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A liquid-crystalline hexa-adduct of [60]fullerene

Thierry Chuard,[a] Robert Deschenaux,*[a] Andreas Hirsch*[b] and Hubert Schönberger[b]

[a] *Institut de Chimie, Université de Neuchâtel, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland. E-mail: robert.deschenaux@ich.unine.ch*
[b] *Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany. E-mail: hirsch@organik.uni-erlangen.de*

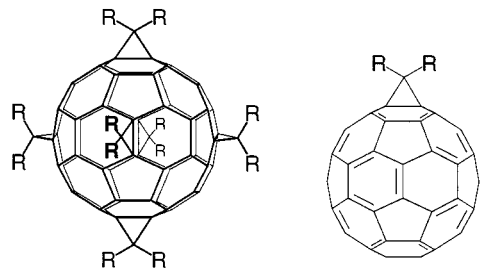
A hexa-adduct of [60]fullerene was synthesized by addition of a mesomorphic twin cyanobiphenyl malonate derivative to C_{60}; whereas the malonate derivative gave a monotropic nematic phase, the fullerene hexa-adduct showed an enantiotropic smectic A phase.

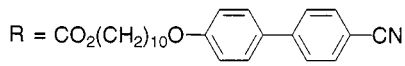
The recent discovery of [60]fullerene-containing thermotropic liquid crystals[1] is of interest considering the current activity devoted to the search of fullerene-based new materials.[2] The unique magnetic, optical and redox properties of [60]fullerene (C_{60}) and its derivatives motivated these studies.[3]

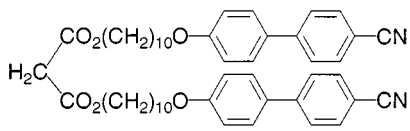
The above liquid-crystalline mono-adduct C_{60} derivatives[1] were prepared by functionalizing the C_{60} core with a mesomorphic malonate framework containing cholesterol as a mesomorphic promoter. These materials showed smectic A phases.

[60]Fullerene offers multiple possibilities for the design of functionalized derivatives.[4] To further explore the capability of C_{60} to give rise to mesomorphic structures, we focussed on hexa-adducts. Observation of liquid-crystalline properties from such an addition pattern would be of interest to rationalize and better understand the *structure–liquid-crystalline properties* relationship for this new family of liquid crystals.

We describe herein the synthesis, characterization and thermal behavior of the fullerene hexa-adduct **1**, which represents a novel example of a mesomorphic C_{60} derivative, and of the fullerene mono-adduct **2**. Compounds **1**† and **2**† were







prepared by addition of the malonate derivative **3**† to C_{60} in 9 and 43% yield, respectively. The thermal properties of **3** are also reported. The liquid-crystalline phases‡ and thermal properties§ of **1**–**3** were investigated by differential scanning calorimetry (DSC, rate: 10 °C min^{-1} under N_2) and polarized optical microscopy (POM).

Malonate derivative **3** gave a monotropic nematic phase (I → N: 87 °C, ΔH = 2.7 kJ mol^{-1}; N → Cr: 57 °C, ΔH = 50 kJ mol^{-1}; peak transitions)¶ which was identified by POM from the observation of typical *schlieren* and homeotropic textures.

Mono-adduct **2** was found to be non-mesomorphic. The only event which was observed was melting of the sample into the isotropic fluid (Cr → I: 114 °C, ΔH = 31 kJ mol^{-1}; peak transition; first heating run).

Hexa-adduct **1** gave interesting results. By DSC, an endotherm was detected at 133 °C (ΔH = 42 kJ mol^{-1}, *i.e.* 3.5 kJ mol^{-1} per cyanobiphenyl group; onset transition) during the first heating run. Reversibility of this transition was observed during the cooling scan. The formation of a liquid-crystalline phase was observed by POM between about 80 and 133 °C. Slow cooling of the sample from the isotropic fluid revealed the formation of focal-conic and homeotropic textures typical of the smectic A phase (Fig. 1). The transition recorded by DSC at 133 °C corresponded to the clearing point. The fact that no melting point was detected by DSC is, most likely, a consequence of the amorphous character of **1** in the solid state (**1** was recovered by evaporation of the solvents after preparative HPLC†); no glass transition was observed by DSC.

