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A surface-alignable micellar nematic

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The lyotropic mesophases of alkali metal salts of 4-*trans*-pentyl cyclohexanoic acid have been studied. The lithium salt is of particular interest in that it forms a lyotropic nematic phase, a hexagonal phase, and another columnar phase, possibly with a rectangular lattice. Unlike most nematics, this phase can assume a parallel alignment on a treated surface in much the same way as thermotropic (molecular) nematics. When the nematic dries, a columnar phase grows into it, showing a strong preferential direction of the column axes. This system should be useful in studying the nematic–columnar transition and in other investigations which require an aligned micellar nematic phase.

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The molecular and micellar phases [1] are in many aspects structurally analogous; they both consist of anisometric units showing orientational but not translational ordering. However, different methods have often to be used to study these phases. Micellar nematics are usually multicomponent systems and generally do not align on surfaces except homeotropically. It is thus not always easy to do controlled experiments on them. Also, the two types of nematic are so different chemically that some of the lore one learns with one type does not apply to another.

There is a class of carboxylic axids which have the acid moeity on the end of a short rigid section which is connected to an alkyl chain on the other side. When these acids dimerize, as they are known to do, the paired carboxyl groups make up a ring, which acts as the centre of a rigid core [2]. The dimer thus has a stiff centre section, local dipole moments, and alkyl tails at each end, just like a normal nematogen. Thus, these acids are often nematogenic. Since these compounds are carboxylic acids, it is possible to make soaps from them, thus giving rise to the possibility of micellar phases. We see that these molecules may help us bridge the gap between micellar and molecular mesogens.

The acid discussed here is 4-*trans*-n-pentyl cyclohexanoic acid (5CHA). The bulk of this paper will be about the lithium salt of 5CHA (Li5CH) and the phases in the Li5CH : water system, which turn out to be interesting on their own, are reported on.

The 5CHA was used as-received from Aldrich. The soaps were made by dissolving the acid in hexane, adding the stoichiometric amount of the appropriate alkali hydroxide, then adding enough water to dissolve the hydroxide. So far, lithium, sodium, potassium, rubidium and caesium salts have been made this way. For all but the caesium salt, gentle heating was needed to make the reaction proceed. The product appeared as a flocculent solid or a gel-like mesophase, quite different in appearance from the reactants. The product was allowed to settle and the hexane decanted off. The soaps are insoluble in hexane, so little was lost on decanting. The product was then dried and dissolved in isopropanol and filtered. Since alkali hydroxides are insoluble in isopropanol, any unreacted base was filtered out by this method. The solution was then dried down in a flow of nitrogen, and washed with hexane. This step was used to remove unreacted acid. Redissolving the washed material in isopropanol produced a clear solution with negligible insolubles. The washed solid product was dried again in an oven at 80°C. This procedure made sure that the only impurities left were those soluble in isopropanol but not in hexane which is an uncommon combination of solubilities.

Contact preparations of the alkali salts versus water were made and examined at room temperature by polarizing microscopy. The phases shown by contact preparation at room temperature are: lithium salt: nematic, columnar (two phases); sodium salt: lamellar (columnar and nematic at higher temperatures); potassium salt: nematic, lamellar; rubidium salt: columnar (at all temperatures up to 100°C); caesium salt: nematic, columnar. The phases are listed in order of increasing soap concentration. The various mesophases were readily identifiable by their distinct optical textures. The nematic showed the characteristic schlieren texture, more fluidity than the other mesophases, and flicker. The lamellar exhibited oily streak textures with homeotropic regions, while the columnar was identified by its broken-fan texture.

The lithium salt was the most thoroughly investigated. At room temperature, it shows a nematic and two columnar phases. The nematic phase at 32·15 wt per cent Li5CH in water is shown in figure 1. This and all other pictures were taken with crossed polarizers. Note the typical schlieren texture and the defect with two brushes. When this preparation was allowed to dry at the edges, the nematic phase was invaded by a viscous phase whose texture is shown in figure 2. The fan texture and high

