Liquid-Crystalline Mixed [5 : 1]Hexa-adducts of [60]Fullerene

Preliminary Communication

by **Sébastien Gottis**, **Cyril Kopp**, **Emmanuel Allard***[1]), and **Robert Deschenaux***

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case postale 158,
CH-2009 Neuchâtel
(e-mail: robert.deschenaux@unine.ch)

A liquid-crystalline mixed [5 : 1]hexa-adduct of [60]fullerene was synthesized by addition of two different malonate derivatives onto C_{60}. The hexa-adduct derivative **2** was prepared by a stepwise synthetic procedure (fullerene → mono-adduct of C_{60} → hexa-adduct of C_{60}). Cyanobiphenyl and octyloxybiphenyl derivatives were selected as mesogens. The malonate derivatives showed either a monotropic nematic phase or a monotropic smectic A phase, and the hexa-adduct derivative gave rise to an enantiotropic smectic A phase.

Introduction. – [60]fullerene-containing thermotropic liquid crystals represent an interesting family of supramolecular materials, as they combine the optical and electrochemical properties of [60]fullerene (C_{60}) with the self-organizing behavior of liquid crystals [1]. Covalent functionalization of C_{60} [1–6] and formation of supramolecular complexes [7] can lead to mesomorphic materials that display a variety of mesophases, including nematic, chiral nematic, smectic A, smectic B, columnar, and cubic phases. Furthermore, the association of C_{60} with various donor moieties, such as oligophenylenevinylene (OPV) [2f], ferrocene [2d,h,n], or tetrathiafulvalene (TTF) [2i] was achieved with the aim to elaborate liquid-crystalline dyads for applications in solar-cell technology and for the development of supramolecular switches.

The versatile chemistry of C_{60} prompted us to design liquid-crystalline hexa-adducts to explore the behavior of mesogens in a spherical environment. The first hexa-adduct of C_{60} was synthesized previously from malonate **1** (see *Scheme* below), which gave rise to a smectic A phase [2c]. Recently, we described a chiral hexa-adduct of C_{60}, which was prepared from a laterally-branched optically active mesogen. A chiral nematic phase was observed [2m]. Besides our work, other mesomorphic hexa-adducts of C_{60} were reported. *Diederich* and co-workers described a hexa-adduct containing eight Et groups and four mesogenic cyanobiphenyl units. This compound afforded a nematic phase during the first heating run [3]. *Felder-Flesch et al.* reported two hexa-adducts of C_{60} containing either twelve mesogenic cholesterol units, or ten mesogenic cholesterol units and two non-mesogenic groups. Both compounds showed a smectic A phase [6]. In all the above-mentioned cases, the observed liquid-crystalline properties are in

---

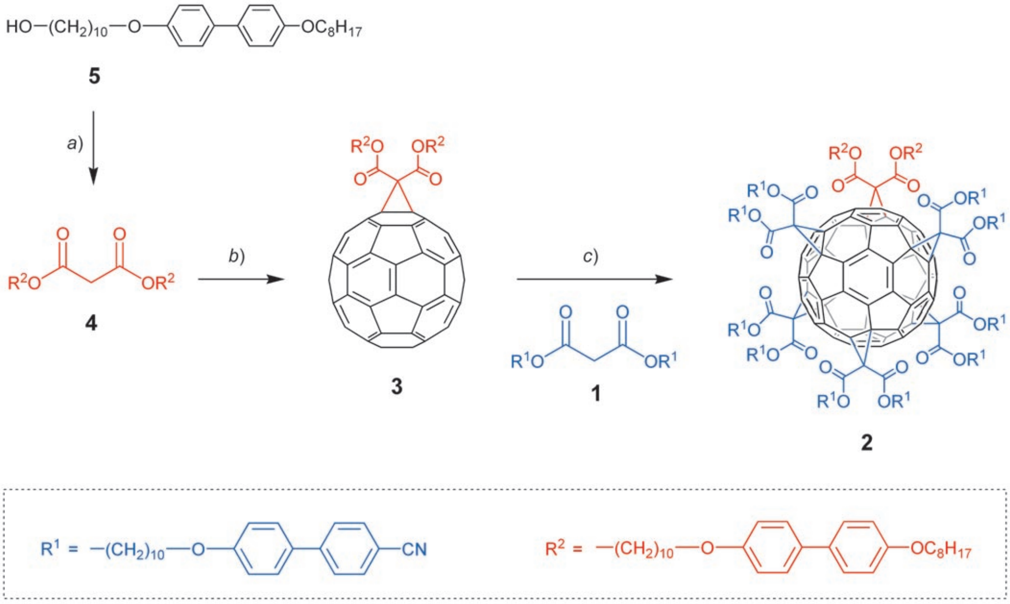
[1]) Current address: Institut Lavoisier UMR-CNRS 8180, Université de Versailles-Saint-Quentin-en-Yvelines, 45 Avenue des Etats-Unis, F-78035 Versailles Cedex (e-mail: allard@chimie.uvsq.fr)

