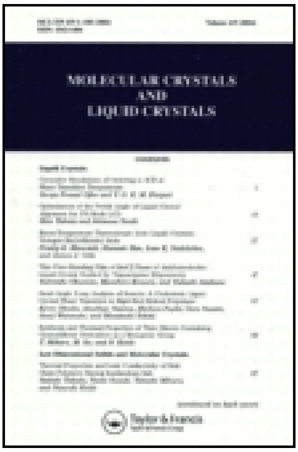

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Correlation Factors in the Nematic and Isotropic Phase of 4-n-octyl-4-cyanobiphenyl (8CB)

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Version of record first published: 24 Sep 2006.

To cite this article: G. M. Tsangaris (1993): Correlation Factors in the Nematic and Isotropic Phase of 4-n-octyl-4-cyanobiphenyl (8CB), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 163-173

To link to this article: http://dx.doi.org/10.1080/10587259308030132

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 163–173
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Printed in the United States of America

Correlation Factors in the Nematic and Isotropic Phase of 4-*n*-octyl-4-cyanobiphenyl (8CB)

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(Received October 1, 1992; in final form November 23, 1992)

Dielectric permittivity of 4-*n*-octyl-4-cyanobiphenyl (8CB) is measured by a shearing Couette cell in the nematic and isotropic phase. Correlation factors are calculated according to Bordewijk and De Jeu for the nematic mesophases and according to Kirkwood for the isotropic liquid.

Activation energy for the nematic reordering is measured dielectrically and the viscous activation energy is measured through the viscometric capability of the shearing cell. A potential barrier of 0.18 eV due to close range intermolecular forces is then obtained.

Keywords: 8CB, dielectric, shear, reordering, correlation-factors

INTRODUCTION

Correlation factor g adopted in Kirkwood's theory[1] for the dielectric permittivity of isotropic liquids can provide information on the nature of the molecular ordering. Bordewijk and De Jeu[2,3] have extended the Kirkwood's theory to account for liquid crystals and their analysis yielded correlation factors $g_{\parallel}$, $g_{\perp}$ due to the anisotropy of permittivity in the mesophase.

In this paper we shall give the correlation factors in aligned and nonaligned phases of 4-*n*-octyl-4-cyanobiphenyl (8CB), calculated from dielectric permittivity data obtained by a shearing Couette cell. Potential barriers to viscous flow and nematic reordering are also calculated.

EXPERIMENTAL

A semi-fixed stator Couette cell was used for dielectric and viscosity measurements which is described in detail elsewhere.[4] Low shear rates can be achieved with this cell since its stator has a fixed alignment along the central axis. Moreover viscosity measurements can be made by measuring the torque exerted to its stator by the liquid. Temperature control was maintained by an oil circulator type C-400 from

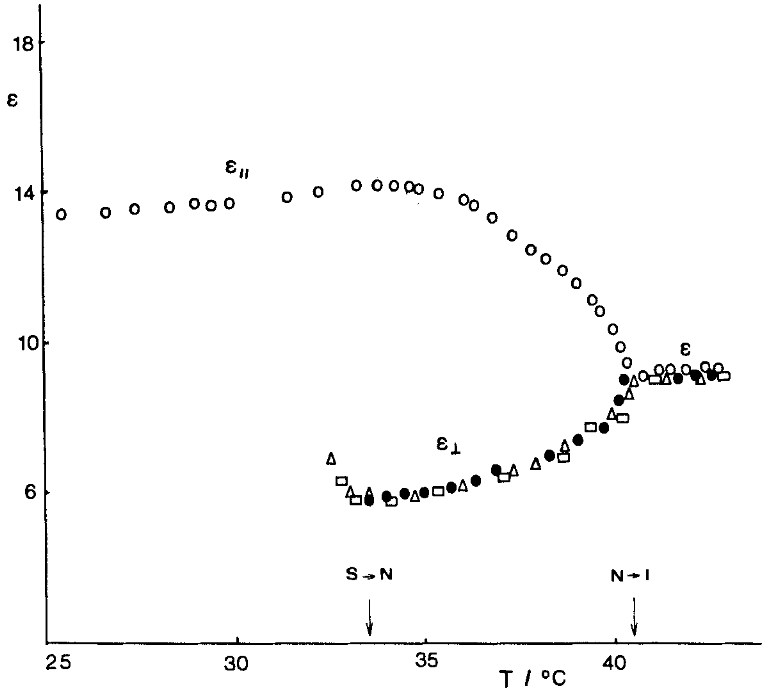

FIGURE 1 Temperature variation of the permittivity of 8CB at different shear rates. ○ = 0 sec^{-1}; ● = 163 sec^{-1}; △ = 655 sec^{-1}; and □ = 1.93×10^4 sec^{-1}.