The bulky C_{60} unit acts as a spacer separating the molecules from each other: for mono-adduct **2**, the intermolecular interactions are too weak to generate mesomorphism. The influence of C_{60} can be thwarted by using malonate derivatives possessing a higher liquid-crystalline character than that of **3**, as we have already demonstrated.[1]

The liquid-crystalline behavior of **1** emphasizes the role played by C_{60} in the case of hexa-addition: assembling twelve cyanobiphenyl units around a focal point generates the required structural anisotropy and intermolecular interactions for mesomorphism to occur. It is noteworthy that polyaddition can be used for the preparation of fullerene-containing thermotropic liquid crystals from addends with low liquid-crystalline tendencies. Observation of a smectic A phase for **1** indicates that the cyanobiphenyl units are not oriented radially around the C_{60} but

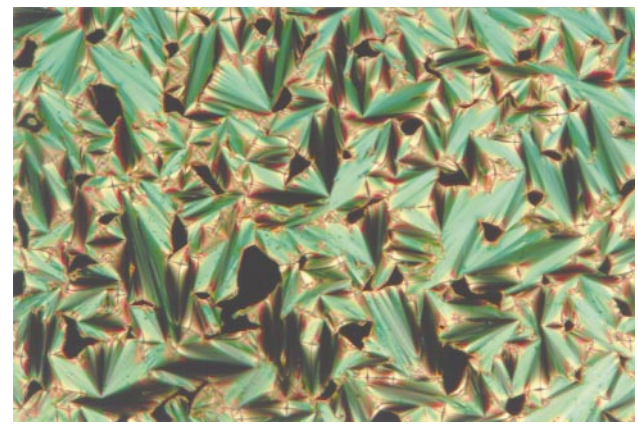


Fig. 1 Thermal optical micrograph of the focal-conic fan texture displayed by **1** in the smectic A phase upon cooling the sample (0.01 °C min^{-1}) from the isotropic liquid to 129 °C.

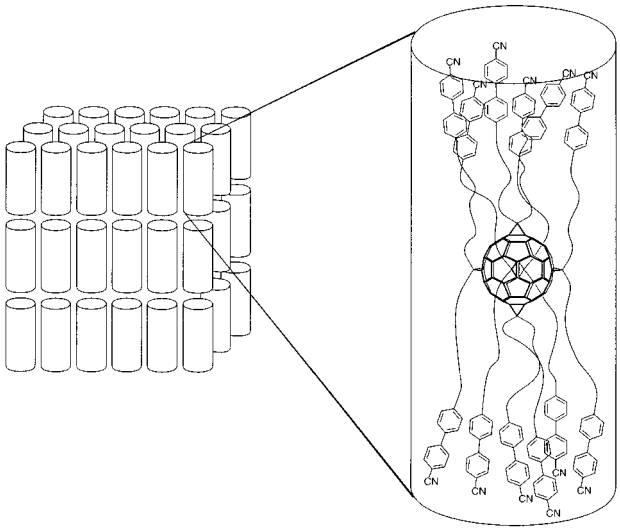


Fig. 2 Proposed model for the organization of **1** within the smectic A phase.

form a cylinder-like structure with the mesogenic fragments oriented upward and downward. Such a structure favors the formation of layers (Fig. 2) as reported for liquid-crystalline dendrimers[5] and siloxysilane derivatives[6] which are analogous to **1**, *i.e.* a central core is functionalized by a large number of mesogenic groups.

The liquid-crystalline properties obtained from the hexa-adduct described above and mono-adducts we recently reported[1] prove that C_{60} can be employed in designing a great variety of mesomorphic materials.

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Notes and references

† Experimental procedure for **3**: prepared from 4′-cyano-4-hydroxybiphenyl, 10-bromodecan-1-ol and malonyl chloride analogously to the synthesis of bis{10-{4-[(cholest-5-en-3β-yloxy)carbonyl]phenoxy}decyl} propanedioate [ref. 1(*a*)]; δ_H(400 MHz, $CDCl_3$) 7.68 (d, 4H, arom.), 7.63 (d, 4H, arom.), 7.52 (d, 4H, arom.), 6.98 (d, 4H, arom.), 4.14 (t, 4H, CO_2CH_2), 4.00 (t, 4H, OCH_2), 3.37 (s, 2H, $O_2CCH_2CO_2$), 1.84–1.77 (m, 4H, aliph.), 1.68–1.61 (m, 4 H, aliph.), 1.51–1.43 (m, 4H, aliph.), 1.37–1.25 (m, 20H, aliph.); δ_C(100 MHz, $CDCl_3$) 166.68, 159.76, 145.22, 132.52, 131.21, 128.28, 127.02, 119.07, 115.04, 110.01, 68.11, 65.61, 41.66, 29.44, 29.39, 29.32, 29.18, 29.15, 28.43, 26.00, 25.74. (Anal. calc. for $C_{49}H_{58}N_2O_6$ (771.01): C, 76.33; H, 7.58; N, 3.63. Found: C, 76.17; H, 7.79; N, 3.61%.