agreement with the nature of the mesogens and the structure of the hexa-adduct materials.

The search for new hexa-adducts of C_{60} prompted us to design mixed fullerene derivatives, *i.e.*, fullerenes that carry two different mesogens. The addition of two mesogens (or more in case of other addition patterns) onto C_{60} could be an elegant means for the design of fullerene-containing liquid crystals with tailor-made properties. For synthetic purposes, we focused our attention first on the [5:1]addition pattern. Indeed, mixed [5:1]hexa-adducts of C_{60} can be prepared by poly-addition of a malonate derivative onto readily available mono-adducts of C_{60}. The addition of the two malonates will follow a stepwise synthetic approach. As a first example, we selected cyanobiphenyl and octyloxybiphenyl derivatives as mesomorphic promoters.

Herein, we report the synthesis, characterization, liquid-crystalline behavior, and supramolecular organization of the mixed [5:1]hexa-adduct **2**, and the synthesis and thermal properties of the mono-adduct **3**, which was used in the preparation of **2**. The synthesis and liquid-crystalline properties of the malonate **1** were already reported [2c].

Scheme



a) Malonyl dichloride, Et_3N, CH_2Cl_2, r.t., 24 h; 79%. *b*) C_{60}, I_2, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, r.t., 19 h; 51%. *c*) 1. 9,10-Dimethylanthracene (DMA), toluene, r.t., 2 h; 2. compound **1**, CBr_4, DBU, r.t., overnight; 7%.

Results and Discussion. – 1. *Synthesis.* The synthesis of **2** and **3** is described in the *Scheme*. Briefly, malonate **4** was prepared in 79% yield by esterification of malonyl dichloride with alcohol **5**. The latter was obtained by analogy to the synthesis of cyanobiphenyl derivatives used for the preparation of **1** [2c]. Subsequent functionalization of C_{60} with **4** *via Bingel* addition [8] led to mono-adduct **3** in 51% yield. Finally, following the methodology developed by *Hirsch et al.* [9], the desired hexa-adduct **2** was obtained in 7% yield by addition of the malonate **1** [2c] to the methanofullerene **3**. All compounds were purified by column chromatography and/or by semi-preparative HPLC, as described in the *Exper. Part.*

2. *Material Properties.* The thermal and liquid-crystalline properties of compounds **2**–**4** were investigated by polarized optical microscopy (POM) in combination with differential scanning calorimetry (DSC). The experimental phase-transition temperatures and enthalpies are reported in the *Table.* The malonate derivative **4** gave rise to a monotropic smectic A phase, as identified by POM from the observation of typical focal-conic and homeotropic textures. The mono-adduct **3** was found to be non-mesomorphic. This behavior is consistent with previous results, and is attributed to steric effects resulting from the presence of the three-dimensional C_{60} unit, which acts as a non-mesomorphic dopant [2c,m].

