First Fullerene[60]-Containing Thermotropic Liquid Crystal

Preliminary Communication

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The synthesis and liquid-crystalline and thermal properties of a fullerene[60] functionalized by a framework containing two cholesterol derivatives through a methanofullerene structure are reported. The targeted fullerene derivative showed high thermal stability.

Introduction. – Owing to its aesthetic structure [1] and remarkable properties, buckminsterfullerene (C_{60}) has generated enthusiastic studies at the frontiers of chemistry (rationale of synthetic strategies for the development of new derivatives [2]), physics (investigation of electrochemical [3], photophysical [4], and magnetic properties [5]), and biology (inhibition of HIV protease (HIVP) [6] and DNA cleavage [7]).

The search for fullerene-based new materials has also attracted much attention [8], and important developments are expected in forthcoming years [2a] [9]. Of particular importance, regarding possible applications, would be the development of fullerene derivatives exhibiting mesomorphic behavior (noncrystalline materials were obtained by combining a fullerene derivative with classical mesogenic groups; however, no liquid-crystalline properties were observed [10]). Such materials could be used in liquid-crystal technology for the elaboration of novel electro-optical devices. Furthermore, fullerene-containing liquid crystals would provide much fundamental information for a better understanding of the factors which govern the formation of supramolecular structures obtained from the organization of fullerene-containing molecular units. Organized molecular films were successfully prepared by either the Langmuir-Blodgett technique
[11] or the self-assembly method [12]; however, further evidence concerning the structure (of the molecular unit)-supramolecular organization relationship are required for obtaining ordered assemblies with tailor-mode properties.

In this communication, we describe the design, synthesis, and mesomorphic properties of C_{60} derivative 1, which represents, to our knowledge, the first fullerene-containing thermotropic liquid crystal. The synthesis and liquid-crystalline behavior of cholesterol intermediates, from which 1 was prepared, are also reported.

Results and Discussion. – The following structural requirements were applied for the successful design of a mesomorphic fullerene[60] derivative: i) to generate strong intermolecular interactions between the mesogenic units, a twin cholesterol framework was selected for the formation of a C_{60} derivative; ii) to lower the transition temperatures, a flexible chain was used as a spacer between the cholesterol derivative and the C_{60} moiety; and iii) owing to the well-established synthetic procedure, the formation of a methanofullerene [2] [13] was chosen to connect the cholesterol fragment to the C_{60}.

The preparation of 1 is illustrated in the Scheme. Treatment of cholesteryl 4-hydroxybenzoate (2) [14] with 10-bromodecan-1-ol led to cholesterol intermediate 3. Condensation of this latter with malonyl chloride gave 4, which was transformed into the bromo derivative 5. Finally, reaction of 5 with C_{60} yielded the targeted compound 1, which was purified by column chromatography (silica gel, toluene) and crystallization (toluene). Its structure and purity were confirmed by 'H- and 'C-NMR spectroscopy and, elemental

Scheme

\[ \text{HO-C} \equiv \text{CO}_2\text{Chol} \]
\[ a \]
\[ \text{HO-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{Chol} \]
\[ b \]
\[ \text{CholO} \equiv \text{CO}_2\text{C-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{C-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{Chol} \]
\[ c \]
\[ \text{CholO} \equiv \text{CO}_2\text{C-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{C-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{Chol} \]
\[ d \]
\[ \text{CholO} \equiv \text{CO}_2\text{C-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{C-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{Chol} \]

\[ \text{HO-} \left( \text{CH}_2 \right)_{10} \text{-O-} \text{CO}_2\text{Chol} \]

\[ 2 \]

\[ 3 \]

\[ 4 \]

\[ 5 \]

\[ 1 \]

\( a \) 10-Bromodecan-1-ol, K_2CO_3, DMF/THF 3:1, 120°C, 20 h; 80%. \( b \) Malonyl chloride, Et_3N, CH_2Cl_2, reflux, 20 h; 75%. \( c \) 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), CBr_4, THF, -40°C, 5 h; 51%. \( d \) C_{60}, NaH, toluene, reflux, 4 d; 40%. 

analysis. Of the four possible isomers which can be formed [2a], $^{13}$C-NMR indicated that the expected [6,6]-closed one was obtained.

