Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Norvez, S. and Simon, J.(1993) 'Epitaxygens: mesomorphic properties of triptycene derivatives', Liquid Crystals, 14: 5, 1389 — 1395

To link to this Article: DOI: 10.1080/02678299308026451

URL: http://dx.doi.org/10.1080/02678299308026451

LIQUID CRYSTALS, 1993, VOL. 14, NO. 5, 1389–1395

Epitaxygens: mesomorphic properties of triptycene derivatives

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The structure of mesophases derived from a triptycene subunit substituted with five paraffinic chains has been determined by X-ray diffraction at small angles. They all show a smectic ordering. This is the first example of a smectogen whose rigid core belongs to the D_{3h} symmetry. A hexagonal order has been observed in the X-ray diffraction patterns; it has been associated with a p31m packing of the rigid cores within the layers. The intralamellar cell parameter is in agreement with the molecular dimensions determined from CPK models. The calculated molecular length is in accordance with the experimental interlamellar distance. The difference in mesomorphic behaviour between the five and six chain derivatives is discussed.

1. Introduction

Conventional smectic phases are formed from oblong molecules, whose molecular cross-section within the layer is often drawn as an ellipse. This shape leads to various types of ordered and disordered smectic phases. We used the triptycene subunit as a rigid core to synthesize a new class of smectic liquid crystals. Due to the peculiar shape of triptycene, an intralamellar ^{2}D-organization was expected (see figure 1).

Triptycene derivatives substituted with five or six long aliphatic chains have been synthesized, following a nine step chemical route already partially published [1]. A different mesomorphic behaviour between the six and five chain derivatives was noticed: the six chain derivatives lead only to highly ordered materials, whereas the five chain compound **I** (see figure 2) presents smectic mesophases.

X-ray characterizations have been carried out in order to determine the precise inter- and intra-lamellar structures of the materials.

2. Results and discussion

2.1. *Experimental section*

Calorimetric measurements have been performed with a Perkin–Elmer DSC7 differential calorimeter. Thermograms have been recorded at 10°C min^{-1}. The textures of the mesophases have been observed using a light polarized hot-stage microscope (Mettler FP 800). X-ray diffraction patterns have been recorded under vacuum, on flat films, with monochromatic (Cu-Kα) X-ray radiation. The samples were contained in Lindemann glass capillary tubes (1·0 mm diameter) and placed in a $\pm 0{\cdot}1$°C regulated oven.

2.2. *Results*

The six chain derivatives give a high number of reflections in their X-ray diffraction pattern, indicating their highly ordered nature. Large angular domains are moreover

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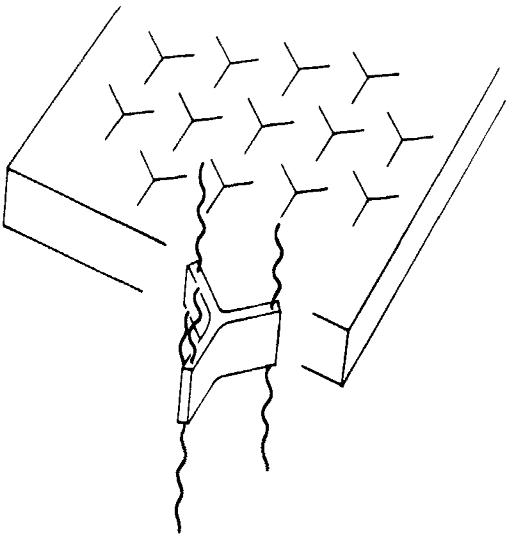
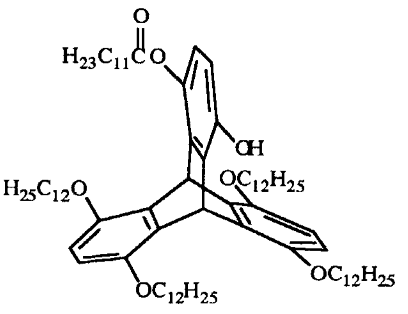


Figure 1. Lamellar organization of triptycene derivatives substituted with long aliphatic chains.



I

Figure 2. Triptycene derivative substituted with five chains of equal length (C_{12}).

observed by light polarized microscopy. No detailed assignments could be achieved. The mesomorphic properties of the five chain derivative can be more easily studied. The results concerning compound **I** are gathered in the table.

