ly excited atoms in some experiments, because of presumed inefficiency of production, could lead to serious error.

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Nature of the Molecular Alignment in a Smectic-*H* Phase

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Quasielastic neutron scattering experiments on terephthal-*bis*-butylaniline (TBBA) show that the phenyl rings do not have a strongly preferred orientation in the smectic-*H* (tilted *B*) phase. This suggests that the Meyer-McMillan model is not quite adequate for this particular system.

Recently, Meyer and McMillan[1] extended to smectic-*B* and -*H* phases a molecular theory[2] of smectic-*C* and -*A* phases, by including a soft-core repulsive interaction in addition to the dipole-dipole interaction used previously. In this theory, this dipole-dipole interaction plays an essential role and is responsible for the tilted character of the smectic-*C* and -*H* phases by orientational ordering of the dipoles. An attempt to confirm the orientational order experimentally was recently made by NMR[3] on a series of smectic compounds. It was found that, while some smectic-*H* phases [in particular that of terephthal-*bis*-butylaniline (TBBA)] are consistent with the idea of a partial freezing out of rotation about the long axis, no freezing of this rotation could be observed in smectic-*C* phases.[4] For similar reasons we have recently studied[5] the smectic-*H* phase of TBBA (in Ref. 5 this was simply called the smectic-*B* phase; other names have been used[6]) using high-resolution quasielastic neutron scattering. The data were found to be consistent with the idea of rapid, uniaxial rotational diffusion of the molecules about their long axis, implying a lack of orientational order. In this Letter, we extend our interpretation of the same

data in terms of a model permitting partial orientational ordering for the phenyl rings and for the N=C–H groups.[7] We find that the value of the orientation parameter consistent with the experiment is much smaller than that predicted by the above-mentioned theory and, in fact, the best fit is obtained for no orientational order at all.

In a hydrogenous system, the scattering of neutrons is almost purely incoherent. The scattering function $S_{\mathrm{inc}}(\vec{Q}, \omega)$ is the Fourier transform in space and time of the self-correlation function $G_s(\vec{r}, t)$ of the protons. In the case of a uniaxial rotational motion, difficulty is encountered in calculating this self-correlation function when an order parameter is introduced. A treatment of this problem will be presented elsewhere.[8] However, the amplitude $A_0(Q)$ (usually called incoherent elastic structure factor) of the $\delta(\omega)$ term which appears in any scattering function of a purely rotational model[9] is the spatial Fourier transform of G_s at infinite time, and may be calculated without resolving the equation of motion. We have

$$A_0(\vec{Q}) = \langle \int G_s(\vec{r} - \vec{r}_0, \infty) \exp(i\vec{Q}\cdot\vec{r})\, d^3r \rangle. \qquad (1)$$

The brackets indicate an average over the initial positions $\vec{r}_0$. The expression of $A_0(Q)$ for the case of uniaxial rotational motion between N sites equally spaced and weighted on a circle was given in Ref. 5. Let us now extend this picture to the case of nonuniform weighting of N sites on the circle. In this way we obtain a model which permits us to take into account the theory of Ref. 1.

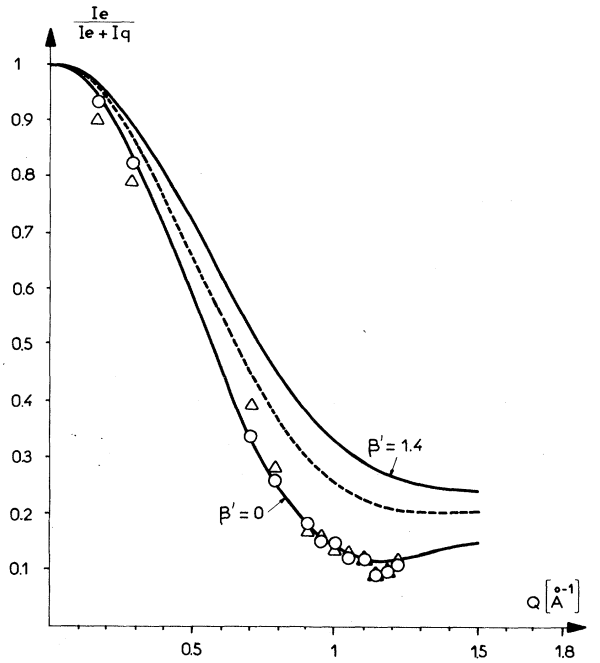

FIG. 1. Elastic to elastic-plus-quasielastic intensity ratio as a function of Q for DTBBA. Circles, data corrected for multiple scattering; triangles, data not corrected for multiple scattering (same points as in Ref. 5, Fig. 2). The full lines represent $A_0(Q)$ calculated from relation (6) for $N=6$, $a=2.50$ Å, and $\beta'=1.4$ and 0. The dashed line represents $A_0(Q)$ calculated from relation (8) for the same values of N and a.

