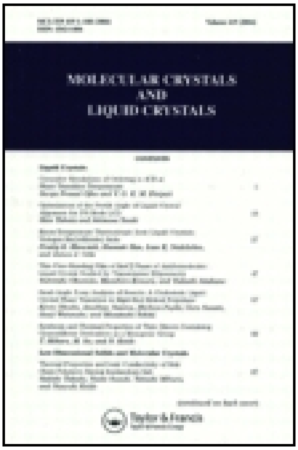


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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

N. Kirov [a] , P. Simova [a] & H. Ratajczak [b a]
[a] Institute of Solid State Physics, 72 Boul., Lenin, 1113, Sofia
[b] Institute of Chemistry, 14 Joliot-Curie, 50-383, Wroclaw

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. II. Molecules with Weak Negative Dielectric Anisotropy, Molecular Crystals and Liquid Crystals, 58:3-4, 299-310

To link to this article: http://dx.doi.org/10.1080/00268948008082129

Mol. Cryst. Liq. Cryst., 1980, Vol. 58, pp. 299–310
0026-8941/80/5803-0299$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

II. Molecules with Weak Negative Dielectric Anisotropy

N. KIROV and P. SIMOVA
Institute of Solid State Physics, 72 Boul. Lenin, 1113 Sofia

and

H. RATAJCZAK
Institute of Chemistry, 14 Joliot-Curie, 50-383 Wroclaw

(*Received August 2, 1979*)

The influence of a.c. electric field (10 kHz) on the IR spectra of the nematic phase of six *p*-alkoxybenzylidene-*p,n*-butylanilines with weak negative dielectric anisotropy was studied and the temperature dependence of the orientational order parameter and threshold voltage have been investigated. The values of band elastic constants K_{33} were calculated for MBBA and EBBA.

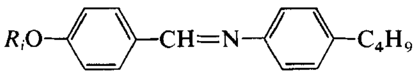
INTRODUCTION

Infrared and Raman spectra of *p*-methoxybenzylidene-*p,n*-butylaniline (MBBA) have been reported a few years ago and tentative assignments were given.[1,3] Recently Vergoten *et al.*[4] published the IR spectra of MBBA and its ethoxy homologue (EBBA) in the region 4000–30 cm^{-1} for samples as a liquid film (isotropic liquid) and for a homeotropic layer in the nematic phase. Assuming that the ring structure of many nematogens has approximately C_{2v} symmetry they gave the assignment of most bands of MBBA and EBBA in the middle IR region. Their results are supported by a normal coordinate analysis and dichroic measurements. However, only Ohnishi[5] has investigated the influence of electric fields on the IR spectrum of liquid crystals with weak negative dielectric anisotropy. He has applied a d.c. electric field up to 10 V 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. No more investigations of their order parameter S_2 have been made up to now.

The aim of the present paper is: (1) to investigate the temperature dependence of orientational order parameter S_2 for homeotropically and homogeneously aligned samples; (2) to study the influence of a.c. electric field on IR spectral characteristics, namely band position, halfwidth, integrated absorption and polarization of liquid crystals *p*-alkoxybenzylidene-*p*,*n*-butilanilines; (3) to calculate their threshold voltages U_c and bend elastic constants K_{33}.

EXPERIMENTAL PART

The general formula for the investigated liquid crystals, usually abbreviated as ABBA is:



where $R_1 = CH_3$ (MBBA), $R_2 = C_2H_5$ (EBBA), $R_3 = C_3H_7$ (P_3BBA), $R_4 = C_4H_9$ (BBBA), $R_5 = C_5H_{11}$ (P_5BBA) $R_6 = C_6H_{13}$ (HBBA).

The first two chemicals were purchased from Eastman Kodak Ltd., while the other four were synthesized in Orsay Liquid Crystal Group. The fifth and sixth homologues form not only nematic but a smectic phase too. Their melting T_M and clearing temperatures T_c determined by us coincide well with those given in Ref. 6. In the literature there are data for the dielectric anisotropy only for the first two homologues. They are as follows: MBBA – $\varepsilon_{\parallel} = 4.7$, $\varepsilon_{\perp} = 5.4$, $\varepsilon_a = -0.7$ (25°C); (7) and EBBA – $\varepsilon_{\parallel} = 4.8$, $\varepsilon_{\perp} = 5.3$, $\varepsilon_a = -0.5$ (35°C) (supplier's data). The equipment, the experimental conditions of the spectra registration and the methods for the preparation of uniform aligned samples are described in Part I. In order to avoid the hydrodynamic effect the frequency of the applied electric field is higher –10 kHz and its intensity changes between zero and 100 V.

