Liquid-Crystalline Fulleropyrrolidines

Preliminary Communication

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A fulleropyrrolidine showing a smectic A phase was synthesized by 1,3-dipolar cycloaddition of a liquid-crystalline aldehyde derivative and sarcosine to C_{60}.

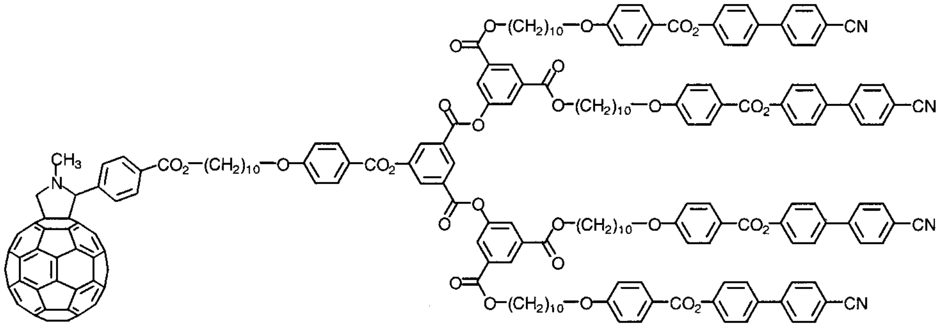
Introduction. – Incorporation of [60]fullerene (C_{60}) into liquid-crystalline assemblies is expected to open the doors toward the development of anisotropic materials with novel properties [1]. Our concept, *i.e.*, addition of mesomorphic malonates to C_{60} (*Bingel* reaction [2]), led to a great variety of fullerene-containing thermotropic liquid crystals [3–6]. The latter compounds displayed smectic A phases and showed good thermal stability and good solubility in common organic solvents. The liquid-crystalline behavior arose from the presence of either cholesterol or cyanobiphenyl derivatives (located on the malonate) acting as mesomorphic promoters. Another contribution reported liquid-crystalline properties of C_{60} derivatives [7]; cyanobiphenyl moieties were introduced onto the C_{60} either by the *Bingel* reaction or by esterification of a C_{60} derivative bearing carboxylic acid functions. The materials showed either nematic or smectic A phases. A concept based on noncovalent interactions was reported by *Nierengarten* and co-workers: the formation of a complex from C_{60} and a mesomorphic cyclotriveratrylene (CTV) derivative led to a liquid crystal that displayed a cubic phase [8].

The field of fullerene-containing liquid crystals is still in its infancy. To further explore the capability of C_{60} to form liquid crystals and to improve our understanding of the *structure-property* relationship for such materials, the design and study of new structures is required. The ultimate goal is the development of liquid-crystalline fullerenes with tailor-made properties.

All of the covalent-like liquid-crystalline fullerenes reported so far [3–7] use the methanofullerene connecting group to assemble mesomorphic malonates to C_{60}. A possible extension for the design of new mesomorphic C_{60} derivatives is the use of other connecting groups that could serve for the functionalization of C_{60} with liquid-crystalline addends.

Fulleropyrrolidines constitute an important family of C_{60} derivatives. They are prepared by 1,3-dipolar cycloaddition of azomethine ylides obtained from α-amino acids and aldehydes [9]. Owing to the accessability of the reactants, numerous fulleropyrrolidines have been prepared and have led to enthusiastic studies [10]. Recently, a hexapyrrolidine derivative of C_{60} was used to elaborate a single-layer organic LED [11]. Liquid-crystalline fulleropyrrolidines appear to be interesting materials.

We report, herein, the synthesis, characterization, and properties of the fulleropyrrolidine derivative **1**, the preparation of which is based on the use of the liquid-crystalline aldehyde derivative **2**. A dendritic addend of second generation was selected as the liquid-crystalline promoter in order to thwart the influence of C_{60}, the size and shape of which lower the tendency of the mono-adducts to form liquid-crystalline phases [3][4][6]. The first modification of C_{60} by a dendritic addend was reported by *Fréchet* and co-workers [12], and was found to be an elegant way to prepare fullerene derivatives with polymer-like properties.



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Results and Discussion. – The synthesis of **1** is outlined in the *Scheme*. Esterification of **3** with benzoic acid derivative **4** gave alcohol intermediate **5**. The latter was esterified with 4-formylbenzoic acid to furnish aldehyde derivative **2**. Addition of **2** and sarcosine to C_{60} gave the fulleropyrrolidine **1**1)). The use of both 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) and 4-pyrrolidinopyridine (4-ppy) as activating agents during the esterification reactions gave better yields. The synthesis of **3**, which was prepared according to a convergent methodology, will be reported in the subsequent full paper. Compound **4** was obtained analogously to the synthesis of 4-[(6-hydroxyhexyl)oxy]benzoic acid [13].