For **1**: Under nitrogen, 9,10-dimethylanthracene (116 mg, 0.562 mmol) was added to a solution of C_{60} (40.5 mg, 0.0562 mmol) in PhMe (60 ml, HPLC grade). The solution was stirred for 2 h. Then **3** (433.6 mg, 0.562 mmol), CBr_4 (186.1 mg, 0.562 mmol) and DBU (171 mg, 1.125 mmol) were added. The mixture was stirred for 3 weeks protected from light and evaporated to dryness. The crude mixture was purified by flash-chromatography on silica gel 60 (0.04–0.063 nm, Merck); elution with hexane (to remove 9,10-dimethylanthracene) and then with PhMe–EtOAc 96 : 4 gave **1** ($R_f \cong 0.25$, PhMe–EtOAc 96 : 4, Riedel-de Haen TLC-Sheets 60 F254) which was detected by mass spectrometry (see below). Further purification of the recovered sample by preparative HPLC (diameter of the column: 2 cm, elution rate: 15 ml min^{-1}) on Nucleosil (5μ) (first: PhMe–EtOAc 95.5 : 4.5, 9.1 min; second: PhMe–EtOAc 97 : 3, 26.3 min) gave pure **1** (26.8 mg, 9%) as a pale yellow solid. δ_H(400 MHz, $CDCl_3$) 7.66 (d, 24 H, arom.), 7.60 (d, 24H, arom.), 7.49 (d, 24H, arom.), 6.95 (d, 24H, arom.), 4.23 (t, 24H, CO_2CH_2), 3.96 (t, 24H, OCH_2), 1.80–1.73 (m, 24H, aliph.), 1.71–1.64 (m, 24H, aliph.), 1.45–1.37 (m, 24H, aliph.), 1.36–1.23 (m, 120H, aliph.); δ_C(100 MHz, $CDCl_3$) 163.84, 159.74, 145.79, 145.13, 141.13, 132.52, 131.24, 128.77, 126.99, 119.00, 115.02, 110.09, 69.13, 68.10, 66.95, 45.45, 29.52, 29.48, 29.41, 29.24, 28.42, 26.06, 25.83; *m/z* (FAB-MS, NBA), 5334 (M^+).

For **2**: To a solution of C_{60} (193 mg, 0.268 mmol) and **3** (201 mg, 0.261 mmol) in dry PhMe (100 ml), were added CBr_4 (93 mg, 0.280 mmol) and then, dropwise, DBU (78 mg, 0.512 mmol). The reaction mixture was stirred at room temperature for 18 h under light protection and concentrated. Purification of the residue by column chromatography (silica gel, 0.070–0.200 mm, SDS; eluent: PhMe) and crystallization (PhMe–EtOAc, overnight at room temperature and then for one day at 8 °C) gave pure **2** (163 mg, 43%). δ_H(400 MHz, $CDCl_3$) 7.68 (d, 4H, arom.), 7.63 (d, 4 H, arom.), 7.51 (d, 4 H, arom.), 6.97 (d, 4 H, arom.), 4.50 (t, 4H, CO_2CH_2), 3.99 (t, 4H, OCH_2), 1.88–1.76 (m, 8H, aliph.), 1.48–1.29 (m, 24H, aliph.) Anal. calc. for $C_{109}H_{56}N_2O_6$ (1489.65): C, 87.89; H, 3.79; N, 1.88. Found: C, 87.89; H, 3.99; N, 1.84%.

‡ Cr = crystal state, I = isotropic liquid, N = nematic phase.

§ For instrumentation, see: R. Deschenaux, F. Turpin and D. Guillon, *Macromolecules*, 1997, **30**, 3759.

¶ Two crystalline forms, which melted at 85 and 96 °C (onset transitions), were observed by POM. Those crystals with the higher melting point, initially present as traces, grew slowly upon annealing the sample at 88 °C.

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