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# Supramolecular liquid crystals formed by hydrogen bonding between a benzocrown-bearing stilbazole and carboxylic acids

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The mesomorphism of hydrogen bonded complexes formed between 4′-carboxybenzo-15-crown-5 stilbazolyl ester (CBCSE) as proton acceptor and carboxylic acids as proton donors is discussed. CBCSE is a monotropic mesogen, forming a nematic phase upon quench cooling. A total of 32 hydrogen bonded complexes has been studied. Hydrogen bonding with carboxylic acids stabilizes the nematic phase, and/or induces a smectic A (SmA) phase. CBCSE forms 1:1 complexes (molar ratio) with alkanoic acids (fatty acids) and 2:1 complexes with alkanedioic acids. None of these proton donors is a mesogen itself, but the hydrogen bonded complexes are. The influence of the chain or spacer length on the transition temperatures is discussed. Besides the homologous series of the alkanoic and alkanedioic acids, the following carboxylic acids were used in this study: diglycolic acid, pyridine-2,6-dicarboxylic acid, 4-dodecyloxybenzoic acid, 3,4-bis(dodecyloxy)benzoic acid, 2,3,4-tris(dodecyloxy)benzoic acid and 3,4,5-tris(dodecyloxy)benzoic acid, phthalic acid, isophthalic acid and terephthalic acid.

## 1. Introduction

It has long been known that in several liquid crystals intermolecular hydrogen bonding is responsible for the existence of the mesophase(s) [1]. Examples of such compounds are the 4-alkoxybenzoic acids [2] and the tris(alkoxy)benzamides [3]. In these cases, the hydrogen bonded complexes are formed between two identical molecules, and the system can be considered as self-complementary. Lehn and coworkers used different complementary molecules to form hydrogen bonded liquid crystals [4]. Simple hydrogen bonded systems with carboxylic acids or phenols as proton donors and pyridyl groups as proton acceptors have been studied intensively by the research groups of Kato, Fréchet, Bruce and Yu [5]. Hydrogen bonding is a powerful tool for stabilizing and inducing mesophases, even in compounds in which the structure largely deviates from that of the classical calamitic liquid crystals. For instance, Tsaih and Yu [6] stabilized the nematic phase and induced a smectic A phase in benzocrown-bearing stilbazoles via hydrogen bonding with 4-alkoxybenzoic acids.

In this paper, we show that in the hydrogen bonded complexes of 4′-carboxybenzo-15-crown-5 stilbazolyl ester (CBCSE, see figure 1) studied by Tsaih and Yu [6], the mesomorphic 4-alkoxybenzoic acids can be replaced by non-mesogenic fatty acids or diacids (alkanoic and alkanedioic acids) without destroying the mesophase. The fatty acids form 1:1 complexes with CBCSE, while the aliphatic diacids form 1:2 complexes (figure 2). The influence of the alkyl chain length on the thermal behaviour is described. Additionally, we show that poly-alkoxy substituted benzoic acids can be used as proton donors, but that hydrogen bonded complexes of the isomers of phthalic acid give rise to behaviour that is more difficult to interpret.

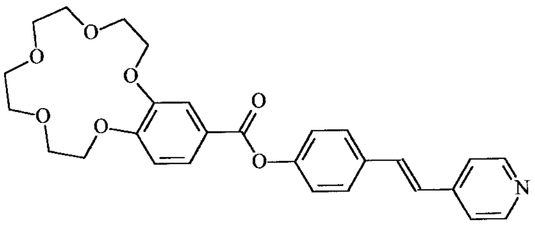

Figure 1. 4′-Carboxybenzo-15-crown-5 stilbazolyl ester (CBCSE).

## 2. Experimental

$^1$H NMR spectra were obtained with a Bruker WM-250 spectrometer (250 MHz), using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. The $\delta$-values are expressed in ppm. IR spectra were recorded with a Bruker FTIR spectrometer IFS66. KBr pellets of

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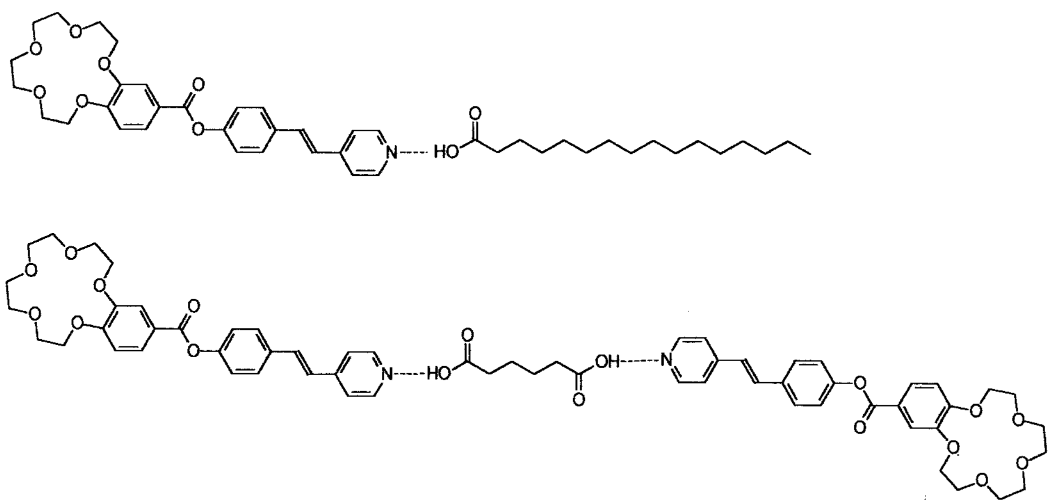


