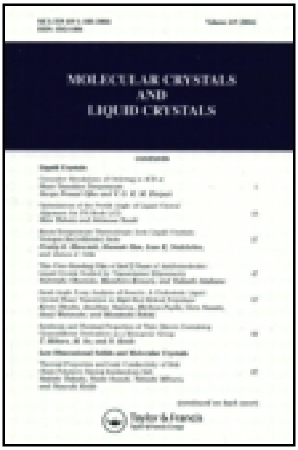

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Dielectric Relaxation and Order Parameters in the Nematic and Smectic Phases of 4-n-octyl-4′-cyanobiphenyl (8CB)

A. Buka [a] [b] & A. H. Price [a]

[a] Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed. SY23 1NE, U.K.

[b] Central Research Institute for Physics, H-1525, Budapest, Hungary

Version of record first published: 20 Apr 2011.

To cite this article: A. Buka & A. H. Price (1985): Dielectric Relaxation and Order Parameters in the Nematic and Smectic Phases of 4-n-octyl-4′-cyanobiphenyl (8CB), Molecular Crystals and Liquid Crystals, 116:3-4, 187-195

To link to this article: http://dx.doi.org/10.1080/00268948508074572

Mol. Cryst. Liq. Cryst., 1985, Vol. 116, pp. 187-195
0026-8941/85/1164-0187/$15.00/0

Printed in the United States of America

Dielectric Relaxation and Order Parameters in the Nematic and Smectic Phases of 4-n-octyl-4′-cyanobiphenyl (8CB)

A. BUKA† and A. H. Price

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed. SY23 1NE U.K.

(*Received June 5, 1984; in final form August 20, 1984*)

The dielectric properties of 8CB in the smectic and nematic phase over the frequency range up to 200 MHz are reported. Two relaxation processes are observed in samples where the director is aligned parallel to the measuring electric field and a broad relaxation process is observed in the perpendicular alignment. The relaxation times do not change significantly at the transition between the smectic and nematic phase, but the activation energy for dipole reorientation appears lower in the smectic phase than in the nematic phase. The results are interpreted to yield the dipole components responsible for the various relaxation processes and also the order parameters.

INTRODUCTION

A study of the frequency variation of the permittivity (ϵ') and the associated dielectric loss (ϵ'') in suitably aligned liquid crystals is expected to show a total of four absorptions.[1] Two of these four absorptions are found when the measuring electric field is parallel to the director (parallel alignment). The absorption occurring at the lower frequency is envisaged as a dipole reorientation about an axis perpendicular to the principal moment of inertia and its intensity depends principally on the longitudinal molecular dipole component

---

†Present address
Central Research Institute for Physics,
H-1525 Budapest, Hungary.

parallel to the principal moment of inertia, while the higher frequency absorption involves the transverse dipole component reorientating about the "long molecular axis". The two absorptions expected when the measuring electric field is perpendicular to the director (perpendicular alignment) again have their origins associated with the longitudinal and transverse dipole components, with the transverse component having a very similar relaxation mechanism (and, hence, relaxation time) to the higher frequency process in the parallel alignment. In practice, resolution of the two absorptions in the perpendicular alignment is difficult and only a broad absorption is often detected (as in the present study). Apart from the measurement of the relaxation times the intensity of the absorptions allow of a calculation of the order parameter and of the dipole component involved in the relaxation[1,2]. Such dielectric studies also give information on the frequency at which the dielectric anisotropy changes sign and this is of interest in dual frequency addressing applications.

The work reported here is a study of the frequency and temperature variation of the dielectric properties of 4-n-octyl-4′-cyanobiphenyl (8CB) in both the nematic and smectic phases and extends the measurements of Druon and Wacreiner[3] into the perpendicular alignment as well as the analysis of the data to include calculation of the dipole components and order parameters.

EXPERIMENTAL RESULTS AND THEIR ANALYSIS

The 8CB sample was used as supplied by BDH Chemicals Ltd., Poole, Dorset, U.K. The dielectric properties were studied over the frequency range between 10^5 and 10^9 Hz and were anlayzed using methods described in previous publications from this laboratory.[4] The liquid crystal alignment in the smectic phase was achieved by cooling from the nematic phase in the presence of an external magnetic field. Both the nematic and smectic phases appear to supercool, with the nematic to smectic transition appearing at 302 K which is 4 K below the normally quoted value.

