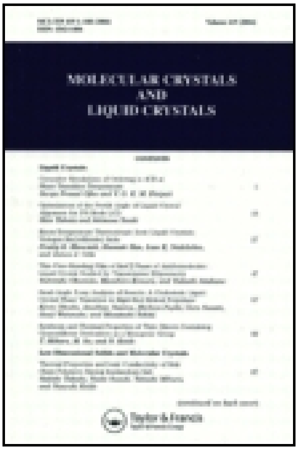

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Influence of a.c. Electric Field on Infrared Absorption Spectra of Liquid Crystals and Determination of Orientational Order Parameter by Infrared Dichroism. I. Molecules with Strong Positive Dielectric Anisotropy

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Version of record first published: 20 Apr 2011.

To cite this article: N. Kirov , P. Simova & H. Ratajczak (1980): Influence of a.c. Electric Field on Infrared Absorption Spectra of Liquid Crystals and Determination of Orientational Order Parameter by Infrared Dichroism. I. Molecules with Strong Positive Dielectric Anisotropy, Molecular Crystals and Liquid Crystals, 58:3-4, 285-298

To link to this article: http://dx.doi.org/10.1080/00268948008082128

Mol. Cryst. Liq. Cryst., 1980, Vol. 58, pp. 285–298
0026-8941/80/5803-0285$04.50/0

Printed in the U.S.A.

Influence of a.c. Electric Field on Infrared Absorption Spectra of Liquid Crystals and Determination of Orientational Order Parameter by Infrared Dichroism

I. Molecules with Strong Positive Dielectric Anisotropy

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(*Received August 2, 1979*)

The influence of a.c. electric field (5 kHz) on the IR and FIR spectra of the nematic phase of three liquid crystals with strong positive dielectric anisotropy ($\varepsilon_a \approx 15$) was investigated. The changes in the half-band widths with increasing electric field intensity are explained by means of the changes in the molecular reorientation in respect to different axes due to the ordering effect of the electric field. The orientational order parameter S_2 for homeotropic and homogeneous samples was calculated and its temperature dependence was studied.

INTRODUCTION

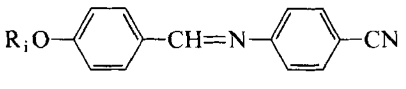
Vibrational spectroscopy (IR and Raman) has been widely used for many years to elucidate molecular structure and to study the intermolecular interactions in condensed phases. It is natural that many research groups applied these techniques to the study of liquid crystals. The first systematic IR measurement of the mesophase began with determination of the order parameter S_2 of first seven members from the homologes series 4,4′-di-*n*-alkoxyazoxybenzenes.[1] Similar studies were made on 2,4-nonadiene, 2,4-

decadiene and 2.4-undecadiene acids.[2] The measurements of the dichroic ratio as a function of temperature for a series of *p,n*-alkoxybenzoic acids (C_1 to C_9, C_{12} and C_{16}) have been done in Ref. 3. In his work Kelker[4] introduced a simplified method for the calculation of S_2 based on the measurement of the integrated absorption of unpolarized light by a homeotropic layer and by an isotopic liquid. Using the dichroic ratio of the bands from the IR spectra of benzonitrile and 4-biphenylcarbonitrile dissolved in nematic liquid crystals, Bulkin[5] calculated the degree of order of *p*-ethoxylbenzylidene *p*-*n*-butylaniline (EBBA) in its mesophase. Recently Fernandes[6] by dichroic measurements in IR and FIR regions determined the absolute order parameter in smectic A and nematic phases of *p*-cyanobenzylidene-*p*, *n*-octyloxyaniline (CBOOA). No other determinations of the orientational degree by IR spectroscopy have been made. There are probably very few papers considering the influence of an electric field on the mesophase as well. First Neff[7] has used a dc electric field to orient a nematic sample of *p*-methoxybenzylidene-*p*-cyanoaniline for the investigations of IR dichroism. The long axis of the molecule is oriented preferentially parallel to the field. The measured dichroic ratio increases with increasing field strength reaching a saturation at approximately 3 kV/cm. Later Ohnishi[8] has applied a dc electric field to a cell filled with MBBA and studied the relative transmittance changes of some bands in the region 4000–1000 cm^{-1} at the conditions of the dynamic scattering mode. The absorption changes have been so small that the difference spectroscopy method had to be employed. Pan and Wang[9] found that in the presence of turbulence due to the application of electric field the intensity of all Raman bands decreases drastically but without any shift in the peak positions.