Figure 2. Hydrogen bonded complexes formed between CBCSE and hexadecanoic acid (upper structure), and between CBCSE and 1,6-hexanedioic acid (lower structure). Analogous complexes were formed between CBCSE and other alkanoic acids (series between pentanoic acid and octadecanoic acid) and other alkanedioic acids (series between malonic acid and 1,12-dodecanedioic acid).

the samples were used for the FTIR spectra. Elemental analyses (CHN) were carried out using a CE Instruments EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC821e module. Samples of 2–5 mg in solid form were put in aluminium pans (40 μl) with a pierced lid, and heated or cooled at a scan rate of 10°C $\mathrm{min}^{-1}$ under a nitrogen flow. Indium metal was used as standard for the calibration of the instrument ($T_m = 156.6 \pm 0.3$°C, $\Delta H_m = 28.45 \pm 0.6\ \mathrm{J\ g}^{-1}$). Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature controller. All chemicals were used as received, without further purification. Organic reagents were obtained from ACROS, Aldrich or Fluka. 3,4,5-Tris(dodecyloxy)-benzoic acid was purchased from the Laboratory of Macromolecular and Organic Chemistry (Eindhoven University of Technology, The Netherlands).

### 2.1. *Synthesis of benzo-15-crown-5*

Benzo-15-crown-5 was synthesized from catechol and 1,11-dichloro-3,6,9-trioxaundecane in the presence of NaOH and butanol [7]. Yield 68%, m.p. 78–79°C (lit. [7] 79–79.5°C). $^1$H NMR (250 MHz, $CDCl_3$, TMS): $\delta = 3.77$ (s, 8H, crown ether $CH_2$), 3.91 (m, 4H, crown ether $CH_2$), 4.14 (m, 4H, crown ether $CH_2$), 6.90 (s, 4H, ArH).

### 2.2. *Synthesis of 4′-acetobenzo-15-crown-5*

4′-Acetobenzo-15-crown-5 was synthesized according to a literature method by acylation of benzo-15-crown-5 with acetic acid anhydride in a polyphosphoric acid/acetic acid mixture at 60°C [8]. Yield 75%, m.p. 95–96°C (lit. [8] 95.5–96.5°C). $^1$H NMR (250 MHz, $CDCl_3$, TMS): $\delta = 2.55$ (s, 3H, $COCH_3$), 3.77 (s, 8H, crown ether $CH_2$), 3.91 (m, 4H, crown ether $CH_2$), 4.19 (m, 4H, crown ether $CH_2$), 6.86 (d, 1H, ArH, $J_o = 8.5$ Hz), 7.51 (d, 1H, ArH, $J_m = 2$ Hz), 7.56 (dd, 1H, ArH, $J_o = 8.5$ Hz, $J_m = 2$ Hz).

### 2.3. *Synthesis of 4′-carboxybenzo-15-crown-5*

4′-Acetobenzo-15-crown-5 was transformed into 4′-carboxybenzo-15-crown-5 by oxidation with NaOBr [9]. Yield 68%, m.p. 188–189°C (lit. [9] 180°C). $^1$H NMR (250 MHz, $CDCl_3$, TMS): $\delta = 3.78$ (s, 8H, crown ether $CH_2$), 3.95 (m, 4H, crown ether $CH_2$), 4.20 (m, 4H, crown ether $CH_2$), 6.87 (d, 1H, ArH, $J_o = 8.5$ Hz), 7.57 (d, 1H, ArH, $J_m = 2$ Hz), 7.72 (dd, 1H, ArH, $J_o = 8.5$ Hz, $J_m = 2$ Hz).

### 2.4. *Synthesis of 4-[(E)-2-(4-pyridinyl)ethenyl]phenol (trans-4-hydroxy-4′-stilbazole)*

4-[(*E*)-2-(4-pyridinyl)ethenyl]phenol was prepared by condensation of 4-hydroxybenzaldehyde with 4-methylpyridine, followed by hydrolysis in dilute HCl solution [10]. Yield 55%, m.p. 175–177°C (lit. [10] 215–217°C; this discrepancy is most probably due to a typing error in the original reference). $^1$H NMR (250 MHz, $d_6$-DMSO, TMS): $\delta = 6.89$ (d, 1H, HC = CH, $J = 16$ Hz), 7.00 (d, 2H, ArH, $J = 8$ Hz), 7.45 (d, 1H, HC = CH, $J = 16$ Hz), 7.50 (m, 4H, ArH), 8.51 (d, 2H, ArH, $J = 5.5$ Hz), 9.81 (s br, 1H, OH).

### 2.5. *Synthesis of 4-[(E)-2-(4-pyridinyl)ethenyl]phenyl 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecane-15-carboxylate (4′-carboxybenzo-15-crown-5 stilbazolyl ester, CBCSE)*