Some typical experimental results are illustrated in Figure 1. The most satisfactory analsysis of the data obtained for the parallel aligned sample was obtained assuming two relaxation processes. Each absorption curve was analysed using the Fuoss-Kirkwood equation.[5]

$$\cosh^{-1}\left(\frac{\epsilon''_m}{\epsilon''}\right) = \beta \ln\left(\frac{f_m}{f}\right)$$

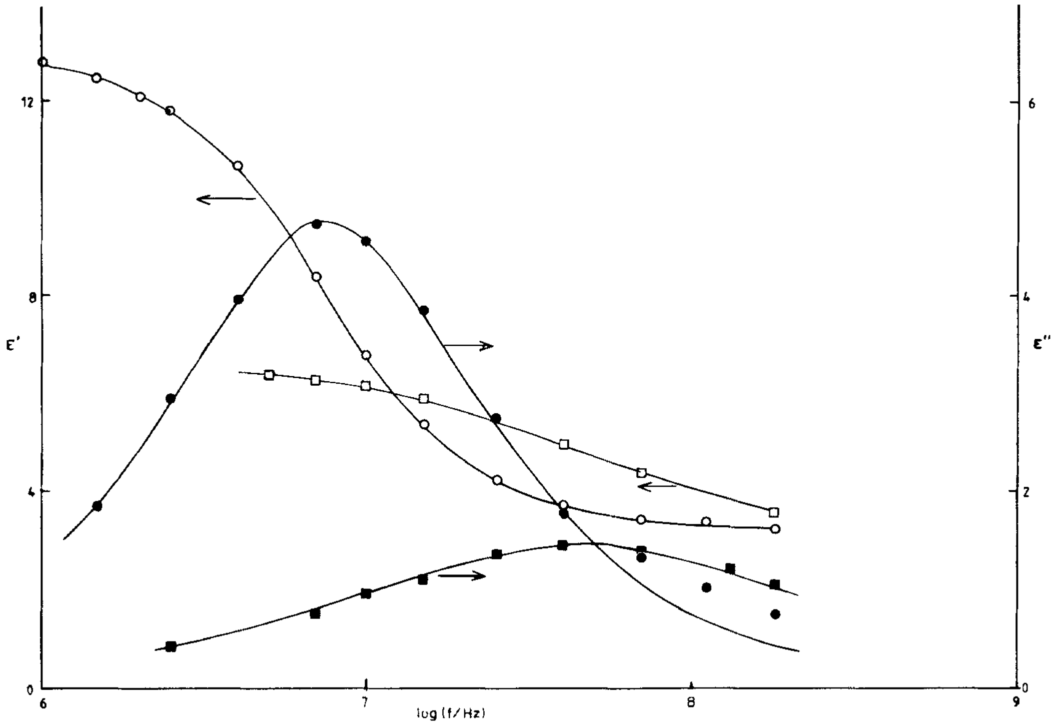

FIGURE 1 Permittivity (ε') and dielectric loss (ε'') in 8CB as measured in the parallel (○, ●) and perpendicular (□, ■) alignments at 310.5K.

where ϵ'' is the dielectric loss at frequency f and the subscript m refers to the parameters at the absorption maximum. The frequency (f_m) of maximum absorption is related to the relaxation time (τ) by $\tau = (2\pi f_m)^{-1}$. β is an empirical parameter describing the width of the absorption and is unity for the simple Debye condition. In the perpendicular alignment the broad absorption curve cannot be realistically resolved into multiple components, and a single Fuoss-Kirkwood equation describes the contour adequately, but with a low β value. The adequacy of the fit was confirmed by extending the measurements at one temperature up to frequencies of 18 GHz using microwave techniques. This procedure differs from the analysis adopted by Wacrenier, Druon and Lippens.[6]

The experimental results are listed in Table I, where ϵ'_{01} and ϵ'_{11}represent the limiting permittivity on the low frequency and on the high frequency side of the first (or low frequency) absorption, ϵ'_{21} the limiting permittivity on the high frequency side of the second (high frequency) absorption in the parallel alignment, and ϵ'_{02} and ϵ'_{12}refer to the equivalent permittivities for the absorption in the perpendicular alignment. Both ϵ'_{21} and ϵ'_{12} approximate to the square of the relevant refractive index. The intensity of the high frequency absorption in the parallel alignment of the mesophase is well characterised, but it is not possible to determine the relaxation time to a sufficient accuracy to detect any temperature variation and a mean value is quoted over the temperature range.