In our previous papers[10, 11] we studied the broadening of some bands from IR spectra of *p*-methoxybenzylidene-*p*, *n*-butylaniline (MBBA), *p*-ethoxybenzylidene-*p*-aminocyaniline (EBCA), *p*-butyloxybenzelidene-*p*-aminocyananiline (BBCA) and *p*-hexoxybenzylidene-*p*-aminocyamamiline (HBCA) under the influence of an electric field (2,000 Hz) and gave a new method for the determination of the threshold voltage U_c. The present work continues these investigations and its main purposes are: (1) to measure the temperature dependence of the orientational order parameter as a function of temperature for aligned nematic liquid crystals: (i) homogenously by rubbing; (ii) homeotropically by treatment of the cell plates with lecithin solution; (iii) homeotropically by means of an electric field. The experimental determination of the order parameter is of significance regarding the molecular statistical theory of nematic liquid crystals. This is due to the fact that empirically determined temperature dependencies of the indicated parameter are needed to provide proof for the results of the theory.[12] (2) To investigate the influence of ac electric field on IR absorption spectra of the same compounds and to connect the electric field influence on the half-width and intensity with the corresponding transition dipole moments. As far as we know from literature data no similar investigations have been made previously.

EXPERIMENTAL PART

The chemicals usually abbreviated as ABCA with general formula



where $R_2 = C_2H_5$ (EBCA), $R_4 = C_4G_9$ (BBCA) and $R_6 = C_6H_{13}$ (HBCA) where purchased from Thompson CSF and were used without further purification. Their melting T_N and clearing temperature T_C was detetermined by us and found to compare well with the literature data.[13] The dielectric anisotropy at the beginning of the temperature interval of the mesophase existence is between 20 and 16.[14]

The ac sinusoidal electric field with a frequency of 5 kHz and intensity up to 50 volts (0–20,000 V/cm) per cell thickness of 25 μm was applied perpendicular to the cell windows. The IR spectra between 4000 and 200 cm^{-1} were recorded by Perkin–Elmer 621 spectrometer. For the registration of molecular vibrations in the far IR region—500–40 cm^{-1} Perkin–Elmer 180 spectrometer was used. All instrumental conditions were carefully chosen and checked in order to give the maximum possible accuracy. For the quantitative measurements of the half-width and integral intensity in the middle IR range the wave number axis was expanded 40 times and the scanning speed was 10 cm^{-1}/min. The integrated absorption of the bands corrected for the effects of finite spectral slit width was estimated following Ramsay procedure.[15] Polarized measurements are done only in the region between 4000 and 250 cm^{-1}. The molecules are arranged parallel (homogenously) to the cell windows by rubbing the plates with filter paper[16] and perpendicular (homeotropically) by treatment the cell surface with 1% solution of lecithin in ether.[17] In the far IR region and for the investigation of the influence of the electric field in the IR absorption spectra Si windows were used as electrode transparent to IR light. In all cases the sample thicknesses of 12 μm or 25 μm for middle IR region and 50 μm for far IR region were held fixed by Teflon spacers. Ten measurements have been carried out for any given voltage and temperature and the results are averaged in all measurements. This allows a considerable decrease in the error of the half-width and integral intensity determination. The standard deviations, the absolute and relative errors for the half-widths and integrated absorption have been calculated for any applied voltage at any temperature. Here we will give as an example only the data for the band at 2223 cm^{-1} from the spectrum of HBCA at 100°C (clearing temperature 103°C) aligned homeotropically. They are as follows: $\bar{\delta} = 11.7 \pm 0.1\ cm^{-1}$ where the absolute error is 0.1 and the relative one is 1 %. The mean integrated absorption is $\bar{A} = 26 \pm 3.3 \cdot 10^3\ cm^{-1}$ with absolute and relative errors 3.3 and 12.5 % correspondingly. The temperature of the sample was read and controlled automatically with a precision of ±0.5°.

