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

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Version of record first published: 28 Mar 2007.

To cite this article: Agnes Buka , Philip G. Owen & Alun H. Price (1979): Dielectric Relaxation in MBBA, Molecular Crystals and Liquid Crystals, 51:3-4, 295-301

To link to this article: http://dx.doi.org/10.1080/00268947908084715

Mol. Cryst. Liq. Cryst., 1979, Vol. 51, pp. 295–302

Printed in Holland

Dielectric Relaxation in MBBA

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(*Received November 20, 1978*)

Dielectric absorption measurements are reported for MBBA in both the parallel and perpendicular alignments. Two absorptions are observed in each alignment. The intensity of the absorptions agree with those calculated using the Maier and Meier mean field theory. In the perpendicular alignment the high frequency absorption is attributed to the internal rotation of the methoxy-group.

Dielectric relaxation measurements on liquid crystals reveal aspects of molecular reorientation in the different phases and alignments. Three theories of dielectric relaxation in nematogens have been proposed.[1–3] The Martin, Meier and Saupe theory[1] and the Pokrovski theory[2] are restricted to nematogens (such as the alkyl-cyanobiphenyls) whose resultant dipole moment lies along the long molecular axis. They are inapplicable to the work on *p*-methoxy-benzylidene-*p*-*n*-butyl aniline (MBBA) described here, since MBBA has a significant dipole component perpendicular to the long molecular axis. The theory proposed by Nordio *et al.*[3] applies generally to molecules whose dipole moment lies at an angle to the long molecular axis. Two relaxation processes are predicted when the measuring electric field is parallel to the aligned nematic director (parallel alignment) and two relaxation processes are also predicted when the measuring electric field is perpendicular to the aligned nematic director (perpendicular alignment). Previous measurements on MBBA[4–6] have been confined to frequencies up to about 10 MHz (a frequency which is too low to establish the complete dielectric spectrum) where only one relaxation process has been reported in both parallel and perpendicular alignments. We now wish to report an

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extension of these measurements to 18 GHz in the perpendicular alignment and to 250 MHz in the parallel alignment.

EXPERIMENTAL

Measurements at frequencies up to 250 MHz were made using a Wayne Kerr B201 Bridge and a Boonton 250A RX meter, fitted with a specially designed rectangular cell. A magnetic field (0.2 T) sufficient to produce maximum alignment of the nematic director could be applied either parallel or perpendicular to the measuring field. Measurements between 250 MHz and 18 GHz were made using the sweep frequency dielectrometer[7,8] with a cell constructed from a length of coaxial line operating in the TEM mode. A magnetic solenoid was wound around this cell and allowed of measurements in the perpendicular alignment. Since MBBA has a negative dielectric anisotropy application of an external electric field also produces an alignment with the director perpendicular to the measuring field and it was not possible to measure in the parallel alignment at these frequencies. All measuring cells were thermostated to ± 0.1 K.

The MBBA sample was supplied by Messrs Eastman Kodak Ltd., dried over molecular sieves and vacuum distilled before use. The clearing temperature was 316 K.

ANALYSIS OF THE RESULTS

The frequency variation of the dielectric loss (ε'') is described by the Fuoss–Kirkwood relation.

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

where the subscript m refers to the absorption maximum. Values of ε''_m were selected to give the best fit for the experimental data and the relaxation time ($\tau = \frac{1}{2}\pi f_m$) is determined from the intercept. β is an empirical parameter describing the width of the absorption ($0 < \beta \leq 1$; $\beta = 1$ corresponds to the Debye equation). Where two absorptions are resolvable, both were analysed using Eq. 1, but the uncertainties in the parameters derived for the high frequency absorption in the perpendicular alignment are very much greater than those derived for the low frequency absorption since the former appears as a shoulder on the main absorption.

