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Dielectric studies of liquid crystals under high pressure: Static permittivity and dielectric relaxation in the nematic phase of pentylcyanobiphenyl (5CB)

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Dielectric studies of a thermotropic-liquid-crystalline substance [pentylcyanobiphenyl (5CB)] under high pressure are reported. Measurements of a complex dielectric permittivity were carried out in the pressure range 0.1–160 MPa, the frequency range 1 kHz–13 MHz, and the temperature range 287–343 K. Static permittivities measured at constant pressures are governed by the $[2S(T)+1]/T$ factor. An increase in permittivity with pressure at a constant temperature is interpreted as a result of an increasing molecular ordering and of a breaking of the dipole-dipole correlations between neighboring molecules. The relaxation time $\tau_{\parallel}$ characterizing molecular rotations around the short axes in the nematic phase is analyzed as a function of temperature and pressure, yielding an activation enthalpy of approximately 60 kJ mol^{-1}, which decreases with increasing pressure, and an activation volume of about 60 cm^3 mol^{-1}, decreasing with increasing temperature. An activation energy in isochoric conditions was evaluated to be 37 kJ mol^{-1} at $V_m = 247$ cm^3 mol^{-1}, 25 kJ mol^{-1} at 243 cm^3 mol^{-1}. A relation between the different activation parameters is discussed.

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INTRODUCTION

Liquid and plastic crystals are of considerable interest because of their mesophase character between the liquid and solid state. The application of pressure has turned out to be particularly relevant since the phase behavior may significantly change under pressure [1].

Dielectric properties of a large number of thermotropic liquid-crystalline (LC) substances have been hitherto studied at atmospheric pressure [2–5]. No dielectric-relaxation studies at high pressure, however, have been reported so far. Measurements at static field give information about the dielectric anisotropy of LC phases, which is related to an electric structure of molecules and, in some cases, to the dipole-dipole correlations between the molecules. Dynamical properties of molecules are investigated by measuring the complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$, as a function of frequency and temperature. The measurements give the values of relaxation times and activation energies characterizing the relaxation processes taking place in LC phases. The results obtained in this way are interpreted on the basis of theoretical models in which several simplifications and phenomenological parameters (e.g., nematic potential, order parameter, symmetry of molecules, etc.) are introduced. It is obvious that the temperature-dependence data are frequently insufficient for the relaxation-process analysis, so the pressure data can give new information on LC phase properties.

In this paper, we present results of dielectric studies of the nematic phase of a LC substance [pentylcyanobiphenyl (5CB)] under high pressure (hp). The analysis of the results concerns mainly the thermodynamic parameters characterizing the molecular reorientations around the short axes in the nematic phase of 5CB (activation enthapy, energy, and volume). The discussion of the results in terms of the theoretical models of the nematic state will be presented in the next paper [6].

Two main modes of dipole relaxation are possible in the LC phases. One is associated with the rotations of molecules around their short axes, the other occurs when the molecules rotate around their long axes. In the nematic phase both relaxation processes are well separated, whereas in the isotropic phase they constitute one broad spectrum of relaxation times. Such different behavior is due to the existence of long-range orientational order of the molecules in the nematic phase, which disappears above the clearing temperature T_c. Molecular rotations around short axes are strongly hindered by the nematic potential, which, together with a large moment of inertia of elongated molecules, causes a relatively slow relaxation process observed at comparatively low frequencies (lf) in the megahertz range. Rotations of molecules around the long axes are not influenced by the nematic potential and the corresponding relaxation process occurs at higher frequencies (hf) in the gigahertz range. Additionally, by orienting the nematic sample in a strong magnetic field, the lf process is detected in the

