optical and Electrochemical Data of **4** in Dichloromethane and in a Toluene/Acetonitrile Mixture (50/50 v/v) Respectively

Optical properties				Electrochemical properties	
Absorption	Emission			Potential (V)[a]	
λ_{max} (nm) E_{max}(eV)	λ_{max} (nm) E_{max}(eV)	Stokes shift (nm)	Φ_f (%)	Oxidation E_{ox}[b]	Reduction E^0_{red}
400 *3.1*	550 *2.26*	150	40	−1.19	1.28

[a] Versus SCE.
[b] Peak potential.

upon excitation of **4**. The excited state could be described as being quinoid-like, thus resulting in a planar conformation, and leading to an intra-molecular two-dimensional charge-transfer (ICT) state emission.

CONCLUSION

In conclusion, the design, synthesis, and mesophase characterization of a new class of disc-like mesogen containing a permanent dipole have been reported. Based on 3,5-dicyano-2,4,6-tristyrylpyridine core, the highly π-conjugated derivatives align in an antiparallel arrangement and form disc-shape "dimeric" units which self assemble over a broad temperature range (80 to 135°C) into columns themselves packed together in a two-dimensional hexagonal lattice. In addition, electrochemical as well photophysical properties of the individual disc-like molecule have been investigated, in solution. Besides two-dimensional charge transfer and photoluminescence, the electron accepting character, evidenced by a high electron affinity, combined with a columnar self-organization seems promising for electron transport and therefore opens the way to applications in optoelectronics.

Because of the versatility of the synthetic pathway, the influence of the strength of the dipolar permanent moment (by varying the nature of the donor group) on mesogenic and electronic properties are currently investigated.

EXPERIMENTAL PART

Full details of the synthesis and characterizations of all the compounds have been reported elsewhere [10].

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