The thermal and liquid-crystalline properties of 1 and 3–5 were investigated by a combination of differential scanning calorimetry (DSC), thermogravimetry, and polarized optical microscopy. The results reported below for 3 and 4 are those obtained during the first heating-cooling cycle.

Cholesterol derivative 3 [C (S$_c$, 93) 125 S$_h$ 148 TGB A 151 N* 206 BP 207 I] presented interesting mesomorphism. On heating, two crystal-to-crystal modifications were observed at 105 and 112° before a S$_h$ phase formed. Then, a TGB A $\rightarrow$ N* $\rightarrow$ BP phase sequence preceded the formation of the isotropic fluid. On cooling, a supplementary monotropic S$_{C-}$ phase was observed at 93°. The liquid-crystalline properties obtained for 3 are similar to those reported for corresponding OH-free analogues [15]. Malonate derivative 4 [C 112 S$_h$ 214 N* 224 BP 225 I] gave enantiotropic S$_h$, N*, and BP phases. Because 5 lacked thermal stability, no reproducible DSC thermograms for successive heating-cooling cycles were obtained. Its liquid-crystalline properties were, therefore, not investigated. The above liquid-crystalline phases were identified from their optical textures.

The DSC thermograms (onset temperatures, if not stated otherwise) registered during the first heating-cooling cycle and second heating run for fullerene derivative 1 are displayed in the Figure. During the first heating (Fig., top), three endotherms were

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Figure. Differential scanning calorimetry thermograms of 1 registered during the first heating (top), first cooling (middle), and second heating (bottom) run. Experimental conditions: sample weight: 2.792 mg; rate: 10°/min; temperature range: 30–240°; under N$_2$.

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1) C: crystalline state; S$_{C-}$: chiral smectic C phase; S$_h$: smectic A phase; TGB A: twist grain boundary smectic A phase; N*: chiral nematic (cholesteric) phase; BP: blue phase; I: isotropic liquid. Monotropic transitions are reported in parentheses. The transition temperatures (in °C) were determined by polarized optical microscopy.

2) S$_c$ phase: schlieren texture; S$_h$ phase: focal-conic and homeotropic textures; TGB A phase: filament texture (see Figs. 2–5 in [16]); N* phase: plane texture (see Plate 109 in [17] and Plate 21 in [18]); BP: platelet texture (see Plates 114 and 115 in [17]).
detected at 170° (peak transition temperature; $\Delta H = 7.8$ kJ/mol), 200°, and 209° ($\Delta H$ (overall value for the last two endotherms) = 61.7 kJ/mol). From polarized optical microscopy, the first transition did not give apparent modifications and was associated to a crystal-to-crystal transition. The second and third endotherms corresponded to the melting of two different crystalline forms into an isotropic fluid. On cooling (Fig., middle), two transitions were observed at 190° ($\Delta H = 6.8$ kJ/mol) and 146° ($\Delta H = 4.6$ kJ/mol) and were indicative of mesomorphic behavior. Polarized optical microscopy revealed the formation of a viscous liquid-crystalline phase between the two exotherms. Identification of the mesophase was not straightforward as a typical texture did not develop; this is often the case for viscous materials. Observation of small droplets pointed to the presence of a focal-conic texture and homeotropic zones. Only a homeotropic texture was observed when optical examinations (temperature stage preheated to 218°) of the liquid-crystalline phase were made with stalarized glasses [19]. The mesophase was thus tentatively identified as a monotropic $S_n$ phase. Further characterization will be provided by X-ray diffraction studies. A poorly defined texture, corresponding to the solidification, appeared near 145°. The viscosity of the mesophase might have prevented a neat crystallization of the sample. During the second heating (Fig., bottom), two endotherms were detected: at 153° (peak transition temperature, $\Delta H = 4.4$ kJ/mol), the liquid-crystalline phase appeared, and cleared at 189° ($\Delta H = 7.4$ kJ/mol). Most likely, the different thermal behavior observed during the first and second heating is a consequence of the cooling process which led to a solid of different nature in comparison with the native crystals.

Importantly, the thermal stability of 1 was confirmed by thermogravimetry (10°/min, under N), which indicated that no decomposition occurred up to ca. 280° (1, 5, and 10% weight loss were measured at 294, 313, and 322°, resp.).