RESULTS AND DISCUSSION

A Determination of orientational order parameter for homogeneously aligned samples

The orientational order parameter S_2 is defined as in Ref. 18

$$S_2 = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) \tag{1}$$

where θ is the angle made by the long axis of any molecule with the direction of molecular alignment. The angular brackets denote averaging over all molecules in the medium. For the determination of S_2 from an IR band one has to know the angle between the vibrational transition moment corresponding to the investigated band and the long molecular axis. Using a homogeneously aligned sample and polarized radiation S_2 can be evaluated from the ratio R between the two absorption coefficients $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, the subscripts $\parallel$ and $\perp$ denote respectively the cases where the incident radiation is polarized parallel and perpendicular to the direction of sample alignment. The spectrum of EBCA in polarized light is given in Figure 1. The most suitable absorption band for the determination of the orientational order is

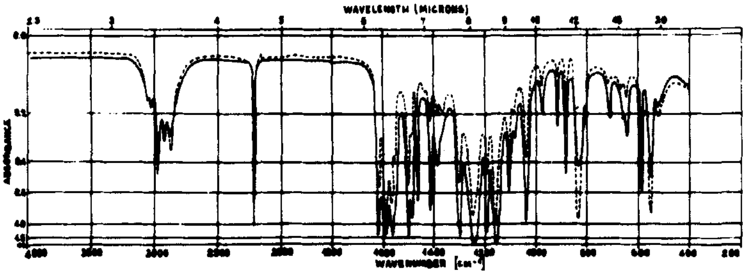


FIGURE 1 IR spectrum of homogeneously ordered EBCA: solid line–electric vector of incident light parallel to the direction of the uniform alignment which coincides with the long molecular axis; dash line = perpendicular; cell thickness = 12μm.

the CN stretching mode at 2223 cm^{-1}. It is a distinct and strong band, free from any overlap with neighboring lines. It has a transition moment nearly parallel to the long molecular axis forming an angle α of almost 10°. If the transition moment is directed along the long axis of the molecule we can write down from Ref. 19 that:

$$S_2 = \frac{R-1}{R+2} \tag{2}$$

The values of the dichroic ratio R^* are related to the observed ones R by the equation $R^* = Rg(\lambda)$ where $g(\lambda) = n_{\parallel}/n_{\perp}$ is a factor taking into account the polarization field anisotropy. In the literature, however, one cannot find available data for the refraction indices $n_{\parallel}$ and $n_{\perp}$ in the IR region for our chemicals. That is why we could not determine the absolute values of S_2 but only the relative ones. On the other hand as Saupe[20] has pointed out the so-called "Lorentz inner field correction" gives rise to only a small systematic increase in the values which do not exceed 10%.

