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X-ray studies of liquid-crystalline phases of polycatenar substances Evidence for a rectangular columnar structure

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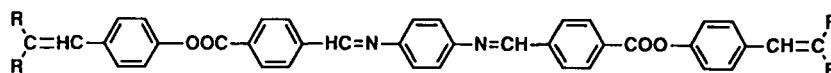
The liquid-crystalline phases of two series of bi-swallow tailed compounds have been investigated using textural observations and X-ray studies. Besides nematic and smectic phases a new phase type has been observed. This is characterized by a rectangular columnar structure.

1. Introduction

In the past 10 years new types of liquid-crystalline structures with columnar building units have been found by the variation of the chemical architecture. In the class of discotic compounds the columns can be approximated by cylinders with circular cross sections caused by the shape of the flat molecules. [1]. In addition polycatenar compounds [2] with a flat lath-like shape have been synthesized which also exhibit columnar liquid-crystalline structures. The term phasmidic has been introduced for substances with a rod-like aromatic core with six long aliphatic chains [3].

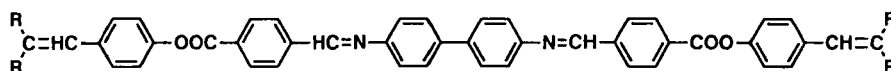
Here the structures of the liquid-crystalline phases observed in bi-swallow tailed compounds with the following structural formulas are discussed:

Series I 5BS_n



R: H_{2n+1}C_nOOC- n: 7, 10, 11, 12, 16

Series II 6BS_n



R: H_{2n+1}C_nOOC- n: 7, 10, 11, 12, 16

2. Results

The optical textures prove clearly the existence of nematic and smectic C phases in both series. Figures 1 and 2 show the transition points of the series as a function of the number of carbon atoms in the chains. The texture of the nematic

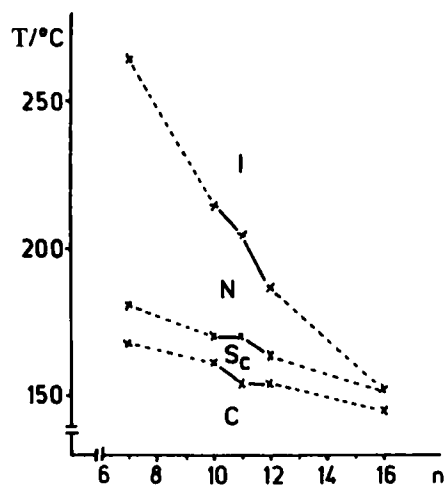


Figure 1. Transition temperatures of series I as a function of the chain length.

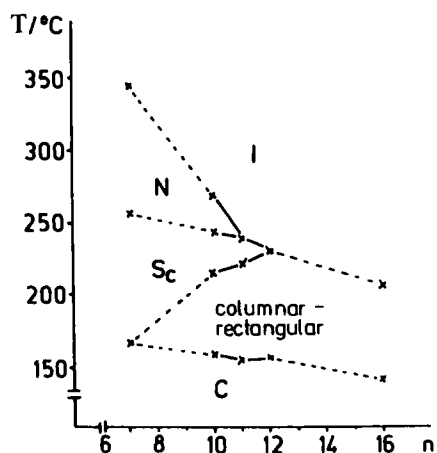


Figure 2. Transition temperatures of series II as a function of the chain length.

phases are characterized by a schlieren texture whereas the smectic C phases appear as schlieren or broken fan shaped textures. Additionally, in series II a phase is generated below the smectic C phase the texture of which is similar to that described in discotic systems. Miscibility studies between the homologues of series I and series II have shown the complete miscibility of the smectic C phases of both series. However, all attempts to find complete miscibility between the smectic C phases of classical rod-like compounds with the smectic C phases of both new series failed. This result is different from miscibility studies between bi-forked and rod-like compounds [6].