Tecam, while thermocouples were checking the temperature of cell electrodes. A DC permanent magnet motor type SM22-36 from ASR Servotron was used to drive the cell and the speed of rotation (rps) was measured by a tachoratiometer type TR 6000 from EAL. Capacitances were measured by a Wayne-Kerr bridge B 642 using its internal frequency 1592 Hz. The strain bridge used for viscosity measurements was the model HWL-D of Welwyn Strain Measurements Ltd. Precision strain gauges, from Romulus, Michigan, were used. 8CD was used as supplied by BDH. It undergoes the following transitions:

$$\text{solid} \xrightarrow[21.5^\circ\text{C}]{} \text{smectic} \xrightarrow[33.5^\circ\text{C}]{} \text{nematic} \xrightarrow[40.5^\circ\text{C}]{} \text{isotropic liquid}$$

RESULTS AND DISCUSSION

(a) Dielectric Properties

The variation of permittivity with temperature and shear for 8CB is shown in Figure 1.

At zero shear, permittivity was measured throughout the temperature range covering smectic, nematic and isotropic phases. Comparing obtained results with

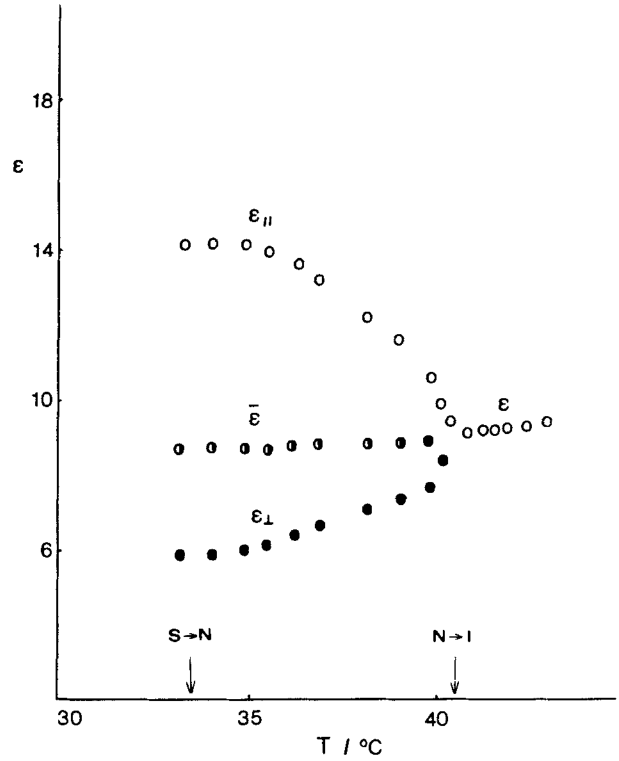

FIGURE 2 Temperature variation of the permittivities $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and the mean $\bar{\varepsilon}$ in the nematic phase and ε in the isotropic phase for 8CB.

existing data[5,6,7] it can be concluded that the permittivity measured was $\varepsilon_{\parallel}$ with the director parallel to the field and normal to the cell surfaces.

On shearing, 8CB molecules were reorientated as shown by a large change in permittivity when in the smectic or the nematic phase. This was essentially complete even at the lowest accessible shear rate available (163 sec^{-1}) although further, very much smaller perturbations could be induced by higher shear rates, including small drops in the isotropic permittivity. Results in the smectic phase are not shown because reproducible readings could not be obtained under shear, although a reduction in permittivity always occured. It is probable that in this state the irreproducibility was the result of void formation in the gap during shear, because of the high viscosity of the smectic phase.

Dielectric data obtained during shearing agree with those already existing[5,6,7] for $\varepsilon_{\perp}$. It is then concluded that even at 163 sec^{-1} the molecules in the nematic phase were aligned in the stream lines of the flow field since flow alignment angle for 8CB is very small[8,9,10] and the director is stable.[11] Thus the application of shear enabled the principal components of permittivity to be readily measured on the same sample.