Table. *Phase-Transition Temperatures* (*T*) *and Associated Enthalpy Changes* (ΔH) *for Compounds* **1**–**4**

Compound	T [°][a])	ΔH [kJ/mol]	Transition[b])	T_g [°][c])
1[d])	87	2.7	(I → N)	–
	57	50	(N → Cr)	
2	151	55.5	SmA → I	80
3	112	43.1	Cr → I	–
4	115	21.6	(I → SmA)	–
	114	12.3	(SmA → Cr)	
	111	37.7	(Cr → Cr′)	

[a]) Transition temperatures are given at the onset of the observed peaks. [b]) I = isotropic liquid, N = nematic phase, SmA = smectic A phase, Cr = crystal; monotropic transitions are given in parentheses. [c]) Glass-transition temperature. [d]) Data taken from [2c].

By DSC, an endotherm was detected for **2** at 151° during the first heating run. This transition was found to be reversible in subsequent heating–cooling cycles. The formation of a liquid-crystalline phase between *ca.* 80 and 151° was observed by POM. Slow cooling of the sample from the isotropic fluid revealed the formation of a smectic A phase. Indeed, typical focal-conic and homeotropic textures were observed (*Fig. 1*). The fact that no melting point was detected by DSC is, most likely, a consequence of the amorphous character of **2** in the solid state.

The liquid-crystalline behavior of **2** emphasizes the role played by C_{60} in the case of hexa-adducts: assembling six malonate derivatives with two different mesogens in a 5:1 ratio around a focal point provides the required structural anisotropy and intermolecular interactions for mesomorphism to occur. In such a system, the mesogenic units form a cylinder-like structure, the self-assembly of which gives rise to lamellar organization (*Fig. 2*). Interestingly, whereas the malonate derivatives gave rise to monotropic mesophases, the hexa-adduct **2** showed enantiotropic mesomorphism.

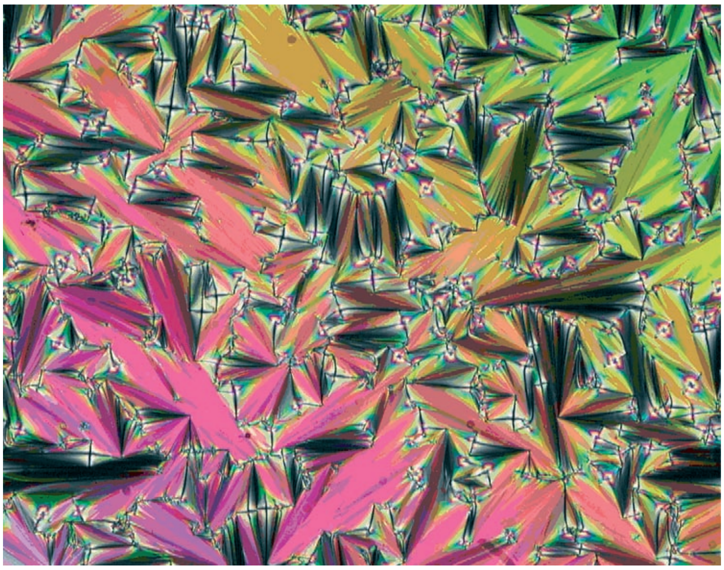


Fig. 1. *Thermal-polarized optical micrograph of the focal-conic fan texture displayed by* **2** *in the smectic A phase upon cooling the sample from the isotropic liquid to a temperature of 151°*