4′-Carboxybenzo-15-crown-5 (5 mmol) was heated for 16 h at reflux with an excess of thionyl chloride (15 ml), in a dry nitrogen atmosphere. The excess of thionyl chloride was removed under reduced pressure and the acid chloride formed was used without further purification for the esterification. The acid chloride was dissolved in dry pyridine (15 ml), 4-[(*E*)-2-(4-pyridinyl)ethenyl]-phenol (5 mmol) was added, and the mixture was heated for 5 h at reflux in a nitrogen atmosphere. Subsequently, the mixture was allowed to cool to room temperature, and poured into dilute aqueous HCl. The organic layer was separated from the aqueous layer, and the aqueous layer was extracted several times with chloroform. The combined organic phases were washed with saturated aqueous $Na_2CO_3$, followed by saturated aqueous NaCl, dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, with chloroform/ethanol 20/1 as the eluent) and by crystallization (twice from acetone). Yield 62%, m.p. 151–152°C (lit. [6] 147–150°C). $^1H$ NMR (250 MHz, $CDCl_3$, TMS): $\delta = 3.79$ (s, 8H, crown ether $CH_2$), 3.94 (m, 4H, crown ether $CH_2$), 4.22 (m, 4H, crown ether $CH_2$), 6.99, 7.31 (2d, 2H, HC=CH, $J = 16$ Hz), 6.93, 7.24, 7.55, 7.66, 7.84 (4d, dd, 7H, ArH, $J_o = 8.5$ Hz, $J_m = 2$ Hz), 7.37, 8.59 (2 dd, 4H, pyr H, $J_o = 4.5$ Hz, $J_m = 1.5$ Hz). MS (CI): $m/z = 492$ ($M^+ + 1$). IR (KBr, $cm^{-1}$): 1731 (s, C=O). Elemental analysis: calc. for $C_{28}H_{29}NO_7$, C 68.42, H 5.95, N 2.85; found, C 67.98, H 5.95, N 2.69%.

### 2.6. *Synthesis of 4-dodecyloxybenzoic acid*

4-Dodecyloxybenzoic acid was synthesized by reaction of ethyl 4-hydroxybenzoate with 1-bromododecane in 2-butanone, using $K_2CO_3$ as the base (reflux time 48 h), and by subsequent hydrolysis of the ethyl ester with KOH in ethanol and workup with dilute aqueous HCl. The crude product was purified by recrystallization from acetic acid. Yield 80%, m.p. 96°C. $^1H$ NMR (250 MHz, $CDCl_3$, TMS): $\delta = 0.88$ (t, 3H, $CH_3$), 1.1–1.6 (m, 18H, $CH_2$), 1.77 (quintet, 2H, $CH_2CH_2O$), 4.02 (t, 2H, $OCH_2$), 6.91 (dd, 2H, ArH, $J = 9$ Hz), 8.03 (dd, 2H, ArH, $J = 9$ Hz).

### 2.7. *Synthesis of 3,4-bis(dodecyloxy)benzoic acid*

3,4-Bis(dodecyloxy)benzoic acid was obtained in a three-step reaction, starting from catechol. First, catechol was transformed into 3,4-bis(dodecyloxy)benzene by reaction with 1-bromododecane (2 eq.) in acetone, with $K_2CO_3$ as the base and with a catalytic amount of KI (yield 85%). Secondly, 3,4-bis(dodecyloxy)acetophenone was obtained by acylation of 3,4-bis(dodecyloxy)benzene with acetic anhydride in a polyphosphoric acid (PPA) /acetic acid mixture at 60°C (yield 65%). Finally, this product was transformed into 3,4-bis(dodecyloxy)-benzoic acid by oxidation with NaOBr. Yield 65%, m.p. 120°C. $^1H$ NMR (250 MHz, $CDCl_3$, TMS): $\delta = 0.88$ (m, 6H, $CH_3$), 1.1–1.9 (m, 40 H, $CH_2$), 4.05, 4.07 (2t, 4H, $OCH_2$), 6.89 (d, 1H, ArH, $J_o = 8.5$ Hz), 7.59 (d, 1H, ArH, $J_m = 2$ Hz), 7.73 (dd, 1H, ArH, $J_o = 8.5$ Hz, $J_m = 2$ Hz).

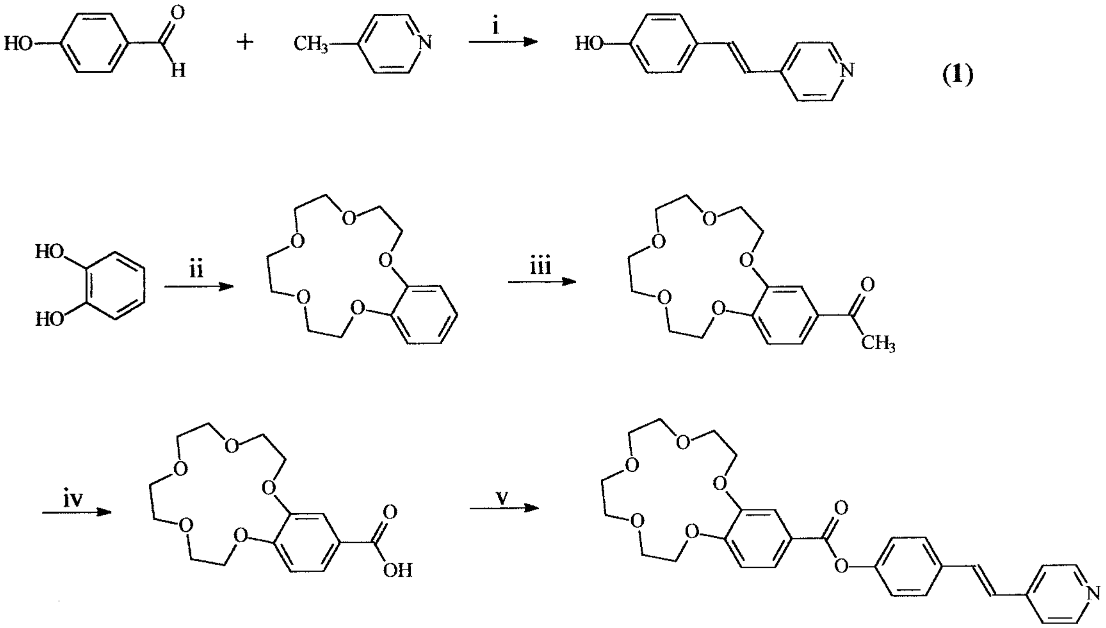
### 2.8. *Synthesis of 2,3,4-tris(dodecyloxy)benzoic acid*