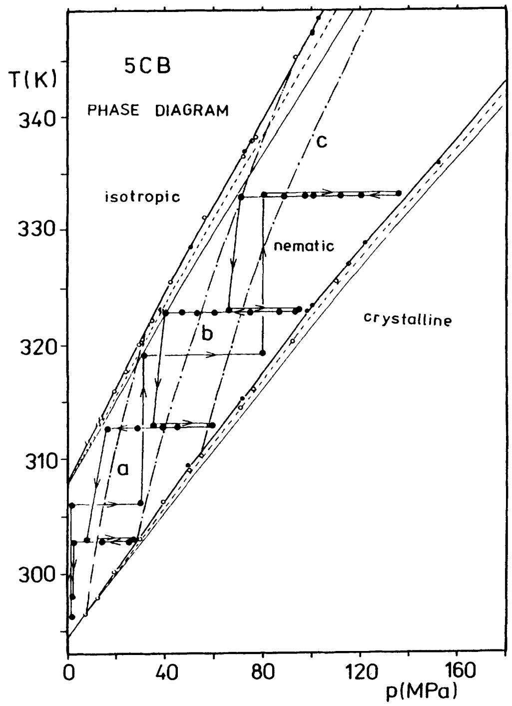

FIG. 1. Temperature-pressure phase diagram for 5CB. Solid lines with points were obtained by the differential-thermal-analysis method [13,14], thin solid lines were obtained by Horn [9], and thin dashed lines by Shashidhar [15]. The lines marked *a*, *b*, and *c* are isochores corresponding to $V_m = 247$, 245, and 243 $\mathrm{cm^3\,mol^{-1}}$ (according to [9]). A typical measurement run is shown.

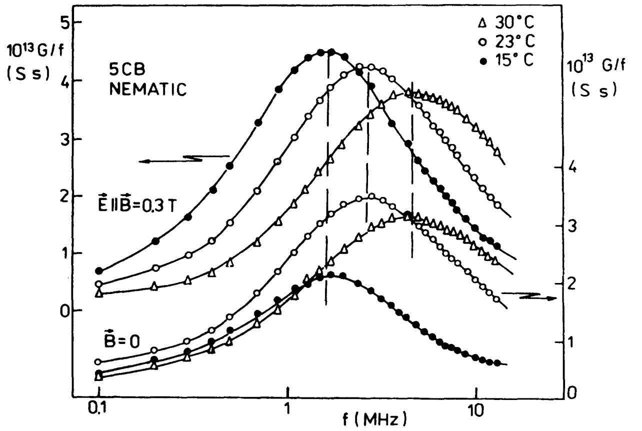

FIG. 2. Comparison of the dielectric losses for the nematic phase of 5CB (atmospheric pressure) measured for samples oriented by magnetic field and unoriented. The capacitor has not been calibrated and therefore the conductivities G are presented.

$\mathbf{E}\|\mathbf{B}$ geometry, while the hf one is detected in the $\mathbf{E}\|\mathbf{B}$ geometry.

Because the relaxation time $\tau_{\|}$ characterizing the lf relaxation process is directly connected with the height of the nematic potential [7], we expected that it should be pressure dependent. The most suitable compounds for the observation of this effect are those with their dipole moments directed along the main molecular axes. For the first study of the influence of pressure on $\tau_{\|}$, we chose 5CB, which has the following advantages. (a) The $p(T)$ phase diagram of this substance, as well as some data for isochoric lines, are known from optical measurements [8,9]—Fig. 1. (b) Relatively low melting and clearing temperatures enable us to perform the measurements in a hp apparatus developed previously for the study of plastic crystals [10]. (c) The compound is easy to handle due to good chemical stability.

EXPERIMENT

The hp setup used for the dielectric measurements was described elsewhere [10,11]. A special capacitor was designed [12] for studying very small amounts of the sample (less than 2 ml for one run). The measurements of the complex permittivity, $\epsilon^* = \epsilon' - i\epsilon''$, were performed in the frequency range of 1 kHz to 13 MHz using a Hewlett-Packard automatic bridge (model HP 4192A) connected to a Commodore 8296 computer. The recorded conductance and capacitance data have to be corrected for the influence of lead impedance. Equations previously derived [10] were improved using the inductance of lead as an adjustable parameter [12]. The corrected capacitance can be expressed as $C = C_0 + \epsilon' C_1$. After calibration with standard liquids, C_0 and C_1 were found to be 0.198 and 9.68 pF, respectively.

