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First Fullerene[60]-Containing Thermotropic Liquid Crystal

Preliminary Communication

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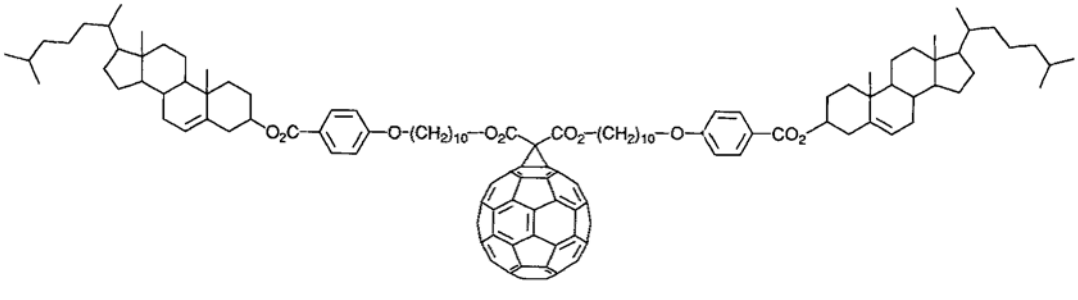
The synthesis and liquid-crystalline and thermal properties of a fullerene[60] functionalized by a framework containing two cholesterol derivatives through a methanofullerene structure are reported. The targeted fullerene derivative showed high thermal stability.

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



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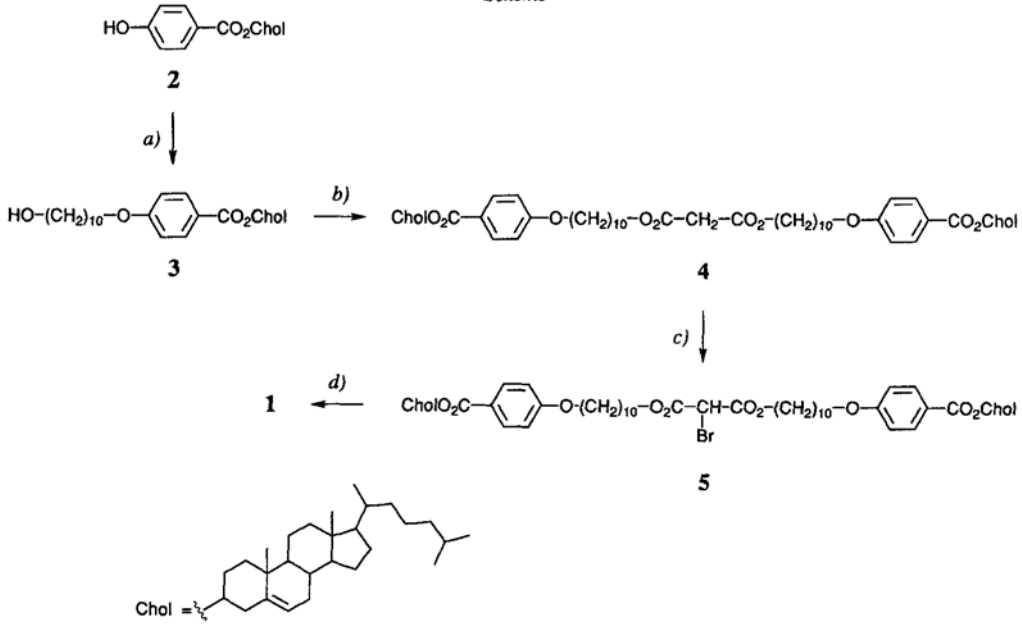
[11] or the self-assembly method [12]; however, further evidence concerning the *structure* (of the molecular unit)-*supramolecular organization* relationship are required for obtaining ordered assemblies with tailor-mode properties.

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 ^{1}H- and ^{13}C-NMR spectroscopy and, elemental

Scheme



a) 10-Bromodecan-1-ol, K_2CO_3, DMF/THF 3:1, 120°, 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°, 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_A 148 TGB A 151 N* 206 BP 207 I][1]) presented interesting mesomorphism. On heating, two crystal-to-crystal modifications were observed at 105 and 112° before a S_A phase formed. Then, a TGB A→N*→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_A 214 N* 224 BP 225 I][1]) gave enantiotropic S_A, 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[2]).