2,3,4-Tris(dodecyloxy)benzoic acid was synthesized in a two-step reaction, by first alkylating pyrogallol [11] and then introducing the COOH group, according to a method described in [12]. Pyrogallol was alkylated at the three OH positions with 3 eq. of 1-bromododecane in acetone, with $K_2CO_3$ as the base and with a catalytic amount of KI. Subsequently, 2,3,4-tris(dodecyloxy)-benzene was lithiated with *n*-butyllithium and carboxylated with solid $CO_2$. To 10 mmol of *n*-butyllithium at ambient temperature and in an argon atmosphere was added dropswise 10 mmol of tetramethylethylenediamine (TMEDA). To this solution, a solution of 2,3,4-tris(dodecyloxy)benzene (10 mmol) in hexane was added by syringe, and the reaction mixture was stirred during 3 h under an argon atmosphere. After this period, *c.* 100 g of solid $CO_2$ was added to the reaction mixture. After evaporation of the excess of $CO_2$, dilute aqueous HCl was added. The aqueous layer was shaken with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$, and filtered; the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica) with heptane/ethyl acetate (90/10) as eluent, followed by recrystallization from acetone/methanol. Yield 32%, m.p. 44°C. $^1H$ NMR (250 MHz, $CDCl_3$, TMS): $\delta = 0.88$ (m, 9H, $CH_3$), 1.0–1.9 (m, 60 H, $CH_2$), 3.97, 4.04, 4.33 (3t, 6H, $OCH_2$), 6.77, 7.87 (2d, 2H, Ar-H, $J_o = 9$ Hz).

## 3. Results and discussion

### 3.1. *Synthesis and thermal behaviour of CBCSE*

4′-Carboxybenzo-15-crown-5 stilbazolyl ester (CBCSE) was synthesized by first preparing 4′-carboxybenzo-15-crown-5 and 4-[(*E*)-2-(4-pyridinyl)ethenyl]phenol, and subsequently coupling them by esterification (see the scheme). Our synthesis methodology differs from that of Tsaih and Yu [6] in that we preferred a convergent route to a linear synthesis sequence. CBCSE melts to an isotropic liquid at 151–152°C (lit. [6] 147–150°C). Upon quench cooling (< 20°C $min^{-1}$), a nematic phase was observed at 81°C. Fast cooling rates were necessary,



**(1)**

Scheme. Synthesis of 4′-carboxybenzo-15-crown-5 stilbazolyl ester (CBCSE). Reagents and conditions: (i) $Ac_2O$, reflux, 55% (ii) $Cl(CH_2CH_2O)_3CH_2CH_2Cl$, NaOH-BuOH, 68%; (iii) $Ac_2O$, PPA, AcOH, 75%; (iv) NaOBr, 68%; (v) (a) $SOCl_2$, (b) **1**, pyridine, 62%.

because CBCSE has a strong tendency to crystallize. CBCSE is an interesting mesogen, because in contradistinction to the majority of mesogenic compounds, it lacks a terminal chain. Because the ring is not rigid in the absence of metal ions, it can be supposed that the crown ether acts as a kind of terminal polyethylene oxide chain. By forming complexes with lanthanide ions, the mesomorphism is destroyed. We prepared 1 : 1 complexes of CBCSE with lanthanide nitrates $Ln(NO_3)_3$ (Ln = La, Ce–Lu except Pm), but none of these complexes was mesomorphic. The metal complexes decompose before melting (at *c.* 240°C).

### 3.2. *Complexes with alkanoic acids*

Contact preparations were made with CBCSE and each member of the homologous series of the alkanoic acids (fatty acids) between pentanoic ($C_4H_9COOH$) and octadecanoic acid ($C_{17}H_{35}COOH$), and these were observed by polarizing optical microscopy in order to obtain a snapshot of the phase diagram. The contact preparations showed that the nematic phase of the ligand is stabilized and that a smectic A phase is induced. Thus in the mixtures, the isotropic to nematic transition occurs at a higher temperature than for pure CBCSE, and the mesophase stability range is larger. Whereas, the I → N transition of CBCSE is at 81°C, in the mixture the transition occurs between 95 and 105°C. The SmA phase is only present in some of the mixtures and not in CBCSE. The nematic phase was determined from its schlieren or marble-like texture, which showed flashes when the cover slip was pressed by a needle. The Brownian motion of the molecules could be observed. The smectic A phase was characterized by its typical focal-conic texture and extinct regions of homeotropic alignment. In all the systems, the highest clearing point was observed for the 1 : 1 mixture (molar ratio). We also investigated the 1 : 1 mixtures by DSC. The 1 : 1 mixtures where prepared by dissolving the two compounds in a 1 : 1 molar ratio in dichloromethane (acetone was added for the mixture with pentadecanoic acid and the higher homologues), and by removing the solvent by evaporation.

For the mixtures with pentanoic and hexanoic acid, only monotropic mesomorphism was found, whereas the mixtures with all the other homologues exhibited enantiotropic mesomorphism. In the case of the 1 : 1 mixtures, both a nematic phase and a smectic A phase could be observed for pentanoic acid, hexanoic acid, heptanoic acid and octanoic acid. From nonanoic acid on, the 1 : 1 mixture exhibited only a smectic A phase and no longer a nematic phase.

