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ANISOTROPY OF ULTRASONIC ATTENUATION IN NEMATIC LIQUID CRYSTALS

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Anisotropic ultrasonic attenuation in nematic liquid crystals is accounted for by an intramolecular mechanism. Anisotropy calculated for n-(p-methoxybenzylidene)-p-butylaniline (MBBA), on the basis of the proposed model, is in good agreement with experimental results.

The attenuation of ultrasonic waves in nematic liquid crystals arises from at least three different processes[1-3]: (i) Shear viscosity effects. (ii) Nonzero response time of the nematic order parameter to temperature and density perturbations. (iii) Intramolecular degrees of freedom. Process (i) dominates at fairly high frequencies ($\nu > 100$ MHz). Process (ii) dominates near the nematic to isotropic transition temperature, T_C, whereas (iii) may dominate at low frequencies ($\nu < 10$ MHz) far from T_C.

The above three contributions to the ultrasonic attenuation coefficient, α, in nematic liquid crystals are anisotropic and depend on the angle formed between the nematic director, $\hat{n}$, and the ultrasonic wave vector $\vec{k}$. (This anisotropy, $\Delta\alpha$, is discussed in terms of the difference between the attenuation coefficients of waves propagating parallel and perpendicular to the director, i.e., $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$). At high frequencies (where (i) dominates) the anisotropy in α can be accounted for in terms of the tensorial nature of the viscosity coefficients in nematics, but no straightforward explanation exists for the anisotropy of processes (ii) and (iii). In this note we discuss an intramolecular mechanism which can result in an anisotropic ultrasonic attenuation coefficient and can thus account for process (iii). As a

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concrete example we analyze the case of the nematic liquid crystal n-(p-methoxybenzylidene)-p-butylaniline (MBBA) whose ultrasonic properties have been extensively studied.

The noncritical component of α in MBBA is thought to arise from rotational isomerism in the butyl end group of the molecule. In analyzing this process it has been customary to assume that the resulting ultrasonic relaxation is purely thermal in nature, i.e. couples only to the ultrasonic temperature perturbations.

The ultrasonic attenuation coefficient due to a single relaxation process can be written as[4]

$$\frac{\alpha}{\nu^2} = \frac{2\pi^2 c}{c_0{}^2} \frac{\varepsilon\tau}{1 + \omega^2\tau^2} \tag{1}$$

where c is the sound velocity, c_0 is the sound velocity at zero frequency, τ is the relaxation time, and ε the relaxation strength. For a thermal relaxation[5] involving an excited energy level of degeneracy g_2 and a ground level of degeneracy g_1,

$$\varepsilon = \frac{g_2}{g_1} (\gamma - 1) \frac{R}{C_p^\infty} \left|\frac{\Delta H_0}{RT}\right|^2 \frac{e^{-\Delta G_0/RT}}{\left[1 + \frac{g_2}{g_1} e^{-\Delta G_0/RT}\right]^2} \tag{2}$$

Here γ is the ratio of the specific heats, C_p^∞ the infinite frequency specific heat at constant pressure, ΔG_0 and ΔH_0 are the Gibbs free energy and the enthalpy differences between the energy levels involved. Although this approach is satisfactory for unoriented samples, it fails to account for the noncritical component of $\Delta\alpha = \alpha_\parallel - \alpha_\perp$. Indeed, in a purely thermal relaxation, local deviations from equilibrium are determined by temperature oscillations and not by the direction of the ultrasonic wave with respect to any reference system associated with an individual molecule in the liquid. We show that under two plausible assumptions (discussed below), a rotational isomeric process results in an anisotropic ultrasonic attenuation.

Consider an MBBA molecule whose axis points along the direction of $\hat{n}$; the butyl end group attached to one of the aromatic rings in the MBBA molecule has four carbon-carbon (C-C) bonds around which the end group or portions of the end group can rotate (see Fig. 1). The lowest energy state, the trans-trans (TT) state, occurs when bond #3 is parallel to bond #1, and bond #2 is parallel to bond #4. Rotation of bond #3 into the two other equilibrium positions will result in the two trans-gauche (TG) states. Similarly, one obtains the two gauche-trans (GT) states by rotating bond #2 to the other two equilibrium positions associated with this bond. The gauche-gauche (GG) states are of higher energy and their contribution to the rotational isomeric process will be neglected here.

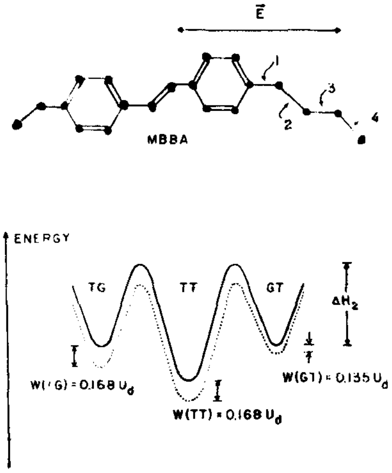

Fig. 1 Schematic representation of an MBBA molecule and the rotational isomeric energy states of its butyl end group. Solid curve: without attractive anisotropic interaction. Dotted curve: with this interaction. The energy shifts are not drawn to scale.