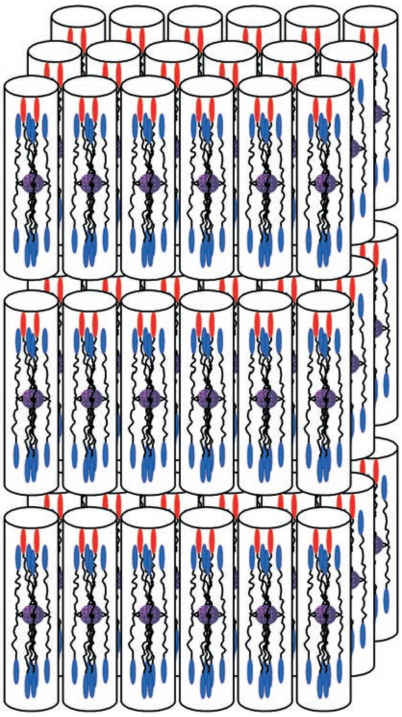


Fig. 2. *Proposed model for the supramolecular organization of* **2** *within the smectic A phase*

Conclusions. – We have demonstrated that liquid-crystalline mixed [5:1]hexa-adducts of C_{60} can be readily synthesized. Interestingly, poly-addition can be used for the preparation of fullerene-containing thermotropic liquid crystals from different mesogens. This result opens the door for the design of further polyfunctional fullerene materials.

R. D. acknowledges the *Swiss National Science Foundation* (Grant No. 200020-111681) and the *State Secretariat for Education and Research* (Grant no 01.0377), *RTN* Project 'Fullerene-Based Advanced Materials for Optoelectronic Utilizations' (FAMOUS) from the *European Union* (HPRN-CT-2002-0071), for financial support.

Experimental Part

General. The synthesis and anal. data of **1** have been described before [2c]. UV/VIS Spectroscopic data are reported as λ_{max} (in nm) and, in parentheses, as ε (in $dm^3 mol^{-1} cm^{-1}$). NMR chemical shifts δ are reported in ppm rel. to the solvent. MS Data are reported in *m*/*z*.

Compound Purification. The intermediate compounds and the methanofullerene **3** were purified by column chromatography (CC) on silica gel, eluting with CH_2Cl_2/heptane 8:2 (for **5**), CH_2Cl_2/heptane 9:1 (for **4**), and toluene/heptane 1:1 and then toluene/AcOEt 7:3 (for **3**). The hexa-adduct **2** was first purified by CC (SiO_2; toluene/heptane 1:1 and then toluene/AcOEt 96:4), and then by semi-prep. HPLC on µ*Porasil Silica* (10 µm; column: 7.8 mm × 300 mm; toluene/heptane/AcOEt 88:10:2, 3 ml/min; t_R 37 min).

Data of **2**. ^{1}H-NMR (400 MHz, CD_2Cl_2): 7.64 (*d*, 20 arom. H); 7.60 (*d*, 20 arom. H); 7.49 (*d*, 20 arom. H); 7.40 (*d*, 8 arom. H); 6.92 (*d*, 20 arom. H); 6.88 (*d*, 4 arom. H); 6.86 (*d*, 4 arom. H); 4.21 (*t*, 12 CO_2CH_2); 3.93 (*t*, 12 CH_2O); 3.91 (*t*, 2 CH_2O); 1.78–1.70 (*m*, 14 $C\mathit{H}_2CH_2O$); 1.65 (*quint.*, 12 $CO_2CH_2C\mathit{H}_2$); 1.41–1.24 (*m*, 164 aliph. H); 0.86 (*t*, 2 Me). ^{13}C-NMR (100 MHz, CD_2Cl_2): 164.03; 160.23; 158.72; 158.68; 146.06; 145.41; 141.58; 133.43; 133.36; 132.94; 131.46; 128.64; 127.81; 127.30; 119.37; 115.33; 115.06; 115.03; 110.42; 69.60; 68.55; 68.49; 68.46; 67.44; 46.23; 32.24; 30.10; 29.95; 29.91; 29.85; 29.79; 29.72; 29.68; 29.64; 28.85; 26.50; 26.43; 26.26; 23.06; 14.27. Anal. calc. for $C_{368}H_{370}N_{10}O_{38}$ (5540.92): C 79.77, H 6.73, N 2.53, O 10.97; found: C 79.64, H 6.82, N 2.54, O 11.00.