The limited mesomorphic behavior of 1, in comparison with that of 4, is due to the C$_{60}$ core which acts as a spacer between the mesogenic molecules. The presence of a strong liquid crystal promoter, the twin cholesterol framework in this case, is, therefore, of prime importance to thwart the unfavorable effects of the C$_{60}$ unit. These results are in agreement with data reported for other mesomorphic systems which also contain a bulky unit, e.g., ferrocene-containing thermotropic liquid crystals [20]. Furthermore, despite the use of flexible alkyl chains, a high-melting compound was obtained. Reduction of the melting point should lead to fullerene derivatives with enhanced liquid-crystal properties.

The first fullerene-containing thermotropic liquid crystal reported herein represents a finding of great importance in view of developing new anisotropic materials. The design and study of further examples will allow to rationalize the structure-mesomorphic properties relationship and to engineer liquid-crystalline behavior for this novel class of thermotropic liquid crystals.

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Experimental Part

General. Instrumentation: Mettler-TG-50 thermobalance connected to a Mettler TA-4000 processor. Cholesteryl 4-hydroxybenzoate was prepared following a literature procedure [14]. Toluene (distilled over NaH), CH₂Cl₂ (distilled over P₂O₅), and THF (distilled over LiAlH₄) were dried prior to use. The synthesis were performed under N₂ (except for the preparation of 3). Fullerene[60] (99.5%) was purchased from Lancaster. Column chromatography (CC): SDS 60 A CC Chromagel (0.060-0.200 mm). DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene.

Cholesteryl-5-en-3β-ol-4'-(10-Hydroxydecyloxy)benzoate (3). A mixture of cholesteryl 4-hydroxybenzoate (14.0 g, 27.6 mmol), 10-bromodeca-1-ol (8.40 g, 35.4 mmol), K₂CO₃ (11.5 g, 83.2 mmol), DMF (210 ml), and THF (70 ml) was stirred at 120°C for 20 h. The mixture was cooled to r.t. and the solid filtered off and washed with THF. Evaporation gave a solid residue which was purified by CC (CH₂Cl₂) and crystallization from EOH: 3 (14.7 g, 80%). [α]D₂⁰ = +31 (c = 0.5, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): 7.98 (d, J = 8.9, 2.4 atom H); 6.90 (d, J = 8.9, 2.4 atom H); 5.42 (d, J = 4.1, CHO (Chol)); 4.77-4.82 (br, m, CHO (Chol)); 4.00 (t, J = 6.5, CH₂O); 3.65 (t, J = 6.5, CH₂OH); 2.45 (d, J = 7.7, 2 H, Chol); 0.69-2.06 (57 H, Chol, CH₃). Anal. calc. for C₃₄H₄₆O₆ (663.05): C 79.71, H 10.64; found: C 79.83, H 10.81.

Bu [10-4-[(cholesteryl-5-en-3β-ol-4'-oxy)carbonyl]phenoxyl]decyl Propanedioate (4). A solution of propane-1,2-diol chloride (0.27 g, 1.92 mmol) in CH₂Cl₂ (5 ml) was added dropwise to a solution of 3 (2.50 g, 3.77 mmol) and Bu₄N (0.48 g, 4.71 mmol) in CH₂Cl₂ (40 ml). The mixture was stirred at reflux for 2 h, cooled to r.t., washed successively with 1 N HCl and sat. aq. NaHCO₃ soln., dried (MgSO₄), and evaporated. Purification of the solid residue by CC (CH₂Cl₂) and crystallization from CH₂Cl₂/hexane gave 4 (1.97 g, 75%). [α]D₂⁰ = +28 (c = 0.3, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): 7.98 (d, J = 8.9, 4 atom H); 6.90 (d, J = 9.0, 4 atom H); 5.41 (d, J = 4.1, 2 H, CHO (Chol)); 4.77–4.87 (br, m, 2 H, CHO (Chol)); 4.14 (t, J = 6.7, 4 H, CO-CH₂); 3.60 (t, J = 6.5, 4 H, CH₂O); 3.37 (t, O₂C-CH₂-CH₂); 2.45 (d, J = 7.5, 4 H, Chol); 0.69–2.05 (114 H, Chol, CH₃). Anal. calc. for C₄₀H₄₇O₁₀ (696.87): C 78.40, H 10.12; found: C 78.37, H 10.03.