RESULTS AND DISCUSSION

Some typical results for the frequency variation of the dielectric absorption (ε'') in MBBA are shown in Figures 1 and 2. Two absorptions are present in both alignments. The second absorption in the perpendicular alignment appears as a shoulder. The dielectric parameters derived for these absorptions are listed in Table I. The uncertainty in these parameters is estimated to be ± 5 percent except for the high frequency absorption in the perpendicular alignment where the uncertainty is estimated to be no better than ± 10 percent.

Previously reported measurements[4–6] for the dielectric relaxation in MBBA were confined to frequencies below about 10 MHz and to the parallel alignment. The present results agree with those previously reported for this alignment and the activation enthalpy for the relaxation process being 63 ± 5 kJ mol^{-1} in good agreement with that of Rondalez.[4] These previous measurements also produced an ε_∞ much greater than the square of the refractive index, indicating the presence of a second absorption at higher frequencies. The limiting high frequency permittivity ($\varepsilon_{\infty 2}$) is now much closer, but still higher, than the square of the refractive index. This difference is accommodated by the presence of an intense absorption in the far infrared spectral region.[9]

In the parallel alignment the low frequency absorption has been ascribed to a molecular reorientation involving rotation about the short molecular

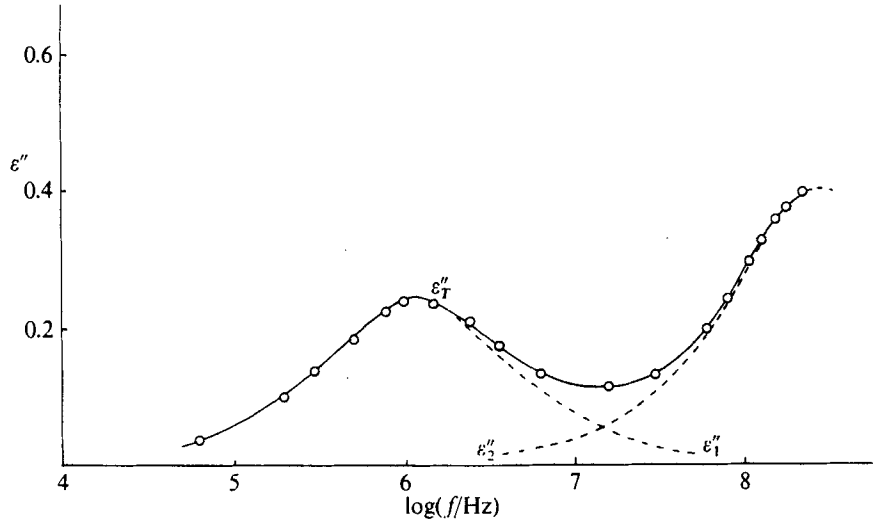

FIGURE 1 Dielectric absorption (ε'') as a function of frequency (f) for MBBA in the parallel alignment at 295 K. ○, experimental results; ——, calculated absorption ($\varepsilon''_T = \varepsilon''_1 + \varepsilon''_2$); – – –, resolved absorptions (ε''_1, and ε''_2).