2.2.1. *Calorimetric measurements*

At least three mesophases are observed by differential scanning calorimetry (see figure 3). The peaks are poorly resolved, but reversible, with only small supercooling in all cases. Due to the small enthalpies observed for the first three transitions, it seems that, even at room temperature, a mesomorphic state is obtained.

2.2.2. *Polarized light microscopy*

When cooling the isotropic liquid down to 166°C, classical elongated bâtonnets of focal-conics appear; they subsequently coalesce in a fan shaped texture characteristic of a smectic A phase (see figure 4).

A homeotropic texture, with crown-like defects, has also been observed confirming the smectic A nature of the high temperature mesophase. Striations appear with

Table 1. Calorimetric measurements, microscopic observations and X-ray diffraction analysis for compound I. *T*, transition temperatures; Δ*H*, enthalpy of transition; *d*, interlamellar spacing; *a*, hexagonal cell parameter; FC, focal conic texture; (1), (2), (3), (4), at 20, 154, 159 and 166°C, respectively.

T/°C		39	156	163	168·8
Δ*H*/J g^{-1}		2–3	2–3	2–3	22·8
Texture	Fixed FC	Sanded FC	FC+ transition bars	FC+ homeotropic	Isotropic
d (lam)	35·3 Å (1)	31·5 Å (2)	30·8 Å (3)	30·0 Å (4)	—
a (hex)	8·0$_4$ Å	8·3 Å	8·3 Å	—	
	Diffuse peak	Halo	Halo	Halo	Halo
Chains	4·2$_8$ Å	4·5 Å	4·5 Å	4·5 Å	4·5 Å (+halo 24 Å)

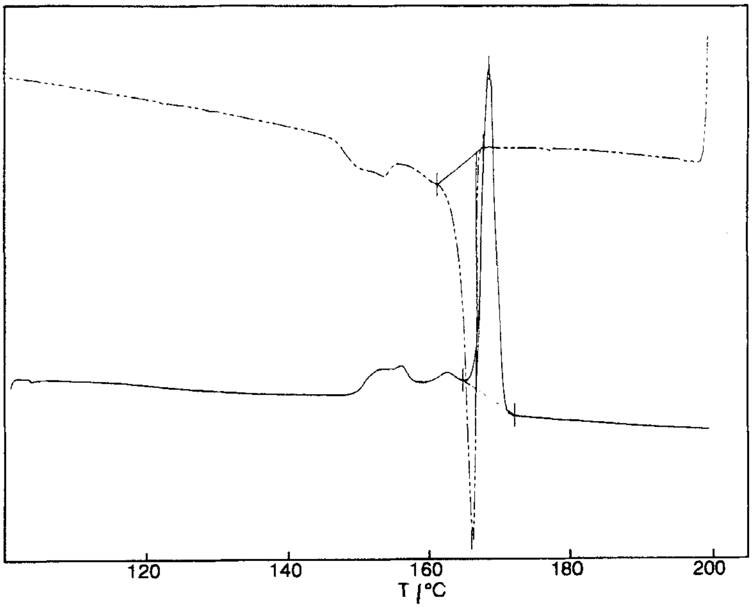


Figure 3. Thermogram of compound I at 10°C min^{-1}.

decreasing temperature; the fan-like texture becomes smooth, and then sanded. The material becomes highly viscous and the texture obtained is stable down to room temperature. No detectable crystallization occurs; this is in agreement with the DSC results.

2.2.3. *X-ray diffraction*

In the isotropic phase, the diffraction pattern shows two diffuse halos at around 4·5 and 24 Å. At 166°C, three peaks appear, whose spacings are characteristic of a lamellar phase, with an inter-reticular distance of 30·0 Å. A weak diffuse halo at small angles always remains. With decreasing temperature, the interlamellar distance increases; at

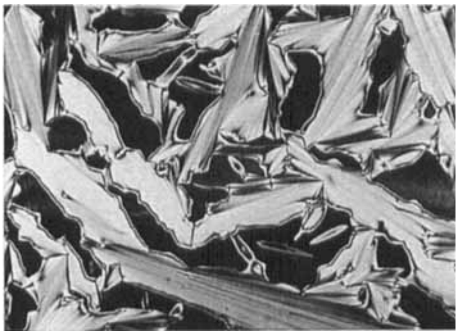


Figure 4. Photomicrograph at 166°C (smectic A phase of compound I) (crossed polarizers).