Data of **3**. UV/VIS (CH_2Cl_2): 426 (2940), 487 (1820), 686 (240). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.46 (*d*, 4 arom. H); 7.44 (*d*, 4 arom. H); 6.95 (*d*, 4 arom. H); 6.92 (*d*, 4 arom. H); 4.50 (*t*, 2 CO_2CH_2); 4.00–3.96 (*m*, 4 CH_2O); 1.88–1.75 (*m*, 12 H, $C\mathit{H}_2CH_2O$, $CO_2CH_2C\mathit{H}_2$); 1.47–1.30 (*m*, 44 aliph. H); 0.89 (*t*, 2 Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.15; 158.64; 145.78; 145.66; 145.57; 145.27; 145.08; 145.04; 145.01; 144.27; 143.49; 143.41; 142.60; 142.31; 141.36; 139.39; 133.71; 128.08; 115.13; 68.50; 68.44; 67.88; 32.26; 29.98; 29.86; 29.81; 29.74; 29.69; 29.66; 29.02; 26.50; 26.43; 23.10; 14.55. MALDI-TOF-MS: 1695.67 ($[M+H]^+$, $C_{123}H_{91}O_8^+$; calc. 1695.67). Anal. calc. for $C_{123}H_{90}O_8$ (1696.06): C 87.10, H 5.35, O 7.55; found: C 87.03, H 5.51, O 7.46.

Data of **4**. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.46 (*d*, 4 arom. H); 7.45 (*d*, 4 arom. H); 6.95 (*d*, 4 arom. H); 6.93 (*d*, 4 arom. H); 4.14 (*t*, 2 CO_2CH_2); 4.00–3.96 (*m*, 4 CH_2O); 3.37 (*s*, $O_2CCH_2CO_2$); 1.80–1.76 (*m*, 4 $C\mathit{H}_2CH_2O$); 1.65 (*quint.*, 2 $CO_2CH_2C\mathit{H}_2$); 1.50–1.30 (*m*, 44 aliph. H); 0.89 (*t*, 2 Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 167.15; 158.63; 158.61; 133.74; 133.70; 128.06; 115.12; 68.50; 68.45; 66.10; 42.12; 32.24; 29.91; 29.86; 29.80; 29.73; 29.68; 29.62; 28.88; 26.48; 26.21; 23.09; 14.54. Anal. calc. for $C_{63}H_{92}O_8$ (977.40): C 77.42, H 9.49, O 13.09; found: C 77.27, H 9.49, O 13.24.

Data of **5**. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.47 (*d*, 2 arom. H); 7.45 (*d*, 2 arom. H); 6.95 (*d*, 2 arom. H); 6.93 (*d*, 2 arom. H); 3.99 (*t*, 2 CH_2O); 3.65 (*t*, $C\mathit{H}_2OH$); 1.80 (*quint.*, 2 $C\mathit{H}_2CH_2O$); 1.59–1.30 (*m*, 24 aliph. H); 0.89 (*t*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 158.61; 133.74; 133.71; 128.07; 115.13; 68.50; 68.47; 63.51; 33.21; 32.24; 29.94; 29.91; 29.80; 29.72; 29.67; 26.47; 26.14; 23.08; 14.54.

Optical and Thermal Studies. Polarized optical microscopy was performed on a *Zeiss-Axioskop* polarizing microscope equipped with a *Linkam THMS-600* variable-temperature stage, under N_2. Transition temperatures and enthalpies were determined on a *Mettler-Toledo-822e* differential-scanning calorimeter at a rate of 10°/min under He/N_2.

REFERENCES

[1] T. Chuard, R. Deschenaux, *J. Mater. Chem.* **2002**, *12*, 1944.