The variation with temperature of the mean permittivity

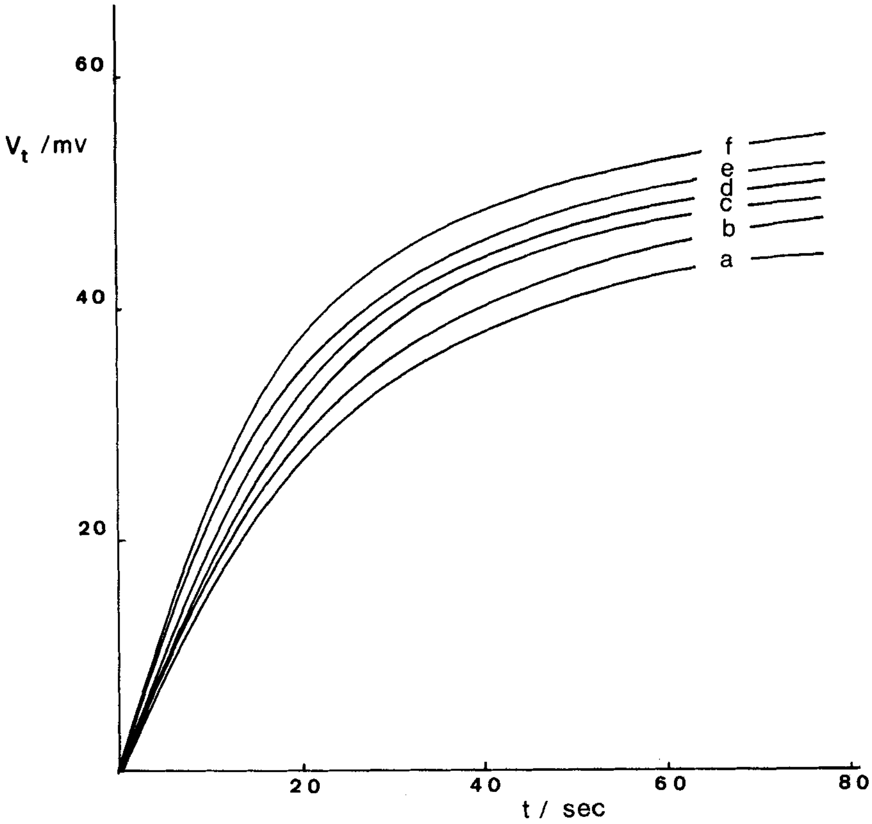

FIGURE 3 The output of the bridge V_t on the Y v.t recorder at different temperatures: a, 38.2°C; b, 37.3°C; c, 36.2°C; d, 35.8°C; e, 35.1°C; f, 34.3°C. The initial shear rate was $G = 163\ \text{sec}^{-1}$.

$$\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp}) \qquad (1)$$

is shown in Figure 2 for the lowest shear rate. It can be seen that curves for $\bar{\varepsilon}$ in the nematic phase and ε in the isotropic phase extrapolated to T_c do not coincide. At the nematic to isotropic phase transition temperature, the mean permittivity of the nematic phase is slightly lower than the permittivity of the isotropic phase. There is evidence[12] that this effect is present in polar compounds regardless of the sign and magnitude of the anisotropy and various explanations[13,14] have been proposed. According to De Jeu[15] this phenomenon is attributed to molecular association.

(b) Correlation Factors

Information of the ordering in the isotropic phase can be obtained from correlation factor g which is derivable from Kirkwood's Equation[1] (2) provided the dipole moment μ is known.