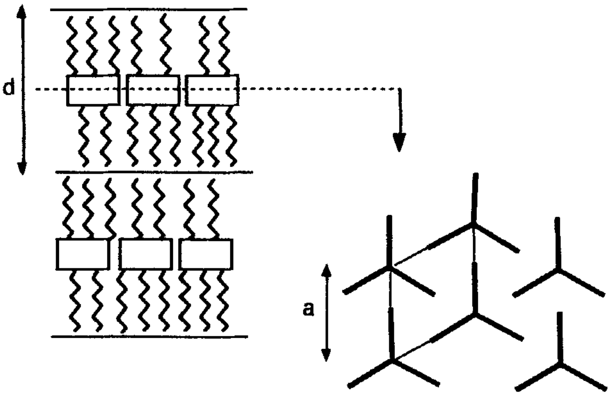


Figure 5. Model of the molecular packing. The rigid cores lead to an intralamellar hexagonal packing.

the same time a second series of peaks appears which may be assigned to a hexagonal structure. The halo associated with disordered chains is observed in all cases. At room temperature, this halo is transformed into a broad peak. When the interlamellar distance decreases, the hexagonal lattice expands (see the table).

2.3. *Structural model*

Figure 5 describes the model proposed for interpreting the X-ray diffraction data. The interlamellar spacing may be estimated from the molecular dimensions [2]. The length of the aliphatic tail has been estimated from Flory's work [3], and Tanford's calculations [4], adapted for thermotropic systems [2]. In this model, disordered aliphatic chains have a length defined by $l_{\text{flex}} = \rho \times l_{\text{ext}}$. The calculated length for extended alkyloxy chains is $l_{\text{ext}} = 1{\cdot}89 + 1{\cdot}265n$. The coefficient ρ depends on the chain length and is approximately equal to 0·72 for dodecyl derivatives [2].

The height of the rigid core is $L = 5{\cdot}4$ Å. The overall molecular length is then $L + 2l_{\text{flex}} = 30$ Å, in good agreement with experimental X-ray diffraction results. The fact that the inter-reticular distance increases with decreasing temperatures may be explained by a greater rigidity of the chains at lower temperatures; the paraffinic chain length then tends to be closer to the fully extended value.

The organization within the smectic layer may be postulated. CPK molecular models indicate that the triptycene subunit should give rise to an in-plane hexagonal parameter of 8 Å (see figure 6). X-ray diffraction data lead to exactly the same value at room temperature and to 8·3 Å for two of the higher temperature phases (at 154°C and 159°C). There is, therefore, a good agreement between theoretical estimations and experimental observations. It is noteworthy that such an organization of the triptycene subunits permits the paraffinic chains to pack easily: closest packing of triptycene cores leads to a 55·4 $Å^2$ cell area. For the hexa-substituted derivative, 18·5 $Å^2$ only are available for each chain. This value only allows crystallized paraffinic chains. This would explain the crystalline behaviour of the hexasubstituted derivative. On the contrary, the five chain derivative leads to an area of 22·2 $Å^2$ per paraffinic chain; this value is compatible with disordered mesophases [5–7].

The areas associated with the paraffinic and triptycene subunits are therefore compatible. Moreover, the symmetries of the two systems are also in agreement, since p31m is a subgroup of p6mm, which is the symmetry of the hexagonal gel phase of soaps [8] or the L_β phase [9]. The compatibility between the two systems imposes a relationship between the cell parameters associated with the hexagonal lattices, a_t for the rigid cores, a_c for the aliphatic tail (see figure 7).

When $a_t = 8$ Å (closest-packing of the triptycene subunits), $a_c = 4{\cdot}6$ Å; this is exactly the distance between the chains at the anchoring points imposed by the triptycene framework. In this way both p6mm and p31m systems are perfectly compatible.

With increasing temperatures, the hexagonal lattice of the rigid cores expands until a disordered smectic phase is reached, in which the hexagonal organization disappears. The molecular size of the triptycene subunit cannot allow a 'local' free rotation of the molecules; the absence of intralamellar order merely indicates the loss of long range positional order.

