Structures, properties and miscibility behaviour of liquid crystalline polycatenar tetrone derivatives

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Structures, properties and miscibility behaviour of liquid crystalline polycatenar tetrone derivatives

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The tetrones represent an interesting new mesogenic building block. The results of this study show that they can be incorporated into a variety of mesophases. A smectic phase was observed in the polycatenar compound with four terminal chains as expected. The phase exhibits a tilted structure (Sc phase) to prevent void formation. The compound with six pendant chains forms a columnar phase. In spite of their structural similarity, the tetrones studied tended not to be completely miscible. However, complete miscibility with a semi-discoid phenylhydrazone was observed. When this hydrazone, which forms a columnar 'D$_{ho}$ phase', was mixed with tetrone which forms a columnar 'D$_{hd}$ phase' a columnar hexagonal phase was produced with enhanced stability. We believe that the stability enhancement derives from a charge transfer interaction between the tetrone and the phenylhydrazone.

1. Introduction

The structures of liquid crystalline phases are essentially determined by the shapes of the molecules [1, 2]. Thus rod-like molecules produce calamatic smectic mesophases (S$_A$, S$_C$, ...) [3] whereas flat, disc-like molecules form mesophases with columnar structures, like N$_D$, D$_{ro}$, D$_{rd}$ [4, 5] and board-like molecules form sanidic mesophases [6].

Polycatenar compounds [7, 8] represent a class of liquid crystal materials between the calamitics and discotics. They consist of two different parts: a rod-like rigid core and one or two half-disc shaped moieties at the end of the core. Depending on the number and the position of the alkyl chains, which are linked directly to the half-disc like moieties, such compounds exhibit nematic and/or smectic and/or columnar mesophases [9, 12]. Often intermolecular hydrogen bonds and/or charge transfer interactions play an important role in the formation and stabilization of these columnar mesophases [13, 14].

Different rod-like cores, including biphenyl, terphenyl and so on, have been used in polycatenar compounds. In the compounds under discussion, tetrones are used as the central core in the polycatenar compounds.

It is known, that the tetrone moiety is not completely flat, but tilted [15, 16]. To study the influence of this group

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on the formation of liquid crystalline phases, the three tetrone derivatives (I–III) shown in figure 1 were synthesized.

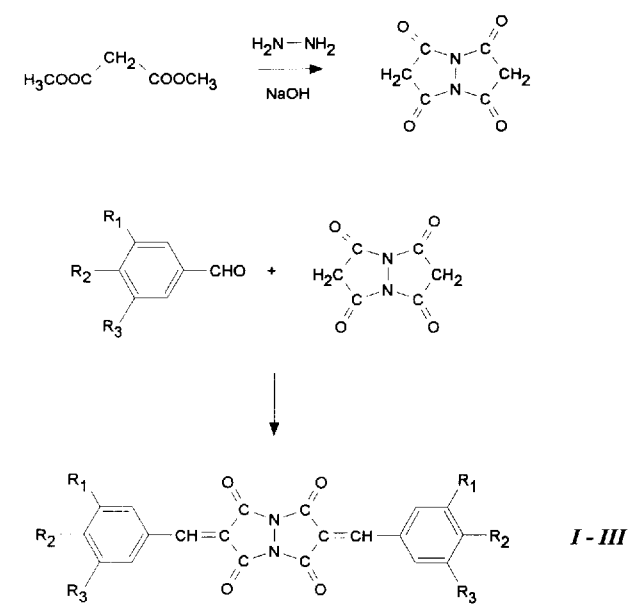## 2. Synthesis and characterization of substituted tetrone derivatives

The synthesis of the tetrone has been achieved by a condensation of dimethyl malonate and absolute hydrazine. The synthesis of the tetrone-containing dyes is shown in the figure 1. A wide range of amphiphilic tetrones is accessible by condensation of substituted aldehydes and tetrone. For the alkoxy- and amino-substituted derivatives, the alkylated aldehyde was first prepared and then the condensation reaction was done. The synthesis of the substituted aldehydes will be described elsewhere. All the compounds were characterized by NMR spectroscopy using a 400 MHz NMR spectrometer (Aspect 3000, Bruker).

3. Results and discussion

3.1. Mesomorphic behaviour of the tetrone derivatives

The phase behaviour of the three tetrones (I–III) is summarized in figure 1. The tetrone I shows only crystalline behaviour, but increasing the number of the methylene groups (compound II) leads to formation of a smectic mesophase. The diffraction pattern of a non-

Figure 1 Synthesis and transition scheme for the tetrone derivatives.