RESULTS AND DISCUSSION

A Determination of orientational order parameter for homogeneously aligned samples

As one can see from Figure 1 where the polarized IR spectrum of *p*-propoxybenzylidene-*p*,*n*-butylaniline is given there are no well pronounced bands, strong and distinct, with no overlap with neighboring bands, and with known

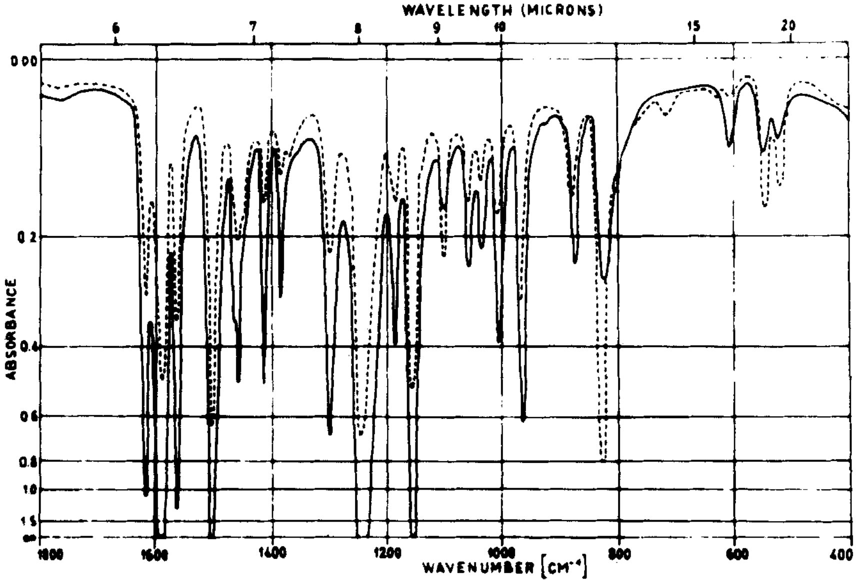


FIGURE 1 IR spectrum (1800–400 cm^{-1}) of homogeneously aligned P$_3$BBA; solid line = electric vector of the incident light parallel to the direction of the uniform alignment which coincides with the long molecular axis; dash line = perpendicular; cell thickness 12 m.

direction of their transition moments as CN stretch vibration in the spectrum of *p*-alkoxybenzylidene-*p*-cyanoanilines. However, the assignment given in Ref. 4 can help us to choose some bands suitable for the calculation of S_2. If, in the normal coordinate analysis we consider a mode with known potential energy distribution which has a component greater than 50% to be a characteristic group frequency, only eight normal modes between 4000 and 200 cm^{-1} can be used for orientational order parameter determination. All these eight bands can be assigned to vibrations of the aromatic part but the degree of coupling is of great importance and none of the modes are due to the single type of molecular vibrations. Seven of them arising from vibrations of the benzene ring are polarized parallel to the long axis while the last one, at 840 cm^{-1} is attributed to CH out of the plane deformation has a transition moment perpendicular to the main axis. For determination of S_2 we choose four bands—namely those at 840 cm^{-1} $S_{10}(B_2)$-70%; 1165 cm^{-1}-$S_8(A_1 + S_9(A_1)$-67%; 1512 cm^{-1}-$S_{20}(A_1)$-50% + $S_{19}(A_1)$-32% and 1598 cm^{-1}-$S_8(A_1$-64% + $S_7(A_1) + S_9(A_1)$. Maier and Englert[8] have used the same bands—837 cm^{-1} and 1600 cm^{-1}—to determine the orientation order parameter of some liquid crystals with central azoxy groups and obtained experimental data close to the theoretical prediction.

