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Thermal Behaviour of the Twist Viscosity in a Series of Homologous Nematic Liquid Crystals

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We have measured the twist viscosity $\gamma_1(T)$ by the rotating field method, over the entire nematic range of the 4,4'-di-*n*-alkoxyazoxybenzenes (mOAB) from $m = 2$ to $m = 7$. The results of these measurements are presented here together with a new development of our previous theory of $\gamma_1(T)$ which accounts for the free volume variation with temperature and gives the following main result:

$$\gamma_1(T) = g \cdot S^2 \cdot \exp \left(\frac{eS}{kT} + \frac{\theta S^2}{T - T_0} \right)$$

where S is the order parameter, eS is the height of the Maier-Saupe potential, T_0 is the temperature of motional "freezing" of the nematic director, and g and θ are nearly constant parameters which may be either computed from other physical data or extracted from the data discussed here. This theoretical result fits very well to the experimental data over the entire nematic range of all the above mentioned materials.

1 INTRODUCTION

Twist viscosity γ_1 is the dissipative coefficient associated with the motion of the director relative to the surrounding fluid in nematic liquid crystals, and it plays a fundamental role in the dynamics of this type of mesophase.¹

Up to now, different expressions have been proposed for the temperature dependence of γ_1 in nematics.²⁻¹¹ Some of them consider only the order parameter dependence of γ_1 as $\gamma_1 \sim S^2$,^{2,4,5} or $\gamma_1 \sim S^9$ and others are of

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the Arrhenius type with a weight factor either proportional to S^2 ³ or proportional to S .^{10,11} However, the S -dependence of γ_1 is not compatible with a general thermodynamic argument^{1,8} that leads to $\gamma_1 \sim S^2$. The molecular statistical theory of $\gamma_1(T)$ presented in Refs. 6, 7 gives an expression for $\gamma_1(T)$ which is still of the Arrhenius type, but with an activation energy proportional to the order parameter S , and presenting a weight factor proportional to S^2 .

The present situation about the thermal dependence of γ_1 is not very clear for two main reasons. First, all of the expressions previously quoted do not have enough generality to fit successfully to all known data. On the other hand, the published data refer to materials with very different structures which do not allow us to gain an insight into the linkage between molecular properties and twist viscosity.

In order to clarify this situation we measured $\gamma_1(T)$ over the entire nematic range of six member of the homologous series of 4,4'-di-*n*-alkoxyazoxybenzenes (mOAB for short) from $m = 2$ (P.A.P.) to $m = 7$. Equivalent data for the first members of this series ($m = 1$: P.A.A.) was already known. We have found that it is possible to give a theoretical description of the full experimental data by using a modified form of the theory proposed by us some years ago.^{6,7} This modified theory simply takes into account free volume effects which were disregarded in the former presentation.

The remainder of this paper is organized as follows. In the next section we discuss the modifications to be introduced in our previous theory^{6,7} in order to account for free volume effects. Our main result is the new expression for $\gamma_1(T)$:

$$\gamma_1 = gS^2 \exp\left(\frac{\epsilon S}{kT} + \frac{\theta S^2}{T - T_0}\right) \quad (1)$$

where S is the order parameter, ϵS is the height of the Maier-Saupe mean field potential,¹² T_0 is the temperature of motional "freezing" of the director, and g and θ are nearly constant parameters which may be either computed from other physical data (see below), or experimentally evaluated. Section 3 displays the experimental data, which is discussed and contrasted with our theory in Section 4. We give the conclusions of this work in Section 5, together with suggestions for further work.

2 THEORY

In this section we present the modifications in our previous theory about $\gamma_1(T)$ in nematics^{6,7} which are needed to account for free volume effects explicitly.

The essential feature of this theory is to relate the characteristic frequency ν_0 of reorientation of a particle (a molecule or a small group of m molecules, to take into account short range steric order) about the director (in equilibrium), and γ_1 . This reorientation consists in rotational jumps of π radians performed by the particle between two minima of the intermolecular mean field potential. The expression linking ν_0 and γ_1 is ⁷

$$\gamma_1 = \frac{kT}{\pi^2 V^a} \cdot \frac{1}{\nu_0} \quad (2)$$

where k is the Boltzmann constant, T is the temperature and V^a is the volume each particle must dispose in order to jump. The characteristic time $1/\nu_0$ is essentially the low-frequency dielectric relaxation time measured with $\mathbf{E} \parallel \mathbf{n}$.

