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Liquid Crystals

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The homologous series of some new six-ring double-swallow-tailed compounds

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A Knoevenagel condensation of the appropriate dialkyl malonate **1** and terephthalaldehydic acid **2** in the presence of piperidine acetate produced the 4-[2,2-bis(alkyloxycarbonyl)ethenyl]benzoic acids **3**. Water formed in the reaction was collected by a water separator. The terminally branched benzoic acids were recrystallized from methanol. Reaction with thionyl chloride yielded the acid chlorides which were esterified with 4-hydroxybenzaldehyde **4** in toluene with triethylamine as base. The 4-formylphenyl 4-[2,2-bis(alkyloxycarbonyl)ethenyl]benzoates **5** can be purified by recrystallization from methanol. The final products **7** ($n=8-14, 16$) were prepared by condensation of 1,2-(4,4'-diaminodiphenyl)ethane **6** with the formyl derivatives **5** by heating under reflux in ethanol under nitrogen. Toluene-*p*-sulphonic acid served as catalyst. After cooling, the precipitates were separated off and recrystallized at least twice from dimethylformamide.

3. Experimental

The phase transition temperatures were determined by calorimetry using a DSC 7 (Perkin-Elmer). The mesophase textures were analysed using a polarizing microscope equipped with a heating and cooling stage. Structural investigations were also performed by X-ray diffraction using the Guinier method.

4. Results

In table 1 the phase behaviour and the transition temperatures of the homologous compounds are presented. The transition enthalpies (in kJ mol^{-1}) are also listed in brackets below the transition temperatures. In figure 1 the phase diagram of the homologous series is shown where the transition temperatures are plotted against the carbon number n of the terminal alkyl chains.

It follows from table 1 and figure 1 that the lower homologues ($n=8-11$) exhibit nematic and smectic C phases. Members with relatively long terminal chains ($n=12-16$) possess columnar mesophases. For the dodecyloxy, tridecyloxy and tetradecyloxy homologues, the interesting situation is observed that both lamellar (smectic C) and columnar (D_{ob}) phases occur for the same substance. But for the tetradecyloxy homologue, the smectic C phase occurs only on cooling the isotropic liquid. It should be mentioned that in this homologous series, the smectic C phase is the high temperature phase with respect to the columnar phase, in contrast to some biforked tetracatenar compounds [3, 4]. Whereas the smectic C phase exhibits a schlieren texture, the texture of the columnar phase reminds one of a fan-shaped texture (see figure 3). As already shown [7] for the dodecyloxy homologue, the unusual phase sequence S_C

Table 1. Transition temperatures in $^{\circ}\text{C}$ and transition enthalpies in kJ mol^{-1} (in parentheses).

$R = C_nH_{2n+1}$

Compound	n	Mesophases									
DS8	8	Cr	–	–	89	S_C	191	N	276	I	
					(24·24)		(1·06)		(–) ^a		
DS9	9	Cr	–	–	91	S_C	197	N	245	I	
					(45·67)		(2·10)		(1·08)		
DS10	10	Cr	–	–	104	S_C	194	N	229	I	
					(52·33)		(2·38)		(0·73)		
DS11	11	Cr	–	–	106	S_C	189	N	219	I	
					(52·12)		(2·47)		(0·39)		
DS12	12	Cr	95	$S_{C(\text{tre})}$	117	D_{ob}	154	S_C	187	N	209
			(54·41)		(0·20)		(0·40)		(2·43)		(0·30)
DS13	13	Cr	–	–	102	D_{ob}	175	S_C	–	184	I
					(101·95)		(1·97)			(2·58)	
DS14	14	Cr	–	–	101	D_{ob}	– ^b	–	180 ^b	I	
					(87·12)				(4·83)		
DS16	16	Cr	–	–	104	D_{ob}	–	–	178	I	
					(101·81)				(5·41)		

Cr=solid crystal; S_C =smectic C; I=isotropic liquid; D_{ob} =oblique columnar phase; N=nematic.

^a The transition enthalpy could not be detected because of partial decomposition of the substance.

^b On cooling the isotropic liquid, a smectic C phase appears which is transformed into the D_{ob} phase at 175°C .