Tetrone	R_1	R_2	R_3	Transition scheme
I	–H	–N(C$_{16}$H$_{33}$)$_2$	–H	Cr 54°C Cr 118°C I
II	–H	–N(C$_{18}$H$_{37}$)$_2$	–H	Cr 116°C S$_C$143°C I
III	–OC$_{12}$H$_{25}$	–OC$_{12}$H$_{25}$		Cr 64°C Dr 112°C D$_h$133°C I

oriented sample of **II** (see figure 2) exhibits four sharp reflections in the small angle range and one diffuse scattering region in the wide angle range. The reflections which are marked *B* to *D* are higher orders of the first reflection (*A*) and are indicative of a layer structure.
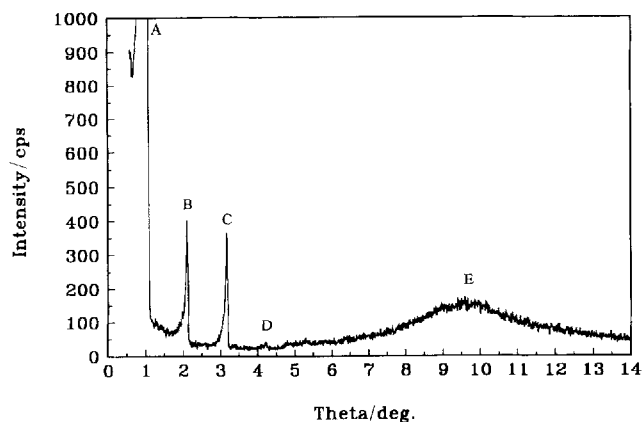

Theta/deg.

Figure 2 Diffraction pattern **II** at 125°C.

The large difference between the molecular length estimated by space filling models ($L = 6·2$ nm) and that measured ($d = 4·2$ nm) implies a tilted alignment of the molecules within the layers. This, together with the schlieren texture observed, is consistent with the phase assignment as S$_C$. The change from four *N* alkyl chains in **II** to six alkoxy chains in **III** anchored directly to the phenyl ring, yields a change from a smectic to a columnar phase.

A dark mosaic texture can be observed by polarizing microscopy at 65°C. A lightening of this mosaic texture with small structural changes was observed at about 112°C. This process is reversible, and DSC measurements (see table 1) show a clear transition at this temperature. The transition enthalpy (ΔH_{tr}) is considerably higher than that at the clearing point (ΔH_{CL}). X-ray measurements using the film method confirmed the transition at about 112°C. The patterns taken in the low temperature phase exhibit two strong and seven very weak reflections in the small angle range and one diffuse scattering region in the wide angle range. This pattern is maintained up to about 110°C.

The reflections observed in the low temperature mesophase (see table 2) can be explained by a rectangular lattice. The extinction rule of reflections ($h0$) and ($0k$) with h, $k = 2n + 1$ proves the existence of a rectangular D$_{r(P2_1/a)}$ lattice with $a = 5·88$ nm and $b = 3·44$ nm.

At the transition into the high temperature phase (110–112°C), the weak reflections disappear and the remaining pattern is consistent with a columnar hexagonal mesophase. The ratio of the small angle reflections in this columnar phase is $1 : \sqrt{3} : 2$. The hexagonal lattice parameter corresponds at 120°C to $a_{hex} = 3·38$ nm and at 95°C to $a_{hex} = 3·49$ nm. The difference between the molecular length ($L = 4·7$ nm) and the hexagonal lattice parameter indicates a disordered arrangement and an interdigitation of the alkyl chains.

The volume increment method [17] has been used to estimate the volume of the molecule (V_{mol}). Calculation of the packing coefficient, V_{mol}/V_{cell}, with two molecules per column disc in both phases, yields a value of 0·7. This leads to a proposed formation of the columns by the hexacatenar tetrone as shown in figure 3. A wrapping of aliphatic chains around the rod-like rigid core assembly, as already known from discotics [18], can be built up by the alkyl chains. Detailed X-ray measurements of the position of the inner reflection (a very strong reflection) as a function of temperature are shown in figure 4. The *d*-values of the inner reflection within the hexagonal mesophase increase with decreasing temperature, the evident change shown corresponding to the transition into the rectangular phase (93·5°C in the cooling mode).