The sample of pentylcyanobiphenyl was produced by R. Dąbrowski of the Military Technical Academy (Warsaw). Transition points of the sample at atmospheric pressure agreed with the literature data.

The capacitor designed and the hp vessel do not allow one to orient the sample by a magnetic field during the measurements. However, our recent study shows that the dispersion and absorption spectra obtained for an unoriented sample or for a sample oriented by a magnetic field give the same relaxation times (see Fig. 2), although the values of permittivity are lower in the former case.

The pressure was transmitted by compressed helium or argon via a moving piston on the sample. For details, see previous papers [10,11]. In Fig. 1 one can see how the pressure and temperature were changed during one selected run. The state points have been passed both on increasing and decreasing pressure, thereby checking the reproducibility of the measurements, which was usually better than 5%. For every state point the data were recorded only after an hour of equilibration.

RESULTS

Phase diagram. In the first stage of the measurements we performed a few runs starting with pressures very close to the nematic-crystal transition line according to the phase diagram published by Horn [8]. However, most of these runs had to be rejected due to unexpectedly frequent leakages of the dielectric cell caused by crystallization of the sample. Therefore, we reestablished the phase diagram with differential thermal analysis using two different hp devices [13,14]. The phase-transition lines are shown in Fig. 1, together with the results of Horn [8] and of Shashidhar and Venkatesh [15]. Our transition lines are shifted significantly towards lower pressures. The $T_c(p)$ values agree well with the results of Wallis and Roy [16]. These discrepancies seem to be connected with an inaccurate measurement of the pressure [16]. Taking into account the suggestion given in [16], we recalculated the Horn data [8] to obtain the proper isochoric lines within the nematic phase of 5CB (Fig. 1).

Static permittivity. In Fig. 3 the static permittivity ϵ_r is plotted as a function of temperature and pressure. The results presented were obtained in many separate measurement runs with different temperature-pressure treatment of the samples. On approaching the clearing temperature, the permittivity decreased strongly and remained essentially constant in the isotropic phase. In the nematic phase ϵ_r is distinctly higher than the mean value $\bar{\epsilon}_0=\frac{1}{3}(\epsilon_{\parallel 0}+2\epsilon_{\perp 0})$, which in turn, is slightly less than ϵ_{is} extrapolated from the isotropic phase[17–21]. The fact that $\epsilon_r \gg \bar{\epsilon}_0$ is probably due to an orientation effect caused by the small conductivity of the sample (the strength of the measuring electric field was approximately 20 V/cm). As seen in Fig. 3(a), the $\epsilon_r(T)$ values obtained at atmospheric pressure are only slightly less than the $\epsilon_{\parallel 0}(T)$ values measured on the samples oriented by a magnetic field [17,19–21] (only values obtained by Menu [18] are markedly large than those).