Now, we must compute V^a and ν_0 . To compute V^a , we assume that the minimum volume that each particle must dispose in order to jump is the volume per particle extrapolated from the isotropic phase to the temperature T . If β is the compressibility and V_N is the volume per particle in the nematic phase, then

$$\frac{V^a - V_N}{V^a} = -\beta \cdot \Delta p \quad (3)$$

where Δp is the variation in the "internal" pressure necessary to the volume expansion. It may be computed from the Maier-Saupe mean field potential per molecule $D(\theta)$ ¹² given by

$$D(\theta) = -\frac{AS}{mV_N^2} \cdot \frac{3 \cos^2 \theta - 1}{2} \quad (4)$$

where A is a parameter giving the strength of the potential and θ is the angle between the long molecular axis and the director; we have:

$$\Delta p = -\left(\frac{\partial \langle D \rangle}{\partial V_N}\right)_S = -\frac{A}{mV_N^3} S^2 \quad (5)$$

Therefore, from (3) and (5) we get

$$\frac{V^a - V_N}{V^a} = \frac{\beta \cdot A}{mV_N^3} \cdot S^2 \quad (6)$$

and substituting this last expression into (2) we conclude that γ_1 is proportional to S^2 , as first proposed in Ref. 3.

The computation of the jump frequency ν_0 is done here in the framework of the theory of rate processes.¹³ The mean field energy of a molecule is minimum for $\theta = 0$ and maximum for $\theta = \pi/2$, and, according to the theory

of rate processes, there is an equilibrium between the number N_a of molecules in the activated state ($\theta = \pi/2$) and the number N_g of molecules in the ground state ($\theta = 0$). Therefore

$$\frac{N_a}{N_g} = \frac{z_a}{z_g} \frac{Z_1^a Z_2^a Z_3^a}{Z_1^g Z_2^g Z_3^g} \cdot \exp\left(-\frac{\Delta\Sigma}{k}\right) \quad (7)$$

where Z_i^a and Z_i^g are the rotational partition functions for each of the three rotational degrees of freedom of the particle in the activated and ground states, respectively, z_a and z_g are the partition functions for all other degrees of freedom, and $\Delta\Sigma$ is the entropy difference between the activated and ground states. The rotational partition functions Z_i may be written in general as

$$Z_i = \left(\frac{2I_i kT}{h^2}\right)^{1/2} \quad (8)$$

where h is the Planck constant and I_i is the appropriate moment of inertia. Assuming that the particles are symmetrical tops ($I_2 = I_3$), and substituting (8) into (7) we get

$$\frac{N_a}{N_g} = \frac{z_a}{z_g} \cdot \frac{I_2^a}{I_2^g} \cdot \left(\frac{I_1^a}{I_1^g}\right)^{1/2} \cdot \exp\left(\frac{-\Delta\Sigma}{k}\right) \quad (9)$$

On the other hand, the number of molecules that jump over the potential barrier per unit time is $\nu_0 N_a$ and it is equal to N_a divided by the mean lifetime τ of the molecules in the activated state. Putting $\tau = \pi/\langle\omega\rangle$, $Y = I_2^a \omega^2/2kT$, and using Boltzmann statistics, we find

$$\tau = \pi \cdot \frac{Z_2^a}{\int_0^\infty d\omega \cdot \omega \cdot \exp(-Y)} = \pi^{3/2} \cdot \left(\frac{2I_2^a}{kT}\right)^{1/2} \quad (10)$$

so that

$$\frac{N_a}{N_g} = \nu_0 \cdot \tau = \nu_0 \cdot \pi^{3/2} \cdot \left(\frac{2I_2^a}{kT}\right)^{1/2} \quad (11)$$

From Eqs. (9) and (11) we obtain an expression for ν_0 which can be put into the form:

$$\nu_0 = \frac{kT}{h} \cdot \frac{z_a}{z_g} \cdot \frac{I_2^a}{I_2^g} \cdot \left[\frac{I_1^a}{I_1^g} \cdot \frac{h^2}{2\pi^3 I_2^a kT} \right]^{1/2} \cdot \exp\left(-\frac{\Delta\Sigma}{k}\right) \quad (12)$$