Table 1.   DSC results for compound **III** (1 ≡ first heating mode, 2 ≡ cooling mode, 3 ≡ second heating mode, heating/cooling rate; 10 K min^{-1}). ΔH_m, melting enthalpy; ΔH_{tr}, transition enthalpy; ΔH_{cl}, clearing enthalpy in J g^{-1}; T_m, melting temperature; T_{tr}, transition temperature; T_{cl}, clearing temperature in °C.

Cycle	Cr	$T_m(\Delta H_m)$	Dr	$T_{tr}(\Delta H_{tr})$	D$_h$	$T_{cl}(\Delta H_{cl}$	I
1	●	54·1 (46·0)	●	112·6 (10·4)	●	131·4 (2·5)	●
2	●	43·6 (− 41·4)	●	93·5 (− 8·1)	●	125·5 (− 1·8)	●
3	●	36·5 (62·3)	●	112·7 (8·8)	●	130·9 (1·8)	●

3.2. *Results and discussion of the mixtures investigated*

To study further the phase behaviour of these interesting tetrone mesogens, mixtures of tetrone **III** with the 2,4-dinitrophenylhydrazone **IV** were prepared and studied. (see figure 5) This mesogen, as a donor (D)/acceptor (A) system, contains electron-rich as well as electron-poor units and forms a columnar hexagonal mesophase, where the packing of the molecules in the columns is stabilized by charge transfer interactions [14]. Other examples of the stabilizing and destabilizing of liquid crystalline mesophases via charge transfer interactions are known from the literature [19].

The diffraction pattern of compound **IV** in the mesophase (see figure 6) shows two Bragg peaks in the small angle region with a Bragg angle ratio of 1 : $\sqrt{3}$ (*A–B* ratio) and three diffuse outer scattering maxima (*C–E*). The disordered state of the alkyl chains yields the diffuse scattering indicated as *D* in figure 6. The packing within the columns corresponds with the diffuse scattering *E*. A fit to the diffuse scattering maxima in the wide angle range is shown in the figure 7. The positions of the diffuse scattering at *C* and *E* (taken from the fit) have nearly a 1 : 2 Bragg angle ratio. That is, the scattering at *E* is twice the period of *C*, which is additional evidence for an alternating arrangement of the molecules within the columns through charge transfer interactions and intermolecular hydrogen bonds as assumed in [14].

Miscibility experiments with the tetrone **III** and the phenylhydrazone **IV** were carried out by the contact method, as well as with mixtures with specific concentra-

tions. The contact method proved the complete miscibility between the two liquid crystalline hexagonal columnar phases. The mosaic texture of the columnar hexagonal phase was observed in the whole contact zone. The binary system (see figure 8) was investigated by DSC, X-ray and optical methods. Mixtures in the middle concentration
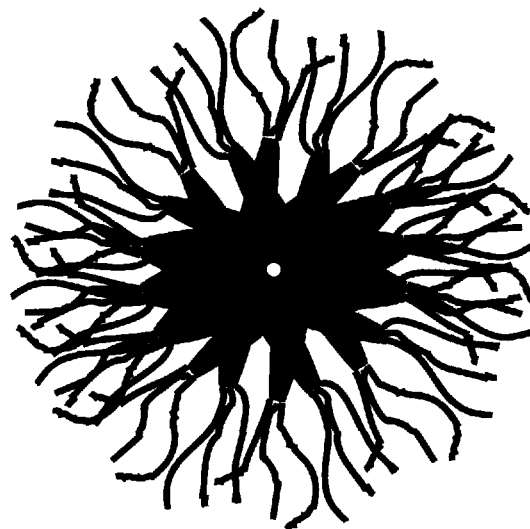

Figure 3.   Assumed arrangement of the molecules of **III** within a column.

Figure 4.   Temperature dependence of the innner reflection (very strong intensity) on the Coolong mode.

Table 2.   Bragg angles (Θ_{exp}), measured (d_{exp}) and calculated (d_{calc}) d-values of **III** at 70°C (film method).