Let φ be the angle characterizing the position of a proton on the circle and φ_0 its value at zero time. If the orientational distribution is peaked at $\varphi = 0$, we can write

$$G_s(\vec{r} - \vec{r}_0, \infty) = A \sum_{j=1}^{N} \exp[\beta' \cos(2\pi j/N + \varphi_0)]\, \delta(\vec{r} - \vec{r}_j), \qquad (2)$$

where, following Ref. 1, in the case of a smectic-H phase, β' is given by

$$\beta' = \beta \mu^2 S_0 / k_B T. \qquad (3)$$

In these expressions, μ is the dipole moment, S_0 is a parameter related to the two-particle correlation function, and β is the orientational order parameter $[\beta = (\cos\varphi_{AV}]$. In addition, the $\vec{r}_j$ define the positions of the N sites on the circle of radius a, and A is a normalizing constant. To a very good approximation (better than 10^{-4} for $N=6$), A is given by[8]

$$A = [N I_0(\beta')]^{-1}, \qquad (4)$$

where I_0 is the zero-order modified Bessel function of the first kind. Using Eqs. (1) and (2), the calculation of $A_0(Q)$ can be performed exactly. The initial distribution $f(\varphi_0)$ is chosen such that

$$f(\varphi_0) = [2\pi I_0(\beta')]^{-1} \exp(\beta' \cos\varphi_0). \qquad (5)$$

The result, after powder average, is[8]

$$A_0(Q) = \frac{1}{N I_0^2(\beta')} \sum_{j=1}^{N} \frac{\sin(2Qa \sin\pi j/N)}{2Qa \sin\pi j/N} I_0(2\beta' |\cos\pi j/N|). \qquad (6)$$

For $\beta' = 0$ (no orientational order), one recovers the result of Ref. 5 [Eq. (2) for $l = 0$].

The numerical value of β' for TBBA can be obtained from Ref. 1. As $\mu^2 S_0 \approx 2k_B T_{AC}$, where T_{AC} is the smectic-A–smectic-C transition temperature, we should have

$$\beta' = 2\beta T_{AC}/T. \tag{7}$$

For TBBA, $T_{AC} = 445$ K. The experiment was performed at $T = 392$ K. With $\beta = 0.6$ (from Fig. 7 of Ref. 1), we obtain $\beta' \approx 1.4$. This value corresponds to the orientational order of the dipole moments predicted by Ref. 1.

We now reexamine the experimental data on the partially deuterated TBBA (DTBBA) sample which were presented in Ref. 5. The experimental values of $A_0(Q)$ are shown in Fig. 1, corrected[10] for multiple scattering, together with the earlier uncorrected data (from Ref. 5) for comparison. These points represent an average incoherent elastic structure factor of all the protons of the DTBBA molecules. The DTBBA molecule contains ten protons, namely the four protons of the central phenyl rings, two protons on each external phenyl ring, and the two protons of the N=C–H groups.[5] If we assume that all these protons are dynamically equivalent regarding rotation around the molecular axis (e.g., if the molecule is rigid), the average structure factor should be given by Eq. (6) with $\beta' = 1.4$. Such a curve, using an average gyration radius of 2.5 Å, is represented in Fig. 1 and is definitely inconsistent with the experimental data. A possibility for reducing this discrepancy is to assume that some or all the protons of the phenyl rings can perform cylindrical, "isotropic" ($\beta' = 0$), rotational motion and that only the protons of the N=C–H groups, associated strongly with the molecular dipolar moments, show the orientational order. However, in this case, an isotropic motion of the central ring is rather unlikely because of steric hindrance. For the two external rings, such a motion seems possible. In this case, the theoretical average structure factor would be

$$A_0'(Q) = 0.6[A_0(Q)]_{\beta'=1.4} + 0.4[A_0(Q)]_{\beta'=0}. \tag{8}$$

The corresponding curve is drawn as a dashed line in Fig. 1, and, again, the discrepancy is