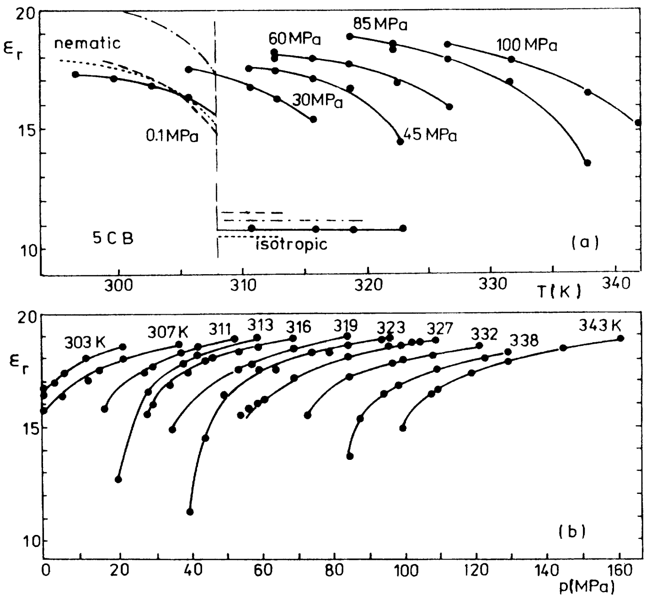

FIG. 3. (a) Dependence of static permittivity ϵ_r on temperature at constant pressures in the nematic and isotropic (at 0.1 MPa only) phases of 5CB; the lines without points show the $\epsilon_{\parallel 0}$ values obtained at 0.1 MPa by Menu [18] (—·—·—), Ratna and Shashidhar [19] (· · · ·), and Cummins *et al.* [20] (— — —). Vertical line corresponds to T_C at atmospheric pressure. (b) Dependence of ϵ_r on pressure at constant temperatures in the nematic phase of 5CB.

Dielectric relaxation in the nematic phase. Figure 4 shows, as an example, the dispersion and absorption spectra (after subtraction of the conductivity effect) obtained at 327 K for different pressures in the nematic phase and for atmospheric pressure in the isotropic phase of 5CB. Loss curves have been fitted to different equations (Cole-Cole, Cole-Davidson, Havriliak-Negami, and Jonscher). We choose the fits obtained with the use of the Jonscher equation assuming $\tau=1/\omega_{\max}$ (for details, see previous papers [11]). Some selected results are presented in Table I. The observed dielectric-relaxation process can be described approximately by a single Debye mechanism, which is in accordance with the results for oriented sample [17]. This is seen in Fig. 5, where one spectrum from Fig. 4 in the form of the Cole-Cole plot is presented. Thus, in the limit of the frequencies used in our experiment, the dielectric spectra of 5CB in the nematic phase are not influenced by the hf relaxation processes observed at higher frequencies for perpendicularly oriented samples [17]. Therefore, the assumption that the relaxation times correspond to $\tau_\parallel$ is justified.

Dielectric relaxation in the isotropic phase. In the case of the isotropic phase the frequency of maximum loss is

TABLE I. Examples of the pressure dependence of the relaxation times $\tau_\parallel$ obtained for the nematic phase of 5CB.

T (K)	p (MPa)	$\tau_\parallel$ (10^{-8} s)
307	0.1	2.34
	5	2.68
	12	3.25
	22	3.92
	38	5.86
316	28	2.15
	30	2.39
	35	2.60
	40	2.83
	45	3.70
	55	4.35
	60	4.75
	67.5	4.87
	70	5.37
327	55	2.22
	70	2.59
	85	3.65
	96.5	4.59
	100	4.95
	105.5	5.51
	110	5.60
343	100	2.10
	109	2.53
	110	2.56
	120	3.04
	130	3.65
	145.5	4.75
	161	5.55

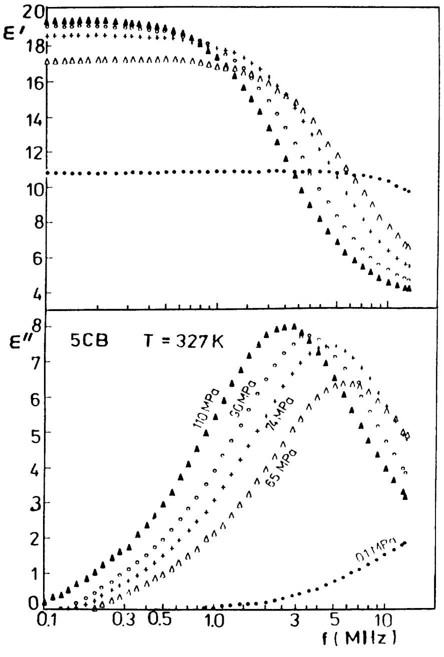

FIG. 4. Dispersion and absorption spectra obtained for the nematic (65, 74, 90, and 110 MPa) and isotropic (0.1 MPa) phases of 5CB.

considerably shifted to higher frequencies beyond 13 MHz (see Fig. 4); therefore only the rising part of the loss curve can be measured with the available instruments. Nevertheless, we also fitted this limited number of experimental points to several loss curves. It was found that the Cole-Davidson equation yielded a much better fit than the Cole-Cole one, which is in agreement with the results of Lippens [17]. However, because of the missing high-frequency data, a reasonable value for ϵ_∞ cannot be obtained. Using the Lippens data we have checked how a limited number of points on the low-frequency part of the loss curve influences the parameters of the Cole-Davidson equation. It was found that the frequency of maximum loss was relatively insensitive to the choice of ϵ_∞. On fixing $\epsilon_\infty=2.75$, we got essentially the same relaxation times when we used all frequencies (up to 1000 MHz) or only a limited number (up to 25 MHz).

