Possible Second-Order Nematic–Smectic-*A* Phase Transition

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NMR measurements of the molecular orientational order in the homologous series 4-*n*-alkoxybenzylidene-4′-phenylazoaniline are compared with the McMillan smectic-*A* theory. The agreement is remarkable. The measurements show a discontinuous drop in the order parameter at the first-order smectic-*A* ⟷ nematic phase transition. The magnitude of the drop decreases with decreasing length of the alkyl end chain, finally approaching that characteristic of a second-order phase transition predicted by McMillan.

Recently, McMillan[1] introduced a specific interaction model which would predict first-order as well as second-order nematic ⟷ smectic-*A* transitions. The treatment was a clever extension of the Saupe-Maier theory by the introduction of an additional order parameter to describe the smectic-*A* order. A number of interesting developments arose from the calculation. It could explain, for example, the role of the alkyl end chains on the molecule in the formation of the smectic phase. A phase diagram quite similar to that actually observed was predicted. More exciting, the theory went further to predict a second-order nematic ⟷ smectic-*A* transition which had yet to be observed. McMillan calculated the temperature dependence of the specific heat, entropy, and order parameters, but little or no data were available for comparison. In this paper we show detailed measurements of the temperature dependence of one of the order parameters, η, for a homologous series of compounds where the length of the alkyl chain is varied from one to fourteen carbons. The prediction by McMillan is remarkable and some measurements are in fact consistant with that calculated for a second-order nematic–smectic-*A* transition.

In the description of the smectic-*A* phase, two order parameters are involved. One is the same as that introduced by Saupe:

$$\eta = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle, \tag{1}$$

where θ is the angle between the long axis of the molecule and its preferred direction of orientation. This parameter was predicted by McMillan to drop discontinuously at a first-order nematic–smectic-*A* transition. The magnitude of the drop depends upon the length of the alkyl chain attached to the molecule. As the number of carbons in the tail is decreased, the magnitude of the drop also decreases until no drop is realized at all, at which point the transition is second order. This parameter can sometimes be measured with precision with NMR, and it is measurements of η which we present in this paper.

In our measurements we use the homologous series of compounds 4-*n*-alkoxybenzylidene-4′-phenylazoaniline. A phase diagram showing the nematic–smectic-*A* transition temperature on the reduced temperature scale versus the length of the alkyl end chains is shown in Fig. 1. There are three regions of interest in the phase diagram. The first region is where the McMillan parameter α has values less than 0.7. Here the smectic-*A* ⟷ nematic transition, if it exists, is predicted to be second order. In our homologous series, only the compound C_2 (two carbons in the end chain) belongs in this region. The identification of this transition will be discussed later. The second region is where the smectic-nematic transition becomes first order ($0.7 < \alpha < 0.98$). The phases in this region were identified by their optical texture. In the third region, $\alpha > 0.98$, the liquid crystal passes directly from the isotropic into the smectic phase. All the compounds above C_{10} (synthesized up to C_{18}) showed this character. These are not shown in Fig. 1.

This series of compounds is particularily well suited for NMR since the magnetic dipole interactions for the adjacent protons in the aromatic rings are easily identified in the magnetic-resonance spectra. The splitting which results from this interaction is well resolved and is the large

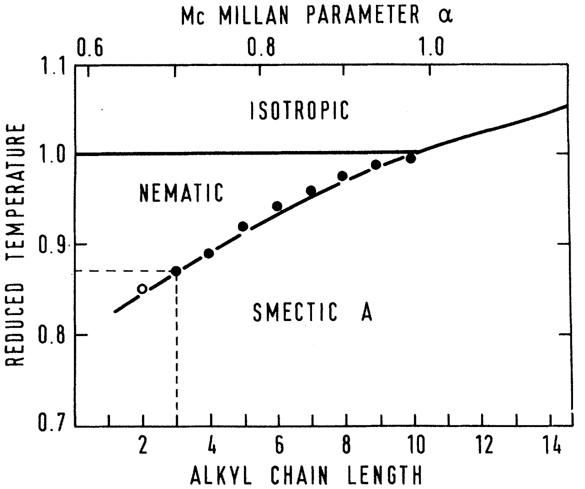

FIG. 1. Phase diagram for the McMillan parameter α (solid line) along with a plot of the ratio of the nematic–smectic-A transition temperature (°K) to the isotropic-nematic transition temperature versus the number of carbon atoms in the end chain for the homologous series 4-n-alkoxybenzylidene-4′-phenylaxoaniline.