Figure 2 represents the orientational order parameter S_2 of our three liquid crystals as a function of temperature calculated in Ref. 2. In the literature there are no other data concerning S_2 for ABCA in order to

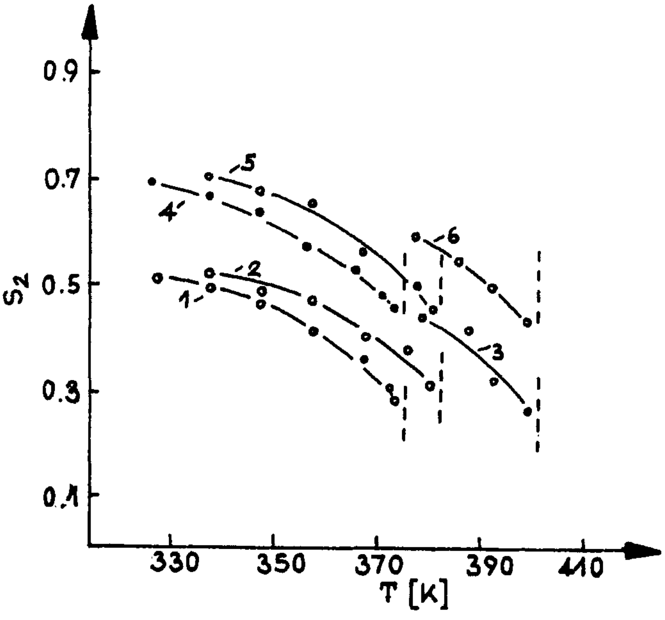


FIGURE 2 Temperature dependence of orientational order parameter S_2: (1) HBCA; (2) BBCA; (3) EBCA (homogeneously aligned); (4) HBCA; (5) BBCA; (6) EBCA (homeotropically aligned).

compare them with our data but the results obtained earlier by other authors for *p*-alkoxyazoxybenzenes and some *p*-alkoxy substituted Schiff's bases with different methods, namely vibrational spectroscopy,[1–6] guest dye dichroism,[21,22] NMR,[23] EPR[24] and coherent neutron scattering[25] for homogeneously aligned samples are close to ours.

B Determination of orientational order parameter for homeotropically aligned samples

When the molecules of liquid crystals are ordered perpendicular to the cell windows the CN absorption is very weak and with almost equal intensity in both polarizations. In this case the "dichroic ratio" R' at a given temperature can be defined as the ratio of the band integrated absorption at the same temperature to that in the isotropic phase just after the clearing point.[4] The following formula connects R' with the orientational order parameter

$$R' = 1 - S_2(1 - \tfrac{3}{2}\sin^2\alpha) \qquad (3)$$

and hence

$$S_2 = \frac{1 - R'}{1 - \frac{3}{2}\sin^2\alpha} \qquad (4)$$

Here α is the angle between the transition dipole moment of the investigated vibration and the long molecular axis.

As was pointed out before the evaluation of S_2 from dichroic studies must include the appropriate corrections for the anisotropy in the refractive indices and the polarizability of the liquid crystal media. In contrast with a homogenously aligned sample where the correction is as much as 10%, for homeotropically ordered sample can be estimated that the necessary correction is within 2%. This is mainly because the difference between the ordinary and extraordinary refractive indices of the liquid crystal is generally greater than that between the ordinary index of the liquid crystal and the index of the isotropic phase. The last two quantities are of interest when a homeotropically aligned sample is used. As the desired correction is less than the experimental uncertainties it is not included in our determinations of S_2. Thus within the experimental accuracy the results for the homeotropic sample give the absolute value of S_2 while for homogeneously aligned molecules we obtained only the relative one. Figure 2 illustrates the temperature dependence of the order parameter for perpendicularly aligned EBCA, BBCA and HBCA. As in the case of homogeneous samples there are no other data in the literature concerning the temperature dependence of of S_2 for these chemicals. Our results confirm quantitatively that the uniform parallel alignment of liquid crystals prepared by rubbing of the cell windows with paper or cloth is not so perfect as the homotropically arrangement achieved by deposition of organic or inorganic thin layer on the cell surface. The rubbing method is highly empirical, not sufficiently reproducible and in general, the characteristics of the surface are not known well to allow a satisfactory explanation of the alignment mechanism.