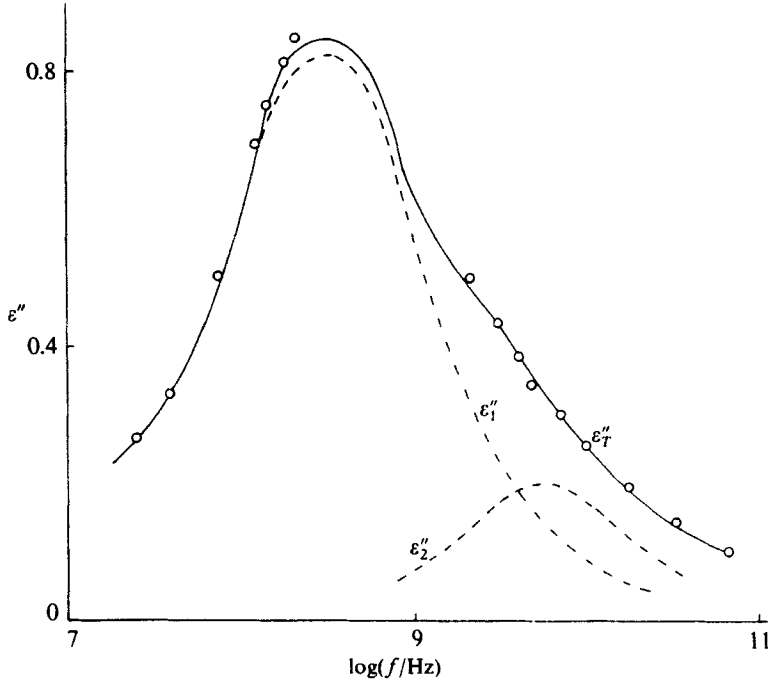

FIGURE 2 Dielectric absorption (ε'') as a function of frequency (f) for MBBA in the perpendicular alignment at 295 K. ○, experimental results; ——, calculated absorption ($\varepsilon''_T = \varepsilon''_1 + \varepsilon''_2$); – – –. resolved absorption (ε''_1 and ε''_2).

TABLE I

Dielectric relaxation parameters for nematic MBBA

	Low frequency absorption				High frequency absorption			
T/K	ε_{01}	$\varepsilon_{\infty 1}$	β_1	τ/ns	ε_{02}	$\varepsilon_{\infty 2}$	β_2	τ_2/ns
Parallel alignment								
290	4.72	4.14	0.9	227	4.14	3.21	0.9	0.70
295	4.58	4.03	0.8	138	4.03	3.17	0.9	0.58
300	4.69	4.13	0.8	102	4.13	3.27	0.9	0.53
305	4.69	4.16	0.8	65.9	4.16	3.33	0.9	0.50
310	4.71	4.25	0.7	52.5	4.25	3.55	0.9	0.58
315	4.75	4.30	0.7	23.5	4.30	3.26	0.9	0.35
Perpendicular alignment								
290	5.20	3.05	0.9	0.76	3.05	2.75	1.0	0.06
295	5.10	3.01	0.8	0.58	3.01	2.59	1.0	0.03
300	5.10	2.90	0.8	0.42	2.90	2.60	1.0	0.02
305	5.10	2.84	0.8	0.33	2.84	2.55	1.0	0.01
310	5.00	2.67	0.7	0.25	2.67	2.40	1.0	0.007
315	5.00	2.56	0.7	0.19	2.56	2.30	1.0	0.004

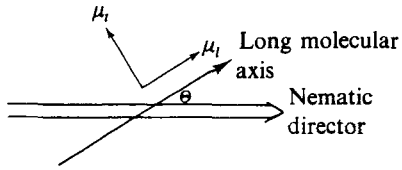

FIGURE 3 Schematic representation of the dipole inclinations in a nematogen.

axis.[4,5] The higher frequency absorption has not been previously reported. Its molecular origin may lie in the reorientation of the dipole component transverse to the long molecular axis. The situation is schematically represented in Figure 3, where μ_t and μ_l are the dipole components perpendicular and parallel to the long molecular axis inclined at a mean angle θ (described by the nematic order parameter S) to the nematic director. In the mean field theory[10] the mean square dipole moment $\langle \mu_\parallel^2 \rangle$ parallel with the director is

$$\langle \mu_\parallel^2 \rangle = \tfrac{1}{3}\mu_l^2(1 + 2S) + \tfrac{1}{3}\mu_t^2(1 - S) \tag{2}$$

and two relaxation processes may arise if the relaxation times associated with μ_l and μ_t are sufficiently different. The intensity of such processes may be calculated from the mean field theory[10] and in the parallel alignment the intensities are given by

$$(\varepsilon_0 - \varepsilon_\infty)_1 = A(\varepsilon_{\parallel\infty} - 1)_1 + B\tfrac{1}{3}\mu_l^2(1 + 2S) \tag{3}$$