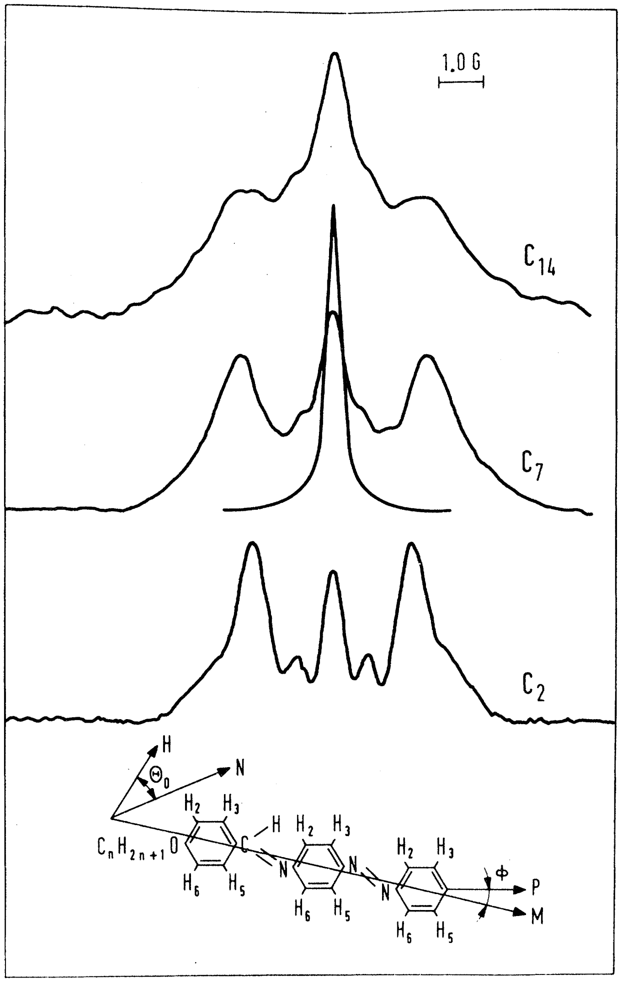

FIG. 2. Absorption line shapes for the proton spins in the C_{14}, C_7, and C_2 compounds of the 4-n-alkoxybenzylidene-4′-phenylazoanilene series near the reduced temperature of 0.9.

splitting shown in Fig. 2. Since the intermolecular interactions are motionally averaged to zero and the interactions within the molecule are only partially averaged, the splitting resulting from the adjacent proton spins in the aromatic rings follows the simple relation[2]

$$H = 3\gamma r^{-3}\eta(\tfrac{3}{2}\cos^2\varphi - \tfrac{1}{2})(\tfrac{3}{2}\cos^2\theta_0 - \tfrac{1}{2}),$$

where γ is the gyromagnetic ratio, r is the internuclear separation, and the angles φ and θ_0 are diagramed in Fig. 2. The term containing φ results from additional averaging due to the free rotation of the molecule about its long axis. In the nematic phase the anisotropy in the magnetic susceptibility forces the preferred direction of orientation to be parallel to the applied magnetic field and $\theta_0 = 0$. If the sample is cooled through the nematic phase into the smectic phase in the presence of a large magnetic field (~ 15 000 G in our experiments), the preferred direction in the smectic-A phase will likewise be parallel to the field. With $r = 2.45$ Å and $\varphi = 10°$ the values of η are determined from the measured splitting. The absorption spectra were recorded by using the boxcar integrator to Fourier transform the free-induction decay from a Bruker pulsed NMR spectrometer. It should perhaps be noted that as the length of the end chain is increased the intensity of the central portion of the spectrum increases. This can only happen if the degree of order of the end chain is much less than the rigid central portion of the molecule since the internuclear spacing for the protons in the end chain is less than in the rings.[3] The end chains therefore show a more fluidlike character than does the rigid portion of the molecule. In addition we should mention that the smectic-A phase can usually be identified by reorientation of the sample in the magnetic field.[4] The NMR line narrows as shown in Fig. 2 in the compound C_7 as the value of θ_0 approaches $\cos^{-1}(\frac{1}{3}\sqrt{3})$. This narrowing relies on there being little distortion in the smectic order resulting from a competition between the container walls and the magnetic field.

