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Determination of Elastic Constant K_{33} for Some Nematic Liquid Crystals with Strong Positive Dielectric Anisotropy by Means of IR Absorption Spectroscopy†

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The influence of a.c. electric field (2000 Hz) on the half-width of some bands from IR spectrum of three liquid crystals with strong positive dielectric anisotropy is investigated and U_c and K_{33} values are calculated.

INTRODUCTION

Two types of hydrodynamic instabilities appear when an a.c. electric field is applied to a thin layer of a nematic liquid crystal.[1] For the first type, named conductive regime, the frequency of the applied electric field ω is smaller than a critical one ω_c and at a given threshold voltage U_c, Williams

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† This investigation began with Dr. G. Vergoten's visit to the Institute of Solid State Physics, Sofia and was completed during Dr. N. Kirov's stay in the Department of Theoretical Chemistry and Chemical Physics, Institute of Chemistry, University of Wroclaw, Poland.

domains appear. In this case the relaxation time of reorientation of liquid crystal molecules is comparatively large. For example, for MBBA the relaxation time upon switching on or off the field is of the order of several milliseconds.[2] On the other hand the broadening of IR absorption bands are related to the mean reorientation time τ_0 in the following way:[3-5]

$$\Delta\delta = \frac{1}{\pi_c \tau_0} \tag{1}$$

As one can see from Eq. (1) the aforementioned relaxation times will cause a broadening of the vibrational band of about 10^{-7} cm^{-1} that can not be determined experimentally.

In the second regime, called a dielectric one, the frequency of the applied electric field is larger than the critical value and molecules oscilate, while the charges are static. Two types of relaxation exist in this case, slow and fast mode, with the relaxation times as follows:[6]

$$T_s = \frac{\eta'}{Kq^2} \qquad T_f = \frac{\rho}{\eta q^2} \tag{2}$$

Here K is the elastic constant of the nematic, q is the distortion wave vector, η and η' which have dimensions of viscosity and ρ is the density of the liquid crystal.

For MBBA with negative dielectric anisotropy ($\varepsilon_{\parallel} = 4.7$; $\varepsilon_{\perp} = 5.4$; $\varepsilon_a = -0.7$)[7] when the molecules are oriented perpendicular to the cell windows and the electric field is also perpendicular to the cell plates and parallel to the long axes of the molecules K is equal to the bend elastic constant K_{33} and $\eta' = \eta_B$ is about 0.16 poise. In this case the wave vector can be expressed approximately by the formula:[6]

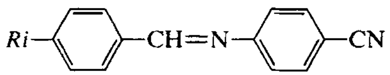
$$q^2 \simeq \frac{2\omega\eta_B}{K_{33}}\left[\frac{\zeta^2 - 2}{\zeta^2}\right] \tag{3}$$

where $\omega = 2\pi\nu$ is the circular frequency and ζ is a constant approximately equal to 3.[1]

If we estimate the wave vector and replace its value in the Eq. (3) the magnitudes of slow and fast relaxation times can be obtained. We found that T_s is about 10^{-4} seconds. Such a relaxation process is quite slow and as a result the broadening of the vibrational bands will be insignificant and cannot be determined experimentally by IR absorption spectroscopy. The relaxation time T_f is of the order of 10^{-10}–10^{-11} seconds and according to Eq. (1) will lead to a broadening of about 1 cm^{-1}. Actually our investigations on homeotropically aligned MBBA molecules confirmed this result.[8]

EXPERIMENTAL PART

The influence of sinusoidal electric field on three liquid crystals with strong positive dielectric anisotropy—*p*-(alkoxybenzylidene) *p*-aminocyananilines (ABCA) was investigated. The general formula of ABCA liquid crystals is:



where $R = —OC_2H_5$ (EBCA), $R_2 = —OC_4H_9$-*n* (BBCA) and $R_3 = —O_6H_{13}$-*n* (HBCA). The chemicals were purchased from Thompson CSF and were used without further purification. The temperature intervals of their mesophase existence determined by us are as follows: EBCA—105–129°C; BBCA—65–110°C; HBCA—56–103°C and coincide well with other results.[9] The data for dielectric anisotropy taken from Ref. 10 are for EBCA at 108°C, $\varepsilon_{\parallel} = 29.5$, $\varepsilon_{\perp} = 9$, $\varepsilon_a = 20.5$ for BBCA at 65°C, $\varepsilon_{\parallel} = 26.8$, $\varepsilon_{\perp} = 8.1$, $\varepsilon_a = 18.7$ and for HBCA at 60°C, $\varepsilon_{\parallel} = 23.3$, $\varepsilon_{\perp} = 7.7$, $\varepsilon_a = 15.6$. All investigations of the influence of electric field on IR spectra of our three liquid crystals have been done at these temperatures.

The a.c. electric field with a frequency of 2000 Hz and intensity up to 25 volts per a cell thickness of 25 μm (0–10000 v/cm) was applied perpendicular to the windows. The IR spectra were recorded by UR-20 (Carl-Zeiss Jena, DDR) and a Perkin-Elmer 621. The dichroism measurements were done by Perkin-Elmer 621. For the region below 200 cm^{-1} Perkin-Elmer 180 with far infrared option was used. The sample thickness of 25 μm was held fixed by a Teflon spacer. The molecules are oriented parallel to the walls by rubbing. Silicon plates served as electrodes transparent to IR light. The spectra were recorded on a percent transmission scale, expanding the wave-number axis 40 times. The scanning speed was 10 cm^{-1} per minute. The "true" half-width was calculated using the method of Ramsay.[11] Ten measurements have been carried out for any given voltage and the results are averaged in all measurements. This allows a considerable decrease in the error of half-width determination. The standard deviations, the absolute and the relative errors for half-widths of all bands investigated at different voltages have been calculated. Here we will give as an example only the data for the band at 559 cm^{-1}. They are as follows: without electric field $\delta = 12.37 \pm 0.14$ where the absolute error is 0.14 and the relative one is 1.11%. When an electric field with an intensity of 25 volts is applied δ increases to 14.3 ± 0.19 with the absolute and relative errors 0.19 and 1.31% correspondingly. The errors for the other bands are in the same limits. The temperature of the sample was read and controlled automatically with a percision of ±0.2°C.

RESULTS AND DISCUSSION

The IR absorption spectra of all three liquid crystals were recorded in the region 4000–33 cm^{-1}. In the limits of error the electric field does not shift the bands. Actually our field is weak ($\sim 10^4$ v/cm) in order to produce any changes in the band position. As some calculations indicate[12] fields with intensity more than 10^5–10^6 v/cm should shift the bands of gaseous HCl with less than 0.1 cm^{-1}. However, the electric field applied on our liquid crystal samples influences mostly band half-widths and the integral intensity. This paper will deal only with the changes of the band widths which are closely connected with the molecular dynamics in condensed phase.

The hindred rotation and translation of the molecules in condensed phases has been studied for a number of years by dielectric and nuclear magnetic resonance and frequently by vibrational spectroscopy too. The correlation function gives a spectral density of the Lorentzian type. Therefore there is a definite relation between the correlation time and the width of the vibrational bands.[3–5] Extensive investigations of Rothshild[13] indicate that the molecular dynamics in condensed phases influences not only the half-width but the band contour too. In our case, however, as one can see from Figure 1, where the points indicate the calculated Lorentzian contour, the electric field does not change the band shape. That's why we investigate only the influence of the electric field on the band half-width δ.

Figure 2 shows the half-width changes of the bands at 889 cm^{-1} (BBCA), 1067 cm^{-1} (HBCA) and 1197 cm^{-1} (HBCA). As one can see from it at approximately 1 volt δ begins to increase and reaches saturation at about 15–20 volts.

How can this effect be explained?