Θ_{exp}/degree	d_{exp}/nm	Intensity	Indices	d_{calc}/nm
1·50	2·94	Very strong	(20), (11)	—
2·55	1·72	Strong	(02)	—
3·00	1·47	Weak	(40), (22)	1·48
3·44	1·30	Very weak	(32)	1·29
3·94	1·12	Very weak	(13)	1·12
4·44	0·99	Very weak	(33)	0·99
4·88	0·90	Very weak	(43)	0·90
5·38	0·82	Very weak	(24)	0·82
5·94	0·74	Very weak	(44)	0·74
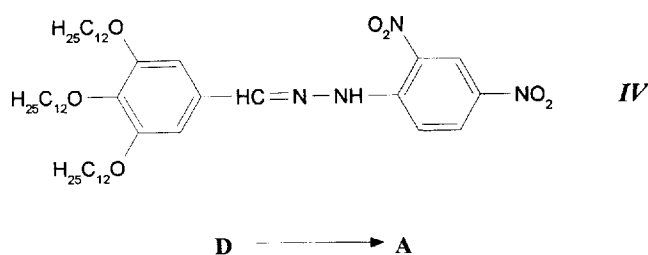
Figure 5. Phenylhydrazone **IV** (Cr 97°C D$_h$ 137°C I);
D = donor, A = acceptor moiety.

Figure 7. Fit of the diffuse wide angle scatterings of compound
IV at 120°C.

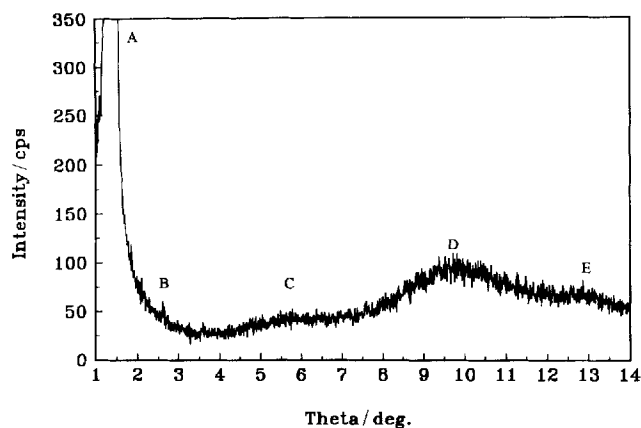Figure 6. Diffraction pattern of **IV** at 120°C.
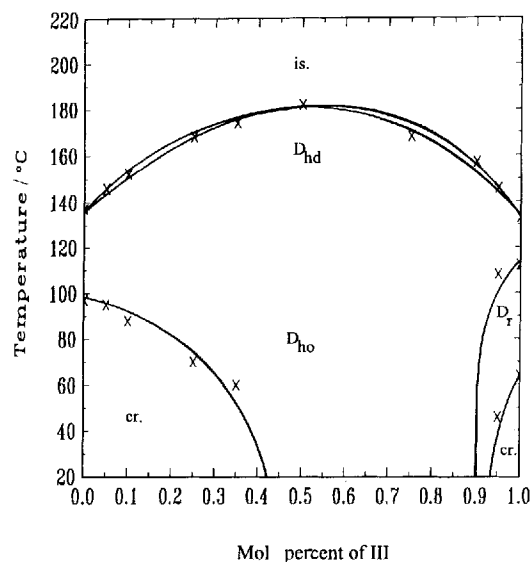
Figure 8. Phase diagram for mixtures of compounds **III**
and **IV**.

range showed an enhanced stability of the liquid crystal-
line phase. The temperature range of the phase was
extended from room temperature up to 180°C. The mosaic
texture of **M50** (concentration 50 mol%) at room tempera-
ture is shown in figure 9. Preliminary IR measurements
have shown that the spectrum of the mixture is quite
different from the spectra of the pure compounds. The
intensities of the CO– as well as those of the NH-vibrations
are essentially reduced in the mixture. This leads one to
suppose that the molecules of both compounds **III** and **IV**
are statistically incorporated in one and the same column.
Further investigations of this special feature are under way
and shall be reported elsewhere.

The diffraction patterns at room temperature and at
100°C of **M50** are shown in figure 10. Both diffraction
patterns show two sharp reflections in the small angle
range. Two diffuse scattering regions can be observed in
the wide angle range at room temperature, whereas only
one region of diffuse scattering exists above 100°C. The
reflections (100) and (110) again relate as 1 : √3, proving
the columnar hexagonal lattice.

