
Preliminary Communication

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A liquid-crystalline mixed [5:1]hexa-adduct of [60]fullerene was synthesized by addition of two
different malonate derivatives onto C₆₀. The hexa-adduct derivative 2 was prepared by a stepwise
synthetic procedure (fullerene — mono-adduct of C₆₀ — hexa-adduct of C₆₀). 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 (C₆₀) with the self-organizing behavior of
liquid crystals [1]. Covalent functionalization of C₆₀ [1 – 6] and formation of supra-
molecular 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 C₆₀ 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 C₆₀ prompted us to design liquid-crystalline hexa-adducts
to explore the behavior of mesogens in a spherical environment. The first hexa-adduct
of C₆₀ 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 C₆₀, 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 C₆₀
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
C₆₀ 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

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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].

**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 functional-
ization 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>T [°C]</th>
<th>ΔH [kJ/mol]</th>
<th>Transition*</th>
<th>T$_g$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>87</td>
<td>2.7</td>
<td>(I → N)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>50</td>
<td>(N → Cr)</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>151</td>
<td>55.5</td>
<td>SmA → I</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>112</td>
<td>43.1</td>
<td>Cr → I</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>115</td>
<td>21.6</td>
<td>(I → SmA)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>114</td>
<td>12.3</td>
<td>(SmA → Cr)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>37.7</td>
<td>(Cr → Cr')</td>
<td>–</td>
</tr>
</tbody>
</table>

* Transition temperatures are given at the onset of the observed peaks. *) I = isotropic liquid, N = nematic phase, SmA = smectic A phase, Cr = crystal; monotropic transitions are given in parentheses. *') Glass-transition temperature. * 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°C.

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.

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Experimental Part

General. The synthesis and anal. data of 1 have been described before [2c]. UV/VIS Spectroscopic data are reported as \lambda_{\text{max}} (in nm) and, in parentheses, as \varepsilon (in dm^3 mol^{-1} cm^{-1}). NMR chemical shifts \delta 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\textsubscript{2}Cl\textsubscript{2}/heptane 8:2 (for 5), CH\textsubscript{2}Cl\textsubscript{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\textsubscript{2}; toluene/heptane 1:1 and then toluene/AcOEt 96:4), and then by semi-prep. HPLC on \mu-Porasil Silica (10 \mu m; column: 78 mm \times 300 mm; toluene/heptane/AcOEt 88:10:2; 3 ml/min; t\textsubscript{R} 37 min).

Data of 2. \textsuperscript{1}H-NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{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); 6.84 (d, 4 arom. H); 4.21 (t, 12 CO\textsubscript{2}CH\textsubscript{2}); 3.93 (t, 12 CH\textsubscript{2}O); 3.91 (t, 2 CH\textsubscript{2}O); 1.78–1.70 (m, 14 CH\textsubscript{2}CH\textsubscript{2}O); 1.65 \textit{quin}, \textit{t} (12 CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}C); 1.41–1.24 (m, 164 aliph. H); 0.86 (t, 2 Me). \textsuperscript{13}C-NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}): 164.03; 160.23; 158.72; 158.68; 145.41; 141.58; 133.43; 133.36; 132.94; 131.46; 128.64; 127.81; 127.10; 119.37; 115.53; 115.06; 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_{118}H_{36}O_{14} (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\textsubscript{2}Cl\textsubscript{2}): 426 (2940), 487 (1820), 686 (240). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{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); 6.50 (t, 2 CO\textsubscript{2}CH\textsubscript{2}); 4.00–3.96 (m, 4 CH\textsubscript{2}O); 1.88–1.75 (m, 12 H, CH\textsubscript{2}CH\textsubscript{2}O, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}C); 1.47–1.30 (m, 44 aliph. H); 0.89 (t, 2 Me). \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): 164.15; 158.64; 154.78; 154.66; 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_{118}H_{34}O_{14}^+; calc. 1695.67). Anal. calc. for C_{118}H_{34}O_{14} (1696.06): C 87.10, H 5.35, O 7.55; found: C 87.03, H 5.51, O 7.46.

Data of 4. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): 7.46 (d, 4 arom. H); 7.45 (d, 4 arom. H); 7.40 (d, 4 arom. H); 6.95 (d, 4 arom. H); 6.93 (d, 4 arom. H); 6.93 (d, 4 arom. H); 6.31 (d, 4 arom. H); 4.83 (t, 2 CO\textsubscript{2}CH\textsubscript{2}); 4.00–3.96 (m, 4 CH\textsubscript{2}O); 3.37 (s, O\textsubscript{2}CCH\textsubscript{2}CO\textsubscript{2}); 1.80–1.76 (m, 4 CH\textsubscript{2}CH\textsubscript{2}O); 1.50–1.30 (m, 16 aliph. H); 1.06 (t, 2 Me). \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): 167.15; 158.63; 158.61; 133.74; 133.70; 128.06; 115.12; 68.50; 68.45; 68.45; 66.10; 42.12; 32.24; 29.80; 28.80; 28.73; 28.68; 28.62; 28.48; 26.21; 23.09; 14.45. Anal. calc. for C_{118}H_{36}O_{14} (27740): C 77.42, H 9.49, O 13.09; found: C 77.72, H 9.49, O 13.24.

Data of 5. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): 7.47 (d, 2 arom. H); 7.45 (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\textsubscript{2}O); 3.65 (t, CH\textsubscript{2}OH); 1.80 (quin, t, CH\textsubscript{2}CO\textsubscript{2}); 1.59–1.30 (m, 24 aliph. H); 0.89 (t, Me). \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): 158.61; 133.74; 133.71; 128.07; 115.13; 68.50; 68.47; 63.51; 32.31; 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\textsubscript{2}. Transition temperatures and enthalpies were determined on a Mettler-Toledo-822e differential-scanning calorimeter at a rate of 10°/min under He/N\textsubscript{2}.
REFERENCES