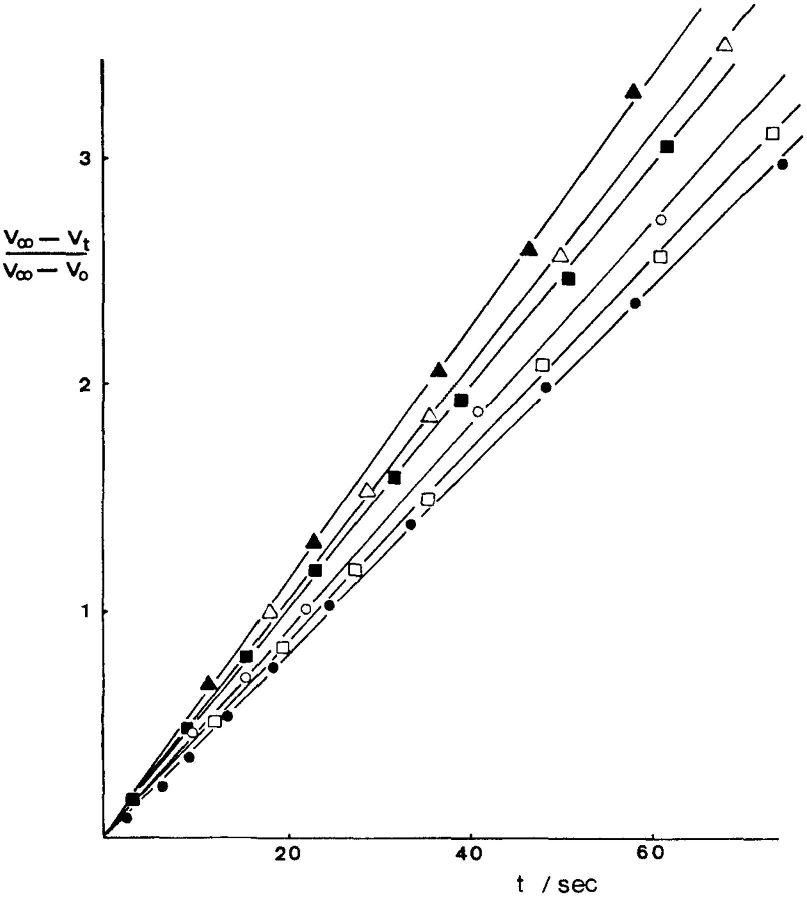

FIGURE 4 The term $(V_\infty - V_t)/(V_\infty - V_0)$ versus time at different temperatures: ● = 38.2°C; □ = 37.3°C; ○ = 36.2°C; ■ = 35.2°C; △ = 35.1°C; and ▲ = 34.3°C.

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{3\varepsilon} = \frac{N}{V\varepsilon_0}\left(\bar{\alpha} + \frac{g\mu^2}{3kT}\right) \tag{2}$$

Kirkwood's equation requires also an estimate of the mean molecular polarizability $\bar{\alpha}$. This may be derived in terms of the principal components of polarizability parallel and normal to the long axis, α_l and α_t, by using the expression (3) due to Vucks[16]

$$\frac{n_j^2 - 1}{n^2 + 1} = \frac{Nd}{3\varepsilon_0 M}\alpha_j \qquad j = l, t \tag{3}$$

in which n_j is the corresponding component of the refractive index and n the refractive index in the isotropic phase, given by the relation

$$n^2 = \frac{1}{3}(n_e^2 + n_0^2) \tag{4}$$

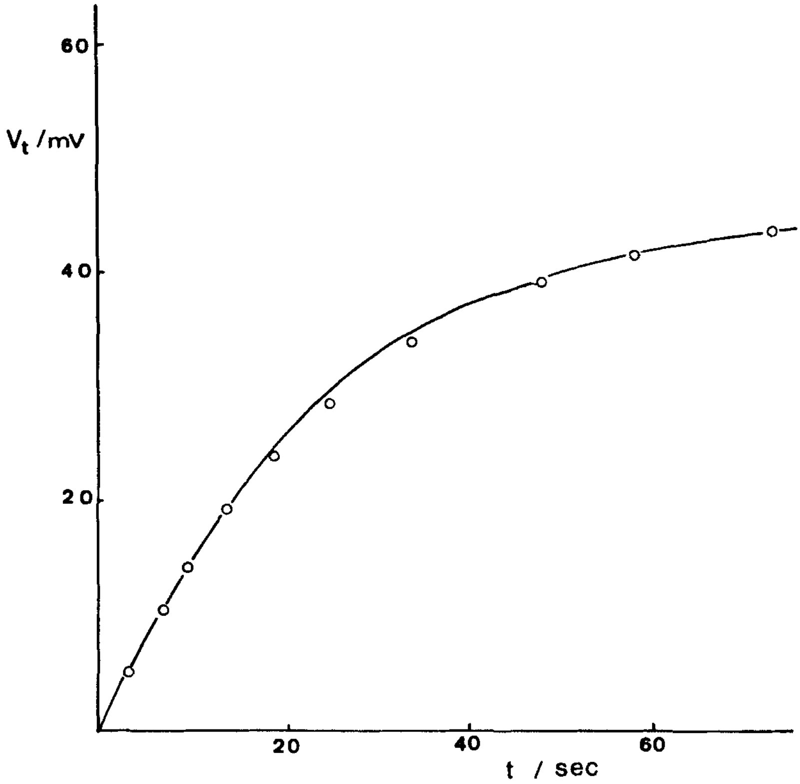

FIGURE 5 V_t versus time at a temperature 38.2°C. Open circles represent calculated points based on a single reorientation time of 24.5 sec.