[2] a) T. Chuard, R. Deschenaux, *Helv. Chim. Acta* **1996**, *79*, 736; b) B. Dardel, R. Deschenaux, M. Even, E. Serrano, *Macromolecules* **1999**, *32*, 5193; c) T. Chuard, R. Deschenaux, A. Hirsch, H. Schönberger, *Chem. Commun.* **1999**, 2103; d) M. Even, B. Heinrich, D. Guillon, D. M. Guldi, M. Prato, R. Deschenaux, *Chem.–Eur. J.* **2001**, *7*, 2595; e) B. Dardel, D. Guillon, B. Heinrich, R. Deschenaux, *J. Mater. Chem.* **2001**, *11*, 2814; f) S. Campidelli, R. Deschenaux, J.-F. Eckert, D. Guillon, J.-F. Nierengarten, *Chem. Commun.* **2002**, 656; g) S. Campidelli, C. Eng, I. M. Saez, J. W. Goodby, R. Deschenaux, *Chem. Commun.* **2003**, 1520; h) S. Campidelli, E. Vázquez, D. Milic, M. Prato, J. Barberá, D. M. Guldi, M. Marcaccio, D. Paolucci, F. Paolucci, R. Deschenaux, *J. Mater. Chem.* **2004**, *14*, 1266; i) E. Allard, F. Oswald, B. Donnio, D. Guillon, J. L. Delgado, F. Langa, R. Deschenaux, *Org. Lett.* **2005**, *7*, 383; j) S. Campidelli, J. Lenoble, J. Barberá, F. Paolucci, M. Marcaccio, D. Paolucci, R. Deschenaux, *Macromolecules* **2005**, *38*, 7915; k) J. Lenoble, N. Maringa, S. Campidelli, B. Donnio, D. Guillon, R. Deschenaux, *Org. Lett.* **2006**, *8*, 1851; l) S. Campidelli, E. Vázquez, D. Milic, J. Lenoble, C. A. Castellanos, G. Sarova, D. M. Guldi, R. Deschenaux, M. Prato, *J. Org. Chem.* **2006**, *71*, 7603; m) S. Campidelli, T. Brandmüller, A. Hirsch, I. M. Saez, J. W. Goodby, R. Deschenaux, *Chem. Commun.* **2006**, 4282; n) S. Campidelli, L. Pérez, J. Rodríguez-López, J. Barberá, F. Langa, R. Deschenaux, *Tetrahedron* **2006**, *62*, 2115.

[3] N. Tirelli, F. Cardullo, T. Habicher, U. W. Suter, F. Diederich, *J. Chem. Soc., Perkin Trans. 2* **2000**, 193.

[4] M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato, E. Nakamura, *Nature* **2002**, *419*, 702; Y. Matsuo, A. Muramatsu, R. Hamasaki, N. Mizoshita, T. Kato, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 432; Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 9586.

[5] R. J. Bushby, I. W. Hamley, Q. Liu, O. R. Lozman, J. E. Lydon, *J. Mater. Chem.* **2005**, *15*, 4429.

[6] D. Felder-Flesch, L. Rupnicki, C. Bourgogne, B. Donnio, D. Guillon, *J. Mater. Chem.* **2006**, *16*, 304.

[7] D. Felder, B. Heinrich, D. Guillon, J.-F. Nicoud, J.-F. Nierengarten, *Chem.–Eur. J.* **2000**, *6*, 3501; M. Kimura, Y. Saito, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, *J. Am. Chem. Soc.* **2002**, *124*, 5274.

[8] C. Bingel, *Chem. Ber.* **1993**, *126*, 1957; J.-F. Nierengarten, A. Herrmann, R. R. Tykwinski, M. Rüttimann, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 293; X. Camps, A. Hirsch, *J. Chem. Soc., Perkin Trans. 1* **1997**, 1595.

[9] A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem., Int. Ed.* **1994**, *33*, 437.

Received January 24, 2007