The attractive van der Waals interactions to which a molecule in a nematic liquid crystal is subjected can be thought of as being due to an isotropic part and an anisotropic part. The ensemble average of the anisotropic attractive energy associated with these interactions is written, using the mean field theory of Maier and Saupe, as

$$U_d = - U_a S^2 \qquad (3)$$

where S is the temperature dependent order parameter, U_a is considered to be temperature independent and is such that at the transition temperature

$$4.55\ k_B T_c = U_a \ . \qquad (4)$$

We characterize the anisotropic part of the interactions by introducing an electric field $\vec{E}$ parallel to $\hat{n}$. This field contains contributions from all enighboring molecules and is in some geometric sense analogous to the average magnetic field a single magnetic dipole would experience in a ferromagnet. In terms of this electric field the anisotropic attractive energy, U_d, can be written as $U_d = -\beta E^2$ where β is the average polarizability of the molecule in the direction of $\hat{n}$. If the polarizability β_b of all bonds b were isotropic U_d would be the same for all configurations. The net result would be a lowering of all energy levels by an equal amount. Since bond polarizabilities are not isotropic (the C-C case is particularly anisotropic) U_d will be different for the different configurations associated with the TT, TG, and GT states. This is because in each case the various bonds of the end group form different angles with $\vec{E}$ (or $\hat{n}$).

In order to calculate the anisotropy in α, we assume that the ultrasonic wave with $\vec{k}\|\hat{n}$ couples more effectively to the TT ↔ GT transitions and the one with $\vec{k}\perp\hat{n}$ couples more effectively to the TT ↔ TG transitions. This can be justified intuitively by noting (for example, by actually constructing a molecular model) that the TT ↔ GT transition reduces the length of the molecule whereas the TT ↔ TG transition reduces its width.

The actual calculation of $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ is carried out as follows. The energy W_b due to the interaction between bond b and the field $\vec{E}$ is written as $W_b = \vec{p}_b \cdot \vec{E}$ where $p_b = \tilde{\beta}_b \vec{E}$ is the induced electric dipole moment and $\tilde{\beta}_b$ the polarizability tensor associated with bond b. Since chemical bonds of the type considered here have approximately axial symmetry, the polarizability tensor can be expressed in terms of a longitudinal component β_ℓ along the direction of the bond and a transverse component β_t perpendicular to it. The interaction energy W can be written as

$$W = -E^2 \sum_b (\beta_\ell^b \cos^2\theta_b + \beta_t^b \sin^2\theta_b) \qquad (5)$$

where the sum extends over the four C-C and nine C-H bonds in the butyl end group, and θ_b are the angles between the direction of $\vec{E}$ and the various bonds. If we assume that all bond angles about each carbon atom are tetrahedral [i.e., equal to $\cos^{-1}(1/3)$], then θ_b (b = 1 to 13) can be expressed in terms of the supplement, μ, of the tetrahedral angle. Using the values[6] $\beta_\ell^{CC} = 1.88$, $\beta_t^{CC} = 0.02$, $\beta_\ell^{CH} = 0.79$, and $\beta_t^{CH} = 0.58$, all in units of Å^3 per molecule, one obtains for each configuration

$$W(TT) = - E^2\{(1 + \cos^2\mu)\beta_\ell^{CC} + (\sin^2\mu)\beta_t^{CC} + (1 + 6\cos^2\mu)\beta_\ell^{CH} + (6\sin^2\mu)\beta_t^{CH}\}$$

$$W(TG) = W(TT)$$

$$W(GT) = - E^2\{(2\cos^2\mu)\beta_\ell^{CC} + (2\sin^2\mu)\beta_t^{CC} + (3 + 4\cos^2\mu)\beta_\ell^{CH} + (4\sin^2\mu)\beta_t^{CH}\} \qquad (6)$$

The value of E^2 can be estimated from the total anisotropic attractive energy $U_d = - \beta E^2$ where β is the average polarizability of the whole molecule in the direction of $\hat{n}$. This total polarizability was calculated here by adding the contributions from the various bonds and the aromatic rings in the MBBA molecule and was found to be 38.8 Å³ per molecule.