Using the values $n_e = 1.661$ and $n_0 = 1.524$ for the extraordinary and ordinary rays quoted for 8CB at 589 nm[17] it is found that $n = 1.570$ and the components of polarizability from (3) are:

$$\alpha_l = 5.13 \times 10^{-39}\ \mathrm{C.m^2}.V^{-1}$$

$$\alpha_t = 3.84 \times 10^{-39}\ \mathrm{C.m^2}.V^{-1}$$

with

$$\bar{\alpha} = \frac{1}{2}(\alpha_l + 2\alpha_t) = 4.26 \times 10^{-39}\ \mathrm{C.m^2}.V^{-1} \tag{5}$$

In Equations (2) and (3) the following notation is used: N is the Avogadro number, M the molecular mass, d the density (for 8CB $d = 985\ \mathrm{kg.m^{-3}}$), V the molecular volume, ε_0 the permittivity of free space and k the Boltzmann constant.

From equation (2) and the mean molecular polarizability (5) with $\varepsilon = 8.20$ at $T = 315$ K, it is found that

$$g^{1/2}.\mu = 15.26 \times 10^{-30}\ \mathrm{C.m} \tag{6}$$

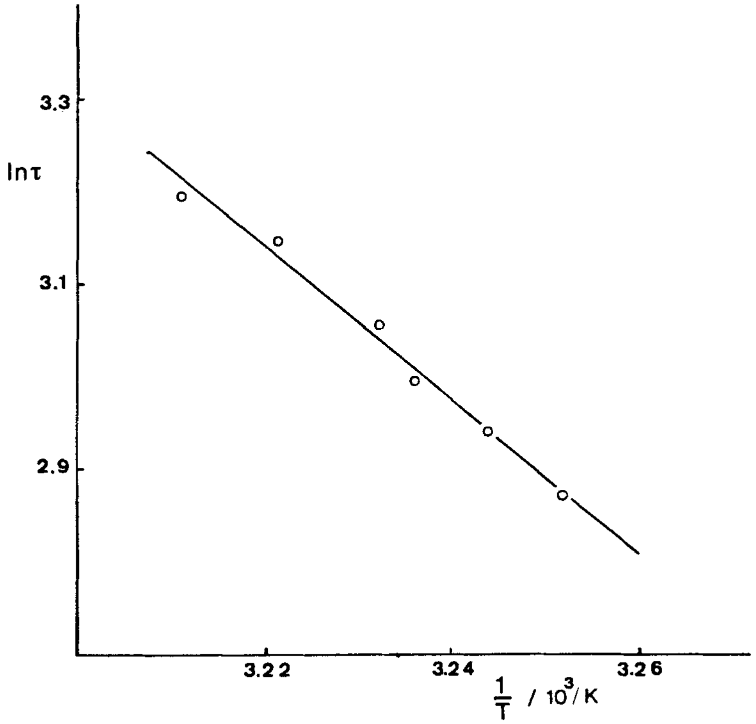

FIGURE 6 The dependence of ln τ on $1/T$. From the slope the activation energy W is obtained.

a value which is similar to that of 11.50×10^{-30} C.m given by Davies *et al.*[18] for the heptyl-cyanobiphenyl and 11.0×10^{-30} C.m evaluated by Cummins[19] for the pentyl-cyanobiphenyl.

Independent dielectric measurements for 8CB in benzene give a value of $\Delta\varepsilon/C = 0.304 \times 10^{-2}$ m³.mol⁻¹ and neglecting the small solution contribution of Δn^2 provide via the Guggenheim[20] relation, an estimate of the dipole moment μ, which is little influenced in dilute non polar solution by dipole-dipole interactions

$$\mu = 16.20 \times 10^{-30} \text{ C.m} \tag{7}$$

A value of $g = 0.887$ for the correlation parameter g in the isotropic phase is then obtained, indicating antiparallel dipolar asssociation, a situation common in highly polar liquids, since the asymmetry of molecules induces packing about the major axis.

For the nematic phase, in which anisotropy of permittivity occurs, two correlation factors are involved referring to ordering of the long and short axis. Bordewijk and De Jeu[2,3] analysis involves the calculation of the field in a cavity in an anisotropic dielectric, with permittivities $\varepsilon_l(l = \parallel, \perp)$, filled with permittivities $\varepsilon_{\infty,l}(l = \parallel, \perp)$. Because anisotropy is present, there are shape parameters Ω_l and the following (8), (9) equations give the correlation factors $g_\parallel$, $g_\perp$.