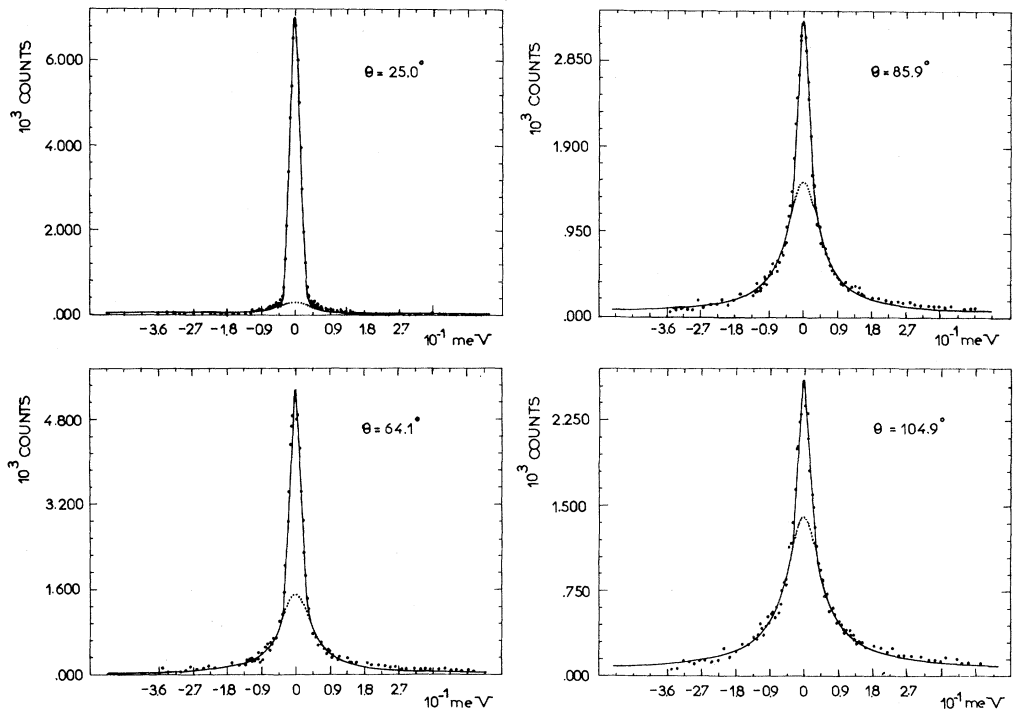

FIG. 2. Quasielastic neutron spectra of DTBBA in the smectic-H phase (119°C). Incident wavelength 9.48 Å. Scattering angles: 25°, 64.1°, 85.9°, 104.9°. The points are experimental, corrected for multiple scattering; the full lines represent the best fit of the "isotropic," uniaxial rotation model of Ref. 5, using $a = 2.56$ Å, $\tau_1 = 1.49 \times 10^{-11}$ sec, and $u^2 = 0.126$ Å^2. The separation between purely elastic and quasielastic contribution is also shown.

rather great. Consequently, the orientational order parameter (if any) is probably much smaller than predicted by the theory of Ref. 1. In fact, fitting expression (6) to the experimental points corrected for multiple scattering and taking β' and a as parameters, the best fit is obtained for $\beta' = 0$ and $a = 2.53$ Å, in excellent agreement with the analysis of Ref. 5. To further emphasize this, we have fitted the uniaxial-rotational model presented in Ref. 5 to the corrected experimental spectra. In Fig. 2 we show four out of the ten spectra, which were all treated in a simultaneous fit.[11] The best fit was obtained for $a = 2.56$ Å, $\tau_1 = 1.49 \times 10^{-11}$ sec, and $u^2 = 0.126$ Å^2, again in good agreement with a simpler analysis based on graphical integration and linewidth measurements.[12] This shows that not only is the incoherent elastic structure factor inconsistent with the high orientational order of the molecules within the plane perpendicular to their long axis, but also that the actual neutron spectra are quite consistent with the presence of rapid "isotropic" rotation around this axis.[13] We can thus conclude that the Meyer-McMillan theory is not very adequate to describe the smectic-*H* phase of TBBA.

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[12]It must be noted that for systems such as the one studied here, and for similar experimental conditions, the multiple scattering affects the total intensity of the quasielastic spectra much more than their shape. This can be seen by comparing our present values of a, τ_1, and u^2 with those of Ref. 5 and with those we obtained by applying the same fitting procedure to the uncorrected spectra.

[15]To be more precise, given the space and time scale of the experimental technique, what we can say is that if a proton of the body was at a given point in space at $t = 0$, it can be considered, to a very good approximation, as uniformly distributed on a circle of average radius 2.5 Å containing this point, at time $t \sim 10(\Delta\omega)^{-1} \approx 2 \times 10^{-10}$ sec ($\Delta\omega$ is the instrumental energy resolution).