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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Liquid-crystalline behaviour of molecules with tetrahedral symmetry

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To cite this Article Eidenschink, R. , Kreuzer, F. -H. and De Jeu, W. H.(1990) 'Liquid-crystalline behaviour of molecules with tetrahedral symmetry', *Liquid Crystals*, 8: 6, 879 – 884

To link to this Article: DOI: 10.1080/02678299008047398

URL: <http://dx.doi.org/10.1080/02678299008047398>

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PRELIMINARY COMMUNICATIONS

Liquid-crystalline behaviour of molecules with tetrahedral symmetry

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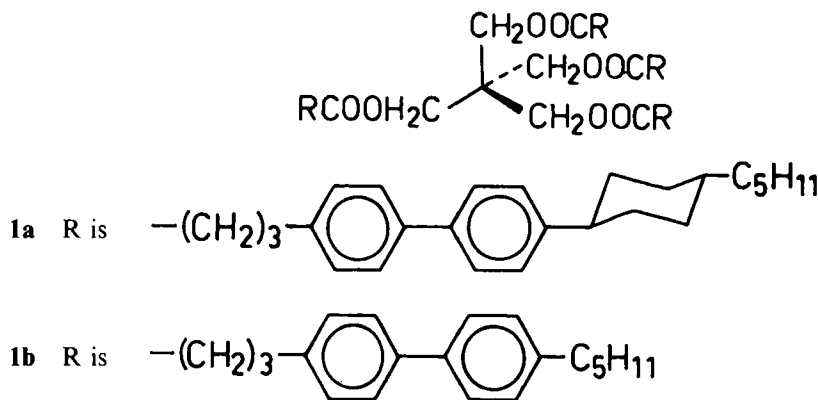
and W. H. DE JEU

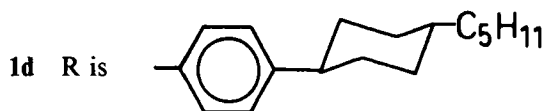
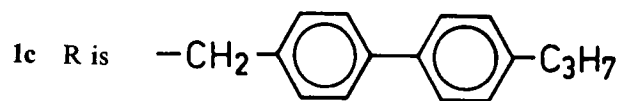
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(Received 5 July 1990; accepted 3 August 1990)

It is shown that molecules with tetrahedral symmetry can give smectic liquid-crystalline phases, both with liquid and with ordered layers. In contrast to the usual behaviour the layering is rather strong, leading to three orders in the X-ray diffraction pattern. A tentative model is given in which the long mesogenic substituents are bent at the spacers with which they are attached to the central carbon atom, such that in spite of the tetrahedral angles a rod-like shape is obtained.

Thermotropic liquid crystal phases are known to be formed by molecules having the non-isometric shapes of rods, discs, or variations on these. It is generally assumed that molecules of cubic symmetry cannot be the basis of anisotropic liquid crystal phases [1]. However, some results from industrial research in silicon chemistry [2, 3] should have already given rise to suspicion towards such a general statement. Here we report on the liquid crystal phases formed by tetrakis[4-(4'-trans-4-pentylcyclohexyl)-biphenyl-4-yl]-butyryloxymethyl]methane (**1a**).





Compound **1a** shows three mesophases. The one at the most elevated temperature has tentatively been classified as smectic A, the next lower one as smectic B. The classification of the third smectic phase is not fully clear yet, but the X-ray results indicate that it is less ordered than smectic B.

Compound **1a** was prepared by fusing pentaerythritol with an excess of the substituted butyric acid under nitrogen at 210°C for 4 hours. Chromatographic purification (silica gel/toluene) was used. The structure has been confirmed by elemental analysis, IR, ^1H NMR and molecular mass (gel liquid chromatography). Compound **1a** precipitated as a liquid crystal from different solvents. Differential scanning calorimetry (Mettler-TA4000, DSC30) shows the transitions (see figure 1)

$$\begin{array}{ccccccc} \text{S}_3 & 152^\circ\text{C} & \text{S}_2 & 229^\circ\text{C} & \text{S}_1 & 275^\circ\text{C} & \text{I} \\ & & & & & & \\ & < 0.5 \text{ kJ mol}^{-1} & & 7.5 \text{ kJ mol}^{-1} & & & 35 \text{ kJ mol}^{-1} \end{array}$$