For liquid crystals with strong positive dielectric anisotropy the onset of instability can be predicted from the theories of Helfrich[15] and Dubois-Violette *et al.*[16] but there are no criteria for determining whether the instability will develop in the dynamic scattering mode. It has been generally assumed that only materials with negative dielectric anisotropy show dynamic scattering. Initially the molecules of ABCA are arranged parallel to the cell windows. With the increasing electric field they began to change their orientation and reach an arrangement perpendicular to the cell windows. At stronger fields the conductive anisotropy no longer favor instability and molecular orientation does not change any more. As a result the half-width reaches saturation. Our microscopic measurements are consistent with IR results. The light transmittance of the samples reaches saturation at about 20 volts when the brightness does not change any more. The same result is obtained by Baise[17] who has studied the light scattered by a layer of another liquid crystal with positive dielectric anisotropy--*p,p'*-dibutyloxyazoxybenzene ($\varepsilon_a = +0.2$).

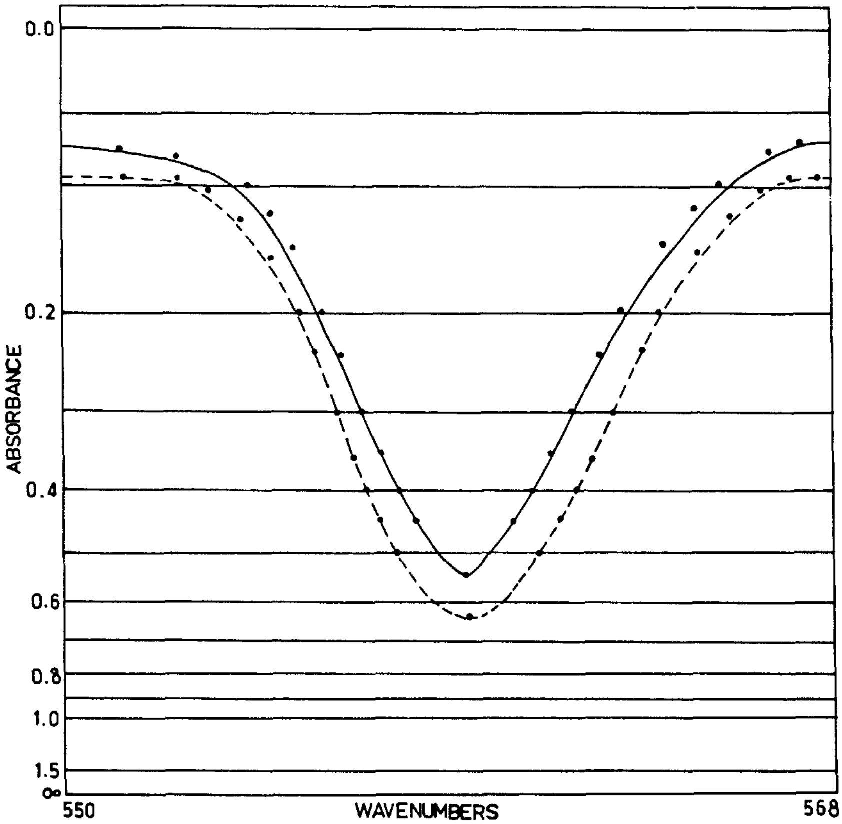


FIGURE 1 The influence of electric field on the contour of the band at 556 cm^{-1}: full line—without electric field; dash line—25 volts.

Two very important liquid crystal characteristics, namely the threshold voltage U_c and bend elastic constant K_{33} can be determined from the electric dependence of the band widths.

Figure 3 represents the dependence of normalized half-width (the half-width at a given voltage δ_U devided to the width at zero voltage δ_0) on the square voltage of the applied electric field in the interval between 1 and 4 volts. As one can see for voltages not far from a critical one this dependence is linear. From it, as it is shown at Figure 3, the threshold voltage can be determined. The results are as follows: EBCA—0.9 volts, BBCA—1.2 volts and HBCA—1.6 volts. The data are averaged on all bands investigated and the mean error is about 0.07 volt.