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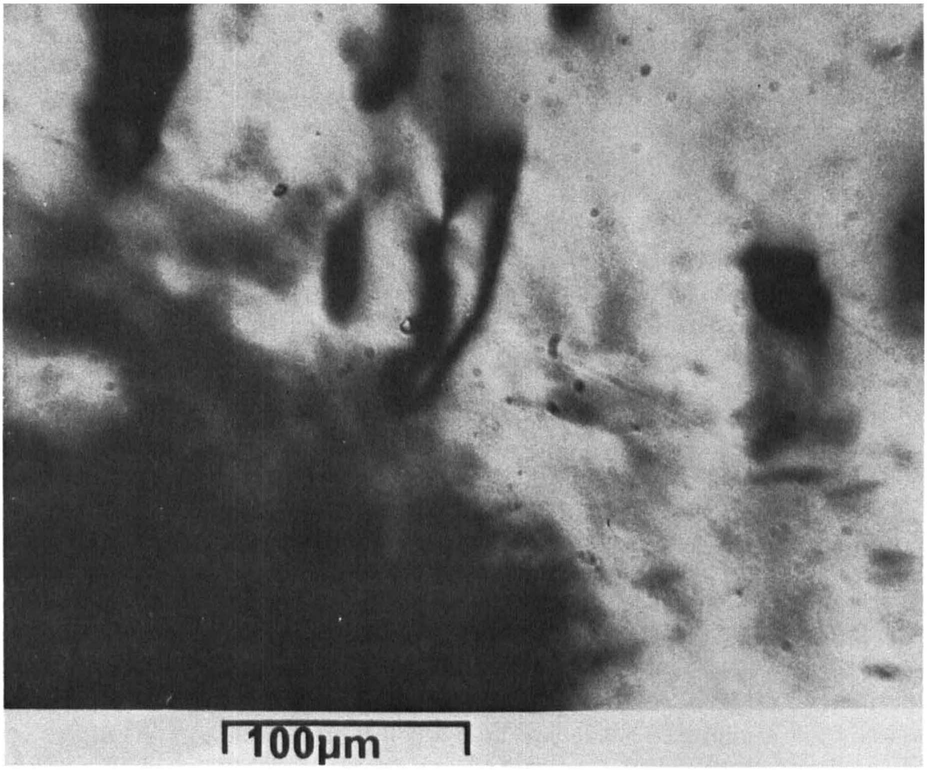

Figure 1. The nematic phase at 32·15 wt per cent Li5CH in water.

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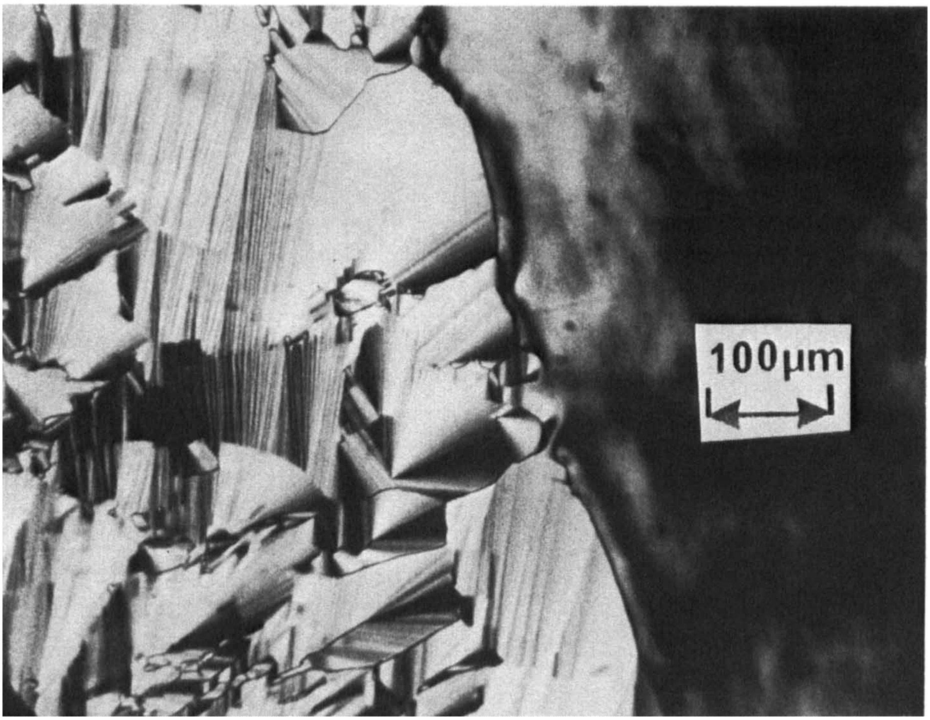

Figure 2. The preparation shown in figure 1 allowed to dry at the edge.

viscosity is typical of the hexagonal columnar phase, e.g. AOT in water. The abruptness of the boundaries between differently oriented areas suggests a columnar rather than a lamellar phase.