Monodomains of different orientations were obtained
by slowly cooling samples of mixtures in glass capillaries.
The X-ray beam can be directed perpendicular to the
column axes (see figure 11 (*a*)) or in such a way that
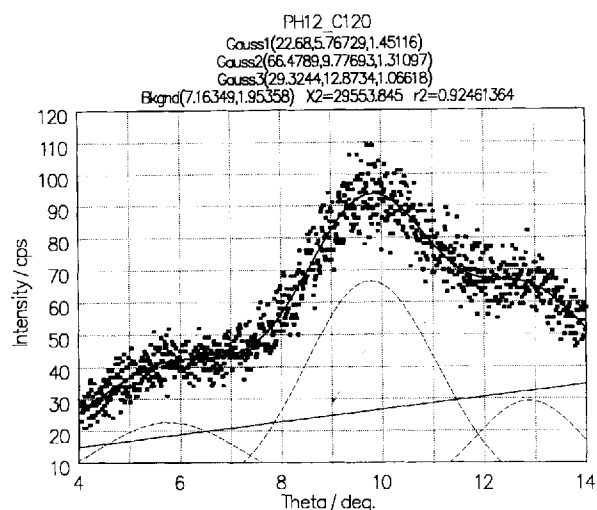the column axes are parallel to the beam (see figure 11 (*b*)).

The latter measurements clearly show the six-fold symme-
try of the lattice. The oriented samples produce four inner
reflections at the equator and different diffuse scatterings
(see table 3). The two outer scattering correspond to the
alkyl chains and to the intracolumnar scattering. An
explanation of the 4 maxima of additional scattering
observed around $\Theta = 5.9°$ between equator and meridian,
cannot be given at present. The increased temperature
range of the columnar hexagonal phase in **M50** offers the
opportunity of studying the scattering related to the
intracolumnar periodicity, which disappears at higher
temperatures. The loss of scattering intensity in this peak
occurs gradually over the range of temperature studied.
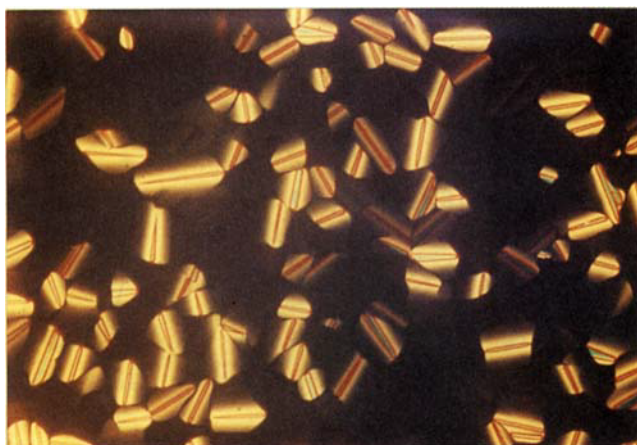Evaluation of the scattering profile via a peak-fit program

Figure 9. Mosaic texture of **M50** observed by optical microscopy at room temperature.
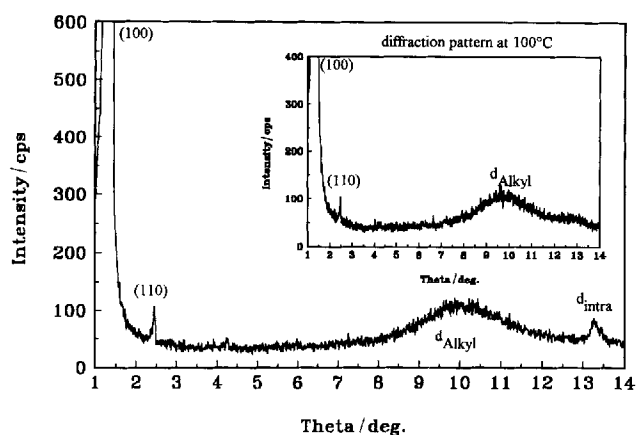

Figure 10. Diffraction pattern of the mixture **M50** at room temperature and 100°C.

Figure 11. Flat camera diffraction pattern of oriented sample of **M50** at room temperature. X-ray beam directed (*a*) perpendicular and (*b*) parallel to the column axes.

Table 3. Reflections observed by flat film camera ($\Theta_{exp.}$ and $d_{exp.}$, measured Bragg angles and distances, respectively; $\Theta_{calc.}$, calculated Bragg angles).

