Pressure-Induced Shifts of Mesomorphic Phase Transition Temperatures

Sir:

The existence of a class of materials, bis(4′-*n*-alkoxybenzal)-1,4-phenylenediamines, having several liquid crystal phases has been reported recently by Arora, Taylor, Fergason, and Saupe.[1] These are large molecules with functional groups which tend to make the structure approximately linear.[2]

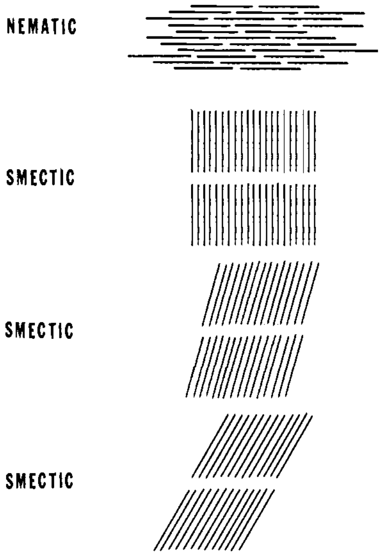

Figure 1. Liquid crystal configurations. The smectic–smectic transitions represent small changes in relative position and orientation.

While above the clearing point the material is isotropic, below that temperature the molecules may align themselves either in layered or nonlayered structures, and these structures transform, one to another, at well-defined temperatures. The nematic phase is characterized by parallel major axes of the molecules; it may be pictured as a number of pencils laid down with a particular orientation. There is not a mechanically stable structure, because the individual molecules are free to slide parallel to their axes or perpendicular to their axes. In this group of compounds, smectic mesomorphs appear at lower temperatures; in these phases the molecules are not only parallel, but also are positioned in space with respect to their neighbors. Specifically, they are arranged in planes. Their axes may be perpendicular to the plane or may form fixed angles with the plane (Figure 1). These planes can slide with respect to each other, and hence can display remarkably low viscosities.

This latter effect was being demonstrated to me recently at the Liquid Crystal Institute at our sister institution, Kent State University. Observing the change in color as the microscope cover glass was displaced very lightly, it occurred to me that the transitory changes were the result of locally transforming the material to a more dense phase by the pressure on the cover glass. The pressure differential was rapidly dissipated, but the effect suggested that the transformations between some of the phases could be influenced by relatively small changes in pressure. Since the structures suggest the probability of discontinuities in the density–temperature relation, isotropic pressure would probably be effective.

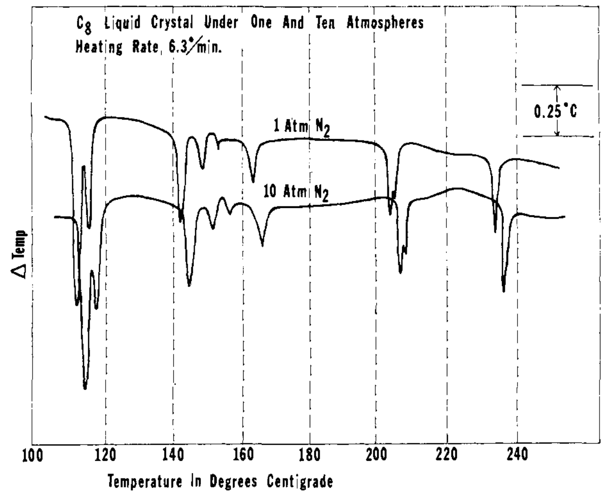

Figure 2. Differential thermal analysis curves of bis(4′-*n*-octyloxybenzal)-1,4-phenylenediamine, under static nitrogen pressure of 1 and 10 atm at 2.0°/min. Transition temperatures shift, although not greatly, by reason of isotropic compression.

To test the hypothesis, I obtained samples of two liquid crystals from the Institute and ran differential thermal analysis curves at 1 and 10 atm of nitrogen. Both showed reproducible changes of transition temperatures with this tenfold change in pressure. Figure 2 shows the curves for the C_8 derivative, bis(4′-*n*-octyloxybenzal)-1,4-phenylenediamine, under 1 and 10 atm of nitrogen. There is not a uniform displacement of temperature with pressure, nor would a uniform displacement be expected. Nevertheless, the range of displacements is small.

Pressure effects on the melting points and clearing points of some materials having only a nematic phase have already been demonstrated.[3,4] Because the smectic–smectic transitions in most cases represent lesser changes in the degree of ordering of the molecules, the pressure effects have apparently escaped notice. The hypothesis may be advanced that easily measurable changes in transition temperature with pressure should be a characteristic of *all* liquid crystal transitions. Other materials supplied by the Liquid Crystal Institute are being studied in order to test this hypothesis.

Tabulations of the pressure shifts are being prepared for the C_6–C_{10} derivatives described by Arora, *et al.*[1] The experimental methods shall be described in appropriate detail in that publication.

Acknowledgment. The author is grateful to the National Science Foundation for its support through institutional and research grants and to the Liquid Crystal Institute for supplying materials.

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Received June 9, 1969