When the transition moment is directed along the long axis of the molecules (symmetry type A_1) we can write from Ref. 9:

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

If the vibrational transition moment is perpendicular to the long axis (symmetry type B_2) we have from Ref. 10:

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

The data for the orientational order parameter S_2 are calculated with formulae (1) and (2) and the results are averaged over all four bands. The temperature dependence of S_2 for the five investigated compounds is shown at Figure 2. In the literature, however, there are no available data for $n_{\|}$ and $n_{\perp}$ in the IR region of our chemicals. That is why the so-called "Lorentz inner field correction" has not been done neither for homeotropic nor for homogeneous samples but as it was pointed out by Saupe[10] this correction gives rise to only small systematic increase in S_2 values which is usually, especially for perpendicular molecular alignment, within the limits of the experimental accuracy. The orientational order parameters only for MBBA and EBBA have been investigated up to now by other methods but it is sufficient to indicate that our data are a little lower than those yielded in Refs. 11 and 12. This disagreement can be attributed to the fact that other authors have achieved homogeneous arrangement not by rubbing but with

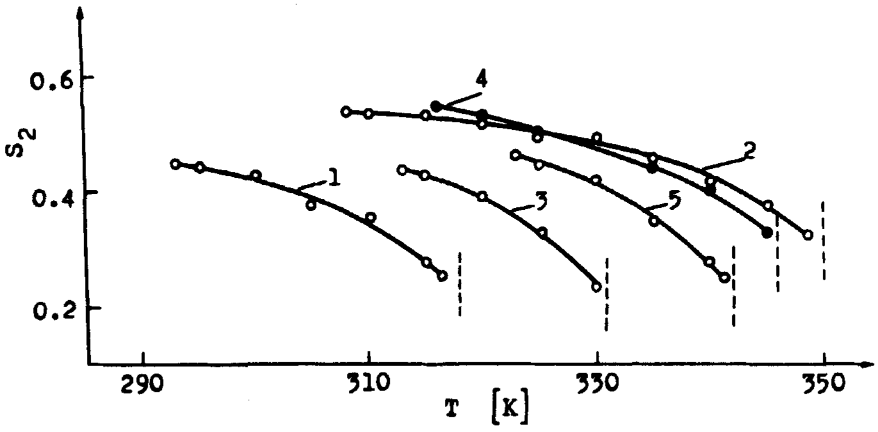


FIGURE 2 Temperature dependence of orientational order parameter S_2: (1) MBBA; (2) EBBA; (3) P_3BBA; (4) BBBA and (5) P_0BBA (homogeneously aligned).

window coating by means of vacuum vaporization of gold which usually gives a better uniform alignment. Our results confirm quantitatively, as in the case with the other liquid crystals investigated in Part I, that the uniform parallel alignment achieved by rubbing of the cell windows, especially IR light transparent plates, with paper or cloth is not so perfect and reproducible as that reached by deposition of organic or inorganic thin layer on the cell surface.

B Determination of orientational order parameter for homeotropically aligned samples

When the molecules are aligned perpendicular to the cell surface the dichroic ratio R cannot be defined and for determination of S_2 we have to use the method given by Kelker[13] and explained in detail in Part I. However, in the spectrum of *p*-substituted Schiff's bases there are not bands with dispersion shape whose integral intensity can be determined using Ramsay's procedure.[14] Thats why for determination of S_2 *via* the infrared spectrum we have examined a 5% solution of 4-biphenylcarbonitrile in our liquid crystals. This solution is dilute enough so that the arrangement in the liquid crystal phase is not changed. From the other size the CN stretch vibration at 2223 cm^{-1} is clear, not overlapped by other bands. Figure 3 gives the temperature dependence of S_2 of five liquid crystals under investigation.

The order parameter S_2 for homogeneous and homeotropic samples exhibits an odd-even alternation with respect to the number of carbon atoms n in the alkoxy C_nH_{2n+1} end group (Figure 4). The similar dependence is found for the same homologous series in the clearing temperature T_c