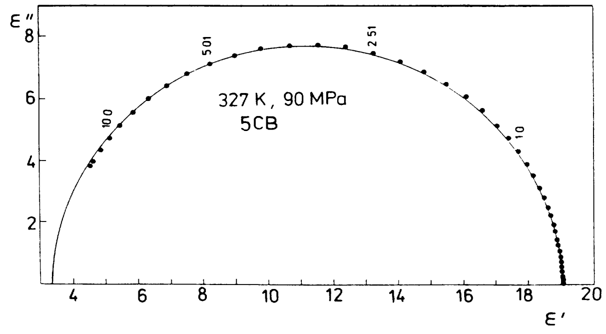

FIG. 5. Cole-Cole plot for one spectrum from Fig. 4.

Therefore, we evaluated our own experimental data in the same manner with the Cole-Davidson equation and $\tau_{is}=1/\omega_{max}$, which resulted in $\tau_{is}=6.73$, 5.60, 5.06, and 4.48×10^{-9} s at 311, 316, 319, and 323 K, respectively (Lippens obtained 5.3×10^{-9} s at 313 K). The calculations gave $\Delta H_{is}=28.5$ kJ/mol at atmospheric pressure,

TABLE II. Activation volumes $\Delta V_\parallel$ ($\pm8\%$), activation enthalpies $\Delta H_\parallel$ ($\pm5\%$), and activation energies $\Delta U_\parallel$ ($\pm10\%$) obtained for the nematic phase of 5CB. The values in parentheses correspond to the isotropic phase.

T (K)	$(\partial \ln\tau_\parallel/\partial p)_T$ (10^{-2} MPa^{-1})	$\Delta V_\parallel$ (cm^3 mol^{-1})	p (MPa)	$[\partial \ln\tau_\parallel/\partial(1/T)]_p$ (K)	$\Delta H_\parallel$ (kJ mol^{-1})	V_m (cm^3 mol^{-1})	$[\partial \ln\tau_\parallel/\partial(1/T)]_V$ (K)	$\Delta U_\parallel$ (kJ mol^{-1})
303	2.43	61.5	0.1	7490.0	62.6	248	5120.4	42.8
307	2.39	61.3		(3477.0)	(28.9)	247	4423.2	37.0
311	2.39	62.1	15	7434.8	61.8			
				(3659.3)	(30.4)	246	3838.7	32.1
313	2.36	61.7	20	(3717.5)	(30.9)			
						245	3421.8	28.6
316	2.31	61.0	30	7669.8	63.8			
				(3839.5)	(31.8)	244	3270.7	27.3
	(1.24)	(32.5)	45	7180.5	59.7			
						243	3188.3	26.4
319	2.23	59.0	60	7361.7	61.2			
						242	2963.8	24.8
	(1.20)	(31.7)	70	6483.2	54.2			
323	2.22	59.9	85	6393.2	53.2			
	(1.17)	(31.3)	90	6227.8	51.8			
327	2.14	58.5	100	6420.1	53.4			
	(1.13)	(30.6)	105	5865.9	48.8			
332	1.83	50.8	110	5861.0	49.0			
338	1.76	49.7						
343	1.59	45.6						
	(1.00)	(27.8)						

which seems to be quite reasonable and compares with a value of 32.8 kJ/mol reported for the activation energy for the isotropic viscosity coefficient [22].

The measurements of the pressure dependence of the dielectric relaxation in the isotropic phase were performed at five temperatures only (316, 319, 323, 327, and 343 K). The values of $(\partial \ln\tau_{\mathrm{is}}/\partial p)_T$ are listed in Table II. They are significantly lower than in the nematic phase, which reflects the ease of molecular reorientations in the isotropic phase.