and

$$(\varepsilon_0 - \varepsilon_\infty)_2 = A(\varepsilon_{\parallel\infty} - 1)_2 + B\tfrac{1}{3}\mu_t^2(1 - S) \tag{4}$$

where

$$A = \frac{\bar{\varepsilon} - \bar{\varepsilon}_\infty}{2\bar{\varepsilon} + \bar{\varepsilon}_\infty}; \qquad B = \frac{\bar{\varepsilon}(\bar{\varepsilon}_\infty + 2)^2(2\bar{\varepsilon} + 1)N}{3(2\bar{\varepsilon} + \bar{\varepsilon}_\infty)^2 \mathbf{k}T\boldsymbol{\varepsilon}};$$

$$\bar{\varepsilon} = \tfrac{1}{3}(\varepsilon_\parallel + 2\varepsilon_\perp); \qquad \bar{\varepsilon}_\infty = \tfrac{1}{3}(\varepsilon_{\infty\parallel} + 2\varepsilon_{\infty\perp});$$

the subscripts 1 and 2 refer to the low and high frequency absorptions respectively. Using the dipole components mentioned above the calculated intensities are compared with the observed intensities at 290 K in Table II. The agreement is good despite the limitations of the mean field theory.

TABLE II

Calculated and observed intensities for MBBA in the parallel alignment at 290 K

	Observed $(\varepsilon_0 - \varepsilon_\infty)$	Calculated $(\varepsilon_0 - \varepsilon_\infty)$
Low frequency absorption	0.58	0.57
High frequency absorption	0.93	0.98

TABLE III

Calculated and observed intensities for MBBA in the perpendicular alignment at 290 K

	Observed $(\varepsilon_0 - \varepsilon_\infty)$	Calculated $(\varepsilon_0 - \varepsilon_\infty)$
Low frequency absorption	2.15	4.09
High frequency absorption	0.30	0.05

In the perpendicular alignment, the intensity of the absorptions is given by

$$(\varepsilon_0 - \varepsilon_\infty)_1 = A(\varepsilon_{\infty\perp} - 1)_1 + B\tfrac{1}{3}\mu_t^2\left(1 + \frac{S}{2}\right) \tag{5}$$

and

$$(\varepsilon_0 - \varepsilon_\infty)_2 = A(\varepsilon_{\infty\perp} - 1)_2 + B\tfrac{1}{3}\mu_t^2(1 - S) \tag{6}$$

and the calculated and observed intensities are compared in Table III. The agreement here is very poor, with the calculated absorption being nearly twice the observed value. Assuming the validity of the mean field theory, a possible explanation for this discrepancy involves the internal rotation of the methoxy group. Group moment calculations[5] show that reasonable agreement is possible between the calculated and observed dipole moment only if free internal rotation of this group occurs. It has been suggested by Nordio *et al.*[3] that the relaxation behaviour in the perpendicular alignment would yield one absorption only, since the two relaxation times would be very similar. In which case, our lower frequency absorption could well arise from molecular reorientation and the high frequency process arises from the internal rotation of the methoxy group. (Its low intensity in the parallel alignment would render it undetectable). The calculated intensity for the low and the high frequency absorptions is now 2.4 and 0.13 respectively, in much better agreement with the observed intensities (see Table III). On this basis one would have anticipated a broad low frequency absorption, but our resolution is insufficient to properly examine this possibility.

CONCLUSIONS

The dielectric spectrum of MBBA reveals two absorptions both in the parallel and in the perpendicular alignments. In the parallel alignment the low frequency absorption is associated with the relaxation of the dipole component parallel to the long molecular axis, while the high frequency absorption arises from the relaxation of the transverse dipole component. The intensity of both processes agrees with that calculated from the mean

field theory. In the perpendicular alignment the high frequency absorption is due to the internal rotation of the methoxy-group, while the low frequency absorption arises from a whole molecule reorientation.

Acknowledgement

The authors wish to thank the Science Research Council for financial support and for a grant towards the purchase of equipment.

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