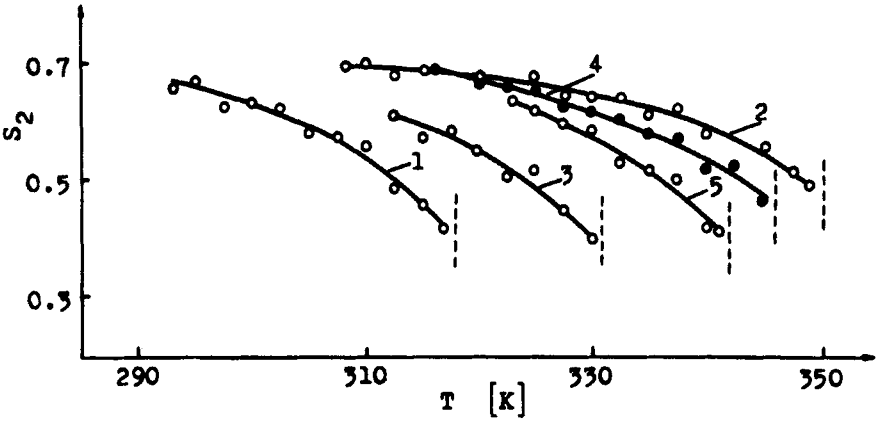


FIGURE 3 Temperature dependence of orientational order parameter S_2: (1) MBBA; (2) EBBA; (3) P_3BBA; (4) BBBA and (5) P_5BBA (homeotropically aligned).

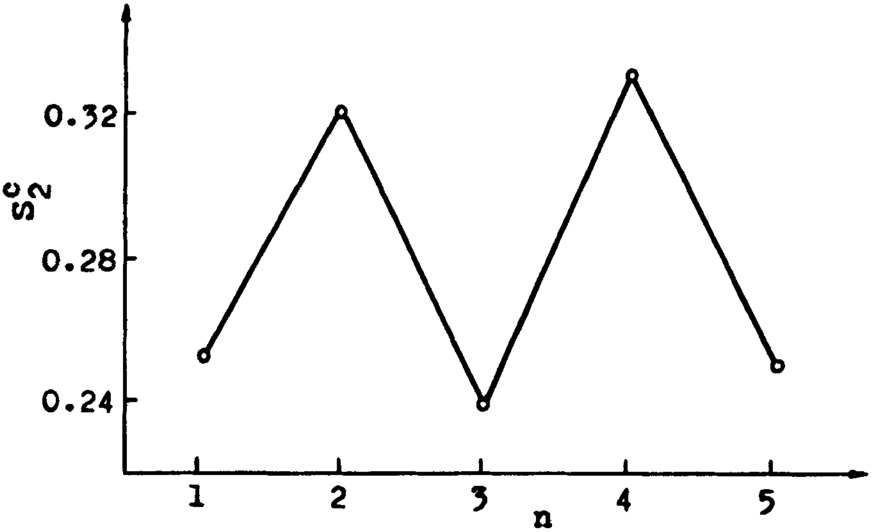


FIGURE 4 Even odd effect in ABBA series (homogeneously aligned) (one degree before T_c).

and in the enthalpies and entropies of the phase transition mesophase—isotropic liquid.[1] An even-odd effect was also observed by us in the pre-orientation potential barrier of the molecules of *p*-alkoxyazoxybenzene nematogens[15] and recently from C_{13} NMR measurements of the same compounds[16] where the two end groups are equivalent. Our results for S_2 presented here are the first spectroscopical evidence of an odd even ordering effect in the homologous series of Schiff's base liquid crystals where the two end groups are not equivalent. Only Chang[7] has observed the same type of alternation in the same homologous series before us by means of optical anisotropy measurements. Although molecular end chains are known to exert important effect on the properties of this mesophase, theories of the liquid crystalline phase have not until recently included their effect explicitly. Now the even-odd effect can be explained with the influence of end chains on the anisotropic interaction between essentially rigid molecules.[17]

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

Figure 5 represents the influence of the electric field with different intensity on the IR spectrum of homeotropically aligned *p*-propoxybenzylidene-*p,n*-butylaniline. As one can see, with increasing of the electric field strength the scattered light increases, transmittance of the sample decreases drastically, most of the bands broaden so much and even merge some details in the