Figure 3 gives an X-ray pattern of an oriented sample in the nematic phase. It clearly indicates the existence of skewed cybotactic groups. The four diffuse maxima in the small angle region condense to Bragg spots at the transition into the smectic C phase. The component q_z of the scattering vector allows us to estimate the length L' of the building units of the cybotactic groups. It can be seen in figure 4 that L' nearly agrees with L (where L is the length of the molecules in their most stretched

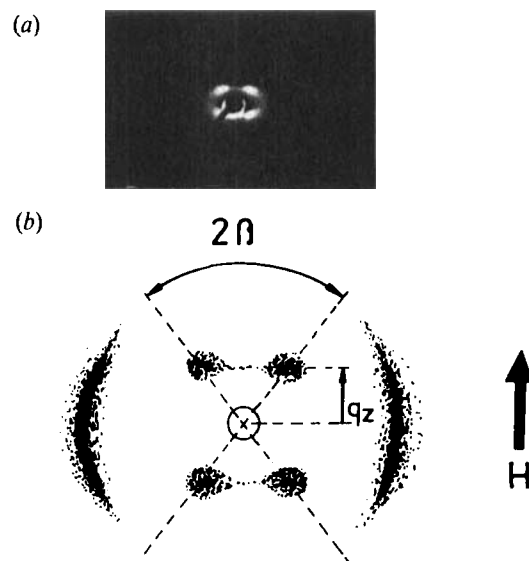


Figure 3. (a) X-ray pattern of an oriented sample in the nematic phase of compound 5BS10. (b) Schematic representation of (a). H shows the directions of the aligning magnetic field.

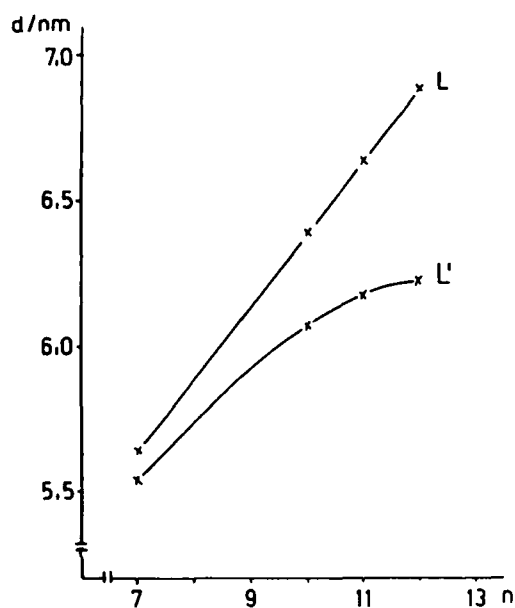


Figure 4. Molecular lengths and lengths of the building units in the cybotactic groups.

shape obtained by CPK models) for the heptyl homologue of series I. With increasing chain length an increasing difference is observed which is explained by the deviation of the chains from their most stretched conformation. Figure 5 shows the temperature dependence of the d values in the smectic C phase of series I. Because of the thermal decomposition of the samples the measurement could not be extended to higher temperatures. Table 1 contains the tilt angles, β , of the molecules in the cybotactic groups (nematic phase near the S_C -H transition) and in the smectic layers in the

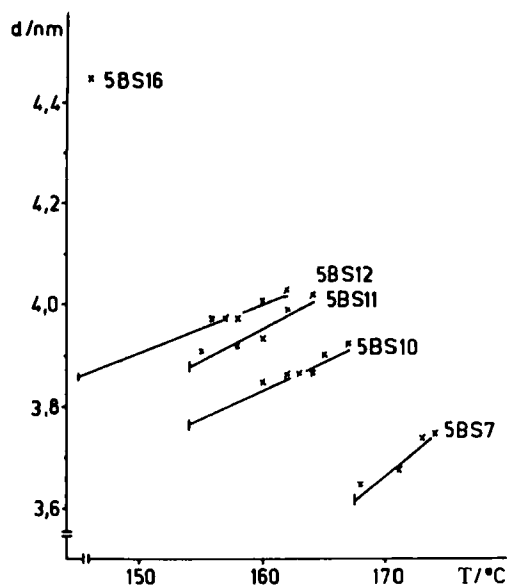


Figure 5. The layer thickness in the smectic C phase in series I as a function of temperature.

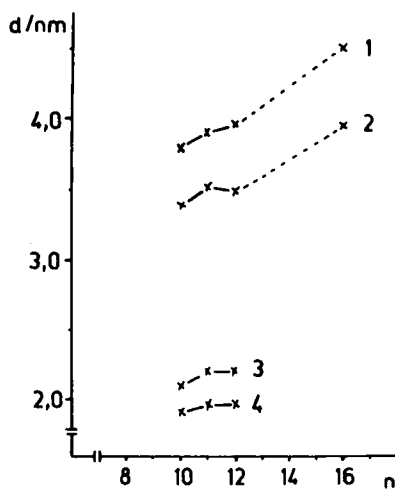


Figure 6. The d values of the observed small angle reflections in the columnar phase.