Now we must compute $\exp(-\Delta\Sigma/k)$. It is essentially the product of two terms: the probability that the particle has enough energy to overcome the potential barrier times the probability that the particle finds enough free

volume to do it. The first term has been computed in Ref. 7 and is given by

$$\exp\left(-\frac{\varepsilon S}{kT}\right)$$

where

$$\varepsilon S = D\left(\frac{\pi}{2}\right) - D(0) = \frac{3}{2} \cdot \frac{A}{mV^2} S. \quad (13)$$

The second factor may be computed by a method analogous to that of Ref. 14; the result is, in our notation,

$$\exp\left(-\gamma \cdot \frac{V^a - V_0}{V_N - V_0}\right) = e^{-\gamma} \cdot \exp\left(-\gamma \cdot \frac{V^a - V_N}{V_N - V_0}\right) \quad (14)$$

where $V^a - V_0$ is the amount of free volume each particle must dispose in order to get the activated state, $V_N - V_0$ is the free volume per particle, and γ is a factor comprised between 0.5 and 1 to account for the free volume overlap. If α is the difference between the thermal expansion coefficients of the nematic phase and of the crystalline phase, we may write

$$V_N(T) - V_0 \simeq \alpha \cdot V_0 \cdot (T - T_0) \quad (15)$$

where $V_0 = V_N(T_0)$ and T_0 is the temperature at which there is no more free volume disposable. Eq. (14) may be further transformed using Eqs. (6) and (15):

$$-\gamma \frac{V^a - V_N}{V_N - V_0} = -\frac{\gamma}{V_0 \cdot \alpha} \cdot \frac{V^a}{V_N} \cdot \frac{\beta A}{mV_N^2} \cdot \frac{S^2}{T - T_0} \quad (16)$$

Therefore we may write

$$\exp\left(-\frac{\Delta \Sigma}{k}\right) = e^{-\gamma} \cdot \exp\left(-\frac{\varepsilon S}{kT} - \frac{\theta S^2}{T - T_0}\right) \quad (17)$$

where

$$\theta = \frac{V^a \gamma}{V_0 \cdot \alpha} \cdot \frac{\beta A}{mV_N^3} \quad (18)$$

Now, substituting (17) into (12) we obtain:

$$v_0 = \frac{kT}{h} \left\{ e^{-\gamma} \frac{z_a}{z_g} \cdot \frac{I_2^a}{I_2^g} \cdot \left[\frac{I_1^a}{I_1^g} \cdot \frac{h^2}{2\pi^3 I_2^a kT} \right]^{1/2} \cdot \exp\left(\frac{-\theta S^2}{T - T_0}\right) \right\} \cdot \exp\left(-\frac{\varepsilon S}{kT}\right) \quad (19)$$

and putting this last expression and Eq. (6) into Eq. (2) we finally arrive to

$$\gamma_1(T) = \left(\frac{2}{\pi} \cdot \frac{I_1^g}{I_1^a} \cdot kT \cdot I_2^a \right)^{1/2} \cdot \frac{z_g}{z_a} \cdot \frac{I_2^g}{I_2^a} \cdot \frac{\beta A e^{\gamma}}{m V_N^3 (V^a - V_N)} \cdot S^2 \cdot \exp \left(\frac{\varepsilon S}{kT} + \frac{\theta S^2}{T - T_0} \right) \quad (20)$$

which may be written in short as

$$\gamma_1(T) = g S^2 \exp \left(\frac{\varepsilon S}{kT} + \frac{\theta S^2}{T - T_0} \right) \quad (21)$$

The factor $\{ \dots \}$ in Eq. (19) was called $\Pi(Z^e, Z)$ in Ref. 7 but it was not given explicitly. As we shall see below, the exponential factor inside $\{ \dots \}$ in Eq. (19), i.e., "the free-volume factor", is the main difference between this theory and that presented in Ref. 7 where the importance of the second term in the r.h.s. of Eq. (17) was not sufficiently recognized. This "free volume factor" is similar to that introduced by Cohen and Turnbull for the translational diffusion in an isotropic liquid of hard spheres.¹⁴

Expression (19) means, in short, that the frequency ν_0 of the rotational jumps of π is given by kT/h , times the probability that the molecule has enough energy to overcome the potential barrier, times the probability that the molecule finds the necessary free volume to jump.