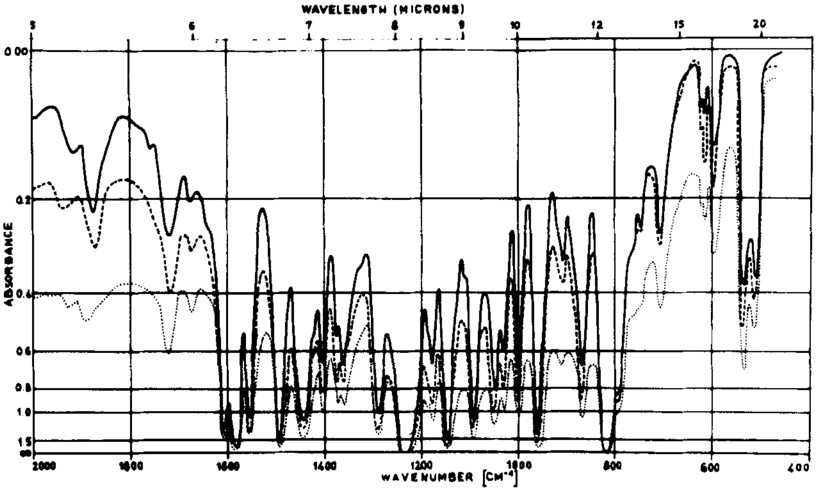


FIGURE 5 IR spectrum (1800–400 cm^{-1}) of EBBA; solid line = without electric field; dash line = 20 V; dotted line = 100 V; cell thickness = 12μm.

spectrum. This behavior of the investigated liquid crystals is just opposite to that of alkoxybenzylidene-*p*, cyananilines where the electric field orders the liquid crystal molecules and as a result the transmittance of the sample increases, the half-widths of most of the bands decrease significantly and the characteristics of the spectrum are improved. However, as in the case of liquid crystals with positive dielectric anisotropy even the most intensive electric field does not shift the IR bands in the region 4000–35 cm^{-1} but influences only on the half-width and integrated absorption. All band polarized parallel to the long molecular axis (type A' if we assume that the investigated molecules have C_s symmetry) broaden with some cm^{-1} and their integral intensity increases, while the others—transversally polarized (A'') become more narrow—with 1 cm^{-1} approximately and their integrated absorption decreases slightly. Here we will deal only with the bands whose half-width increases. As Figure 6 indicates the electric field begins to act not immediately but after reaching a given voltage-threshold voltage U_c whose value depends on the molecular length. The influence of the electric field usually reaches saturation between 15 and 40 volts depending on the structure of the liquid crystal-line molecule—as longer is the alkoxy side chain as higher is the value of the saturation.

How can the broadening of the bands with increasing field strength be explained? The electric field orders the molecules with negative dielectric anisotropy perpendicular to its direction. Initially the samples are arranged perpendicular to the cell windows and the order parameter S_2 is about 0.6

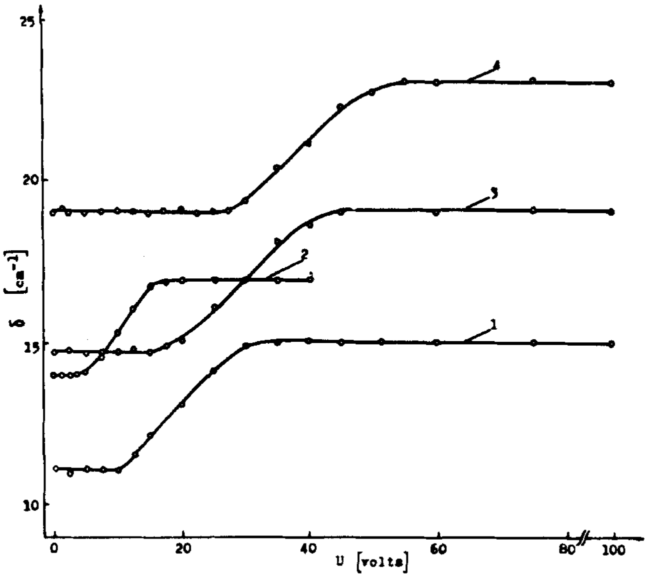


FIGURE 6 Influence of electric field on the half-widths of the bands: (1) 888 cm^{-1} (EBBA); (2) 728 cm^{-1} (MBBA); (3) 972 cm^{-1} (P_3BBA) (4) 1305 cm^{-1} (BBBA).