However, the mixtures with a higher CBCSE content than the 1 : 1 mixture formed only a nematic phase and the mixtures with a higher fatty acid content showed only a smectic A phase. These systems could be observed using contact preparations of the 1 : 1 mixtures with CBCSE and also contact preparations of the 1 : 1 mixture with each of the homologues of the alkanoic acids series.

For these studies a 1 : 1 mixture was brought into contact with pure CBCSE or the corresponding alkanoic acid (in the isotropic phase for both components).

It should be noted that obtaining contact preparations of the pure compounds proved to be difficult for nonanoic acid and the lower homologues because of their high volatility at the melting point of CBCSE. It was necessary to add regularly new acid to compensate for these volatility losses. The mesophase behaviour of the 1 : 1 mixtures of CBCSE with alkanoic acids is summarized in table 1. In figure 3, the DSC thermogram of the 1 : 1 mixture of CBCSE with tridecanoic acid is shown.

Table 1. Transitions and thermal data for the hydrogen bonded complexes formed between CBCSE and monocarboxylic acids in a 1 : 1 molar ratio.

| Carboxylic acid | Transition | Temperature /°C | $\Delta H$/J g$^{-1}$ |
|---|---|---|---|
| Pentanoic acid | Cr → I | 108 | 48.1 |
| | I → N | 99 | − 0.5 |
| | N → SmA | 83 | —[a] |
| Hexanoic acid | Cr → I | 106 | 57.8 |
| | I → N | 95 | − 1.1 |
| | N → SmA | 86 | − 0.6 |
| Heptanoic acid | Cr → SmA | 92 | 57.3 |
| | SmA → N | 95 | 1.1 |
| | N → I | 101 | 0.9 |
| Octanoic acid | Cr → SmA | 100 | 56.5 |
| | SmA → N | 101 | 1.3 |
| | N → I | 103 | 0.5 |
| Nonanoic acid | Cr → SmA | 90 | 51.4 |
| | SmA → I | 104 | 5.6 |
| Decanoic acid | Cr → SmA | 87 | 47.3 |
| | SmA → I | 109 | 4.2 |
| Undecanoic acid | Cr → SmA | 87 | 37.5 |
| | SmA → I | 113 | 4.9 |
| Dodecanoic acid | Cr → SmA | 90 | 51.5 |
| | SmA → I | 117 | 8.6 |
| Tridecanoic acid | Cr → SmA | 89 | 49.0 |
| | SmA → I | 119 | 7.9 |
| Tetradecanoic acid | Cr → SmA | 92 | 55.5 |
| | SmA → I | 122 | 8.5 |
| Pentadecanoic acid | Cr → SmA | 92 | 49.4 |
| | SmA → I | 124 | 8.2 |
| Hexadecanoic acid | Cr → SmA | 93 | 52.2 |
| | SmA → I | 126 | 8.6 |
| Heptadecanoic acid | Cr → SmA | 94 | 54.0 |
| | SmA → I | 129 | 8.8 |
| Octadecanoic acid | Cr → SmA | 94 | 57.5 |
| | SmA → I | 130 | 8.5 |

[a] This transition could not be measured by DSC, because of overlap with the crystallization peak.

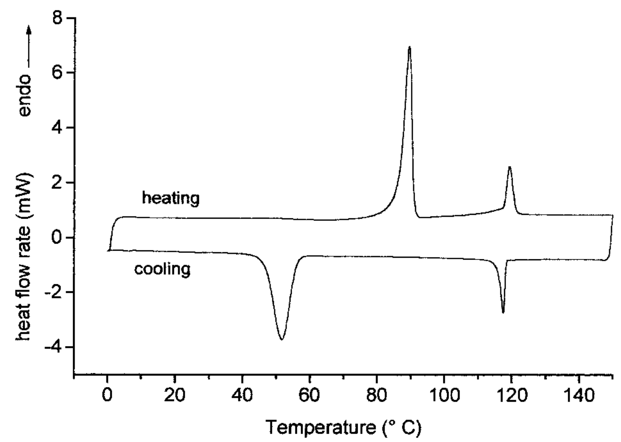


Figure 3. DSC thermogram of the hydrogen bonded complex formed between CBCSE and tridecanoic acid (1 : 1 molar ratio). The second heating and cooling runs are shown; endothermic peaks point upwards.

### 3.3. *Complexes with alkanedioic acids*

Hydrogen bonded complexes of CBCSE with the following aliphatic dicarboxylic acids (alkanedioic acids) were investigated: malonic acid, succinic acid, glutaric acid, 1,6-hexanedioic acid (adipic acid), 1,7-heptanedioic acid (pimelic acid), 1,8-octanedioic acid, 1,9-nonanedioic acid, 1,10-dodecanedioic acid and 1,12-dodecanedioic acid. Also the complex with diglycolic acid was prepared. It is to be expected that by self-assembly the alkanedioic acids form twin-like structures with CBCSE (see figure 2), by analogy with the molecular twins of alkanedioic acids and the stilbazolyl esters studied by Kato *et al.* [5(*d*)]. In the mixtures with the alkanedioic acids, the nematic phase of the ligand is stabilized, but no smectic mesophase is induced. The highest clearing point was observed for CBCSE : dicarboxylic acid in a 2 : 1 molar ratio. These mixtures were studied by polarizing optical microscopy and by DSC.