As the temperature decreases, the available free volume per particle ($V_N - V_0$) decreases too, and due to the increasing packing of the molecules the mobility of the holes also decreases. When the temperature reaches T_0 , γ_1 becomes infinitely large and the nematic director would "freeze" at this temperature if a phase transition did not occur before.

Returning back to Eq. (21), when $T_0 \ll T$ Eq. (21) reduces to the form proposed by us in Ref. 7:

$$\gamma_1 = c S^2 \exp \left(\frac{\varepsilon S}{kT} \right) \quad (22)$$

but if this condition is not fulfilled, the free volume factor dominates the temperature dependence of γ_1 and Eq. (21) may then be approximated by

$$\gamma_1 = g_1 S^2 \exp \left(\frac{\theta S^2}{T - T_0} \right) \quad (23)$$

3 EXPERIMENTAL RESULTS

We measured $\gamma_1(T)$ by the rotating magnetic field technique^{15,16} over the entire nematic range of six members of the homologous series 4,4'-di-*n*-

alkoxyazoxybenzenes (mOAB for short) from $m = 2$ to $m = 7$. The experiments were carried out with the apparatus existent in the Centre de Recherches Paul Pascal at Talence (France) which is described in Ref. 16.

The samples were purchased from Eastman Chemicals and were first purified by chromatography and after recrystallized from ethyl acetate. The magnetic field used was about 10 K Gauss and the temperature control was done with a calibrated thermocouple immersed with the sample in a thermostated oil bath; we estimate the precision of the temperature measurements to be better than 0.05 K.

Figure 1 shows γ_1 as a function of $T_{\text{NI}} - T$, where T_{NI} is the nematic-isotropic transition temperature, for the odd members of this series, including the data for 10AB quoted from Refs. 12 and 18–20, for the sake of completeness. Figure 2 displays similar data for the even members. The conversion of kinematic viscosity γ_1/ρ to γ_1 was done by using the density data of Linsert.¹⁷ The full curves shown in both Figures 1 and 2 were calculated from a least squares fit of expression (23) to the data, and were drawn by the computer. In these computations we used the expression for $S(T)$ proposed in Ref. 21. Table I presents the best parameters g_1 , θ , and T_0 together with the root mean square error of the fits.

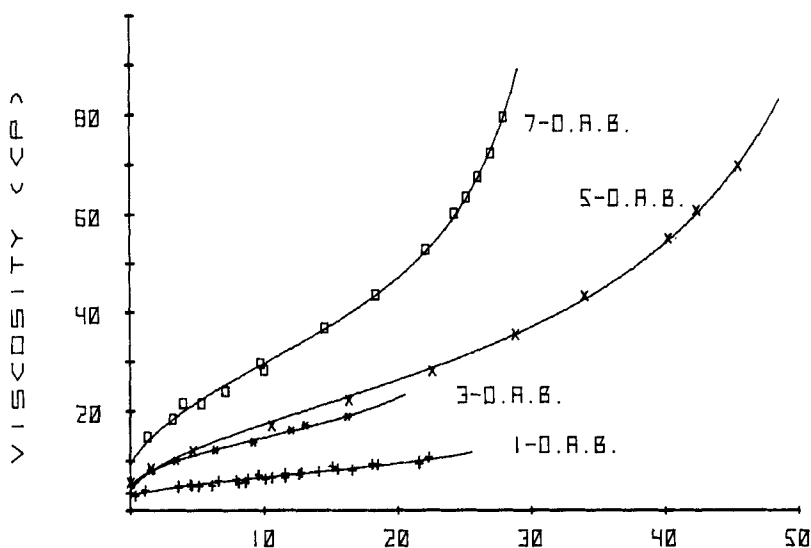


FIGURE 1 Thermal behaviour of the twist viscosity γ_1 for the members with $m = 1, 3, 5, 7$ of the series of di-alkoxyazoxybenzenes (mOAB) as a function of $T_{\text{NI}} - T$.