Θ_{exp}/degree	d_{exp}/nm	Indices	Θ_{calc}/degree
1·42	3·11	100	—
2·42	1·82	110	2·45
3·78	1·17	210	3·76
4·29	1·03	300	4·26
5·95	0·74	?	—
10·32	0·43	d_{Alkyl}	—
13·29	0·32	d_{intra}	—

also shows a continuous decrease of the correlation within the columns (see figure 12). This continuous gradual change from a so-called 'D_{ho}' to a 'D_{hd} pattern' implies that both phases belong to one and the same phase type and that there is only a gradually changing difference in the packing of the molecules within the columns.

4. Experimental

4.1. *Experimental*

The thermal analysis of phase behaviour was carried out using a Perkin–Elmer DSC-7. A Leitz LUX 12 POL S polarizing microscope equipped with a Linkam TP 600 hot stage was used to observe and to characterize the textures of the liquid crystalline phases of the tetrone compounds and of the mixtures with the phenylhydrazone. The X-ray studies (CuK$_\alpha$ radiation, $\lambda = 0.154$ nm) of the mesophases were performed using a Guiner goniometer (Huber G644, Germany) and a Guinier film camera for the non-oriented samples and a flat camera for the oriented samples. The
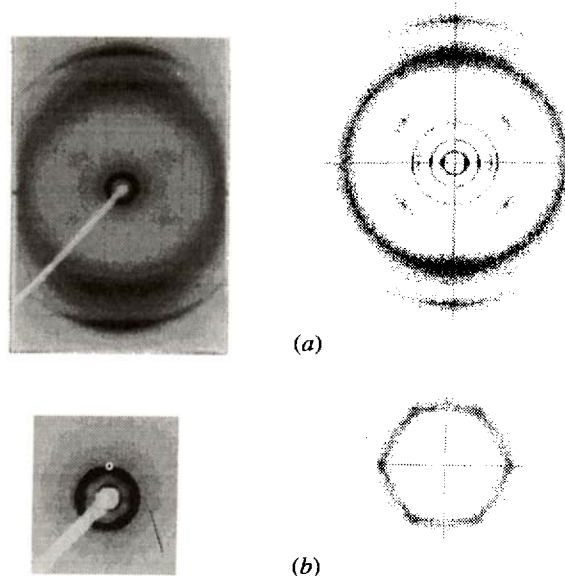
samples were molten in glass capillaries with diameters of 0·7 and 1 mm. The sample temperature was controlled by a Huber temperature device HYC 9634 (Guinier-Goniometer/film camera) or by a home made oven (flat camera) in conjunction with a temperature controller Eurotherm-Model 91. IR measurements were performed using a Bruker IFS25.

4.2. *Preparation of 3,7-(4,4'-di*(N,N-*dihexadecyl)-aminobenzylidene)-1,5-diazabicyclo[3,3,0]octan-2,4,6,8-tetraone*

1 g of 1,5-diazabicyclo[3,3,0]octan-2,4,6,8-tetrone and 2·6 g of 4-*N,N*-dihexadecylaminobenzaldehyde were mixed in 100 ml of *N,N*-dimethylformamide and heated for 2 h at 90°C. After cooling the red precipitate was filtered off and recrystalized twice from *N,N*-dimethyl-formamide. Yield: 2·0 g; Cr 54°C Cr 118°C I.
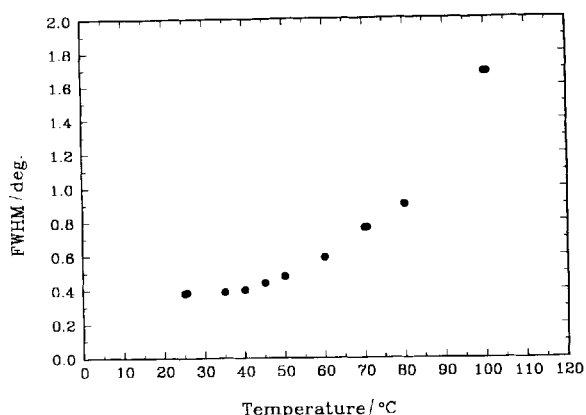
Figure 12.　Temperature dependence of the full width at half maximum of the intracolumnar scattering of the mixture **M50**.

4.3.　Preparation of 3,7-(4,4'-di(N,N-dioctadecyl)amino-benzylidene)-1,5-diazabicyclo[3,3,0]octan-2,4,6,8-tetraone

1 g of 1,5-diazabicyclo[3,3,0]octan-2,4,6,8-tetraone and 2·8 g of 4-N,N-dioctadecylaminobenzaldehyde were mixed in 100 ml of N,N-dimethylformamide and heated for 2 h at 90°C. After cooling the red precipitate was filtered off and recrystallized twice from N,N-dimethylformamide. Yield: 2·5 g; Cr 116°C S_C 143°C I.