On further drying, pictures such as figures 3 and 4 were obtained. In figure 3, we see the broken-fan texture, and in the lower left, some banding across the fans. This banding is stronger in figure 4 in which the sample has lost more water than that in figure 3. The texture change shown in figures 3 and 4 is very reminiscent of the paramorphotic texture change on a smectic B → smectic E transition [3], and probably arises for similar reasons. In the smectic case, the bands result from the breaking of a discrete symmetry as the hexagonal packing of the high-temperature phase changes to a rectangular packing. Any of three equivalent hexagonal axes can become the long axis of the rectangular cell, so different areas within a fan take on different colours as they make different choices. By analogy, if the wetter phase is hexagonal and the dryer one rectangular, a similar banding should take place. Of course, considerations of symmetry dictate that the columns become elliptical in the rectangular phase, instead of round or hexagonal as in the hexagonal phase.

Li5CH : water is not the first system known to have a nematic–hexagonal transition, but it is one of the first to show a nematic that can be parallel-aligned on surfaces. Two alignment methods were tried. In one, a cell was made using rubbed nylon-coated glass as described by Goodby *et al.* [4], and filled with a 34 wt per cent Li5CH in water sample in the nematic phase. At this composition, the nematic occurs at around 70°C, and there is a columnar phase but no banding down to room temperature. Good alignment was obtained until sufficient water diffused out of the sample to cause the formation of a columnar phase.

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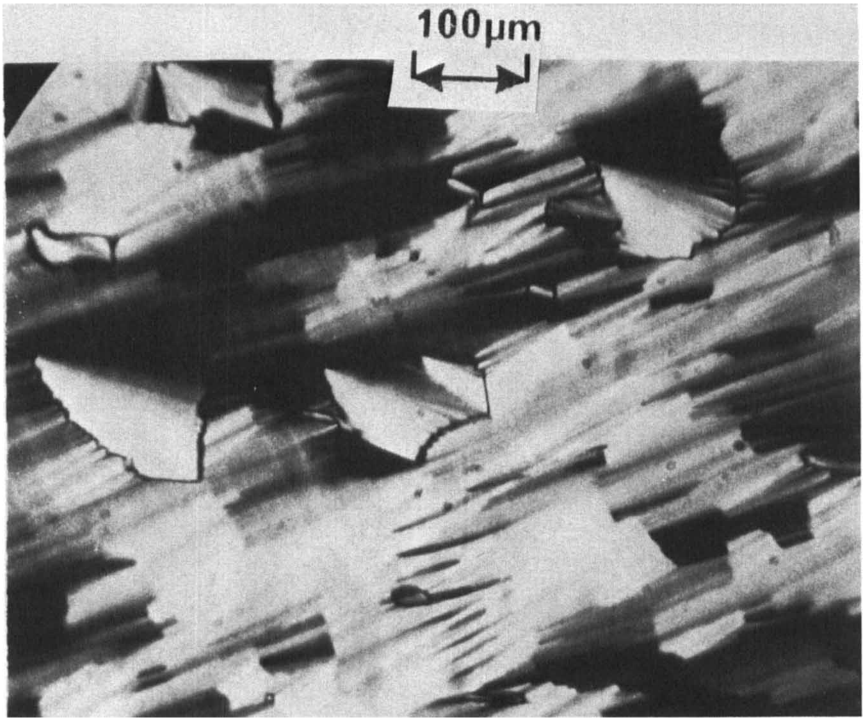


Figure 3. As for figure 2, but after further drying.