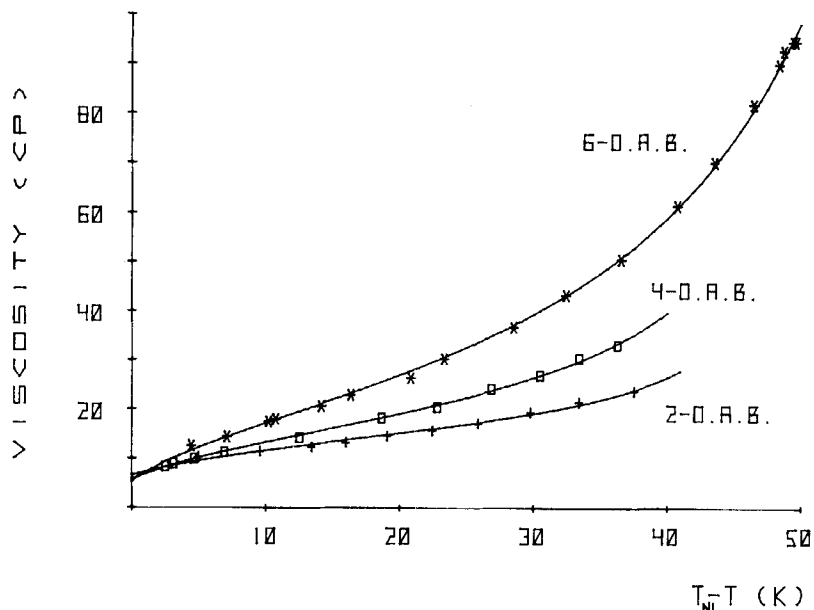


FIGURE 2 Thermal behaviour of the twist viscosity γ_1 , for the members with $m = 2, 4, 6$ of the series of di-alkoxyazoxybenzenes (mOAB) as a function of $T_N - T$.

TABLE I

material	$g_1(\text{cP})$	$\theta(\text{K})$	$T_0(\text{K})$	r.m.s. error (cP)
1OAB	18.070	10.41	368	0.373
2OAB	23.337	10.61	386	0.419
3OAB	30.694	10.97	364	0.259
4OAB	23.549	28.37	345	0.310
5OAB	30.141	58.31	316	0.594
6OAB	23.734	77.60	313	0.745
7OAB	46.695	13.52	357.5	0.774

4 DISCUSSION

A first look over Figures 1 and 2 shows that expression (23) fits fairly well to our experimental data about $\gamma_1(T)$ over the entire nematic range of all those materials. This strongly supports the theory presented in this paper and Ref. 7. We may go one step further and check some other implications of our theory.

Eq. (2) provides a relation between twist viscosity, and the frequency ν_0 of the rotational jumps of π performed by the molecules, in equilibrium. This frequency is expected to be close to the inverse of the low frequency dielectric

relaxation time $\tau_{11}^{(1)}$ which is measured with $\mathbf{E}||\mathbf{n}$ and corresponds to the orientational motion of the component of the permanent electric dipole parallel to the long molecular axis. Therefore one must have

$$\tau_{11}^{(1)} \simeq \frac{\pi^2 V}{kT} \cdot \gamma_1 = \frac{1}{\nu_0} \quad (24)$$

A comparison between the values of $1/\nu_0$ computed through Eq. (24) and the data reported in Ref. 22 about $\tau_{11}^{(1)}$ for the homologues 4, 5, 6 and 70AB shows that Eq. (24) is indeed correct to a good approximation.²³

Eq. (6) provides another way of checking our theory: the volume needed by one particle to jump is expected to be of the order of the volume per molecule as extrapolated from the isotropic phase where the molecules rotate freely. Therefore, we may write for $T = T_{\text{NI}}$

$$V_0 \cdot \alpha \cdot \theta \cdot S^2(T_{\text{NI}}) \simeq \Delta V_{\text{NI}} \quad (25)$$