Our last comment concerns the diffuse peak, observed at room temperature at $4{\cdot}2_8$ Å, for the five-chain derivative. This peak is very probably associated with the paraffinic chains rather than the rigid cores. For paraffinic chains arranged in a pseudo-hexagonal array, this value would lead to a cell parameter of $4{\cdot}9_5$ Å, a little more than the value found in hexagonal gel phases of soaps ($4{\cdot}7_9$ Å) [8] or for paraffins in their

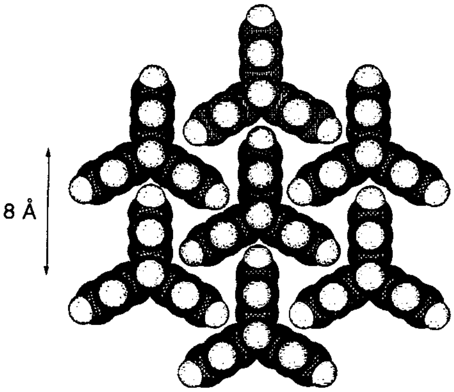
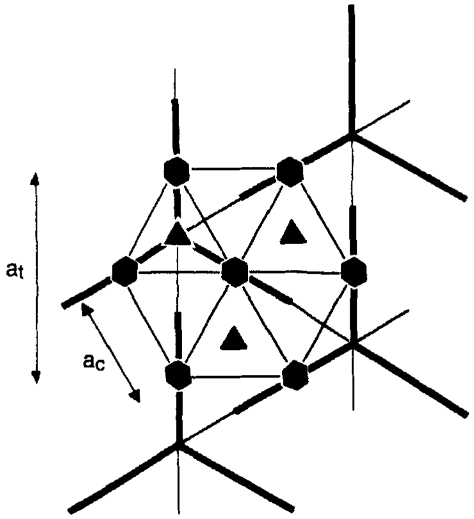


Figure 6. Cell parameter estimated with CPK models for a p31m arrangement of the triptycene subunits.



$$a_c = \frac{a_t}{\sqrt{3}}$$

Figure 7. Adequacy of the rigid and flexible moieties.

rotator phase ($4{\cdot}7_7$ Å) [10]. The chains are therefore in a slightly more disordered state than required for free rotation. This value of $4{\cdot}9_5$ Å corresponds to a 21·1 Å^2 cell, which is still compatible in area with triptycene packing (22·2 Å^2).

At higher temperatures, the hexagonal lattice expands and the area available per chain becomes 23·9 Å^2, corresponding to a disorganized state of the chains. Consequently, the broad peak at $4{\cdot}2_8$ Å is transformed into a conventional diffuse halo at 4·5 Å.

3. Conclusion

The smectic behaviour of a penta-substituted triptycene derivative has been demonstrated. X-ray diffraction shows the occurrence of a lamellar spacing, and a hexagonal organization; this latter has been associated with a p31m packing of the rigid cores within the layers. At higher temperatures a disordered liquid-crystalline phase is formed whose properties are similar to those found for the conventional smectic A phase.

The perfect symmetry and area agreements between the rigid cores and the paraffinic chains led us to propose the term 'epitaxygens' to designate this new class of mesogens [1].

Appendix

Four-chain substituted anthraquinone and anthracene derivatives, obtained as necessary intermediates during the synthesis, also exhibit mesomorphic properties. They will be subsequently described.

We gratefully thank L. Bosio for the X-ray diffraction measurements. The work was performed within the Groupe de Recherches Interdisciplinaires sur les Matériaux Moléculaires (GRIMM).

References

[1] NORVEZ, S., and SIMON, J., 1990, *J. chem. Soc. Chem. Comm.*, p. 1398.
[2] NORVEZ, S., 1991, Thesis, Pierre et Marie Curie University, Paris.
[3] FLORY, P. J., 1969, *Statistical Mechanics of Chain Molecules* (Interscience), p. 147.
[4] TANFORD, C., 1974, *J. phys. Chem.*, **78**, 2469.
[5] WEBER, P., GUILLON, D., and SKOULIOS, A., 1991, *Liq. Crystals*, **9**, 369.
[6] GUILLON, D., SKOULIOS, A., and BENATAR, J. J., 1986, *J. Phys., Paris*, **47**, 133.
[7] GUILLON, D., SKOULIOS, A., PIECHOCKI, C., SIMON, J., and WEBER, P., 1983, *Molec. Crystals liq. Crystals*, **100**, 275.
[8] SKOULIOS, A., 1967, *Adv. Coll. Int. Sci.*, **1**, 79.
[9] SMALL, D. M., 1977, *J. Coll. Int. Sci.*, **58**, 581.
[10] DENICOLÒ, I., DOUCET, J., and CRAIEVICH, A. F., 1983, *J. chem. Phys.*, **78**, 1465.