We did not succeed in crystallizing compound **1a**. Binary mixtures with some nematogenic compounds gave rather different phase diagrams depending on the value of the nematic–isotropic transition temperature of the other component; details will be reported later. The compounds **1b** and **1c** exhibited monotropic smectic liquid-

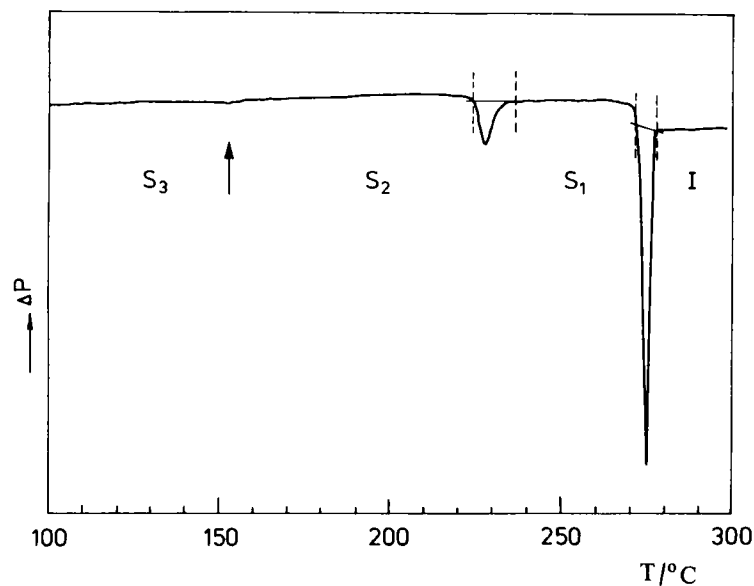


Figure 1. The DSC plot for compound **1a** (heated at 10°C/min).

crystalline phases that could not be identified

- 1b** m.p. 143°C (smectic at 120°C),
1c m.p. 168°C (smectic at 130°C),
1d m.p. 99°C.

Powder X-ray diffraction patterns were obtained as a function of temperature using a Guinier–Simon camera (Enraf–Nonius). The sample was sealed in a 0.3 mm \emptyset Lindeman glass tube under a helium atmosphere. Subsequently it was exposed to the X-rays during a heating/cooling cycle between 50 and 250°C at a rate of 20°C/h.

Typical textures at the smectic–isotropic phase transition and in the three mesophases are shown in figure 2. They are not very informative, but seem to indicate either highly ordered smectic phases or possibly even columnar mesophases. No clear focal conics have been observed as would typically be the case for a smectic A or smectic C phase with liquid layers. Nevertheless in figure 2(b) (first mesophase) some thin stripes are seen which could indicate rudimentary small focal conics. These small features disappear in the second mesophase (see figure 2(c)). In the third mesophase a limited number of clear extra lines appear (see figure 2(d)). No homeotropic textures were observed which would indicate uniaxiality. On the other hand, nothing reminiscent of schlieren textures was found as expected for tilted structures. Summarizing, the textures are not very conclusive regarding the exact nature of the three mesophases.

The powder X-ray diffraction patterns are relatively simple and therefore very informative. In all three mesophases two reflections are observed at small angles (though the second one is very weak in the high temperature phase), which indicate smectic layering. The ratio of the peak positions is 1 : 1.5 leading to an indexing as 002 and 003, respectively (see the table). This gives rise to an 001 reflection at 48–50 Å, but this reflection is not observed because it just falls below the experimental small angle limit of the camera. Within each of the three mesophases there is hardly any temperature dependence of the reflections. At large Bragg angles there is in all phases a single reflection around 4.8–4.9 Å, which is typical for a lateral distance between mesogenic units [4]. In the high temperature phase this reflection is diffuse indicating a liquid structure within the layers. It condenses on cooling at the phase transition to the second smectic phase. The absence of any other reflection in this region indicates a hexagonal structure and hence a smectic B phase. Interestingly this sharp reflection broadens again at the transition to the third mesophase, indicating again a less ordered situation. However, the reflection does not become completely diffuse as

Bragg spacings in the various smectic phases.