where ΔV_{NI} is the volume jump per molecule at the nematic-isotropic transition. Again Eq. (25) is verified to a rather good approximation. For instance, for 4OAB we have $S(T_{\text{NI}}) = 0.475$,²¹ $\alpha \simeq 8.9 \times 10^{-4} \text{ K}^{-1}$,²¹ $T_0 = 345 \text{ K}$ (from Table I) so, from the density data¹⁷ we find $V_0 \simeq 320 \text{ cm}^3/\text{mol}$ and $V_0 \cdot \alpha \cdot \theta \cdot S^2(T_{\text{NI}}) \simeq 1.82 \text{ cm}^3/\text{mol}$ which is close to the value of $\Delta V_{\text{NI}} \simeq 1.15 \text{ cm}^3/\text{mol}$ reported.¹² On the other hand, from Eqs. (20) and (23) it follows that the quantity g_1 is given by the following expression:

$$g_1 = \frac{z_g}{z_a} \cdot \frac{I_2^g}{I_2^a} \cdot \left(\frac{I_1^g}{I_1^a} \right)^{1/2} \cdot \frac{\beta A e^\gamma}{m V_N^3 (V^a - V_N)} \cdot \left(\frac{2}{\pi} k T I_2^a \right)^{1/2} \cdot \exp\left(\frac{\epsilon S}{kT} \right) \quad (26)$$

For 1OAB and for $T = 400 \text{ K}$ we have: $I_2^g = 7.5 \times 10^{-37} \text{ g cm}^2$,²⁴ $\beta = 7 \times 10^{-11} \text{ cm}^3 \text{ erg}^{-1}$,²⁵ $V_N = 223.8 \text{ cm}^3 \text{ mol}^{-1}$ and $V^a - V_N \simeq 4.4 \text{ cm}^3 \text{ mol}^{-1}$.¹² Assuming $z_g \simeq z_a$, $I_1^g \simeq I_1^a$ and $I_2^g \simeq I_2^a$, and using the following equation¹²

$$\frac{A}{m V_N^2} = 4.55 k T_{\text{NI}} \quad (27)$$

we find, by substitution of these values in Eq. (26), $g_1 \simeq 7.7 \text{ cP}$ for $\gamma = 0.5$ and $g_1 \simeq 12.7 \text{ cP}$ for $\gamma = 1$. Both values are lower than the experimental one, but they are probably an underestimation of g_1 because it was implicit in its computation that only one molecule was jumping. A better estimation is provided by taking a small group of 4 molecules in a cubic packing: then, the computation of g_1 must be corrected by a factor $\mu = (I_{\text{group}}/I_{\text{molecule}})^{1/2}$ which is about 2, for this case, giving $g_1 \sim 20 \text{ cP}$. This result is also compatible with a calculation of short range order effects in 1OAB which gives for the nematic phase a coordination number $m \simeq 4$.²⁶

Another interesting point to be discussed is the correlation between the alkyl chain length and the temperature behaviour of γ_1 . Here, we shall recall some of the main features presented by our data:

a) Close to the nematic–isotropic transition temperature the members from 2OAB up to 6OAB have nearly the same value of the twist viscosity which is about 5 cP. For 7OAB, $\gamma_1(T_{NI})$ is about twice this value ($\simeq 10$ cP) and for 1OAB, $\gamma_1(T_{NI}) \simeq 3$ cP.

b) As the temperature decreases, γ_1 increases faster for the higher homologous members than for the low ones. For instance, $\gamma_1(T_{NI} - 30) \simeq 37$ cP for 6OAB and $\gamma_1(T_{NI} - 30) \simeq 19$ cP for 2OAB.

c) The parameter g_1 shows a general increase with the increasing of the alkyl chain length, and presents an odd-even effect.

All these features may be explained by considering the contribution of the alkyl chains to the nematic order. Up to $m = 3$, $\gamma_1(T)$ can also be described to a good approximation by Eq. (22) which does not take free volume effects into account. Therefore, the amount of free volume present in the nematic phase of these materials is large. It has been shown²⁷ that the creation of holes in a low molecular-weight liquid is more favourable than in a high molecular-weight liquid. This fact and the relative disorder of the alkyl chains leads to a rather free reorientation of the molecules: from Table I one sees that the parameter θ is nearly the same for these materials. An unpleasant consequence of this is that the precision at which T_0 is computed for these materials is low. As the alkyl chain length increases further, the amount of free volume per molecule decreases, and the “free volume factor” in Eq. (21) dominates then the thermal dependence of γ_1 which can no longer be described by Eq. (22). For these materials Eq. (21) or its simpler form Eq. (23) must be used. The free volume effect is shown clearly in Table I where the parameter θ increases rapidly from 3OAB to 6OAB, which means that as the chain length increases it becomes more difficult to find enough free volume to allow for the reorientational jumps. This suggests also that the chains become more rigid as their length increases in agreement with what is found by calorimetry²⁸ and X-ray measurements.²⁹