Bu [10-4-[(cholesteryl-5-en-3β-ol-4'-oxy)carbonyl]phenoxyl]decyl 2-Bromopropanedioate (5). A solution of CB₄₃ (0.45 g, 1.36 mmol) in THF (20 ml) was added dropwise to a solution of 4 (1.89 g, 1.36 mmol) and DBU (0.21 g, 1.36 mmol) in THF (120 ml) cooled to −40°C. The mixture was stirred at −40°C for 5 h and hydrolyzed with 1N HCl. Et₂O was added to favor phase separation, the aq. phase extracted twice with CH₂Cl₂, the combined org. phase dried (MgSO₄) and evaporated, and the solid residue purified by CC (CH₂Cl₂/hexane 9:1) and crystallization from acetone: 5 (1.02 g, 51%). [α]D₂⁰ = +29 (c = 0.3, CHCl₃). ¹H-NMR (400 MHz, CDCl₃): 7.98 (d, J = 9.0, 4 atom H); 6.89 (d, J = 9.0, 4 atom H); 5.41 (d, J = 3.7, 2 H, CHO (Chol)); 4.77–4.87 (br, m, 2 H, CHO (Chol)); 4.83 (s, CHBr); 4.22 (t, J = 6.7, 4 H, CO-CH₂); 3.99 (s, J = 6.5, 4 H, CHO₂); 2.44 (d, J = 7.7, 4 H, Chol); 0.69–2.03 (114 H, Chol, CH₃). Anal. calc. for C₅₀H₄₀BrO₈ (873.00): C 74.20, H 9.51, Br 5.42; found: C 74.42, H 9.37, Br 5.12.

Bu [10-4-[(cholesteryl-5-en-3β-ol-4'-oxy)carbonyl]phenoxyl]decyl 1,2-Methanediolether[60] 66,61-dicarboxylate (1). To a soln. of fullerene[60] (0.162 g, 0.225 mmol) in toluene (180 ml), 60% NaH oil dispersion (ca. 0.150 g, ca. 3.25 mmol) and S (0.465 g, 3.16 mmol) were added. The mixture was stirred under reflux for 4 days, cooled to r.t., and hydrolyzed with 1N HCl. The org. phase was dried (MgSO₄) and evaporated: dark residue. Purification of this latter by CC (toluene) gave a purple band (unreacted C₆₀) followed by a deep-red band which contained the desired product (a 3rd brown-red fraction containing probably fullerene bis-adducts was also collected; so far, this fraction has not been investigated). The 2nd fraction was concentrated under vacuum to 10 ml and left at −30°C overnight. A solid, which crystalized, was recovered by filtration and dried to yield 1 (0.191 g, 40%). VIS (λmax in nm (ε in 1 mol⁻¹ cm⁻³)): CH₂Cl₂): 426 (2500), 490 (1540), 687 (200). ¹H-NMR (400 MHz, CDCl₃): 7.97 (d, J = 8.9, 4 atom H); 6.87 (d, J = 8.5, 4 atom H); 5.41 (d, J = 3.7, 2 H, CHO (Chol)); 4.78–4.86 (br, m, 2 H, CHO (Chol)); 4.49 (s, J = 6.5, 4 H, CO-CH₂); 3.98 (s, J = 6.5, 4 H, CHO₂); 2.45 (d, J = 7.6, 4 H, Chol); 0.69–2.03 (114 H, Chol, CH₃). ¹C-NMR (100 MHz, CDCl₃): 166.47, 164.38, 163.46, 146.05, 145.93, 145.85, 145.55, 145.36, 145.31, 145.28, 144.54, 143.76, 143.70, 143.65, 142.86, 142.58, 141.63, 140.46, 139.65, 132.21, 123.72, 123.36, 114.64, 74.87, 72.36, 68.82, 68.12, 57.38, 56.82, 55.31, 50.73, 43.01, 40.43, 40.21, 39.00, 37.75, 37.35, 36.88, 36.49, 32.63, 32.57, 36.23, 30.20, 30.08, 29.91, 29.83, 29.29, 28.33, 20.71, 20.64, 20.71, 26.71, 26.69, 24.99, 24.53, 23.52, 23.26, 21.75, 20.10, 19.41, 12.56. Anal. calc. for C₃₄H₄₆O₆ (2112.75): C 85.84, H 6.58; found: C 85.88, H 6.82.
REFERENCES