C Influence of a.c. electric field (homogenous configuration)

Figures 3 and 4 give the overall spectra (4000–40 cm^{-1}) of 12 μm layer of EBCA without an electric field and with an applied electric field of 50 volts. As one can see there are no changes in the band position even in the far IR

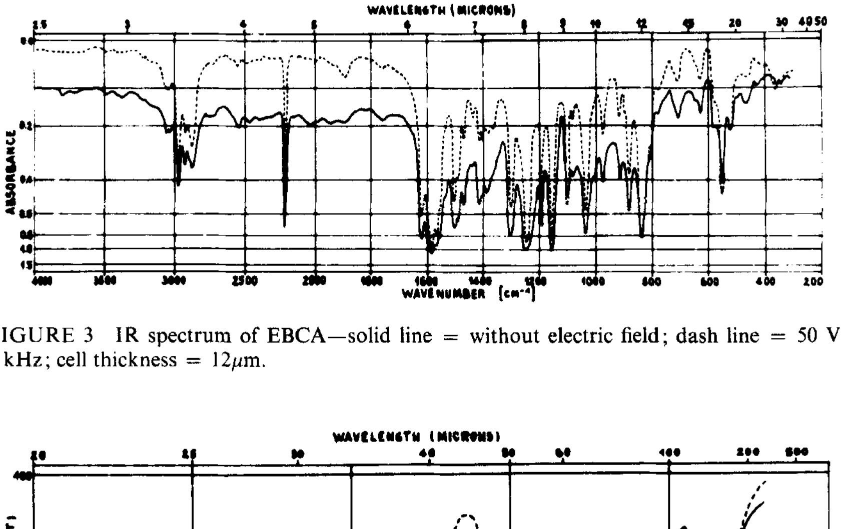


FIGURE 3 IR spectrum of EBCA—solid line = without electric field; dash line = 50 V, 5 kHz; cell thickness = 12μm.

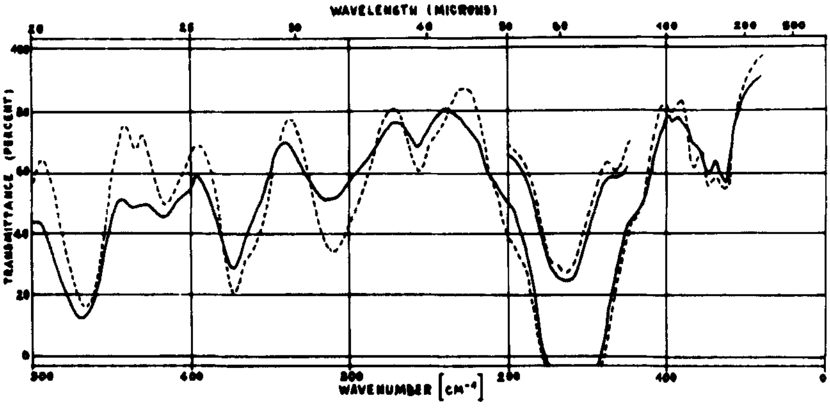


FIGURE 4 FIR spectrum of EBCA = solid line = without electric field; dash line = 50 V, 5 kHz; cell thickness = 35μm.

region. Actually our field is very weak (2.10^4 V/cm) in order to produce any shift of the bands. As some calculations[26] indicate field with intensity of 10^5 V/cm should shift the bands of gaseous HCl with about 10^{-6} cm^{-1}, and will broaden the bands with approximately 10^{-1} cm^{-1}. These changes are far below the precision of the modern spectrophotometers. Much more intensive fields (equal to interatomic ones) must be applied in order to cause significant changes in the vibrational spectrum. Only theoretically it has been shown that a field with 10^8 V/cm will shift the bands from the IR spectrum of HCl with several wave numbers but the increase of the half-width will be about 10 cm^{-1}. Such intensive electric fields cannot be achieved experimentally. However, as Figures 3 and 4 indicate, weaker electric fields change the IR spectrum of investigated liquid crystals significantly ... the scattered light decreases, transmittance of the sample increases, and the bands are outlined and resolved better. The half-width and intensity of most of the bands from the spectra of all chemicals decrease. Figure 5 illustrates the changes of δ for the band at 2223 cm^{-1} (HBCA) as a function of the electric field at different temperatures. The half-width decrease of the other bands is even more drastic, e.g. the band assigned to the benzene ring–oxygen stretch vibration at 1253 cm^{-1} narrows more than two times. As one can see from Figure 5 at higher temperatures the half-width changes with