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

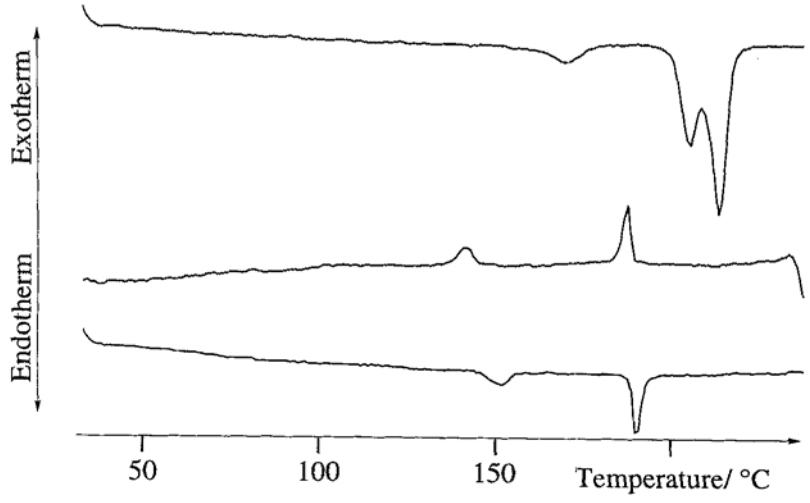


Figure. *Differential scanning calorimetry thermograms of* **1** *registered during the first heating* (top), *first cooling* (middle), *and second heating* (bottom) *run.* Experimental conditions: sample weight: 2.792 mg; rate: 10°/min; temperature range: 30–240°; under N_2.

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[1]) C: crystalline state; S_{C^*}: chiral smectic C phase; S_A: 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_A 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° (ΔH (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 silanized glasses [19]. The mesophase was thus tentatively identified as a monotropic S_A 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_2), 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.

We acknowledge Dr. *V. Vill*, University of Hamburg, for helpful discussions concerning the mesomorphism of compound **3**.

Experimental Part

General. Instrumentation, see [14] [21]. Themogravimetry: *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), CH_2Cl_2 (distilled over P_2O_5), and THF (distilled over $LiAlH_4$) were dried prior to use. The syntheses were performed under N_2 (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.

Cholest-5-en-3β-yl 4-(10-Hydroxydecyloxy)benzoate (**3**). A mixture of cholesteryl 4-hydroxybenzoate (14.0 g, 27.6 mmol), 10-bromodecan-1-ol (8.40 g, 35.4 mmol), K_2CO_3 (11.5 g, 83.2 mmol), DMF (210 ml), and THF (70 ml) was stirred at 120° 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 (CH_2Cl_2) and crystallization from EtOH: **3** (14.7 g, 80%). $[\alpha]_{365}^{20} = +31$ ($c = 0.5$, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.98 (*d*, $J = 8.9$, 2 arom. H); 6.90 (*d*, $J = 8.9$, 2 arom. H); 5.42 (*d*, $J = 4.1$, C=CH (Chol)); 4.77–4.92 (br. *m*, CHO (Chol)); 4.00 (*t*, $J = 6.5$, CH_2O); 3.65 (*t*, $J = 6.5$, CH_2OH); 2.45 (*d*, $J = 7.7$, 2 H, Chol); 0.69–2.06 (57 H, Chol, $(CH_2)_8$). Anal. calc. for $C_{44}H_{70}O_4$ (663.05): C 79.71, H 10.64; found: C 79.83, H 10.81.

Bis{10-{4-[(cholest-5-en-3β-yloxy)carbonyl]phenoxy}decyl} Propanedioate (**4**). A soln. of propanedioyl chloride (0.27 g, 1.92 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a soln. of **3** (2.50 g, 3.77 mmol) and Et_3N (0.48 g, 4.71 mmol) in CH_2Cl_2 (40 ml). The mixture was stirred at reflux for 20 h, cooled to r.t., washed successively with 1N HCl and sat. aq. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated. Purification of the solid residue by CC (CH_2Cl_2) and crystallization from CH_2Cl_2/hexane gave **4** (1.97 g, 75%). $[\alpha]_{365}^{20} = +28$ ($c = 0.3$, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.98 (*d*, $J = 8.9$, 4 arom. H); 6.90 (*d*, $J = 9.0$, 4 arom. H); 5.41 (*d*, $J = 4.1$, 2 H, C=CH (Chol)); 4.77–4.87 (br. *m*, 2 H, CHO (Chol)); 4.14 (*t*, $J = 6.7$, 4 H, CO_2CH_2); 4.00 (*t*, $J = 6.5$, 4 H, CH_2O); 3.37 (*s*, $O_2CCH_2CO_2$); 2.45 (*d*, $J = 7.5$, 4 H, Chol); 0.69–2.05 (114 H, Chol, $(CH_2)_8$). Anal. calc. for $C_{91}H_{140}O_{10}$ (1394.10): C 78.40, H 10.12; found: C 78.57, H 10.03.