The 2 : 1 mixture with malonic acid melted at 128°C and showed upon cooling a monotropic nematic mesophase at 113°C. However, the mixture had a low thermal stability, and decomposed above the melting point. Therefore it was necessary to heat the mixture rapidly to the isotropic state, and then cool it rapidly (20°C min$^{-1}$) without any long thermal annealing in the isotropic state. If thermal decomposition occurred, the nematic phase could no longer be observed.

The 2 : 1 mixtures with the other dicarboxylic acids were thermally more stable. All mixtures showed a monotropic nematic phase, except those with glutaric acid and glycolic acid, which exhibited an enantiotropic nematic phase. The mesophase behaviour of the 2 : 1 CBCSE : glutaric acid mixture can be summarized as Cr • 124 • N • 139 • I, and that of the 2 : 1 CBCSE : diglycolic acid mixture as Cr • 117 • N • 132 • I. The DSC thermogram of the 2:1 mixture of CBCSE and glutaric acid is shown in figure 4. In contradistinction to the mixtures with the alkanoic acids, for the dicarboxylic acids, the tendency to crystallize increases as the methylene spacer lengthens. Thus, the mesophase stability range of the mixture with dodecanedioic acid was much smaller than, for instance, that of the mixture with succinic acid.

It is interesting to note that whereas the mixtures with the aliphatic dicarboxylic acids crystallize upon cooling, the mixture with diglycolic acid supercooled to a glassy state. During the cooling cycle, the viscosity of the nematic phase increased at *c.* 70°C, and between 40 and 50°C the nematic phase solidified to a glass. The texture of the nematic phase is retained in the glassy mesophase. During a subsequent heating run, the viscosity decreased at *c.* 60°C, but was still high for a nematic phase. At this stage, it was not possible to observe the Brownian motion or any flashing effect. However, a schlieren texture could be observed. In the DSC thermogram, a glass transition with a relaxation peak could be observed. Only at about 100°C did the viscosity have a low value of a typical nematic phase, and both the flashing effect and the Brownian motion could be observed. When the glassy mesophase was held at room temperature (instead of directly heating again), crystallization of the sample was observed. Subsequent heating resulted in the same mesophase behaviour as for the neat sample.

The mesophase behaviour of the 2:1 mixtures (molar ratio) of CBCSE and the dicarboxylic acids is summarized in table 2.

### 3.4. *Complexes with alkoxy substituted benzoic acids*

Hydrogen bonded complexes were prepared between CBCSE and the following alkoxy substituted benzoic acids: 4-dodecyloxybenzoic acid, 3,4-bis(dodecyloxy)benzoic acid (figure 5), 2,3,4-tris(dodecyloxy)benzoic acid and 3,4,5-tris(dodecyloxy)benzoic acid. Except for 4-dodecyloxybenzoic acid (Cr • 95 • SmC • 133 • N • 139 • I), none of these benzoic acids exhibits mesomorphism in the pure state. Mesomorphism is induced by complexation. The highest clearing points of the first two hydrogen bonded complexes were observed for the 1:1 mixtures. In these complexes, an enantiotropic smectic phase is induced, and the clearing point decreases with increasing number of alkyl chains. No nematic phase was observed. The texture of the 1:1 mixture of CBCSE with 4-dodecyloxybenzoic acid is a focal-conic texture, typical for the SmA phase. The mesophase behaviour can be summarized as Cr • 119 • SmA • 165 • I. The melting enthalpy is 49.9 J g$^{-1}$ and the clearing enthalpy 6.3 J g$^{-1}$. This mixture was also studied by Tsaih and Yu [6], and these author report the mesophase behaviour as Cr • 115 • SmA • 156 • I. For the texture of the 1:1 mixture of CBCSE with 3,4-bis(dodecyloxy)benzoic acid, bâtonnets were observed upon cooling from the isotropic phase, and the bâtonnets coalesced to a focal-conic texture. This 1:1 mixture was totally miscible with the 1:1 mixture of CBCSE with 4-dodecyloxybenzoic acid. The

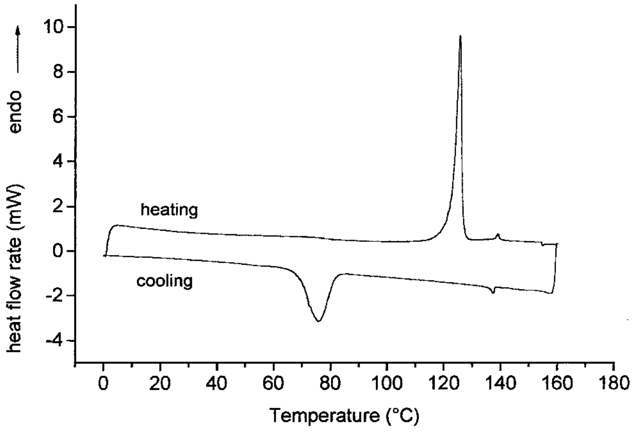


Figure 4. DSC thermogram of the hydrogen bonded complex formed between CBCSE and glutaric acid (2:1 molar ratio). The second heating and cooling runs are shown; endothermic peaks point upwards.