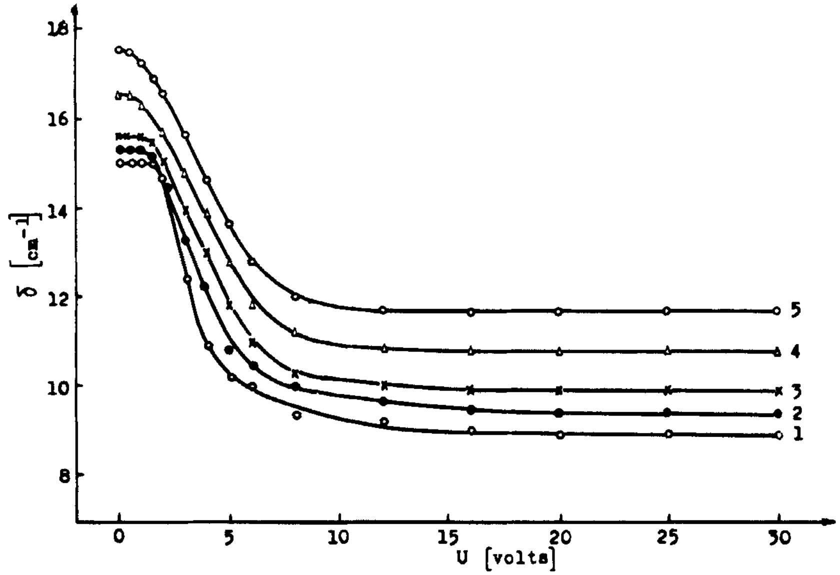


FIGURE 5 Dependence of "true" half-width δ of the band at 2223 cm^{-1} from the spectrum of HBCA on the intensity of electric field: 1 = 333 K; 2 = 343 K; 3 = 353 K; 4 = 363 K and 5 = 373 K.

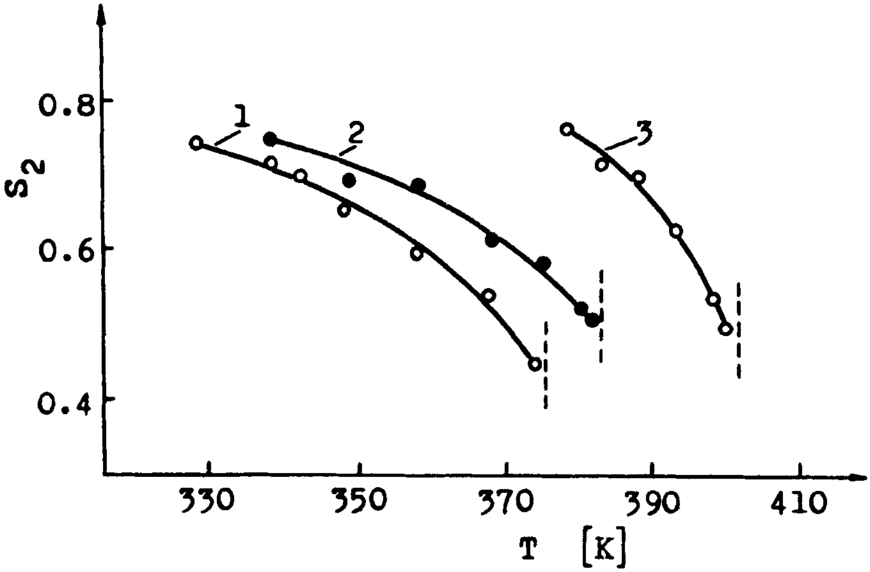


FIGURE 6 Temperature dependence of order parameter S_2 for liquid crystals aligned homeotropically with a.c. electric field: (1) HBCA; (2) BBCA; (3) EBCA.