4.4.　Preparation of 3,7-(3,4,5,3',4',5'-di(trido-decyloxybenzylidene)-1,5-diazabicyclo[3,3,0]octan-2,4,6,8-tetraone

1 g of 1,5-diazabicyclo-[3,3,0]octan-2,4,6,8-tetraone and 3 g of 3,4,5-triodecyloxybenzaldehyde were mixed in 100 ml of N,N-dimethylformamide and heated for 2 h at 90°C. After cooling, the orange precipitate was filtered off and twice recrystallized from N,N-dimethylformamide. Yield: 2·1 g; Cr 64°C D_r 112°C D_h 133°C I.

5.　Analysis

All NMR measurements were done using CDCl₃ and solvent.

3,7-(4,4'-Di(N,N-dihexadecyl)aminobenzylidene)-1,5-diazabicyclo[3,3,0]octan-2,4,6,8-tetraone (**I**)

C₈₄H₁₄₂N₄O₄, (MW 1270): calculated C, 79·3; H, 11·2; N, 4·4; found C,79·7; H, 11·7; N, 4·5 per cent.

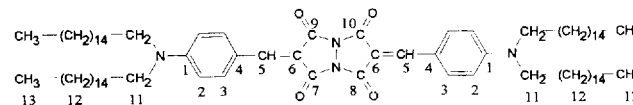*3,7-(4,4'-Di(N,N-dioctadecyl)aminobenzylidene)-1,5-di-azabicyclo[3,3,0]octan-2,4,6,8-tetraone* (**II**)

C₉₂H₁₅₈N₄O₄, (MW 1382): calculated C, 79·8; H, 11·5; N, 4·0; found C, 79·9; H, 12·3; N, 4·2 per cent.

¹H NMR of substance **I**:
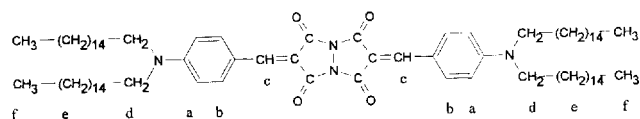
(*a*) 6·65 ppm, (*b*) 8·45 ppm, (*c*) 7·75 ppm, (*d*) 3·35 ppm, (*e*) 1·1–1·7 ppm, (*f*) 0·95 ppm.

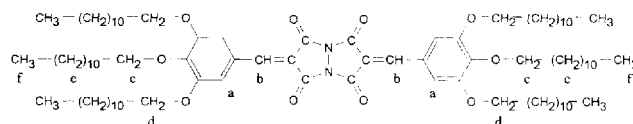### ¹³C NMR (CDCl₃) of substance **I**:

(1) 154 ppm, (2) 112 ppm, (3) 140 ppm, (4) 121 ppm, (5) 154 ppm, (6) 109 ppm, (7), (8), (9), (10) 158 ppm, 158 ppm, 156 ppm, 156 ppm, (11) 51 ppm, (12) 27–32 ppm, (13) 14 ppm.

¹H and ¹³C NMR (CDCl₃) data for compound **II** are analogous to those for compound **I**.

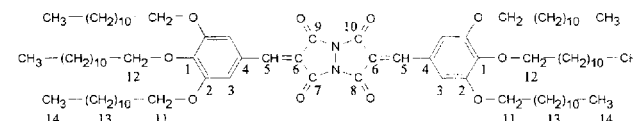*3,7-(3,4,5,3',4',5'-Di(tridodecyloxybenzylidene)-1,5-di-azabicyclo[3,3,0]octan-2,4,6,8-tetraone* (**III**)

C₉₂H₁₅₆N₂O₁₀, (MW 1448): calculated C, 79·8; H, 11·5; N, 4·1; found C,79·9; H11·8; N, 4·3 per cent.

¹H NMR of substance **III**:

(*a*) 7·90 ppm, (*b*) 8·00 ppm, (*c*) 4·20 ppm, (*d*) 4·05 ppm, (*e*) 1·1–1·9 ppm, (*f*) 0·85 ppm.