The liquid-crystalline properties of **1**, **2**, and **5** were investigated by polarized optical microscopy (POM)2)) and differential scanning calorimetry (DSC)2)). Compounds **1**, **2**, and **5** gave rise to liquid-crystalline behavior (*Table*). They all showed smectic A

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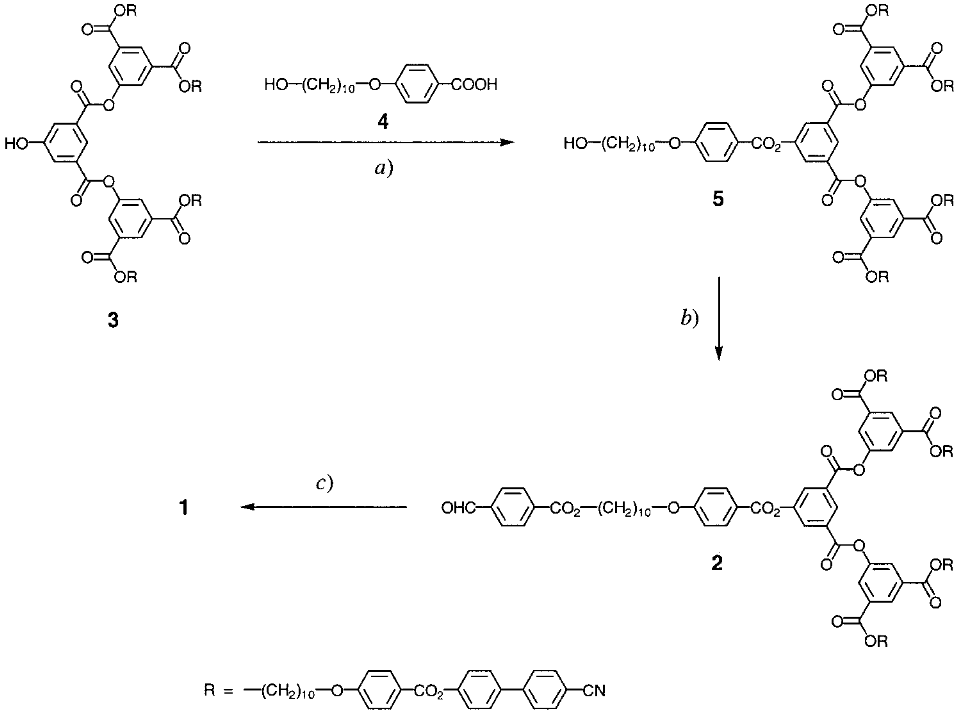
1) Selected data of **1**: VIS (λ_{max} in nm (ε in $dm^3 mol^{-1} cm^{-1}$)): 430 (3740), 701 (350). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.93 (*t*, 1 arom. H); 8.64 (*t*, 2 arom. H); 8.36 (*d*, 2 arom. H); 8.14 (*d*, 12 arom. H); 8.11 (*d*, 4 arom. H); 7.96–7.82 (br., 2 arom. H); 7.74–7.61 (series of *d*, 24 arom. H); 7.32 (*d*, 8 arom. H); 6.97 (*d*, 10 arom. H); 5.00 (*s*, CHN); 4.99 (*d*, 1 H, CH_2N); 4.36 (*t*, 4 CO_2CH_2); 4.30 (*t*, CO_2CH_2); 4.28 (*d*, 1 H, CH_2N); 4.03 (*t*, 5 CH_2O); 2.80 (*s*, MeN); 1.85–1.76 (*m*, 5 $CO_2CH_2CH_2$, 5 CH_2CH_2O); 1.58–1.26 (*m*, 60 aliph. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 166.40; 164.86; 164.79; 164.42; 164.08; 163.66; 163.05; 151.65; 151.56; 150.51; 147.30; 146.26; 146.19; 146.11; 145.92; 145.79; 145.68; 145.52; 145.33; 145.24; 145.19; 144.84; 144.68; 144.49; 144.38; 144.30; 143.11; 142.67; 142.55; 142.19; 142.12; 142.04; 141.92; 141.84; 141.77; 141.66; 141.51; 140.18; 139.85; 139.46; 136.67; 135.93; 135.61; 132.63; 132.60; 132.33; 131.10; 129.06; 128.44; 128.32; 127.67; 127.00; 122.54; 121.19; 120.28; 118.86; 114.54; 114.34; 110.98; 83.11; 69.04; 68.32; 65.86; 65.24; 39.98; 29.45; 29.41; 29.31; 29.21; 29.07; 28.63; 25.96; 25.93. Anal. calc. for $C_{231}H_{171}N_5O_{29}$ (3480.91): C 79.71, H 4.95, N 2.01; found: C 79.46, H 5.22, N 2.02.

2) Optical studies were made with a *Zeiss-Axioscop* polarizing microscope equipped with a *Linkam THMS-600* variable-temperature stage, under N_2. Transition temperatures and enthalpies were determined with a *Mettler 822* differential scanning calorimeter at a rate of 10° min^{-1} under He.

Scheme



a) *N,N'*-Dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS), 4-pyrrolidinopyridine (4-ppy), CH_2Cl_2, room temperature, 24 h; 83%. *b*) 4-Formylbenzoic acid, DCC, DPTS, 4-ppy, room temperature, 15 h; 91%. *c*) C_{60}, sarcosine, toluene, reflux, 20 h; 53%.