T/°C	Small angles d/Å	Large angles d/Å
80	24.4 (002) 16.3 (003)	4.8 (broad)
180	24.9 (002) 16.5 (003)	4.9 (sharp)
250	24.0 (002) 16 (003 very weak)	4.9 (diffuse)

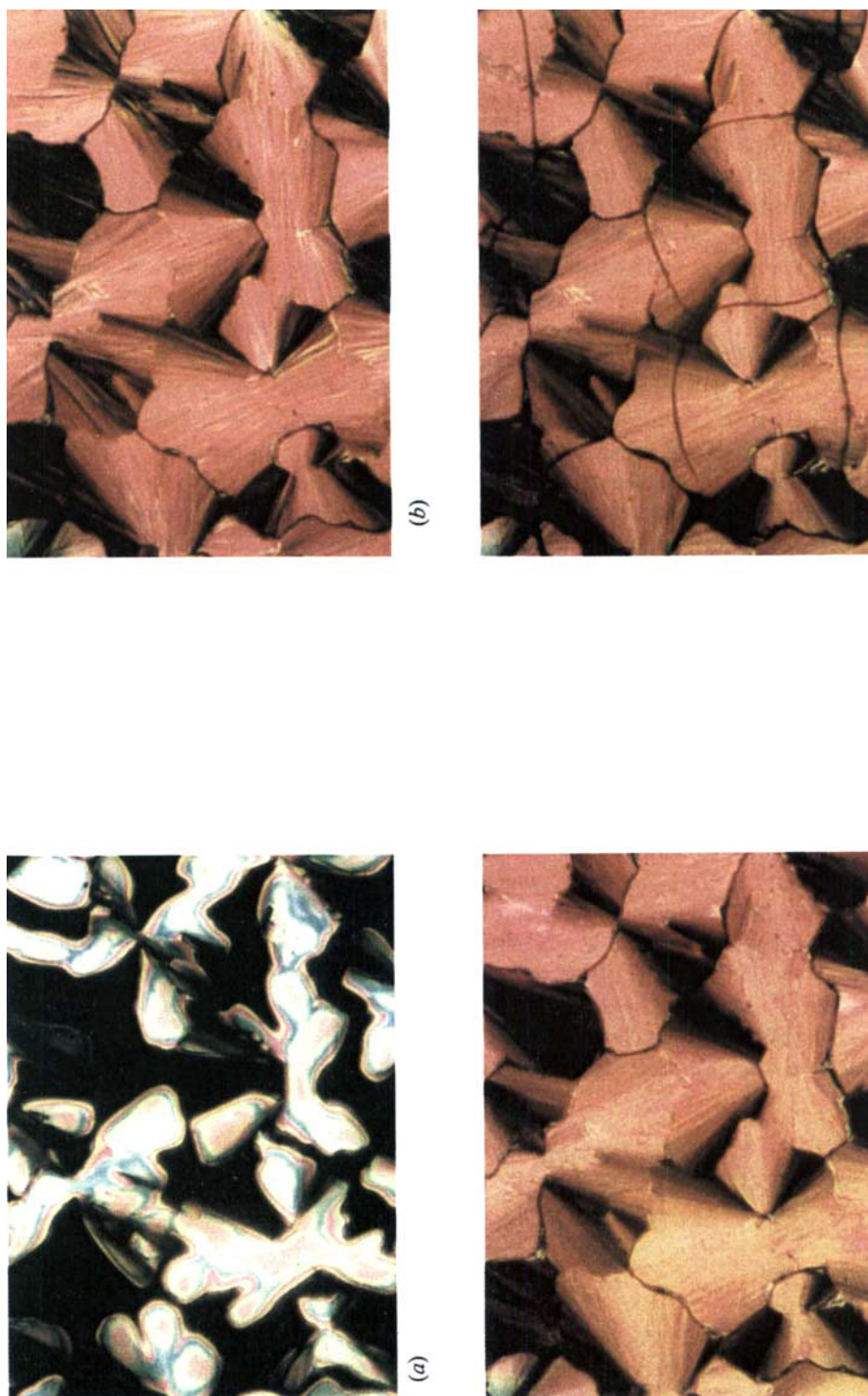


Figure 2. Microscopic textures of compound **1a** at various temperatures (same area of sample, crossed polarizers, $\times 253$): (a) isotropic-smectic transition at 269°C, (b) smectic A phase at 200°C, (c) smectic B phase at 70°C, (d) smectic 3 phase at 245°C.

before, broadening approximately by a factor of the order of three. Quantitative, high resolution measurements on an oriented sample are needed to clarify this point. Anyhow, these results again suggest either a smectic A phase but with strong short range order, or possibly a hexatic smectic B phase.