the electric field are smaller in comparison with temperatures at the beginning of the mesophase existence. This is due to the increased thermal molecular motion at higher temperatures which decreases the orientational role of the electric field. Only a few bands, those at 556, 889, 1067 and 1197 cm^{-1} in all investigated compounds broaden with approximately 1.5 cm^{-1} and their intensity increases slightly.[11] It is clear from Figure 5. and from the plots given in our previous publications[10,11] that the electric field begins to act approaching the threshold voltage, and its influence reaches saturation at about 15–20 V. Initially the molecules of ABCA are arranged parallel to the cell windows. With the increasing electric field they began to change their orientation and constantly reach an arrangement perpendicular to the cell windows. As a result the spectrum does not change any more. Our microscopic observations confirmed this conclusion. The light transmittance of the sample reaches saturation at about 20 V when the brightness stops to increase. In Figure 6 we have recorded the temperature dependence of S_2 for all liquid crystals investigated by us and aligned by an electric field. No other similar investigations have been done by means of vibrational spectroscopy except Neff's IR study.[7] He has calculated that the degree of order of EBCA aligned with a dc electric field 3 kV/cm at 106° is only 0.33. This is far below our value 0.75. Probably this is due to the fact that dc electric field induces domain formations in the thin films, so that the orientation is not uniform. It is also possible that electrolysis can start with the application of a dc electric field especially if the sample is not very pure.

To answer the question why some bands broaden slightly when the electric field is applied but others become much narrower, let us look at the polarized spectrum of one of the chemicals—EBCA for example (Figure 1). It is obvious from the comparison between Figures 1 and 3 that all bands with the transition dipole moment along the long (main) molecular axis become narrower with increasing electric field while those polarized perpendicular to the main axis broaden slightly. The last bands have been the subject of our previous publications.[10, 11] We will explain the reasons for the observed narrowing.

It is a well-known fact that one part of the half-width of a vibrational band from the spectrum of a condensed phase is related to the mean molecular reorientational motion. In general, the motion of this type is described in terms of the self-correlation function of random orientation of the molecules. The correlation function is essential in discussing the relation between the shapes of the vibrational bands and the Brownian rotational motion in condensed phases. The widely used approximation is such that the function is the exponential one of the following type:

$$I(t) = \text{const.}\exp\left(-\frac{t}{\tau_{\mathrm{OR}}}\right) \tag{5}$$

where τ_{OR} is the mean period of the reorientation of the molecules, usually several picoseconds. The Fourier transformation of this function gives the band contour of the Lorentzian type. It is well known that in many cases the vibrational bands fit well to the Lorentzsian curves, the analysis of the band shapes on the basis of this approximation may provide us with a great deal of information on molecular dynamics. Sobelman,[27] Gordon[28] and Shimizu[29] have reported the theoretical details of this aspect of molecular spectroscopy. Rakov[30] has first received the qualitative results connecting the half-width broadening with the Brownian motion in simple organic liquids. A few years later Rotshild studied the molecular motion in condensed phases. He studied rotational and translational diffusion in weakly associated systems,[31] liquid methylene chloride,[32] methyl iodide,[33] chloroform,[33] cyclohexane,[33] in highly polar and strongly associated systems,[34] quinoline,[33] etc., by means of IR and Raman spectroscopy. The relaxation processes in nematic liquid crystals have been studied.[36]