The determination of K_{33}, however, is not so simple. The value of the bend elastic constant depends on the boundary conditions, i.e. on orientational order and on the elastic properties of the liquid crystal.[1] Small deviations

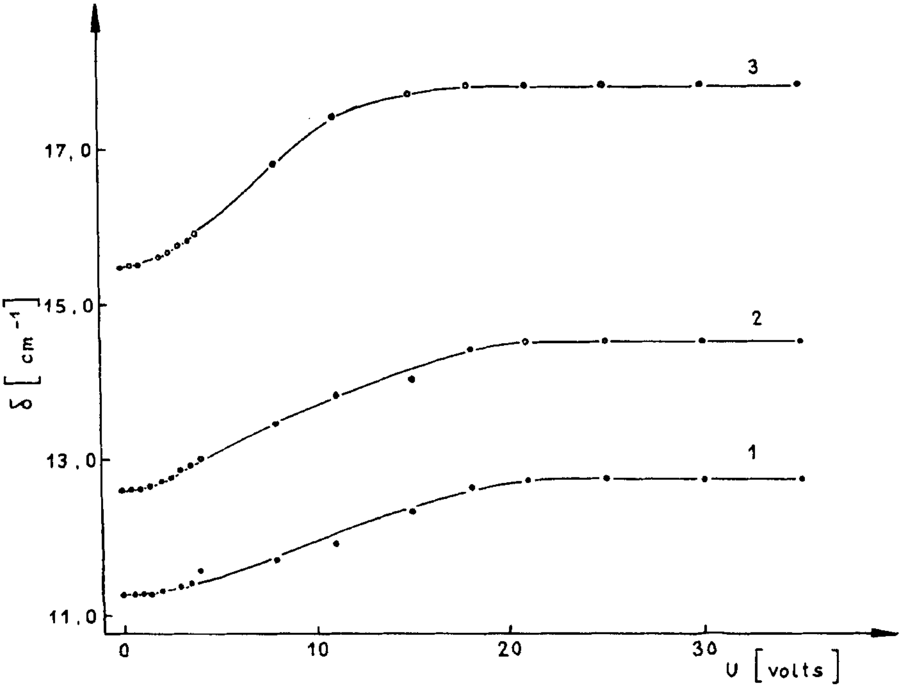


FIGURE 2 Dependence of "true" half-width δ of the bands: 1—1196 cm^{-1} (HBCA); 2—889 cm^{-1} (BBCA) and 3—1067 cm^{-1} (BBCA) on the intensity of applied electric field; cell thickness—25 μm.

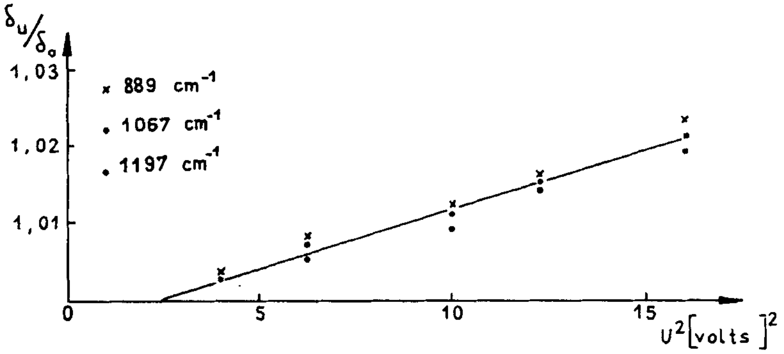


FIGURE 3 Dependence of the normalized half-width δ_U/δ_0 for the bands 1196 cm^{-1}, 1067 cm^{-1} and 889 cm^{-1} (HBCA) on the square voltage of applied electric field.

from the best possible alignment will give a K_{33} value lower than the real one. For this reason before every experiment we checked the order parameter S which characterizes the molecular arrangement

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{4}$$

was checked. In our case the orientational order without any electric field applied was checked by dichroism ratio $R = \varepsilon_{\parallel}/\varepsilon_{\perp}$ where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the absorption coefficient for the light polarized parallel and perpendicular to the long molecular axis.

