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Optically Active Smectic Liquid Crystal

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Abstract—The discovery is reported of the first optically active smectic liquid crystal to consist of only one compound and to permit supercooling to room temperature. The compound is bis-(*p*-6-methyloctyloxybenzylidene)-2-chloro-1,4-phenylenediamine.

It has recently been shown[1–5] that some smectic liquid crystals are biaxial rather than uniaxial. The biaxial nature is due to a uniform tilt of the constituent rodlike molecules from the direction normal to the smectic layers, the tilt angle often being about 45°. There are also theoretical predictions[6] and experimental indications[7] that the molecular orientation spirals as one progresses in the direction normal to the layers, if the tilted smectic liquid crystal is made up of optically active molecules or is mixed with such molecules. In the following we report on the discovery of the first spiraling or "conical" smectic liquid crystal to consist of only one compound and to permit supercooling to room temperature.

The optically active compound we synthesized is very similar to an inactive compound known to have a tilted smectic phase.[1] The structural formulas and names of the active and inactive compounds are given in Fig. 1. Both materials have two mesophases, the higher-temperature phase being nematic in the case of the inactive compound.[1] Using differential thermal analysis we found that in both substances the mesophases are separated by a first order phase transition. The three transition temperatures between the solid and isotropic liquid states of the active and inactive compounds were 29, 94.4, 146.5 and 66.4, 111.2, 166.5 °C, respectively. The lower-temperature mesophase of the active compound could be

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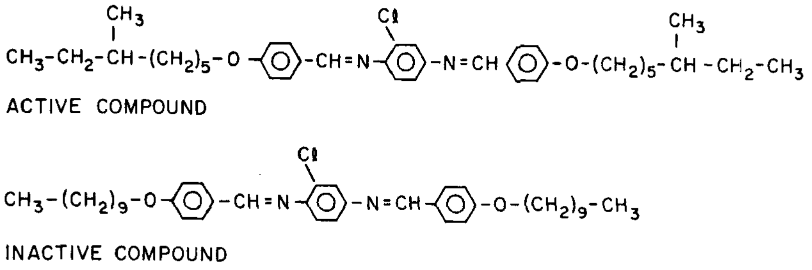

Figure 1. Structural formulas. The optically active compound is bis-(*p*-6-methyloctyloxybenzylidene)-2-chloro-1,4-phenylenediamine. The two active carbon atoms are in S configuration. The inactive compound is bis-(*p*-*n*-decyloxybenzylidene)-2-chloro-1,4-phenylenediamine.

supercooled to room temperature where most measurements were made. We also measured the clearing point and the transition temperatures between the two mesophases for mixtures of the active and inactive compounds. Both transition points varied smoothly and monotonously with concentration, being sharp and practically equal for rising and falling temperature. This may serve to show that the results of Taylor *et al.*[1] and ours are consistent.

As expected, both mesophases of the new material were optically active. In our experiments the liquid crystal was sandwiched between two glass plates and studied under a binocular Bausch and Lomb polarizing microscope. Most samples were wedge-shaped, the cells being about 2 cm long with a $\frac{1}{2}$ mil ($= 13\mu$) thick spacer at one end and no spacer at the other. When formed by cooling, both mesophases looked yellow and turbid and no optical activity was seen. Satisfactory transparency was obtained by sliding the cover glass back and forth. In the clear state both phases appeared very uniformly colored. The color varied through the whole visible spectrum, depending on sample thickness and on the settings of polarizer and analyzer. The color and intensity of the transmitted light did not change when polarizer and analyzer were rotated by the same angle. These properties of the clear state indicate optical activity and rotatory dispersion; birefringence was not noted in our experiments. We may also conclude that the helical or spiral axis was parallel to the light, which implies that the cholesteric or smectic layers were parallel to the glass. Figure 2 shows the dependence of

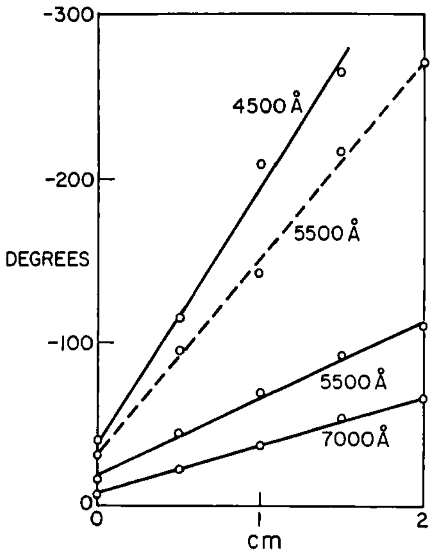

Figure 2. Optical rotation in degrees as function of position for the lower temperature (——) and higher-temperature (----, ca. 115°C) mesophases of the active compound. The sample was wedge-shaped with a ½ mil spacer at 2 cm and none at 0 cm. The nonvanishing intercept demonstrates that the sample thickness could not be made zero in any of our samples, perhaps because of capillary forces.

the angle of rotation on sample thickness, for a few wavelengths, as measured with narrow band pass filters. The optical rotatory power is negative (levorotatory) and for the lower-temperature mesophase about 23,000°/mm at 4500 Å. Inspecting the whole visible spectrum we found the rotatory power and its derivative with respect to wave length to decline (in absolute value) towards longer waves. This suggests that the lower-temperature mesophase represents a configuration resembling a left-handed screw and that its pitch is too small to be measured with visible light.

The higher-temperature mesophase formed Grandjean striations if the glasses of the wedge-shaped cell were uniformly rubbed with a cotton swab before the cell was assembled. Also, it contained the mobile threads (i.e., disclinations) characteristic of nematic and cholesteric mesophases. Neither feature was observed when the wedge-shaped samples were in the lower-temperature mesophase. On the other hand, drops which were in this state and not covered by glass displayed numerous parallel lines along their edges when viewed in transmitted light under the microscope (magnification up to 60 times). The phenomenon seems to be a sign of the so-called terraced-drop texture typical of smectic liquid crystals. We conclude from all these observations that the higher-temperature mesophase is cholesteric and the other conical smectic. The interpretation is supported by the fact that there is normally no more than one nematic or cholesteric phase. In addition, the lower-temperature mesophase was like a wax up to the transition to the other, much more fluid, mesomorphic state.

A remarkable property of the conical smectic phase was the absence of a measurable effect of temperature on optical rotation. In contrast, the cholesteric phase showed a strong variation of activity. The insensitivity appears plausible if the tilt angle does not depend on temperature, as is usually found.[5] Then one may expect the pitch to be controlled by the interaction between smectic layers rather than between individual molecules.

Another liquid crystal with two optically active phases was found earlier by Leclerq *et al.*[8] who thought that both were cholesteric. It seems likely that their lower-temperature mesophase was also a conical smectic liquid crystal.

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