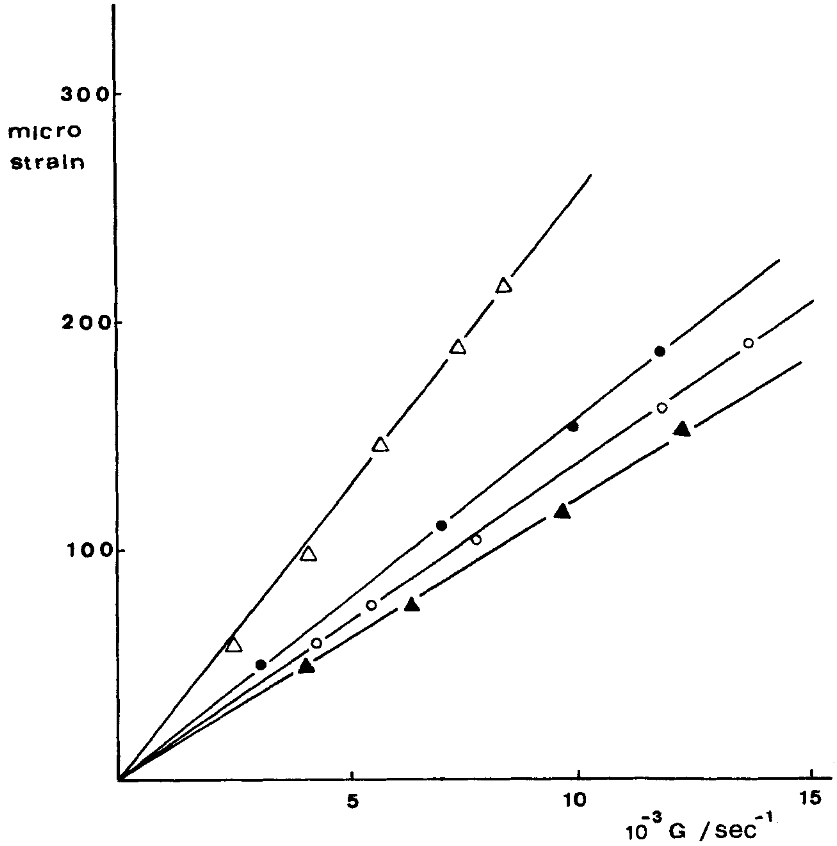

FIGURE 7 The dependence of strain on the shearing rate at different temperatures: ▲ = 39.1°C; ○ = 38.1°C; ● = 37.0°C; and △ = 34.8°C.

$$g_{\parallel} = \frac{3kT\left(1 - \dfrac{Nd}{\varepsilon_0 M}\alpha_l\Omega_l\right)^2 (\varepsilon_{\parallel} - \varepsilon_{\infty\parallel})[\varepsilon_{\parallel} + (\varepsilon_{\infty\parallel} - \varepsilon_{\parallel})\Omega_{\parallel}^{\varepsilon}]}{\dfrac{Nd}{\varepsilon_0 M}(1 + 2\langle S\rangle)\varepsilon_{\parallel}\mu^2} \tag{8}$$

$$g_{\perp} = \frac{3kT\left(1 - \dfrac{Nd}{\varepsilon_0 M}\alpha_l\Omega_l\right)^2 (\varepsilon_{\perp} - \varepsilon_{\infty\perp})[\varepsilon_{\perp} + (\varepsilon_{\infty\perp} - \varepsilon_{\perp})\Omega_{\perp}^{\varepsilon}]}{\dfrac{Nd}{\varepsilon_0 M}(1 - \langle S\rangle)\varepsilon_{\perp}\mu^2} \tag{9}$$

where

$$\Omega_l = 1 - w^2 + \frac{1}{2}w(w^2 - 1)\ln\frac{w + 1}{w - 1} \tag{10}$$

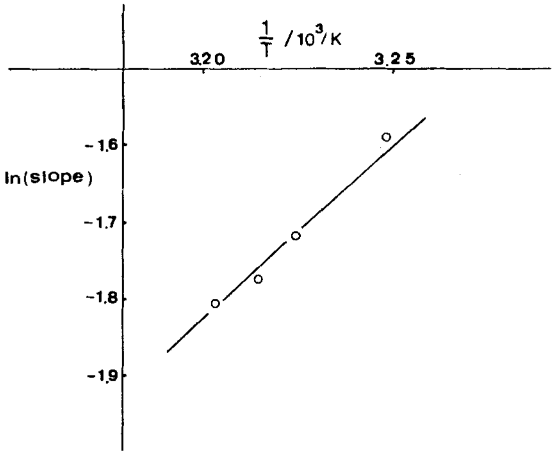

FIGURE 8 The ln(slope) versus $1/T$ dependence. From the slope of this line, the activation energy W_{visc} is obtained.