DISCUSSION

The low frequency limiting permittivity agree with previously published data.[7,8] The dielectric anisotropy changes from positive to negative at about 10 MHz in the nematic phase and at about 5 MHz in the smectic phase. This cross-over frequency moves to slightly higher frequencies as the temperature is increased and the relaxation times decrease.

The temperature variations of the relaxation time in the nematic, smectic, and isotropic phases are shown in Figure 2. The Arrhenius activation energy (in units of kJ mol^{-1}) for dipolar reorientation is (44 ± 6), (67 ± 8) in the parallel alignment of the smectic and nematic phases respectively and (41 ± 6) in the isotropic phase. These values are in close agreement with those quoted by Druon and Wacreiner[3] for the 8CB mesophases. The dipolar reorientation responsible for the low frequency absorption in the parallel alignment is envisaged

TABLE I

Dielectric absorption parameters in the smectic, nematic and isotropic phases of 8CB.

Parallel alignment

Phase	T/K	*Low frequency absorption*				*High frequency absorption*			
		ϵ'_{01}	ϵ'_{11}	β	τ/ns	ϵ'_{11}	ϵ'_{21}	β	τ/ns
Smectic	290	13.0	3.2	1.0	88.4	3.2	2.8	$\beta = 1$ throughout	$\tau = 0.32$ throughout
	294	13.3	3.1	1.0	69.0	3.1	2.8		
	296	13.0	3.2	1.0	61.0	3.2	2.8		
	299	13.2	3.2	1.0	51.3	3.2	2.8		
	301	13.3	3.2	1.0	45.5	3.2	2.8		
Nematic	303	13.7	3.2	1.0	40.8	3.2	2.7		
	305	13.6	3.2	1.0	35.4	3.2	2.7		
	307	13.4	3.2	1.0	29.5	3.2	2.7		
	309	13.4	3.3	1.0	25.7	3.3	2.7		
	310.5	13.0	3.4	1.0	21.2	3.4	2.7		

Perpendicular alignment

Phase	T/K	ϵ'_{02}	ϵ'_{12}	β	τ/ns
Smectic	290	5.4	2.2	0.5	3.18
	294	5.5	2.3		
	296	5.7	2.3		
	299	5.8	2.2		
	301	5.9	2.1		
Nematic	305	5.9	2.7	0.7	3.18
	307	6.3	2.9		
	309	6.8	2.9		
	310.5	6.9	2.7		

Isotropic phase

T/K	ϵ'_0	ϵ'_∞	β	τ/ns
313	9.5	3.3	0.9	6.24
316	10.0	3.4	0.9	5.30
320	10.0	3.3	0.9	4.40
323	10.0	3.1	0.9	3.80

A second absorption with ϵ_∞ of 2.6 and τ = 0.3 ns is also observed.

as a reorientation of the longitudinal dipole component (μ_l) parallel to the "long molecular axis". It is surprising that the activation energy in the smectic phase appears lower than in the nematic phase. The relaxation time itself shows little change at the transition between the two phases. This behaviour may have a parallel with that of rotator