(Figure 2). With increasing the electric field intensity above U_c the molecules begin to change slowly their orientation from homeotropic to a homogeneous one. When the parallel alignment is achieved the electric field has no further influence, and as a result the spectrum does not change. Polarized measurements of ABBA samples oriented homogeneously by a.c. electric field indicate that the alignment is much lower in comparison with the initial one. Calculations of orientational order parameter S_2 confirm this conclusion quantitatively. Actually the initial values of S_2 for all studied liquid crystals is between 0.6 and 0.65 while those of the same samples aligned homogeneously by electric field is much lower—0.2–0.25. This is natural because in this case the molecules can reorientate in the xy plane (the z-axis is perpendicular to the cell surface) while for the homeotropic alignment the only possible molecular rotational relaxation is reorientation around the long axis. As a result the part of the half-width due to the rotational diffusion around the short axes will increase. This will lead, according to formula (6), Part I to broadening with several wavenumbers of all bands with transition dipole moment along the long molecular axis.

Two very important results come from theoretical and experimental points of view which are characteristic of liquid crystals, namely the threshold voltage U_c and bend elastic constant K_{33} can be determined from the electric behavior of the half-width. The method for U_c calculation is explained in detail in Refs. 18 and 19 and here we will give only the results. The U_c data for the nematic phase averaged on all investigated bands are as follows: MBBA-3.5 (298 K), EBBA-9.5 (309 K), P_3BBA-17 (313 K), BBBA-23 (316 K), P_5BBA-30(323 K) and HBBA-36.5(333 K). The mean error is about 0.1 V. The U_c value for MBBA obtained by us coincides very well with other results reported in Ref. 20, while for EBBA and other higher homologues there are no other data in the literature.

The calculation of K_{33}, however, is not so simple. The value of the band elastic constant depends on the boundary conditions, i.e. on orientational order and on the elastic properties of the liquid crystal media. Small deviations from the best possible alignment will give a K_{33} value lower than the real one. In general, as many methods indicate, the S_2 values for nematics liquid crystals ordered homeotropically with deposition of a thin layer of different chemicals on the cell surface is between 0.5 and 0.7. Therefore our data coincide well with other literature data and we can consider that the boundary conditions will not decrease the K_{33} values. By means of the equation

$$K_{33} = \frac{U_c^2 \varepsilon_a \varepsilon_\perp}{4\pi^3 \varepsilon_\parallel} \tag{3}$$

we calculated that K_{33} for MBBA and EBBA are correspondingly $(8.8 \pm 0.4) \cdot 10^{-7}$ dynes (298 K) and $(44.1 \pm 1) \cdot 10^{-7}$ dynes (308 K). Our data for

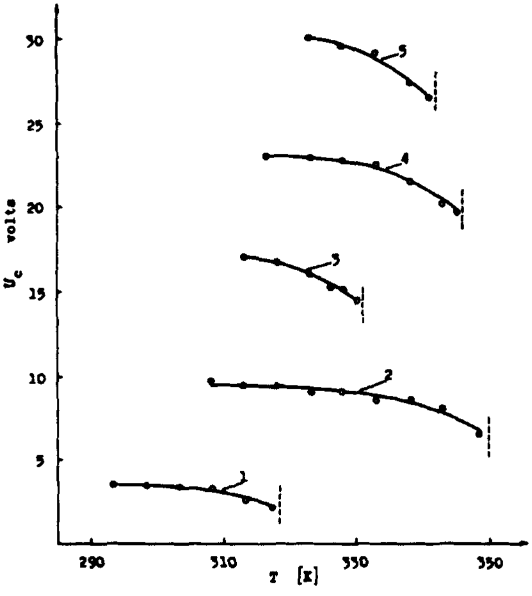


FIGURE 7 Temperature dependence of the threshold voltage (1) MBBA; (2) EBBA; (3) P_3BBA; (4) BBA (5) P_5BBA in their nematic phase.

K_{33} (MBBA) and those obtained by other non-spectroscopical methods are compared in Ref. 21, while for K_{33} and U_c for EBBA there are no other data in the literature.

Figure 7 gives the temperature dependence of the threshold voltage for all investigated compounds. As one can see U_c increases with decreasing temperature which coincides with the theoretical predictions. There are no other investigations on the temperature dependence of U_c except the data of Robert *et al.*[22] for MBBA which are close to ours.

CONCLUSION

The orientational order parameter S_2 for six alkoxybenzylidene-*p*,*n*-butylanilines have been calculated and their temperature dependence investigated. The experimental determination is of significance regarding the molecular statistical theory of nematic liquid crystals. This is due to the fact that empirically determined temperature dependence of the indicated parameter are needed to provide proof for the results of the theory.