Substitution of $E^2 = - U_d/\beta$ along with the numerical values of μ, β_ℓ^{CC}, β_t^{CC}, β_ℓ^{CH}, β_t^{CH}, and β into Eq. (6) yields

$$W(TT) = .168\, U_d;\ W(TG) = .168\, U_d;\ W(GT) = .135\, U_d.$$

These are the energy shifts which the different rotational isomeric configurations undergo because of the presence of the anisotropic attractive energy. Hence, whatever intrinsic energy difference, $\Delta H_0(TT,GT)$, there was between the TT and GT states must be modified by adding the quantity $W(GT) - W(TT) = -0.033\, U_d$. The same is true for $\Delta H_0(TT,TG)$ but the correction $W(TG) - W(TT)$ is equal to zero.

In view of the coupling assumed previously between the direction of the ultrasonic wave and the rotational isomeric transitions, one has

$$\Delta H_0^{\perp} = \Delta H_0;\ \Delta H_0^{\parallel} = \Delta H_0 + 0.033|U_d| = \Delta H_0(1 + \delta)$$

where $\delta = 0.033|U_d|/\Delta H_0$. Substitution of the above enthalpy difference into Eq. (2) for the relaxation strengths, yields

$$\varepsilon_{\perp} = \frac{(\gamma - 1)}{C_P^{\infty}}\, 2R\left[\frac{\Delta H_0}{RT}\right]^2 e^{-\Delta G_0/RT} \qquad (7a)$$

$$\varepsilon_{\parallel} = \frac{(\gamma - 1)}{C_P^{\infty}}\, 2R\left[\frac{\Delta H_0}{RT}\right]^2 e^{-\Delta G_0/RT}(1 + f(T)\delta) \qquad (7b)$$

where $f(T) = 2 - \Delta H_0/RT$ is only weakly temperature dependent. Typically $f(T)$ would vary between 1.3 and 1.4 over the temperature range of interest.

Three approximations were made in writing Eq. (7). Firstly, the exponential term in the denominator of Eq. (2) was neglected with respect to one. The second and third approximations made consist in having neglected terms in δ^2 and having expanded $\exp(-\Delta H_0 \delta/RT)$. As is shown below, $\delta \doteqdot 0.15$, hence these latter approximations result in about a 3% - 4% error.

The relaxation strength for the parallel case can be written as

$$\varepsilon_{\parallel} = \varepsilon_{\perp}(1 + g(T)\delta)$$

and consequently, the anisotropy in the relaxation strength is

$$\varepsilon_{\parallel} - \varepsilon_{\perp} = \varepsilon_{\perp} g(T)\delta \quad .$$

Recalling the definition of δ and using Eq. (3) one has

$$\varepsilon_{\parallel} - \varepsilon_{\perp} = 0.033\ g(T)\ \varepsilon_{\perp}\ U_a S^2/\Delta H_0 \quad . \qquad (8)$$

The above expresses the anisotropy of the relaxation strength (and therefore, the anisotropy in the attenuation coefficient) which (a) is related to the thermal relaxation occurring in the butyl end group of the molecule, (b) is of the correct sign (i.e., $\varepsilon_{\parallel} > \varepsilon_{\perp}$), and finally, (c) has a temperature dependence, chiefly through S^2, which agrees with that found experimentally.[7]

The order of magnitude of $\varepsilon_{\parallel} - \varepsilon_{\perp}$ at room temperature can be calculated using $U_a = 2.86$ Kcal mole^{-1} (from Eq. (4) with $T_c = 314$°K), $\Delta H_0 \doteqdot 0.4$ Kcal mole^{-1} (from Ref. 1), $S = 0.8$ (from Ref. 8), and $h(T) = 1.35$, one finds $\delta = 0.15$ and

$$\varepsilon_{\parallel} - \varepsilon_{\perp} = 0.20\ \varepsilon_{\perp} \ . \qquad (9)$$

For an order of magnitude calculation we can replace $\varepsilon_{\perp}$ with the relaxation strength ε of an unoriented sample. From the data of Ref. 2 one has $\varepsilon = 0.033$, consequently $\varepsilon_{\parallel} - \varepsilon_{\perp} = 0.0066$. This value can be compared to a value of 0.0102 obtained from existing data on velocity anisotropy.[9] From this we conclude that there is order of magnitude agreement. Another check on Eq. (9), one independent of the numerical value given to the relaxation strength $\varepsilon_{\perp}$ (or ε), can be made by comparing the measured low frequency value of $\Delta\alpha/\alpha$ with that expected from Eq. (9). Using measurements of $\Delta\alpha$ and of α by us as well as by others,[2,3] one finds a value of 0.27 at 2 MHz and 0.30 at 1 MHz (both values refer to room temperature). These values compare favorably with the value 0.20 expected on the basis of Eq. (9).

In conclusion, we have shown that an intramolecular mechanism, such as rotational isomerism of the butyl end group in MBBA, can give rise to anisotropic ultrasonic attenuation. The anisotropy calculated on the basis of a simplified model is in good agreement with experimental data.

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