Bis{10-{4-[(cholest-5-en-3β-yloxy)carbonyl]phenoxy}decyl} 2-Bromopropanedioate (**5**). A soln. of CBr_4 (0.45 g, 1.36 mmol) in THF (20 ml) was added dropwise to a soln. of **4** (1.89 g, 1.36 mmol) and DBU (0.21 g, 1.36 mmol) in THF (120 ml) cooled to −40°. The mixture was stirred at −40° for 5 h and hydrolyzed with 1N HCl. Et_2O was added to favor phase separation, the aq. phase extracted twice with CH_2Cl_2, the combined org. phase dried ($MgSO_4$) and evaporated, and the solid residue purified by CC (CH_2Cl_2/hexane 9:1) and crystallization from acetone: **5** (1.02 g, 51%). $[\alpha]_{365}^{20} = +29$ ($c = 0.3$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.98 (*d*, $J = 9.0$, 4 arom. H); 6.89 (*d*, $J = 9.0$, 4 arom. H); 5.41 (*d*, $J = 3.7$, 2 H, C=CH (Chol)); 4.77–4.87 (br. *m*, 2 H, CHO (Chol)); 4.83 (*s*, CHBr); 4.22 (*t*, $J = 6.7$, 4 H, CO_2CH_2); 3.99 (*t*, $J = 6.5$, 4 H, CH_2O); 2.44 (*d*, $J = 7.7$, 4 H, Chol); 0.69–2.03 (114 H, Chol, $(CH_2)_8$). Anal. calc. for $C_{91}H_{139}BrO_{10}$ (1473.00): C 74.20, H 9.51, Br 5.42; found: C 74.42, H 9.37, Br 5.12.

Bis{10-{4-[(cholest-5-en-3β-yloxy)carbonyl]phenoxy}decyl} 1,2-Methanofullerene[60]-61,61-dicarboxylate (**1**). To a soln. of fullerene[60] (0.162 g, 0.225 mmol) in toluene (180 ml), a 60% NaH oil dispersion (*ca.* 0.130 g, *ca.* 3.25 mmol) and **5** (0.465 g, 0.316 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 ($MgSO_4$) and evaporated: dark residue. Purification of this latter by CC (toluene) gave a purple band (unreacted C_{60}) 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 *ca.* 10 ml and left at −30° overnight. A solid, which crystallized, was recovered by filtration and dried to yield **1** (0.191 g, 40%). VIS (λ_{max} in nm (ε in $l \cdot mol^{-1}\ cm^{-1}$), $CHCl_3$): 426 (2500), 490 (1540), 687 (200). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.97 (*d*, $J = 8.9$, 4 arom. H); 6.87 (*d*, $J = 8.9$, 4 arom. H); 5.41 (*d*, $J = 3.7$, 2 H, C=CH (Chol)); 4.78–4.86 (br. *m*, 2 H, CHO (Chol)); 4.49 (*t*, $J = 6.5$, 4 H, CO_2CH_2); 3.98 (*t*, $J = 6.5$, 4 H, CH_2O); 2.45 (*d*, $J = 7.6$, 4 H, Chol); 0.69–2.03 (114 H, Chol, $(CH_2)_8$). ^{13}C-NMR (100 MHz, $CDCl_3$): 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, 53.15, 50.73, 43.01, 40.43, 40.21, 39.00, 37.75, 37.35, 36.88, 36.49, 32.63, 32.57, 30.23, 30.20, 30.08, 29.91, 29.83, 29.29, 28.93, 28.71, 28.64, 26.71, 26.69, 24.99, 24.53, 23.52, 23.26, 21.75, 20.10, 19.41, 12.56. Anal. calc. for $C_{151}H_{138}O_{10}$ (2112.75): C 85.84, H 6.58; found: C 85.68, H 6.82.