Table 2. Phase transitions and thermal data for the hydrogen bonded complexes formed between CBCSE and dicarboxylic acids in a 2:1 molar ratio.

| Carboxylic acid | Transition | Temperature /°C | $\Delta H$/J g$^{-1}$ |
|---|---|---|---|
| Diglycolic acid | Cr → N | 117 | —[a] |
| | N → I | 131 | − 1.3 |
| Malonic acid | Cr → I | 128 | 68.6 |
| | I → N | 113 | —[b] |
| Succinic acid | Cr → I | 168 | 85.5 |
| | I → N | 155 | − 1.5 |
| Glutaric acid | Cr → N | 125 | 52.8 |
| | N → I | 139 | 0.7 |
| 1,6-Hexanedioic acid | Cr → I | 164 | 88.8 |
| | I → N | 149 | − 1.9 |
| 1,7-Heptanedioic acid | Cr → I | 152 | 91.2 |
| | I → N | 133 | − 1.3 |
| 1,8-Octanedioic acid | Cr → I | 174 | 108.6 |
| | I → N | 144 | − 2.3 |
| 1,9-Nonanedioic acid | Cr → I | 143 | 63.1 |
| | I → N | 130 | − 1.4 |
| 1,10-Decanedioic acid | Cr → I | 153 | 64.7 |
| | I → N | 138 | − 1.7 |
| 1,12-Dodecanedioic acid | Cr → I | 157 | 75.0 |
| | I → N | 138 | − 1.5 |

[a] No accurate melting enthalpy is available, because in the first heating run the mixture was not homogeneous, and the mixture solidified to a glass upon cooling. No crystallization of the glass was observed in the second heating run.

[b] Transition could not be observed by DSC, because of the strong tendency of the mixture to crystallize.

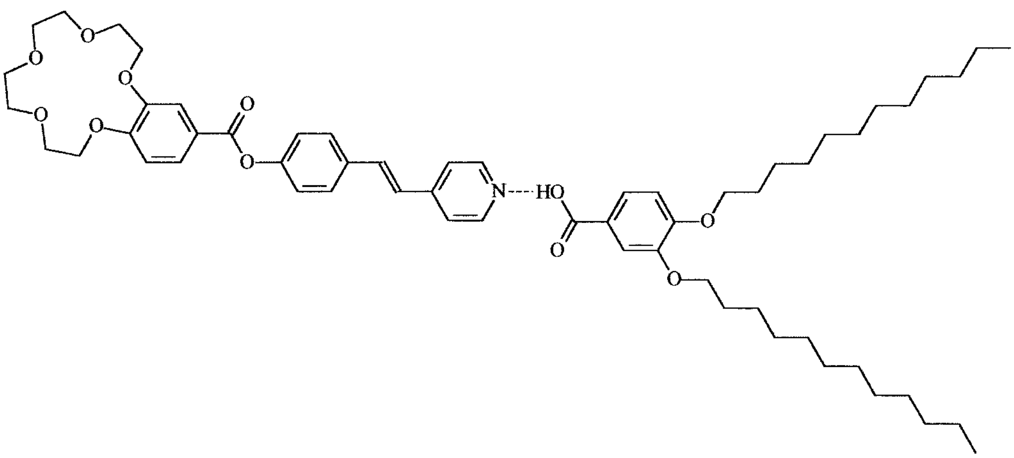


Figure 5. Hydrogen bonded complex formed between CBCSE and 3,4-bis(dodecyloxybenzoic) acid.

mesophase behaviour is Cr • 124 • SmA • 148 • I. The mesomorphism of the hydrogen bonded complexes of CBCSE with the trialkoxy substituted benzoic acids, 2,3,4-tris(dodecyloxy)benzoic acid and 3,4,5-tris(dodecyloxy)benzoic acid is more difficult to describe. For 2,3,4-tris(dodecyloxy)benzoic acid, it was not possible to obtain stable stoichiometric 1:1 mixtures by dissolving the components in a solvent and removing the solvent. During the first heating run, phase separation took place, and the transition temperatures were not reproducible. However, the mesomorphic behaviour as studied by contact preparation of the pure components was reproducible. A monotropic mesophase was formed, with clearing point 92°C. According to the texture, the mesophase was SmA. For 3,4,5-tris(dodecyloxy)benzoic acid, a monotropic SmA mesophase was induced (phase determination by optical microscopy). The highest clearing point was not now observed for the 50:50 (or 1:1) mixture, but for CBCSE and 3,4,5-tris(dodecyloxy)benzoic acid in a 60:40 molar ratio. The 60:40 mixture was thermally not very stable, and during annealing, phase separation was observed. The mixture melted over a broad biphasic range, and upon cooling, the monotropic SmA phase was formed at 132°C. The melting enthalpy was 24.1 J g$^{-1}$ and the clearing enthalpy 3.6 J g$^{-1}$.

### 3.5. *Complexes with aromatic dicarboxylic acids*

Mixtures (2:1 molar ratio) of CBCSE with different aromatic dicarboxylic acids were investigated: pyridine-2,6-dicarboxylic acid, phthalic acid, isophthalic acid and terephthalic acid. The 2:1 mixture of CBCSE with pyridine-2,6-dicarboxylic acid melts at 147°C and forms a monotropic nematic phase at 120°C. The nematic phase solidifies to a glassy mesophase. A glass transition was observed in the DSC thermogram ($T_g = 40°$). However, the mixture is thermally not very stable, and prolonged heating in the isotropic phase caused thermal decomposition. The 2:1 mixture of CBCSE with isophthalic acid forms an enantiotropic nematic phase: Cr • 147 • N • 157 • I. The melting enthalpy is 43.13 J g$^{-1}$ and the clearing enthalpy 0.4 J g$^{-1}$. Upon cooling, the nematic phase solidifies to a glassy mesophase ($T_g = 49°C$). During the second heating run, the glass crystallizes at *c.* 110°C. This mixture again has a rather low thermal stability. It was not possible to obtain reproducible results from the mixtures with phthalic acid and with terephthalic acid.