Table. *Phase-Transition Temperatures*[a]) *and Enthalpy Changes of Compounds* **1**, **2**, *and* **5**

Compound	Tg/°C	$S_A \rightarrow I$/°C	ΔH/kJ mol^{-1}
5	38	185	14
2	35	185	13
1	44	168	13

[a]) Tg = Glass transition temperature, S_A = smectic A phase, I = isotropic liquid. Temperatures are given as the onset of the peak obtained during the second heating; the Tg were determined during the first cooling.

phases, which were identified by POM from the formation of typical focal-conic textures and homeotropic areas. In the case of **1**, the focal conics formed only when the sample was cooled very slowly (0.2° min^{-1}) from the isotropic fluid. No melting points were determined for **1**, **2**, and **5** during the first heating run. Glass transition temperatures were detected for all compounds from the first cooling. No decomposition was observed for the investigated materials either by DSC or POM.

Compound **1** shows a lower isotropization temperature than **2** and **5**. This result reflects the influence of the C_{60} sphere when incorporated into liquid-crystalline structures: its bulkiness renders the intermolecular interactions more difficult (in comparison with the corresponding fullerene-free materials), the consequence of which is a decrease in the stability of the liquid-crystalline phase. This behavior was already observed for other fullerene-containing liquid-crystals [3][6].

The molecular organization of **1** within the smectic A phase can be explained as follows (*Fig.*): the cyanobiphenyl moieties, the flexible chains, and the C_{60} unit form cylinder-like structures, which arrange to form the lamellar mesophase. The formation of a bilayer is also possible.

Conclusion. – The mesomorphic properties observed for **1** indicates that fulleropyrrolidines are valuable molecules for the elaboration of liquid crystals. Furthermore, fulleropyrrolidines lead to stable reduced species [14] (this is not the case for the *Bingel* adducts, which undergo the *retro-Bingel* reaction upon chemical [15] or electrochemical [16] reduction). This electrochemical stability could be an elegant means for the development of fullerene-based redox-active liquid-crystalline molecular switches. Current investigations are devoted to the design and study of further liquid-crystalline fulleropyrrolidines and to their electrochemical behavior.

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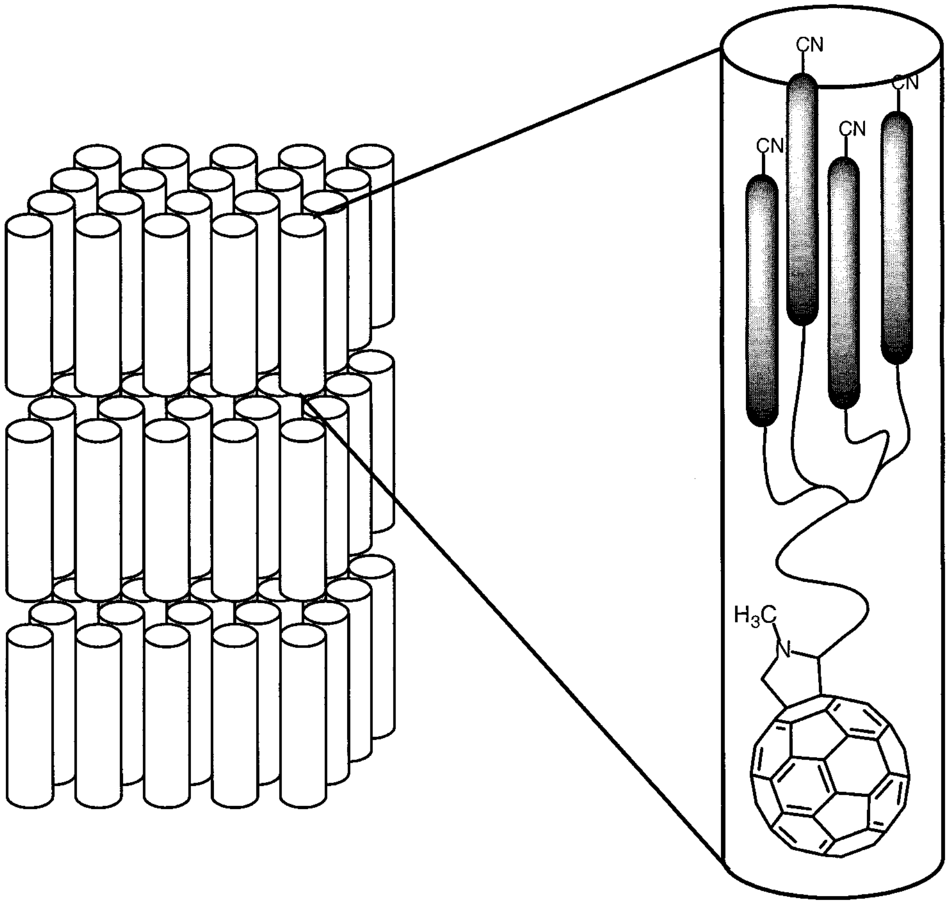

Figure. *Proposed model for the organization of* **1** *within the smectic A phase*

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