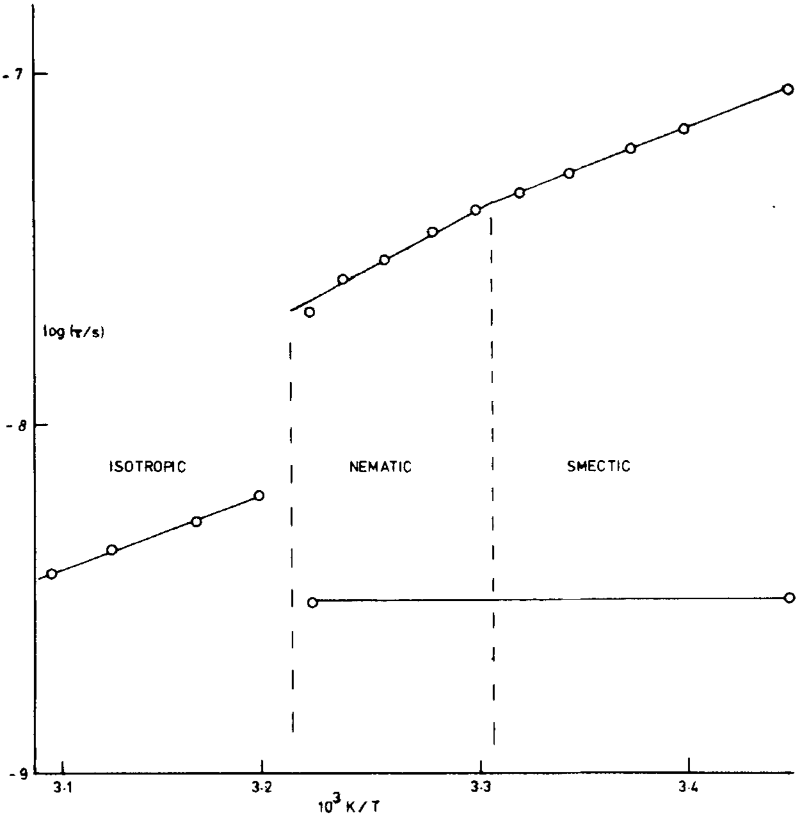

FIGURE 2 Arrhenius plot for the temperature variation of the relaxation times observed in 8CB.

phase solids[9] where again the activation energy for dipole reorientation often appears lower in the solid than in the liquid phase. The regular molecular arrangement found in the solid phase allows of an easier reorientation than is possible in the liquid phase. Perhaps a similar explanation applies in the behaviour of 8CB on transition from the nematic to the more ordered smectic A phase.

The Martin, Meier and Saupe[10] theory of dielectric relaxation in nematogens involves the concept of a "nematic ordering potential" which is primarily responsible for the long range molecular ordering in this phase. The major effect of this "nematic potential" is found on the low frequency relaxation in the parallel alignment, but has little effect on the dielectric relaxation observed in the perpendicular alignment. A similar ordering potential is present in the smectic phase and its magnitude may be estimated from the temperature dependence of the relaxation time. The results quoted here lead to a potential of about 7 kJ mol in both phases. This compares reasonably with the value of 7.7 kJmol^{-1} evaluated[11] for 7CB. The experimental uncertainties preclude distinguishing between the potential existing in the smectic and in the nematic phases.

The intensity of the absorptions depend on the square of the dipole moment component vector reorientating in the direction of the applied field vector. In 8CB the dipole moment is dominated by the cyano-group dipole whose direction lies along the C(aromatic) – C≡N axis. However, the principal moment of inertia is probably offset from this direction by the extended alkyl chain which is quoted[11] as being 38° to this dipole direction. The intensity of the low frequency absorption in the parallel alignment is dependent[1] on $\mu_l^2\ (1 + 2S)$, where μ_l is the longitudinal dipole moment component parallel to the "long molecular axis," and the high frequency absorption in the parallel alignment is dependent on $\mu_t^2\ (1 - S)$, where μ_t is the transverse dipole component. S is the order parameter. The intensity in the perpendicular alignment depends on $\left(\mu_l^2\,(1 - S) + \mu_t^2\left(1 + \frac{S}{2}\right)\right)$. Hence, analysis of the intensities allows of a determination of the dipole components and of the order parameter. The results are quoted in Table II and the order parameters are compared with those deduced from the mean field theory. The general trend is established in the order parameter. The interpretation of the order

TABLE II

Dipole moment components and order parameters determined from the absorption intensity.