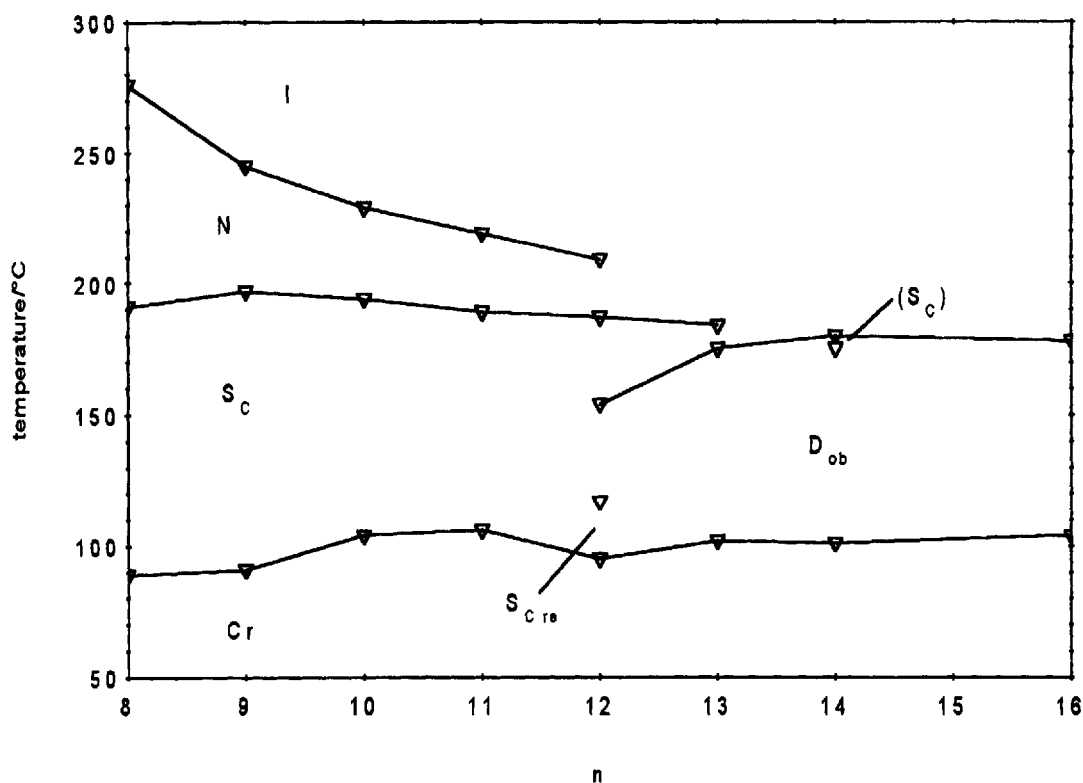


Figure 1. Transition temperatures and phase behaviour as a function of the lengths of the terminal chains ($n=8\text{--}14, 16$).

$D_{ob} S_C N$ was found with increasing temperature, meaning that, on cooling the columnar phase, a re-entrant smectic C phase appears. These phase transitions

could be clearly observed by microscopy, as well as by calorimetry and during X-ray studies [7].

For some representative members of the series, the

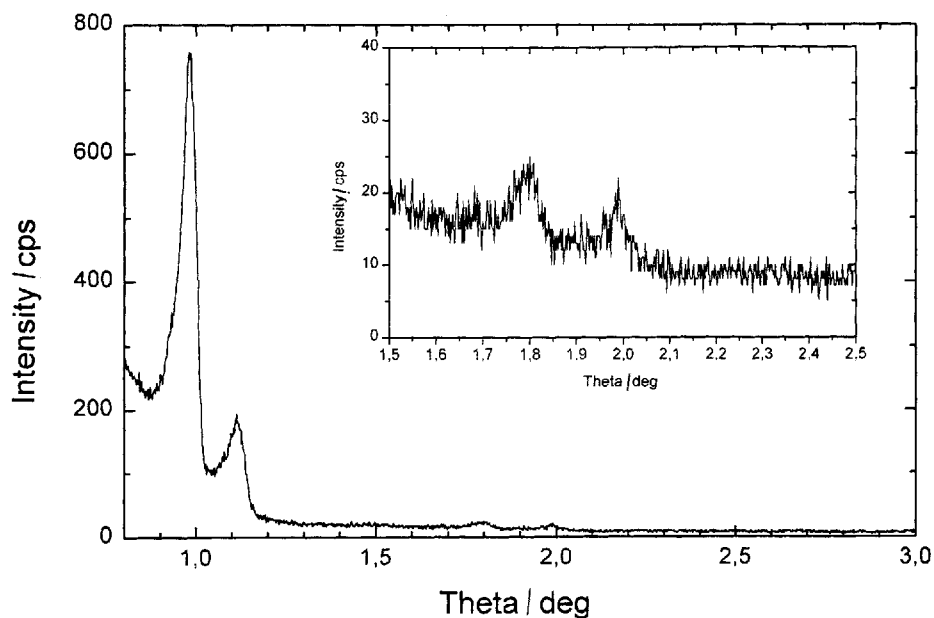


Figure 2. X-ray diffraction pattern of the D_{ob} phase of compound DS16 ($\theta=120^{\circ}\text{C}$). The inset displays the scattering profile of the curve between $1.5^{\circ} \leq \theta \leq 2.5^{\circ}$ on an enlarged scale.