When an electric field up to 100 V, 10 kHz is applied on a thin layer of a nematic liquid crystal with negative dielectric anisotropy the results are exactly opposite to those obtained for liquid crystals with strong positive dielectric anisotropy; the transmittance of the sample decreases drastically with increasing field strength, all bands polarized along the long molecular axis broaden by several wavenumbers while those with transition dipole moment perpendicular to it become more narrow about 1 cm^{-1} approximately. Initially the liquid crystals are arranged homeotropically and S_2 for all investigated compounds is between 0.6 and 0.65. In this case the only possible molecular motion is the rotation around the long molecular axis. When the intensity of the electric field reaches the U_c value the molecules begin slowly to change their orientation from a homeotropic to a homogeneous one. In the last case the orientational order parameter is much lower (0.2–0.25) and the molecules can pre-orient not only around the long axis but also in the plane parallel to the cell surface. Consequently the increased molecular freedom will lead to broadening of all bands with vibrational dipole moment parallel to the long molecular axis.

Our results give a quantitative picture of how the increasing of the ordering in a condensed system changes the half-width and integral intensity of the IR absorption bands. On the other side, knowing initially only the sign of the dielectric anisotropy of the molecules from the electric behavior of the band half-widths we can estimate the direction of the transition dipole moments of the bands which help the precise assignment of the frequencies in the IR spectra of liquid crystals.

References

1. B. J. Bulkin, T. Kennelly, and Wai Bong Lock, *Liquid Crystals and Ordered Fluids*, Edited by J. F. Johnson and R. S. Porter (1974).
2. J. P. Heger and R. Mercier, *Helv. Chim. Acta*, **45**, 886 (1972).
3. E. Sciensinska, J. Sciensinski, J. Twardowski, and J. A. Janic, *Mol. Cryst. Liq. Cryst.*, **27**, 125 (1975).
4. G. Vergoten, G. Fleury, R. Norman Jones, and A. Nadeau, *Mol. Cryst. Liq. Cryst.*, **36**, 327 (1976).
5. Y. Ohnishi, *Jap. J. Appl. Phys.*, **12**, 1079 (1973).
6. R. Chang, F. B. Jones, Jr., and J. J. Ratto, *Mol. Cryst. Liq. Cryst.*, **33**, 13 (1976).
7. D. Diquet, F. Roudeler, and G. Durand, *Compt. rendu Acad. Sci.*, (Paris), **B271**, 954 (1970).
8. W. Maier and G. Englert, *Z. Electrochem.*, **64**, 689 (1960).
9. V. D. Neff, *Liquid Crystals and Plastic Crystals*, Edited by G. Gray and P. Winsor (1975).
10. A. Saupe and W. Maier, *Z. Naturforschung*, **16a**, 816 (1961).
11. Shen Jen, N. A. Clark, P. S. Pershan, and E. B. Priestly, *Phys. Rev. Lett.*, **31**, 1552 (1973); P. S. Pershan, *Proceeding of the First Soviet-American Symposium*, Moscow, May 26–30, 1975, Edited **1**, 61 (1977).
12. I. N. Dozov and I. I. Penchev, *Acta Phys. Polonica*, **A54**, 649 (1978).
13. H. Kelker, R. Hatz, G. Hatz, and G. Wirzing, *Z. Anal. Chem.*, **267**, 161 (1973).
14. D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).
15. P. Simova and N. Kirov, *Adv. Molec. Relax. Proc.*, **5**, 233 (1973).
16. A. Pines, D. J. Ruben, and S. Allison, *Phys. Rev. Lett.*, **33**, 1002 (1974).
17. S. Marcelja, *J. Chem. Phys.*, **60**, 3599 (1974).
18. P. Simova, N. Kirov, H. Ratajczak, G. Vergoten, and G. Fleury, *Mol. Cryst. Liq. Cryst.*, **46**, 137 (1978).
19. N. Kirov, P. Simova, and H. Ratajczak, *J. Mol. Struct.*, **46**, 487 (1978).
20. P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford (1977).
21. N. Kirov, P. Simova, and S. Sainov, *Spectr. Lett.*, **10**, 783 (1977).
22. J. Robert, G. Labrunie, and J. Borel, *Mol. Cryst. Liq. Cryst.*, **23**, 197 (1973).