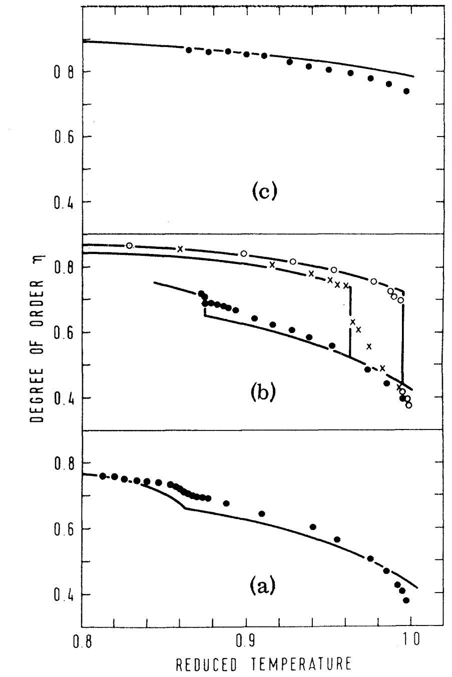

FIG. 3. Measured values of the order parameter η, along with the theoretical values (solid lines), versus the reduced temperature in the homologous series 4-*n*-alkoxybenzylidene-4′-phenylazoaniline for (a) C_2; (b) C_{10} (open circles), C_7 (crosses), C_3 (closed circles); (c) C_{14}.

Measurements of the temperature dependence of η for several compounds in the homologous series are shown in Fig. 3 along with the theoretical values computed from the McMillan theory for the appropriate values of α. The agreement is quite good, particularly in the smectic phase. In the compound C_3 the sample froze into a solid immediately upon entering the smectic phase. In the nematic-phase pretransition effects are indeed obvious. This is particularly noticeable in the compound C_7. At the first-order transition the value of η changes discontinuously as predicted. Perhaps the most interesting, however, is the compound C_2 which shows a variation in η not unlike that predicted by the theory for a second-order smectic-*A* ↔ nematic phase transition. Careful observations with the microscope did in fact show a transition at this temperature but the change in texture was so subtle that it was not clear whether or not it is a transition into the smectic-*A* phase. Reorientation of the sample in the magnetic field did not give a narrowing of the NMR line as is usually characteristic of the smectic-*A* phase; however, it was surprising to discover that the compound C_5 which definitely exhibits the smectic-*A* phase only showed little narrowing in this phase as compared with C_{10} where the line could be appreciably narrowed by a factor of 50. It appears as if the deformation constants[5] are becoming weaker as the first-order transition becomes weaker, allowing more distortion. This could be why C_2 does not appear to narrow at all in the large magnetic field. X-ray data on this series of compounds would be most helpful.

For completeness the transition temperatures for C_2, C_3, C_7, and C_{10}, are 199, 179, 168, and 164°C, for the isotropic-nematic transition and 133, 123, 151, and 162°C for the nematic-smectic-*A* transition, respectively. For C_{14} the isotropic-smectic transition occurs at 159°C.

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[1] W. L. McMillan, Phys. Rev. A 4, 1238 (1971).

[2] G. H. Brown, J. W. Doane, and V. D. Neff, Crit. Rev. Solid State Sci. 1, 303 (1970).

[3] L. E. Sutton, Chem. Soc., Spec. Publ. 11 (1958).

[4] R. A. Wise, D. H. Smith, and J. W. Doane, to be published.

[5] F. C. Frank, Discuss. Faraday Soc. 25, 19 (1958).