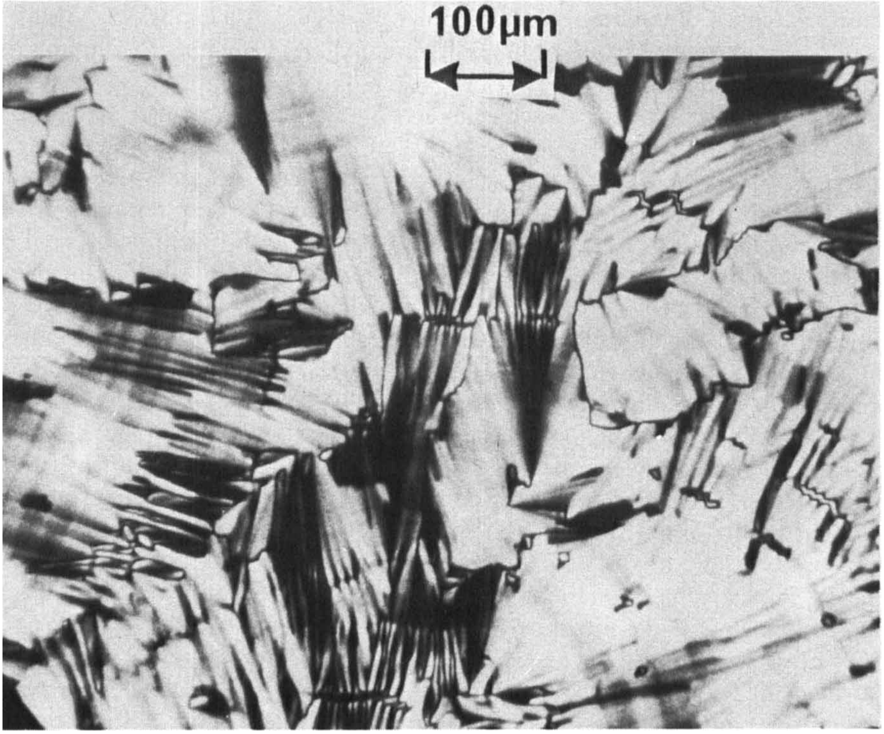
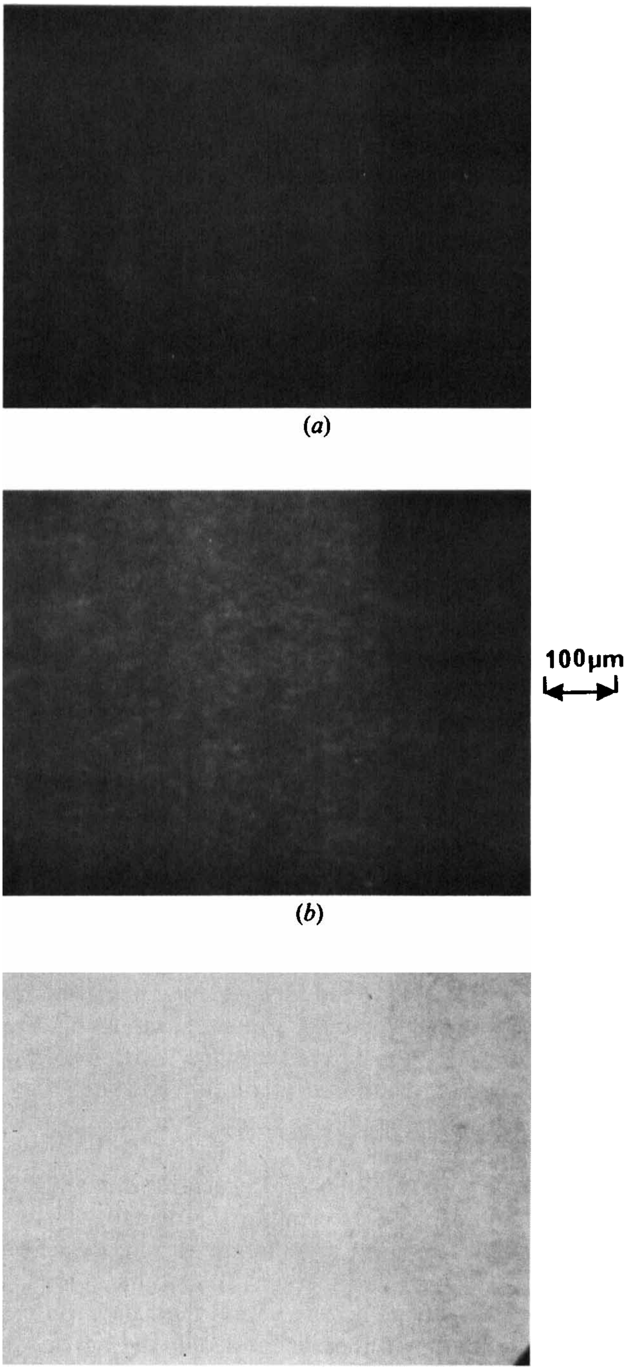


Figure 4. As for figure 3, but after still further drying.