The behaviour of the parameter g_1 along an homologous series may be approximately inferred from Eq. (26). In this expression the quantities that should present a stronger dependence on the molecular length l are: the moment of inertia about the short molecular axis, I_2 , and the molecular volume. With increasing l , we expect that $V \sim l$, and $I \sim \rho \cdot V \cdot l^2$, so

$$g_1 \sim \frac{\sqrt{I}}{V} \sim l^{1/2} \quad (28)$$

For 6OAB and 1OAB the ratio between the molecular lengths at the extended trans conformation is about 1.68; from (28) one finds $g_1(6\text{OAB}) \sim 1.296 \times g_1(1\text{OAB}) \sim 23$ cP, which is near the experimental value (see Table I). Of course it is obvious that an expression like (28) cannot account for the peculiarities of the variation of g_1 along this series, and it is expected to give only a rather crude idea about the variation of g_1 along the series. For instance, for 7OAB expression (28) predicts $g_1 \sim 24$ cP, and the experimental value is about 47 cP. Nevertheless such a high change in the value of g_1 may also be explained by an increase in the coordination number as discussed before.

At this point, some comments about the odd-even effect are in order. For the twist viscosity this effect is not so neat as it is for the order parameter and for the clearing temperature. However the odd-even effect is implicit in the order parameter dependence of γ_1 , for instance, and it is apparent from the variation of g_1 with the alkyl chain length too. Here we note that g_1 is, in general, greater for the odd members (3OAB, 5OAB, 7OAB) in contrast to what is found with S or T_{NI} .

To conclude this section, we remark that our measured values of γ_1 for 2OAB and 7OAB are significantly greater than those presented in Refs. 18 and 30, respectively. For 2OAB our values are about twice those given.¹⁸ One possible explanation for this difference may be found in the fact that the data reported¹⁸ were computed from early Tsvetkov's measurements of the "critical angular speed" observed in the rotating magnetic field experiment. As discussed in Refs. 12 and 18, this method leads to an underestimate of γ_1 . For 7OAB our values are about 50% greater than those reported by Meiboom and Hewitt in Ref. 30 where a different experimental technique was used. This technique has not been so largely tested as the rotating magnetic field method used in our experiments has been, so that it is difficult to compare the performances of both methods.

5 CONCLUSION

Our previous molecular interpretation of the twist viscosity of nematic liquid crystals^{6,7} has revealed rather successful in fitting to the experimental data so far available for nematics composed of short, rigid, molecules. On the other hand, with longer, flexible, molecules the measured viscosity generally appears to increase faster than predicted by our old expression (22) as the temperature decreases. Here we have shown that the basic idea of our previous interpretation of $\gamma_1(T)$ is indeed correct, and that to bring the theory into agreement with experience *in all cases* we only need to introduce some correction in the details of the previous derivation of expression (22). This

correction simply takes explicitly into account free volume effects which were not sufficiently recognized.^{6,7} The new result proposed in this paper, expressions (21) or (23), can adequately describe the thermal dependence of γ_1 over the full nematic range of a series of homologous compounds, and reduces to the old one when free volume effects are negligible. We thus think it is a meaningful result.

To our knowledge, the experimental data presented here is the first set of systematic measurements of $\gamma_1(T)$ over a series of homologous compounds. In order to better understand the behaviour of γ_1 in terms of molecular properties, e.g. chain length, and to test more closely the predictions of our theory, new systematic measurements of $\gamma_1(T)$ should be endeavoured for other homologous series of liquid crystals. On the other hand, measuring γ_1 as a function of pressure would be a particularly useful way of testing the significance of the free volume concept in the field of molecular transport in liquid crystals. Further work along these lines is most welcome.

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