Table 1. Tilt angles in the, β , nematic and smectic C phases.

	5BS7	5BS10	5BS11	5BS12
N	48°	51°	52°	51°
S _C	47°	50°	50°	50°

Table 2. Observed reflections in the columnar phases and the calculated lattice parameters.

	$\theta/^\circ$	hkl	a/nm	b/nm	L/nm
6BS10	1.16	110	6.78	4.59	6.8
	1.30	200			
	2.10	120			
	2.32	220			
6BS11	1.13	110	7.06	4.71	7.1
	1.25	200			
	2.00	120			
	2.25	220			
6BS12	1.11	110	6.99	4.82	7.3
	1.27	200			
	2.00	120			
	2.24	220			
6BS16	0.98	110	7.92	5.51	8.3
	1.12	200			

smectic C phase. The former angle has been measured from the patterns of oriented samples whereas the latter angle has been calculated from $\cos^{-1} L'/L$ with the assumption that the conformation of the molecules is nearly the same in both phases. The high transition temperatures have prevented similar investigations for the compounds of series II.

The X-ray patterns of the additional phase in series II are characterized by four sharp reflections in the small angle region and a diffuse scattering in the wide angle region. ($\theta_{\text{max}} = 10.4^\circ$). Figure 6 shows the position of the reflections as a function of the chain length. The ratios of the Bragg angles (e.g. $\theta_1:\theta_2:\theta_3:\theta_4 = 1:1.12:1.81:2.00$) clearly eliminates the interpretation of the structure in terms of a lamellar or hexagonal one. However, it is possible to explain the observed reflections on the basis of a two dimensional rectangular cell as shown in table 2. The lattice parameters a agree well with the lengths L of the molecules.

3. Discussion

Whereas the smectic C phases under discussion exhibit conventional lamellar structures, the structure of the additional phase must be columnar. With respect to the molecular shape it has been derived from the class of polycatenar compounds. Malthête *et al.* [3] have synthesized phasmidic compounds as a special case of polycatenar materials. They found two types of structure: a hexagonal (Φ_h) and an oblique phase (Φ_{obl}). The phase under discussion represents another structural type namely a rectangular columnar structure. Series II is a further example in which the transition from a columnar phase into a lamellar structure can be observed with increasing temperature [4]. Because of the relatively small number of X-ray reflections in unoriented samples the elaboration of the structure at a molecular level is precarious. The difficulties arising in the interpretation have been pointed out [5].

The condition of dense packing should be fulfilled by the model. On the basis of this presumption a model shown in figure 7 is proposed. Several molecules (six or seven, if a density of 1 g/cm^3 is assumed) are packed side by side (see figure 7(a)) to form the lattice unit (see figure 7(b)). The hatched regions indicate the aromatic

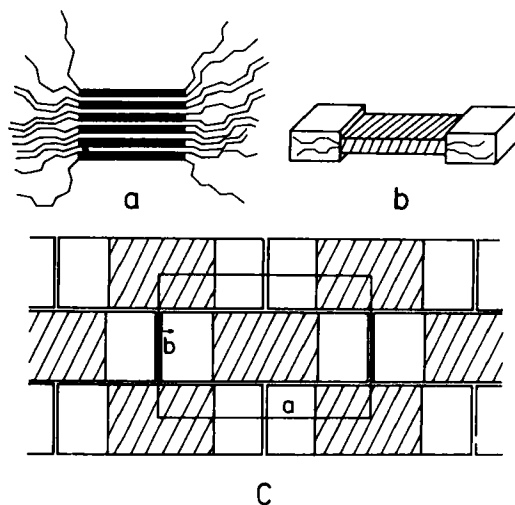


Figure 7. The proposed structural model of the columnar phase; the hatched areas indicate the aromatic moiety.

moiety which requires less space than the aliphatic regions. These different moieties have been packed alternately leading to a two dimensional centred cell (see figure 7(c)). In this way the lattice parameter a can be explained by the length of the molecules. The gaps caused by the small waist (aromatic moieties) can be filled by the aliphatic chains of adjacent regions. Experimental hints for the kind of packing of the units within the columns could not be found.

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