(*a*)

(*b*)

(*c*)

Figure 5. The aligned nematic at 32·15 wt per cent Li5CH, between crossed polars. (*a*) Maximum extinction, (*b*) 1° off maximum extinction, (*c*) 5° off maximum extinction.

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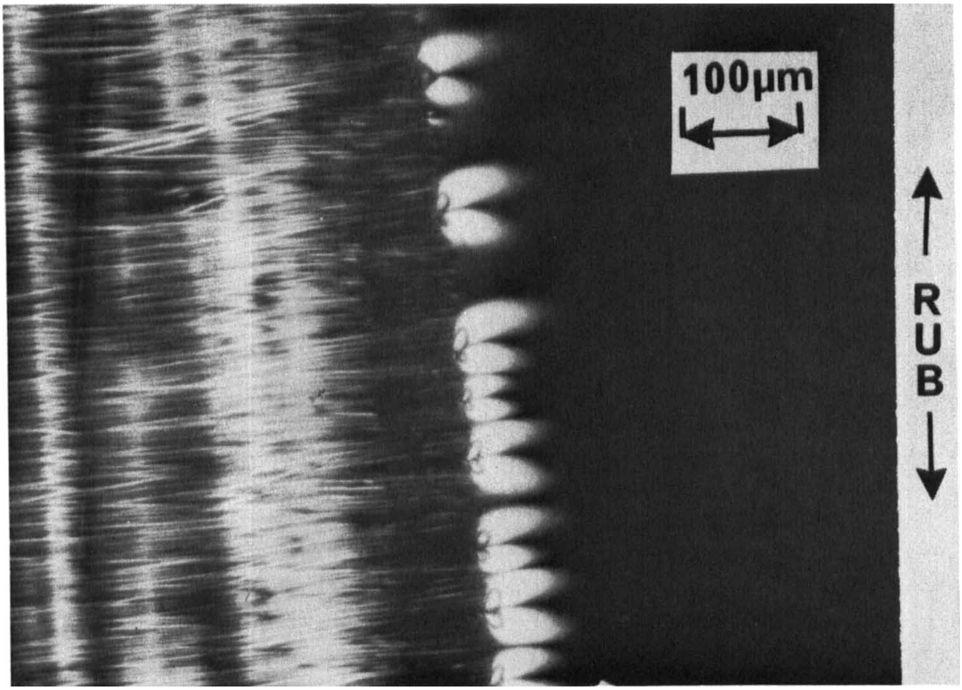

Figure 6. Columnar phase of Li5CH : water growing into an aligned nematic.

The other attempt was with a 32·15 per cent sample in which the nematic occurred at room temperature. Glass slides were cleaned with Deconex-11, treated with ACM-72 and rubbed. The material was squeezed between the slides with no spacer to make a rather thin sample. The sample was heated to the clearing point and allowed to cool. The resulting alignment is shown in figures 5 (*a*, *b*, *c*). Here, the nematic is shown between crossed polarizers at maximum extinction, 1° away, and 5° away from maximum extinction. The pictures were taken with the same exposure. We have therefore alignment as good as that found for molecular nematics. Unfortunately, no clear conoscopic figure could be obtained, so it was impossible to estimate the tilt angle, if any. In figure 6 we see the columnar phase starting to grow-in on drying. Note the aligned growth of the columnar-phase domains and the distortion of the nematic around them. The columnar-phase grains grew with their long axes perpendicular to the rubbing direction.

The columnar phase grew in from the open edge as water was lost. In figure 7, we see some grains of columnar phase growing in the nematic. Here, the sample was allowed to dry from its edge to form a columnar region, then heated to drive the sample back to nematic. Figure 7 was taken as the sample cooled. The long axis of each grain is parallel to the rubbing direction, and there are striations perpendicular to the rub axis. When the columnar phase is formed by drying, only the striations are visible.