The broadening of the half-width due to the Brownian rotational motion is given by:

$$\Delta\delta^{\mathrm{R}}(T) = \frac{1}{\pi_c \tau_{\mathrm{OR}}} \tag{6}$$

Hence the whole half-width of a vibrational band can be expressed as a sum of the component widths coming from the reorientations of the molecules, which is strongly temperature dependent and that coming from the vibrational relaxation, inter and intra molecular interactions and other factors which are not explained yet in detail, i.e.:

$$\delta = \delta_0 + \Delta\delta^{R}(T) \tag{7}$$

If $\Delta\delta^{R} \ll \delta$ rotational relaxation clearly plays a minor role in the band broadening in this particular contour. Therefore, there is a definite relation between the rotational diffusion and the width of the spectrum or spectral density. The shorter the correlation time the easier the molecular reorientation and broader become the vibrational bands. If the molecule can be regarded as spherical bodies they will have only one correlation time. In general, however, many compounds have an elongated shape with three different axes x, y and z. Normal paraffins are typical examples. Therefore, they will have three different correlation times corresponding to the rotational difiusion in relation to the three principal axes. However, for rod-shaped molecules the moments of inertia around the two short axes are very close, while that concerned with rotation in relation to the long axis is about one degree smaller. Rotschild[32] has shown that calculating the correlation functions corresponding to vibrational bands with different transition moments it is possible to calculate $\tau^{x}_{\mathbf{OR}}$, $\tau^{z}_{\mathbf{OR}}$ and $\tau^{z}_{\mathbf{OR}}$ and hence, to evaluate the rotational diffusion tensor. For example, molecules with C_{2v} point symmetry group have IR active vibrations with transition dipole moment parallel to any of the axes of inertia. If the various fundamental and combination bands are sufficiently well separated it is possible to obtain the rotational diffusion tensor using bands belonging to transition moments of three symmetry species A_1, B_1 and B_2. For C_s point group symmetry to which most of the liquid crystal molecules belong we have two types of normal vibrations—A' and A''. The bands from the second group—A'' with transition dipole moment perpendicular to the long molecular axis are sensitive to hindered rotation around it, while the half-width of longitudinally polarized modes symmetry type A' will increase when the rotational diffusion is in relation to the short axes. The initial homogeneous alignment with Si windows is not better than 0.4. It is a well known fact that in the liquid crystal phase the reorientation around the main molecular axis is very easy. However, due to the lower degree of order it is possible, although difficult, reorientation around the short axes. This increased rotational degree of freedom will lead, according to Eq. (6), to broadening of all bands with dipole moment coinciding with the long molecular axis (A'). When the electric field is applied the molecules change their orientation from homogeneous to homeotropical and S_2 increases significantly, reaching 0.75. This is almost a monocrystal and the rotational diffusion in relation to the short axes is at least very difficult. As a result the contribution of the hindered rotation around the short axis in the half-width will decrease and all longitudinally polarized bands become more narrow. Another example can prove this conclusion, that is the orientational order parameters for homeotropically aligned liquid crystals, by treatment of the cell windows with lecithin and by electric field, are almost the same and as a result the half-width of all bands belonging to the symmetry type A' are equal. The significant narrowing of all modes A' clearly indicate that the rotational relaxation plays a major role in the band broadening of these particular contours.

CONCLUSION

The orientational order parameter S_2 for three *p*-alkoxy-benzylidene-*p'*-cyanoanilines nematic liquid crystals with strong positive dielectric anisotropy was calculated and its temperature dependence was investigated.

The ac electric field applied on a thin layer of liquid crystal with positive dielectric anisotropy aligns the molecules perpendicular to the cell surface and as a result S_2 increases up to 0.75–0.80. This is almost a monocrystal and the rotation around the short axes is very difficult. As a result that part of the half-width of the bands polarized along the long axis determined by the hindered rotation around the short axes disappear and the half-width of longitudinally polarized bands decrease drastically. Further investigations of the influence of an ac electric field on the IR spectra of liquid crystals with similar molecular structure, but possessing weak negative dielectric anisotropy, are in progress.

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