The powder X-ray diffraction results lead rather unambiguously to the classification of the phases with decreasing temperature as $I-S_A-S_B-S_3$. There seems to be no room for an interpretation of the small angle reflections different from that as the 002 and 003 of a layer structure. The observation of just a single X-ray peak at large angles leads necessarily to orthogonal phases. The question now is whether this is fully compatible with the other observations, and how to construct a satisfactory molecular model.

The observed values $\Delta H_{S_{A1}}$ of 35 kJ/mol and $\Delta H_{S_{B}S_A}$ of 7.5 kJ/mol fit well into the frame of S_A to I and S_B to S_A transitions, respectively [5], taking into account the four mesogenic groups of **1a** and the associated large molecular mass of 1632.

The observed textures, though not incompatible with the X-ray results, are somewhat puzzling. That no homeotropic textures are observed could very well be related to the large molecular mass in combination with the absence of a nematic phase. The absence of clear focal-conic textures (fingerprints of a liquid layer structure) poses another question. The X-ray results give a strong 002 reflection which is very unusual in a smectic A phase [6], while to the best of our knowledge a third order of the layer reflection has never been previously observed. This indicates a layer structure that is very well packed compared to the situation in a classical monomeric smectic A phase, where the layer structure is best described as a weak sinusoidal density modulation. In this respect the present results compare better with smectic liquid-crystalline side chain polymers, where also sometimes several orders of the layer reflection may be observed [7]. The more pronounced layer structure could lead to an increased resistance against bending of the layers, which then explains the absence of focal-conic textures. If this explanation is correct it should also lead to a relatively large value for the elastic constant K_1 . Measurements of K_1 (which in principle require a nematic phase) are needed as a further test.

A molecular model compatible with the observations can be constructed as follows. The four side chains can be supposed to bend easily at the positions of the flexible spacers which connect the four mesogenic units to the central carbon atom. Optimization of the packing could then lead to two pairs of parallel mesogenic units with their preferred axes in approximately opposite directions (see figure 3). Note that due to the tetrahedral angles at the central carbon the planes of each of the two pairs are perpendicular to each other. A space filling molecular model shows that the type of bending required for the model of figure 3 can easily be realized in combination with a favourable packing. It leads to an almost perfect parallelism of the mesogenic

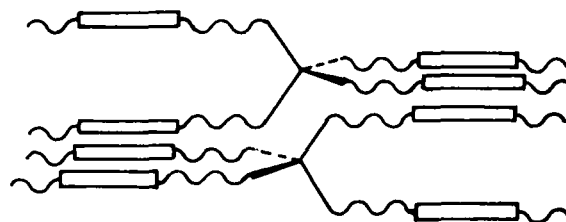


Figure 3. A model for the tetrahedral molecules in a smectic phase.

groups. From the space filling model we estimate 52–53 Å for the total length of the molecule (alkyl end chains in their most extended configuration). The observed smectic layer periodicity of 48–50 Å is 5–10 per cent smaller, which seems quite reasonable. Hence it seems most likely that we deal with a simple direct packing of the molecular units in layers.

In conclusion the observation of smectic phases in compounds with tetrahedral symmetry bridges the gap between traditional monomeric rod-like mesomorphic compounds and liquid-crystalline side chain polymers. The central atom then should be considered as the ultimate limit of a polymer chain to which the mesogenic side-groups are attached via flexible spacers. This type of structure opens a new route to the synthesis of liquid-crystalline materials, and could widen the variation in values for macroscopic physical properties (for example elastic constants). From this point of view it could also be of importance for applications. Further work on both the more fundamental aspects (X-ray measurements on oriented samples) and the practical applications (especially the possibilities of mixtures) is in progress.

We wish to thank Ms. B. Nagel (Nematel), Ms. S. Ehmann (Consortium für Elektrochemische Industrie) and Mr. F. van der Horst (Solid State Physics Laboratory, University of Groningen) for technical assistance. WHdJ is supported via the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for the Fundamental Research of Matter, FOM) by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research, NWO).

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