## 4. Conclusions

In this paper, we have described the stabilization and induction of mesophases via hydrogen bonding in 4′-carboxybenzo-15-crown-5 stilbazolyl ester (CBCSE) systems. A total of 32 hydrogen bonded complexes were prepared by reaction between CBCSE and mono- or di-carboxylic acids. Although neither the alkanoic nor the alkanedioic acids display mesomorphic behaviour by themselves, they can stabilize the nematic phase of CBCSE and/or induce a smectic A phase. For the hydrogen bonded complexes of CBCSE with alkoxy-substituted benzoic acids, the stability range of the induced smectic A phase decreases with increasing number of alkoxy chains. The 2:1 complex between CBCSE and pyridine-2,6-dicarboxylic acid exhibits a monotropic nematic phase, and an enantiotropic nematic phase was found for the 2:1 complex with isophthalic acid.

The formation of hetero-intermolecular hydrogen bonds is a powerful approach for stabilization or induction of mesophases. The appealing part of working with hydrogen bonded mesogens is the easy synthesis, since dissolving the components in a suitable solvent, followed by evaporation of this solvent, gives the desired product in quantitative yield. Although the hydrogen bond is not as stable as a covalent bond, the majority of the hydrogen bonded complexes have a thermal stability which is comparable to that of classical liquid crystals. We have restricted ourselves to a detailed description of supramolecular 1:1 or 2:1 complexes (depending on whether the proton donor is monoprotic or diprotic) because the largest mesophase stability range was observed for these mixtures. However, mixtures can be prepared for any ratio of the proton donor and acceptor [1(*b*)], and the use of non-stoichiometric mixtures provides another degree of freedom besides chain length for fine-tuning the mesomorphic properties.

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## References

[1] (*a*) Paleos, C. M., and Tsiourvas, D., 1995, *Angew. Chem. int. Ed. Engl.*, **34,** 1696; (*b*) Kato, T., 1998, in *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Weinheim: Wiley-VCH), Chap. XVII.

[2] Gray, G. W., and Jones, B., 1953, *J. chem. Soc.*, 4179.

[3] Beginn, U., and Lattermann, G., 1994, *Mol. Cryst. liq. Cryst.*, **241,** 215.

[4] (*a*) Brienne, M. J., Gabard, J., Lehn, J. M., and Stibor, I., 1989, *J. chem. Soc. chem. Commun.*, 1868; (*b*) Kotera, M., Lehn, J. M., and Vigneron, J. P., 1994, *J. chem. Soc. chem. Commun.*, 197.

[5] (*a*) Kato, T., and Frèchet, J. M. J., 1989, *J. Am. chem. Soc.*, **111,** 8533; (*b*) Kato, T., Wilson, P., Fujishima, A., and Frèchet, J. M. J., 1990, *Chem. Lett.*, 2003; (*c*) Kato, T., Frèchet, J. M. J., Wilson, P. J., Saito, T., Uryu, T., Fujishima, A., Jin, C., and Kaneuchi, F., 1993, *Chem. Mater.*, **5,** 1094; (*d*) Kato, T., Fujishima, A., and Frèchet, J. M. J., 1990, *Chem. Lett.*, 919; (*e*) Fukumasa, M., Kato, T., Uryu, T., and Frèchet, J. M. J., 1993, *Chem. Lett.*, 65; (*f*) Bruce, D. W., and Price, D. J., 1994, *Adv. Mater. opt. Electron.*, **4,** 273; (*g*) Willis, K., Price, D. J., Adams, H., Ungar, G., and Bruce, D. W., 1995, *J. mater. Chem.*, **5,** 2195, (*h*) Kihara, H., Kato, T., Uryu, T., Ujiie, S., Kumar, U., Frèchet, J. M. J., Bruce, D. W., and Price, D. J., 1996, *Liq. Cryst.*, **21,** 25; (*i*) Willis, K., Luckhurst, J. E., Price, D. J., Frèchet, J. M. J., Kihara, H, Kato, T., Ungar, G., and Bruce, D. W., 1996, *Liq. Cryst.*, **21,** 585; (*j*) Price, D. J., Willis, K., Richardson, T., Ungar, G., and Bruce, D. W., 1997, *J. mater. Chem.*, **7,** 883; (*k*) Yu, L. J., Wu, J. M., and Wu. S. L., 1991, *Mol. Cryst. liq. Cryst.*, **198,** 407; (*l*) Yu, L. J., and Pan, J. S., 1993, *Liq. Cryst.*, **14,** 829.

[6] Tsaih, J. J., and Yu, L. J., 1997, *Mol. Cryst. liq. Cryst.*, **302,** 339.

[7] (*a*) Pedersen, C. J., 1967, *J. Am. chem. Soc.*, **89,** 2495; (*b*) Pedersen, C. J., 1967, *J. Am. chem. Soc.*, **89,** 7017; (*c*) Pedersen, C. J., 1970, *J. Am. chem. Soc.*, **92,** 391.

[8] Taima, A. G., van Vossen, H., Sudhölter, E. J. R., van Eerden, J., and Reinhoudt, N. D., 1985, *Synthesis*, 680.

[9] Bourgoin, M., Wong, K. H., Hui, J. Y., and Smid, J, 1975, *J. Am. chem. Soc.*, **97,** 3462.

[10] Chiang, M. C., and Hartung, W. H., 1945, *J. org. Chem.*, **10,** 21.

[11] (*a*) Praefcke, K., Singer, D., and Gündogan, B., 1992, *Mol. Cryst. liq. Cryst.*, **223,** 181; (*b*) Gündogan, B., 1996, PhD thesis, TU Berlin, Germany.

[12] Broaddus, C. D., 1970, *J. org. Chem.*, **35,** 10.