REFERENCES

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature (London)* **1985,** *318,* 162.

[2] a) F. Diederich, L. Isaacs, D. Philp, *Chem. Soc. Rev.* **1994,** *23,* 243; b) A. Hirsch, *Synthesis* **1995,** 895.

[3] C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* **1995,** *78,* 1334, and ref. cit. therein.

[4] C. S. Foote, *Topics Curr. Chem.* **1994,** *169,* 347.

[5] P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, J. D. Thompson, *Science (Washington)* **1991,** *253,* 301; P. W. Stephens, D. Cox, J. W. Lauher, L. Mihaly, J. B. Wiley, P.-M. Allemand, A. Hirsch, K. Holczer, Q. Li, J. D. Thompson, F. Wudl, *Nature (London)* **1992,** *355,* 331.

[6] S. H. Friedman, D. L. DeCamp, R. P. Sijbesma, G. Srdanov, F. Wudl, G. L. Kenyon, *J. Am. Chem. Soc.* **1993,** *115,* 6506; R. Sijbesma, G. Srdanov, F. Wudl, J. A. Castoro, C. Wilkins, S. H. Friedman, D. L. DeCamp, G. L. Kenyon, *ibid.* **1993,** *115,* 6510.

[7] H. Tokuyama, S. Yamago, E. Nakamura, T. Shiraki, J. Sugiura, *J. Am. Chem. Soc.* **1993,** *115,* 7918; A. S. Boutorine, H. Tokuyama, M. Takasugi, H. Isobe, E. Nakamura, C. Hélène, *Angew. Chem. Int. Ed.* **1994,** *33,* 2462.

[8] A. G. Avent, P. R. Birkett, C. Christides, J. D. Crane, A. D. Darwish, P. B. Hitchcock, H. W. Kroto, M. F. Meidine, K. Prassides, R. Taylor, D. R. M. Walton, *Pure Appl. Chem.* **1994,** *66,* 1389.

[9] D. R. Huffman, *Mater. Lett.* **1994,** *21,* 127.

[10] S. Ravaine, F. Vicentini, M. Mauzac, P. Delhaes, *New. J. Chem.* **1995,** *19,* 1.

[11] U. Jonas, F. Cardullo, P. Belik, F. Diederich, A. Gügel, E. Harth, A. Herrmann, L. Isaacs, K. Müllen, H. Ringsdorf, C. Thilgen, P. Uhlmann, A. Vasella, C. A. A. Waldraff, M. Walter, *Chem. Eur. J.* **1995,** *1,* 243, and ref. cit. therein.

[12] L. M. Lander, W. J. Brittain, V. A. DePalma, S. R. Girolmo, *Chem. Mater.* **1995,** *7,* 1437, and ref. cit. therein.

[13] C. Bingel, *Chem. Ber.* **1993,** *126,* 1957.

[14] R. Deschenaux, C. Masoni, H. Stoeckli-Evans, S. Vaucher, J. Ketterer, R. Steiger, A. L. Weisenhorn, *J. Chem. Soc., Dalton Trans.* **1994,** 1051.

[15] V. Vill, J. Thiem, *Z. Naturforsch., A* **1990,** *45,* 1205.

[16] A. J. Slaney, J. W. Goodby, *J. Mater. Chem.* **1991,** *1,* 5.

[17] G. W. Gray, J. W. Goodby, 'Smectic Liquid Crystals', Leonard Hill, Glasgow, 1984.

[18] D. Demus, L. Richter, 'Textures of Liquid Crystals', Verlag Chemie, Weinheim, 1978.

[19] A. Soldera, J.-F. Nicoud, A. Skoulios, Y. Galerne, D. Guillon, *Chem. Mater.* **1994,** *6,* 625.

[20] R. Deschenaux, J. W. Goodby, in 'Ferrocenes', Eds. A. Togni and T. Hayashi, VCH Verlagsgesellschaft, Weinheim, 1995, Chapt. 9.

[21] R. Deschenaux, I. Kosztics, B. Nicolet, *J. Mater. Chem.* **1995,** *5,* 2291.