The nematic phase shows flicker, but in an unusual way. The flickering region seems to be longer in the direction perpendicular to the rub axis than parallel. This effect resembles that seen near a nematic–smectic A transition as the elastic constants become anisotropic, and in polymers whose elastic constants are anisotropic. We can understand the appearance of the flicker if we assume that the elastic constants are

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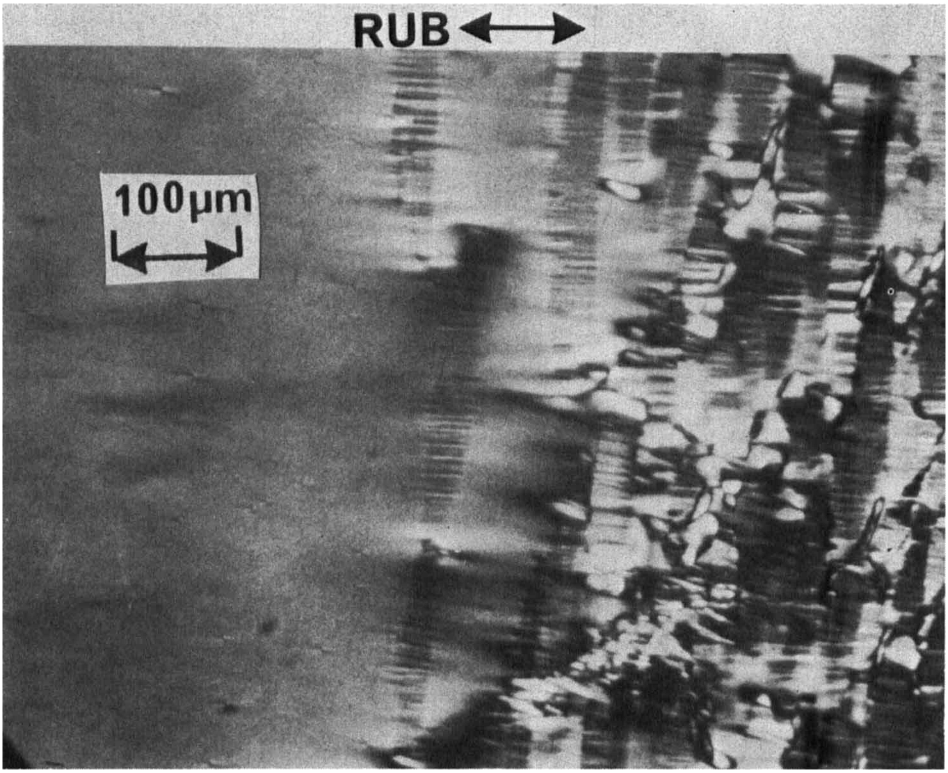

Figure 7. Isolated columnar grains of Li5CH : water growing into an aligned nematic.

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anisotropic due to the constituent micelles having a very large length/width ratio. Suppose the columnar domains grow parallel to the director. Then, the director must be parallel to the rubbing direction, and the fluctuations correlated over longer distances perpendicular to the rub axis than parallel to it. If the correlation length for some time scale is longer in the perpendicular direction than parallel, then the elastic constants governing the variations of the director perpendicular to itself must be larger than those for parallel fluctuations. The perpendicular constants are splay and twist, and the parallel fluctuations are controlled by bend. The fluctuations are observed with crossed polars and the sample near extinction; this is an orientation in which twist produces only a second-order contribution to the intensity. Since the stiff direction seems to be the one in which twist and splay contribute, then the splay constant is concluded to be the stiff one. This is exactly what happens when the nematic is made of long objects. In addition theory implies that the twist and splay constants both diverge near a nematic–columnar transition [5].

It is concluded that the nematic is made of long micelles that link up and correlate to form the columnar phase. The columnar grains grow with their optic axes parallel to the nematic director, as expected.

Li5CH is an amphiphile with several interesting properties. It forms nematic and columnar phases with anisotropic elastic constants, and has the ability to align on rubbed surfaces. It is speculated that the alignability may be due to the close resemblance of the Li5CH molecule to a thermotropic mesogen. Perhaps the micelles on the surface are half-micelles, sitting with their interiors exposed to the substrate. If so, there might be surface forces tending to align the surface micelles, which in turn would align the others in the bulk. This material holds promise as an easily obtained micellar nematogen which can have its orientation controlled like a molecular nematogen.

References

[1] The terms 'molecular' and 'micellar' are used instead of the older 'lyotropic' and 'thermotropic' because they are more descriptive and lead to less confusion than the latter.

[2] Lydon, J. E., 1981, *Molec. Crystals liq. Crystals*, **72**, 79.

[3] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals: Textures and Structures* (Leonard Hill).

[4] Goodby, J. W., Patel, J. S., and Leslie, T. M., 1984, *Ferroelectrics*, **59**, 137.

[5] Swift, J., and Andereck, B. S., 1982, *J. Phys. Lett., Paris*, **43**, L437.

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