with

$$w^2 = \frac{a^2}{a^2 - b^2} \tag{11}$$

in which a, b are the dimensions of long and short axis of the molecular ellipsoid.

$$\Omega_{\parallel}^{\varepsilon} = \frac{\varepsilon_{\parallel}}{\varepsilon_{\parallel} - \varepsilon_{\perp}} - \frac{\varepsilon_{\parallel}\varepsilon_{\perp}^{1/2}}{(\varepsilon_{\parallel} - \varepsilon_{\perp})^{3/2}} \operatorname{arctg}\left(\frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{\varepsilon_{\perp}}\right)^{1/2} \tag{12}$$

$$\Omega_{\perp}^{\varepsilon} = \frac{\varepsilon_{\parallel}\varepsilon_{\perp}^{1/2}}{2(\varepsilon_{\parallel} - \varepsilon_{\perp})^{3/2}} \operatorname{arctg}\left(\frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{\varepsilon_{\perp}}\right)^{1/2} - \frac{\varepsilon_{\perp}}{2(\varepsilon_{\parallel} - \varepsilon_{\perp})} \tag{13}$$

To calculate the ratio a/b of the axis the following procedure was adopted: a is taken equal to the length of the fully extended molecule and calculated in terms of bond lengths and angles to be 2.20 nm, a value also supported by X-ray studies on 8CB.[23]

Using the density $d = 985$ kg.m^{-3} and the molecular mass of 8CB $M = 291 \times 10^{-3}$ kg.mol^{-1}, the volume of an 8CB molecule is obtained $V = 49.0 \times 10^{-29}$ m^3. Considering that the volume available to a molecule in the nematic phase is equal to the volume $V = \pi(b/2)^2 a$, then b has the value of 0.52 nm while $w^2 = 1.059$ (11) and $\Omega_l = 0.069$ (10). At $T = 310$ K, $\varepsilon_{\parallel} = 13.350$, $\varepsilon_{\perp} = 6.130$, $\Delta\varepsilon = 7.220$. Order parameter $\langle S \rangle = 0.478$ was estimated from Maier-Saupe[21,22] theory. Values of $\varepsilon_{\infty\parallel}$ and $\varepsilon_{\infty\perp}$ were obtained by multiplying n_e^2 and n_0^2 by 1.05 to account for the atomic polarization. The value of dipole moment μ was that found previously from Guggenheim's equation.[20] With this data correlation factors for the nematic phase was calculated as:

$$g_{\parallel} = 0.618 \qquad g_{\perp} = 1.042 \tag{14}$$

The less than unity values of g in the isotropic and $g_{\parallel}$ in the nematic phase indicate antiparallel ordering of the molecular dipoles, along the axis of the nematic director. Dipole interactions of the two cyano groups favours this configuration. Such local order possessed by the dipoles along the nematic director implies a substantial barrier to reorientation which is calculated in (c). The almost unity value of $g_{\perp}$ establishes that perpendicular to the nematic director there is random orientation of the dipole components. The lack of order perpendicular to the director is associated with the smaller dipolar component in that direction and with much lower barrier to the orientation of that component of the molecular dipole.

(c) Rates of Orientation

The ability to align molecules in the nematic phase by the shearing flow, provides a way of evaluating the reorientation time and activation energy involved in the reordering to the perpendicularly orientated state.

To do this it is only necessary after cessation of shear, to measure the recovery of the dielectric properties of the still liquid. This is so, provided that the shear rate is low enough, so that disturbances due to the liquid surge do not influence the measurements in the time scale and that the dielectric recovery is not too rapid.