Phase	T/K	$10^{30}\mu_l$/ C m	$10^{30}\mu_t$/ C m	$10^{30}\mu$/ C m	Order Parameter S	
					S	MS*
Smectic	290	10.4	1.4	10.5	0.39	0.59
	296	10.5	1.3	10.5	0.37	0.57
	299	10.9	1.0	10.9	0.35	0.55
Nematic	301	11.2	0.62	11.2	0.33	0.54
	305	10.8	2.4	11.1	0.39	0.52
	307	10.0	2.4	10.2	0.41	0.49
	309	10.2	2.7	10.5	0.37	0.48
	310	10.3	3.2	10.8	0.33	0.46

*MS refers to the order parameter deduced from the mean field theory.

parameter in 8CB is complicated by a high degree of short range antiparallel dipolar association which must influence the long range order characterised by the order parameter. The longitudinal dipole component is effectively constant at (10.5 ± 0.5) × 10^{-30} C m, but the transverse component appears to increase on going from the smectic to the nematic phase. The overall dipole moment ((10.7 ± 0.5) × 10^{-30} C m) compares well with the value calculated by Dunmur[8] from static permittivity mearuements, but is lower than the (14 to 16) × 10^{-30} C m determined using a dilute solution.[8,12] This difference implies association in the pure phase into an antiparallel arrangement. The absolute values of the Kirkwood "*g*" factors are difficult to determine since the longitudinal and transverse dipole components (μ_{11} and μ_1) in the isolated molecule must be known. However the relative magnitude of the Kirkwood "*g*" factors applying to the longitudinal and transverse dipole components may be estimated by assuming that the μ_l and μ_t values listed for the pure mesophases in Table II are related to the properties of the isolated molecule by $\mu_l^2 = g_{11}\ \mu_{11}^2$ and $\mu_t^2 = g_1\mu_l^2$. Assuming a molecular dipole moment of 15 × 10^{-30} C m inclined at an angle of 10° to the "long molecular axis" yields a g_{11} and g_1 of 0.51 and 0.99 respectively, showing that the association arises chiefly from the interaction between the longitudinal dipole components.

CONCLUSIONS

Three dielectric relaxation processes are observed in 8CB and these do not change significantly at the transition from the smectic to the nematic phase. The activation energy for dipolar reorientation however appears to be lower in the smectic phase than in the nematic phase. The calculated order parameters are lower than those expected from the mean field theory. The dielectric relaxation data confirm the presence of a high degree of molecular association in the system. This association chiefly involves the longitudinal dipole component, with the transverse component being only slightly involved.

Acknowledgments

The authors wish to thank BDH Chemicals Ltd. for the gift of the 8CB.

References

1. M. F. Bone, A. H. Price, M. G. Clark, and D. G. McDonnell, *Liquid Crystals and Ordered Fluids* (Eds. A. C. Giffin and J. F. Johnson), Plenum Publishing Corporation, 1984, p. 799.
2. V. K. Agarwal and A. H. Price, *Mol. Cryst. Liq. Cryst.*, **98**, 193 (1983).
3. C. Druon and J. M. Wacrenier, *Mol. Cryst. Liq. Cryst.*, **98**, 201 (1983).
4. A. Buka, P. G. Owen and A. H. Price, *Mol. Cryst. Liq. Cryst.*, **51**, 273 (1979).
5. R. M. Fuoss and J. G.Kirkwood, *J. Amer. Chem. Soc.*, **63**, 385 (1941).
6. J. M. Wacrenier, C. Druon, and D. Lippens, *Mol. Phys.*, **43**, 97 (1981).
7. L. Bata and A. Buka, Central Research Institute for Physics, Hungarian Academy of Sciences, Budapest, Report KFKI-1977-66.
8. D. A. Dunmur, M. R. Manterfield, W. H. Miller, and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.*, **45**, 127 (1978).
9. N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "*Dielectric Properties and Molecular Behaviour*", van Nostrand Reinhold Co., London, 1969, p. 393.
10. A. J. Martin, G. Meier, and A. Saupe, *Faraday Soc. Symposium*, No. **5**, 119 (1971).
11. M. Davies, R. Moutran, A. H. Price, M. S. Beevers, and G. Williams, *J. Chem. Soc. Faraday II*, **72**, 1447 (1976).
12. A. J. Leadbetter, J. L. A. Durrant, and M. Rugman, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 231 (1977).