liquid crystalline phases were characterized by X-ray investigations. For example, for the smectic C phase of the octyloxy homologue, a layer period d of 39.4 Å was measured, whereas the molecular length for the most extended conformation is 66 Å. The X-ray patterns of the columnar mesophases show a diffuse scattering in the wide angle region at about 10° , corresponding to the average distance between the alkyl chains and the

aromatic cores. In addition, there are four sharp reflections in the small angle region which can be related to a two-dimensional oblique lattice of columns. As an example, figure 2 shows the X-ray diffraction pattern of the D_{ob} phase of compound DS16 obtained by the Guinier method. The positions of the interferences in the patterns of the investigated homologues are definitely not compatible with a two-dimensional hexagonal or rectangular cell. Therefore the patterns have been evaluated on the basis of an oblique cell, for which the resulting lattice parameters are presented in table 2.

Figure 4 shows the broken fan-shaped texture of the metastable smectic C phase of compound DS14 which exists only on cooling the isotropic liquid. In this case

Table 2. Lattice parameters of the D_{ob} phase of homologues with $n=13$ and 16.

n	$a/\text{Å}$	$b/\text{Å}$	$\gamma/^\circ$
13	42.5	38.5	112.5
16	51.4	45.3	118

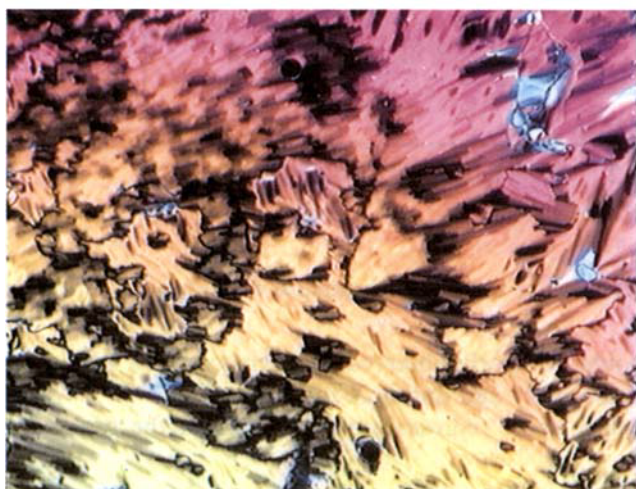


Figure 3. Texture of the oblique columnar phase of compound DS13 at 169°C (magnification: 100 ×).



Figure 5. Texture of the oblique columnar phase of compound DS14 at 174°C (magnification: 100 ×, the same sector as in figure 3).

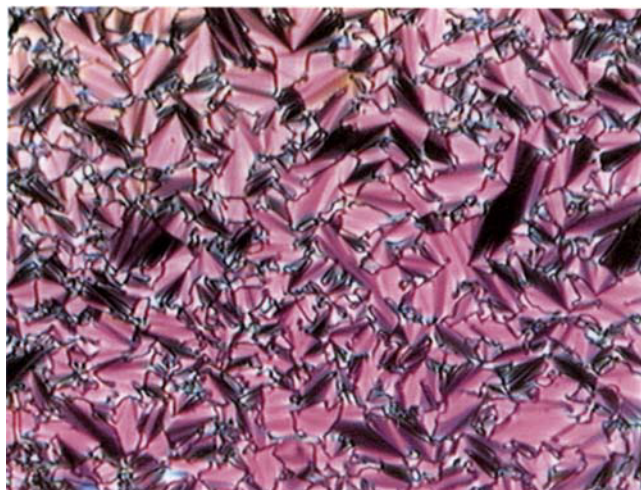


Figure 4. Broken fan-shaped texture of the smectic C phase of compound DS14 at 179°C (magnification: 100 ×).



Figure 6. Mosaic texture of the oblique columnar phase of compound DS16 at 173°C (magnification: 100 ×).

the oblique columnar phase arises as a paramorphotic texture which reminds one of the preceding smectic C texture (figure 5). It is remarkable that contrary to the homologues DS12–DS14, the oblique columnar phase of the DS16 homologue exhibits a mosaic texture (figure 6). It was found that both oblique columnar phases are not completely miscible, but X-ray studies give no hints of clear structural differences.

It is impossible to obtain more detailed structural information because the columnar mesophases could not be oriented homogeneously. According to references [3, 8], the X-ray data can be interpreted by a model where three polycatenar molecules are associated into disc-like clusters which are stacked one over another. The columns are arranged in a two-dimensional oblique lattice. Contrary to the corresponding tetracatenar compounds, in the series of biforked compounds [3] the columnar phase is the low temperature phase with respect to the smectic C phase. Further comparative structural investigations are necessary to find the origin of this different behaviour.

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