Graphs in Figure 3 were obtained by a y v.t recording the bridge capacitance output, on a V v.t recorder. The liquid crystal was aligned by a shear rate of 163 $\sec^{-1}$ prior to stopping the motor and decay curves measured at a series of temperatures. The data shown in Figure 3 represent a first order process as shown by Figure 4 from which a simple first order reorientation times τ_j were obtained as a function of temperature. Typical agreement between data found for a sample run and estimated on the basis of a single reorientation time are shown in Figure 5. The temperature dependence of τ_j is of the Arrhenius type as shown by Figure 6 and provides an activation energy of 70.4 KJ mol^{-1}.

Reorientation undoubtedly involves viscous flow and in order to obtain the activation energy for viscous flow the viscometric capability of the apparatus was employed. Torque measurements using the 0.015 cm beam and attached strain gauge bridge, were undertaken as a function of shear, at a number of selected temperatures in the nematic phase (Figure 7). The slope of these lines are proportional to viscosity and an Arrhenius plot (Figure 8) of the data from Figure 7 provides an estimate of the viscous activation energy of 53.0 KJ mol^{-1}.

These two activation energies do not agree and it is reasonable to assume that the difference, between the activatioin energy for the nematic reordering measured dielectrically and the viscous activation energy, relates to a potential barrier due to close range intermolecular forces. Its magnitude is 17.4 KJ.mol^{-1} or 0.18 eV. The reasonableness of this assumption is supported by the value of 0.10 eV reported[24] for *N*-*p*-methoxybenzylidine-*p*-*n*-butulaniline and that of 0.22 eV for *p*-azoxy-anisole[25] putting 8CB in the middle of this range.

The relative magnitudes of the activation energy barrier for viscous flow and the potential barrier needed to overcome local ordering forces appear to be in the right relation to each other since viscous flow would presumably require the destruction of long range order and the complete rotation of molecules.

References

1. J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).
2. P. Bordewijk, *Physica*, **75**, 146 (1974).
3. P. Bordewijk and W. H. De Jeu, *J. Chem. Phys.*, **68**, 116 (1978).
4. H. Block and G. M. Tsangaris, *J. Phys. E: Sci. Instrum.*, **16**, 896 (1983).
5. T. K. Bose, B. Campbell and S. Yagihara, *Phys. Rev.* **A 36**, 5767 (1987).
6. G. Druon and J. M. Wacrenier, *J. Phys.* (Paris), **38**, 47 (1977).
7. B. R. Ratna and R. Shashidbar, Pramāna, Vol. 6, No. 5, 278 (1976).
8. W. W. Beens and W. H. De Jeu, *J. de Phys. Lett.*, **44**, L 805 (1983).
9. "Thermotropic Liquid Crystals, Fundamentals," by G. Vertogen and W. H. De Jeu, Spriger-Verlag, (1988) p. 152.
10. "The Physics of Liquid Crystals," by P. G. de Gennes, Oxford, 1975, p. 175.
11. K. Skarp, et al., *Mol. Cryst. Liq. Cryst.*, **66**, 199 (1981).
12. W. H. De Jeu, *Solid State Phys. Suppl.*, **14** (1978).
13. A. J. Derzhanski and A. G. Petrov, *Phys. Lett.*, **A34**, 427 (1971).
14. N. V. Madhusudana and S. Chandrasekhar, *Proc. Bangalore Liq. Cryst. Conf.*, 57 (1975).
15. W. H. De Jeu and T. W. Lathouwers, *Mol. Cryst. Liq. Cryst.*, **26**, 225 (1973).
16. M. F. Vucks, *Optics and Spectroscopy*, **20**, 361 (1966).
17. B. D. H. catalogue.
18. M. Davies, R. Moutran and A. Price, *J. Chem. Soc. Faraday II*, **72**, 1447 (1976).
19. P. G. Cummins, D. A. Dunmur and D. A. Laidler, *Mol. Cryst. Liq. Cryst.*, **30**, 109 (1975).
20. E. A. Guggenheim, *Trans. Far. Soc.*, **45**, 714 (1949).
21. W. Maier and A. Saupe, *Z. Naturforsch*, **14A**, 882 (1959); **15A**, 287 (1960).
22. E. B. Pristley, P. J. Wojtowicz and Sheng Ping, "Introduction to Liquid Crystals," Plenum Press, New York and London, 1975. Chap. 3,4.
23. J. E. Lydon and C. J. Coakley, *J. de Phys. Colloque C3*, **40**, c3-234 (1979).
24. E. Rondelez, D. Dignet and G. Durand, *Mol. Cryst. Liq. Cryst.*, **15**, 183 (1971).
25. G. Meier and A. Saupe, *Mol. Cryst.*, **1**, 515 (1966).