If the vibrational induced dipole moment is directed along the long axis of the molecule[18]

$$S = \frac{R-1}{R+2} \tag{5}$$

To measure the degree of order in our nematics we chose the 2227 cm^{-1} band ($C \equiv N$ stretch vibration) which has a vibrational dipole moment nearly parallel to the long molecular axis.[19] We obtained the following data: EBCA—0.58 (108°C), BBCA—0.63 (65°C) and HBCA—0.60 (60°C). These calculations have been made without a correction for the effect of the molecules on the polarized electric field of the radiation, the so-called "Lorentz inner field correction," but as it was shown such correction gives rise only to a small systematic increase of S values, not more than 2%.[20] As far as we know there are no data in the literature concerning the order parameter of *p*-(*p*-alkoxybenzylidene)*p*-amino cyananilines; however S for the other liquid crystals has been measured by various authors and we can do some comparisons. Maier and Englert[21] using the dichroism ratio of some IR bands of PAA oriented by rubbing obtained a mean value of S at the beginning of mesophase existence interval equal to 0.51. Konstantinov *et al.*[22] studied the order parameter of ten mesomorphic *p*,*n*-alkoxybenzoic acids and obtained for their nematic phase values between 0.35 and 0.68. Fernandes[20] by CN stretch vibration band from the IR spectrum of *n*-*p*-cyanobenzylidene *p*,*n*-octyloxyaniline obtained $S = 0.62$ at the beginning of the nematic phase interval existence. Prasad[23] calculated that S for 4,4′-bis(pentyloxy)azoxybenzene at a temperature very near to the phase transition crystal–nematic crystal is about 0.65. R. Chang[24] has found that at 20°C S for MBBA aligned by rubbing is equal to 0.618. The similar result is obtained recently by NMR,[25] Raman scattering measurements[26] and C-13 proton double resonance data.[27] In general, as many different methods indicate the order parameter values for nematic liquid crystals ordered only by rubbing, vary between 0.35 and 0.65. Therefore, our data coincide well with other data available in the literature and we can consider that the boundary conditions will not decrease the K_{33} values.

By means of Equation[1]

$$U_c^2 = \pi^2 \frac{\varepsilon_{\parallel} K_{33}}{\varepsilon_a \varepsilon_{\perp}} \tag{6}$$

we determine that K_{33} for EBCA, BBCA and HBCA are correspondingly $5.3 \pm 0.8 \cdot 10^{-7}$ dynes; $8.3 \pm 1 \cdot 10^{-7}$ dynes and $14.3 \pm 1.2 \cdot 10^{-7}$ dynes, where 0.8, 1.0 and 1.2 are the absolute errors. The relative errors are as follows: 15.5% (EBCA), 11.7% (BBCA) and 8.7% (HBCA). As far as is known there are no data in the literature concerning elastic constants of our liquid crystals. There are data only for compounds with similar structure. Maize and Johnson[28] used a mixture of phenylbenzoate esters with strong positive dielectric anisotropy ($\varepsilon_a = 14.5$) and found that for a 105 μm thick cell this mixture has a U_c approximately 0.7 volts and the K_{33} constant is equal to $11.8 \cdot 10^{-7}$ dynes. Karat and Madhusudana[29] determined the elastic constants for some *p,n*-alkyl *p*-cyanobiphenyls and the data two degrees below the nematic–isotropic transition are between $8 \cdot 10^{-7}$ and $9 \cdot 10^{-7}$ dynes.

CONCLUSION

The following conclusions can be drawn having in mind our results:

1) Under the influence of an a.c. electric field (2000 Hz) the half-widths of the bands studied from the IR absorption spectra of three liquid crystals with strong positive dielectric anisotropy, namely EBCA, BBCA and HBCA begin to increase at about 1 volt and reach saturation at 15–20 volts.

2) The following data for U_c were obtained: EBCA—0.9 volts, BBCA—1.2 volt and HBCA—1.6 volts. By Eq. (6) we determined that K_{33} for HBCA, BBCA and EBCA are correspondingly: $14.3 \pm 1.2 \cdot 10^{-7}$ dyne, $8.3 \pm 1.0 \cdot 10^{-7}$ dynes and $5.3 \pm 0.8 \cdot 10^{-7}$ dynes. No other data for U_c and K_{33} on these liquid crystals are available in the literature up to now.

This work demonstrates the power of IR spectroscopy as a tool not only for the investigation of intermolecular forces in condensed phases, but for the determination of elastic constants whose values are very important from theoretical and practical points of view.

A more complete description including observed changes in the integral intensity with electric field and temperature dependence of K_{33} and U_c is under preparation and will be published soon.

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