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Anomalous Densities in Liquid Crystalline bis-(4-n-alkoxybenzal)-1, 4-phenylenediamines

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Anomalous Densities in Liquid Crystalline bis-(4-*n*-alkoxybenzal)-1,4-phenylenediamines

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Recently Arora, Taylor, Fergason and Saupe[1,2] investigated the homologous series of the bis-(4-*n*-alkoxybenzal)-1,4-phenylenediamines. In contradiction to Gray,[3] who found in this series only one nematic and one smectic modification, they observed besides one nematic modification a number of smectic phases, up to five for several substances. The greatest number of phase transitions were found in the case of the heptyloxy- up to the decyloxy-derivatives.

In order to confirm the phase transitions and to characterize the liquid crystalline modifications, we also prepared bis-(4-*n*-heptyloxybenzal)- and bis-(4-*n*-octyloxybenzal)-1,4-phenylenediamine.

By a heating stage polarizing microscope we were able to confirm all phase transitions given by Arora *et al.*[1] with negligible temperature differences. But we have found some differences concerning the so-called " smectic 5 " modification. Usually it does not have a characteristic texture of a liquid crystal; it is not viscous but hard and brittle; the two lowest transitions for both substances can be markedly supercooled. Truly, the transitions at the lowest temperatures are transitions in the solid crystalline state, and both substances possess only four smectic modifications.

We investigated the temperature dependence of the densities in the liquid crystalline state by means of a capillary method. The results of the measurements are given in Fig. 1 and Fig. 2. Three discontinuities in the curves, which verify the transitions between the four smectic modifications, are clearly recognizable.

As usual the density within the temperature intervals of the different smectic modifications continuously decreases and decreases discontinuously at the transitions, smectic 4/smectic 3 and smectic 2/

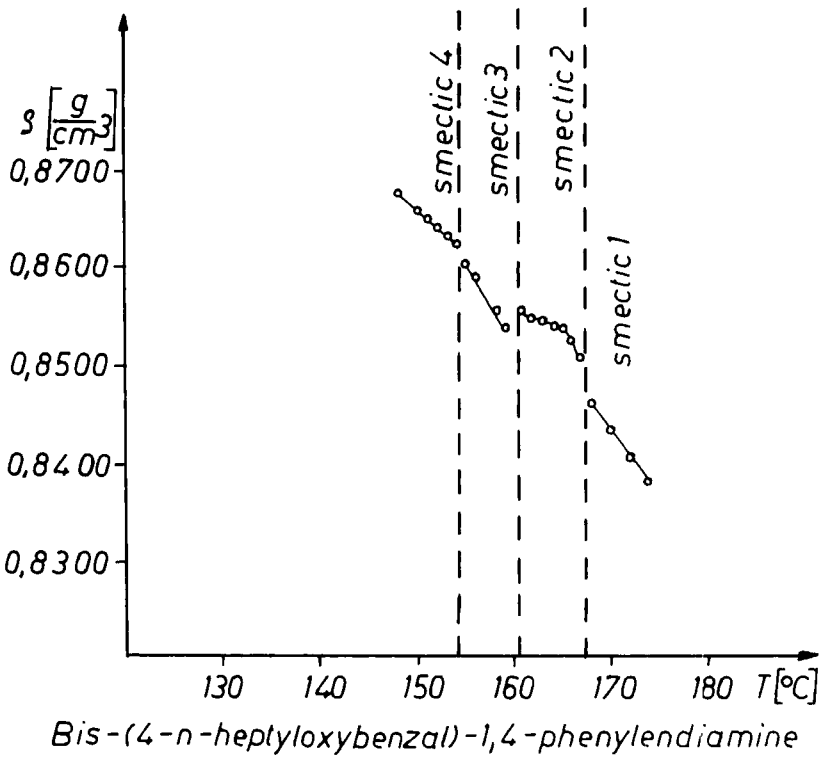

Figure 1.

smectic 1. Curiously the density increases discontinuously at the transition smectic 3/smectic 2. An anomaly of such a type has never been recognized at transitions in the liquid crystalline state. It points to structural peculiarities of the smectic modification 2 for both substances.

Garn[4] investigated the transition temperatures of bis-(4-*n*-octyloxybenzal)-1,4-phenylenediamine under the influence of a static pressure of 10 atmospheres and found a slight increase of all transition temperatures. According to the equation of Clausius and Clapeyron

$$\frac{dT}{dp} = \frac{T\Delta V}{\Delta H} \approx \frac{\Delta T}{\Delta p}$$

there is to be expected a decrease in the temperature of the transition

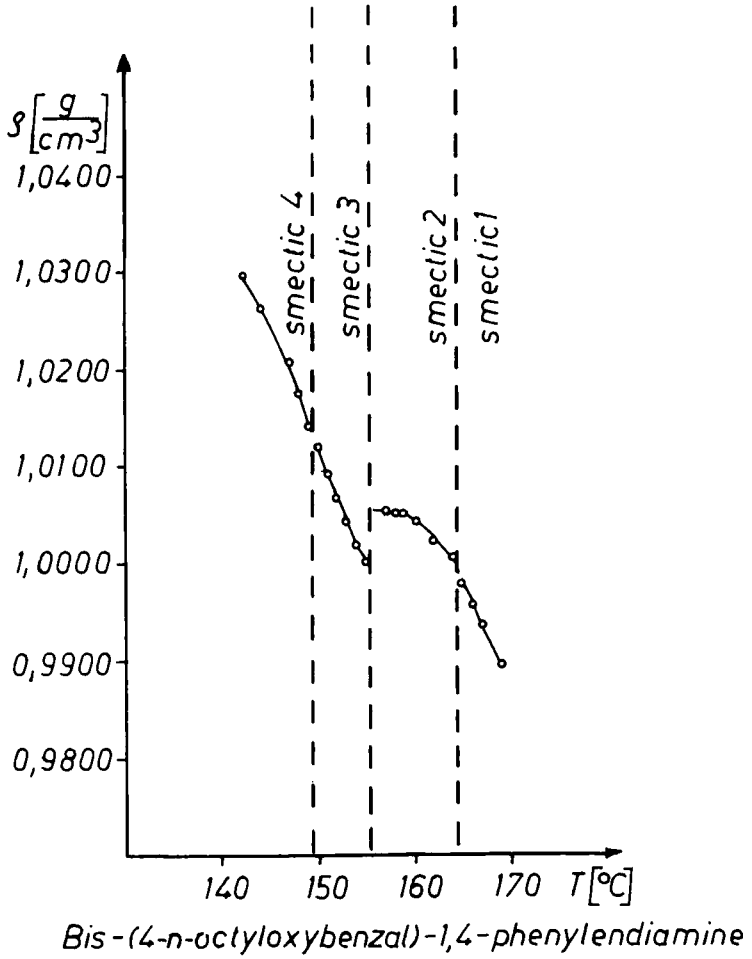

Figure 2.

smectic 3/smectic 2; with the values $\Delta V = -2.9$ cm^3/mole, $\Delta H = 89$ cal/mole[7], $T = 433.8$ °K and $\Delta p = 10$ atm we calculate $\Delta T = -3.4°$.

In order to clarify this difference between experiment and calculation, it would be of interest to undertake measurements up to higher pressures.

For the purpose of classification[5,6] of the smectic modifications of the homologous series of the bis-(4-*n*-alkoxybenzal)-1,4-phenylenediamines we are conducting further investigations.

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