¹³C NMR of substance **III**:

(1) 128 ppm, (2) 147 ppm, (3) 115 ppm, (4) 115 ppm, (5) 158 ppm, (6) 153 ppm, (7), (8), (9), (10) 157 ppm, 156 ppm, 155 ppm, 154 ppm, (11) 69 ppm, (12) 74 ppm, (13) 26–32 ppm, (14) 14 ppm.

6.　Summary

The results discussed prove the known feature that polycatenar compounds with four terminal chains mostly form smectic phases. Whereas one double swallow tailed compound exhibits only crystalline phases, the other forms a smectic phase (S_C); the packing in a tilted structure prevents the formation of gaps in the layer. By way of contrast the compound with six chains produces two columnar phases with a D_h and D_r structure. In spite of the

chemical similarities between compounds **II** and **III**, complete miscibility between the two could not be observed. However complete miscibility of the two hexagonal columnar mesophases, with an enhanced stability of the phase, has been observed in mixtures of the hexacatenar tetrone (**III**) and the semi-disoid phenylhydrazone (**IV**). Furthermore a continuous transition of disordered 'D$_{hd}$ phase' at high temperature to ordered 'D$_{ho}$ phase' at low temperature has been proved for several mixtures by X-ray measurements. These results imply, that the D$_{hd}$ and D$_{ho}$ phases belong to one and the same columnar mesophase type.

References

[1] CHANDRASEKHAR, S., and RANGANATH, G. S., 1991, *Rep. Prog. Phys.*, **53**, 57.

[2] CHANDRASEKHAR, S., 1991, *Liq. Crystals*, **14**, 3.

[3] DEMUS, D., DIELE, S., GRANDE, S., and SACKMAN, H., 1983, *Adv. Liq. Crystals*, **6**, 1.

[4] DESTRADE, C., GASPAROUX, H., Tinh, N. H., MALTHETE, J., and JACQUES, J., 1983, *J. Chem. Phys.*, **80**, 137.

[5] DESTRADE, C., FOUCHER, P., GASPAROUZ, H., TINH, N. H., LEVELUT, A. M., and MALTHETE, J., 1984, *Molec. Crystals liq. Crystals*, **106**, 121.

[6] RINGSDORF, H., TSCHIRNER, P., SCHÖNHERR, O. H., and WENDORFF, J. H., 1987, *Makromolek. Chem.*, **188**, 1431.

[7] MALTHETE, J., TINH, N. H., and DESTRADE, C., 1993, *Liq. Crystals*, **13**, 2.

[8] MALTHETE, J., LEVELUT, A. M., and TINH, N. H., 1985, *J. Phys. Lett., Paris*, **46**, L–875.

[9] LEVELUT, A. M., MALTHETE, J., DESTRADE, C., and TINH, N. H., 1987, *Liq. Crystals*, **2**, 877.

[10] MALTHETE, J., COLLET, A., and LEVELUT, A. M., 1989, *Liq. Crystals*, **5**, 123.

[11] LIN, C., Ringsdorff, H., Ebert, M., Kleppinger, R., and WENDORFF, J. H., 1989, *Liq. Crystals*, **5**, 1841.

[12] TINH, N. H., DESTRADE, C., LEVELUT, A. M., and MALTHETE, J., 1990, *Liq. Crystals*, **8**, 797.

[13] BEGINN, U., LATTERMANN, G., FESTAG, R., and WENDORFF, J. H., 1993, *22. Freiburger Arbeitstagung Flüssigkristalle*.

[14] PAULUS, W., RINGSDORF, H., DIELE, S., and PELZL, G., 1991, *Liq. Crystals*, **9**, 807.

[15] VOIGT-MARTIN, I. G., SIMON, P., ZHON, E., GARBWLLA, R. W., PAULUS, W., and RINGSDORF, H., 1992, 232. Freiburger Arbeitstagung Flüssigkristalle.

[16] VOIGT-MARTIN I. G., ZHON, E., SIMON, P., GARBELLA, R. W., YAN, D., PAULUS, W., and RINGSDORF, H., 1993, *Adv. Mater Opt. Electron.*, **2**, 245.

[17] KITAIGORODSKI, A. I., 1979 (Akademie Verlag).

[18] COTRAIT, M., MARSAU, P., PESQUER, M., and VOLPHILHAC, V., 1982, *J. Phys. Paris*, **43**, 355.

[19] RINGSDORF, H., WÜSTEFELD, R., ZERTA, E., EBERT, M., and WENDORFF, J. H., 1989, *Angew. Chem.*, **101**, 934.