ANALYSIS OF THE RESULTS

Molecular correlations. Measured static ϵ_r values differ, of course, from the true static $\epsilon_{\parallel 0}$ values, which can be measured in the case of a well-oriented sample only. However, the ϵ_r obtained at atmospheric pressure are comparable with the $\epsilon_{\parallel 0}$ values reported in [19–21] [but those are markedly lower than in [18]; see Fig. 3(a)]. It prompted us to draw some conclusions from $\epsilon_r(p,T)$ behavior. Figure 3(a) shows that ϵ_r increases with decreasing temperature at each pressure. It is a normal property of $\epsilon_{\parallel 0}$ in the nematic phase at atmospheric pressure [2–5,17–19]. On the other hand, the ϵ_r is an increasing function of pressures over the whole range of the nematic phase of 5CB—Fig. 3(b) (stronger changes are observed near the clearing temperatures). Such behavior is observed for both the increase and decrease in pressure.

The rise of $\epsilon_{\parallel 0}$ with both the decrease in temperature at $p=\mathrm{const}$ and the increase in pressure at $T=\mathrm{const}$ can be discussed taking into consideration the well-known formula derived for the nematic phase by Maier and Meier [2–5,23]:

$$\epsilon_{\parallel 0}-1=(NhF/\varepsilon_0)(\langle\alpha\rangle_{\parallel}+F\langle\mu_{\parallel}^2\rangle/k_BT)\ , \qquad (1)$$

with

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

S is the usual order parameter depending on temperature and pressure. N denotes the number of molecules per unit volume. $\langle\alpha\rangle_{\parallel}$ is the polarizability averaged over the orientations of all molecules. Factors h and F depend on the average values of permittivity $\bar{\epsilon}_0=\frac{1}{3}(2\epsilon_{\perp 0}+\epsilon_{\parallel 0})$ and polarizability $\bar{\alpha}=\frac{1}{3}(2\alpha_t+\alpha_l)$ and can roughly be treated as constants within the nematic phase. The same concerns the density expressed by N. Additionally, due to the fact that a large dipole moment of the 5CB molecule is directed along its main axis, the dipole polarization distinctly overcomes the induced polarization ($\epsilon_{\parallel 0}\gg\epsilon_\infty$), so we neglect the component $\langle\alpha\rangle_{\parallel}$ and assume $\mu_l\simeq\mu$. Thus, formula (1) is reduced to

$$\epsilon_{\parallel 0}-1\propto(2S+1)/T\propto\epsilon_r-1\ . \qquad (2)$$

To verify this simplified relation (2), we considered the results of the static permittivity, $\epsilon_{\parallel 0}$, measurements of Menu [18] (atmospheric pressure) and the $S(T)$ values of Horn [8,9]. Figure 6(a) shows that the static permittivity is governed solely by the temperature dependence of the order parameter and the temperature in the nematic phase of 5CB. The same can be said about the $\epsilon_r(S)$ at $p=\mathrm{const}$ [Fig. 6(b)]. However, in the case of $\epsilon_r(S)$ at $T=\mathrm{const}$ [Fig. 6(c)], marked discrepancies are observed: the permittivities change more strongly than formula (2) predicts, especially near the clearing temperatures. This effect could be correlated with the character of molecular interactions in the substance under study. It is well known that the alkylcyanobiphenyl molecules exhibit strong antiparallel dipole-dipole correlations in the LC phases [2,18,24,25], as well as in the isotropic phase [18]. Thus it seems to be a justifiable conclusion that relatively low pressure distinctly influences the monomer-dimer equilibrium, causing breaking of dipole-dipole correlations between neighboring molecules in 5CB. An increasing number of monomers having markedly larger dipole moments than the moments' dimers, causes an increase in static permittivity [cf. Eq. (1)]. Such a phenomenon should manifest itself in other parameters characterizing the molecular reorientations around their short axes.

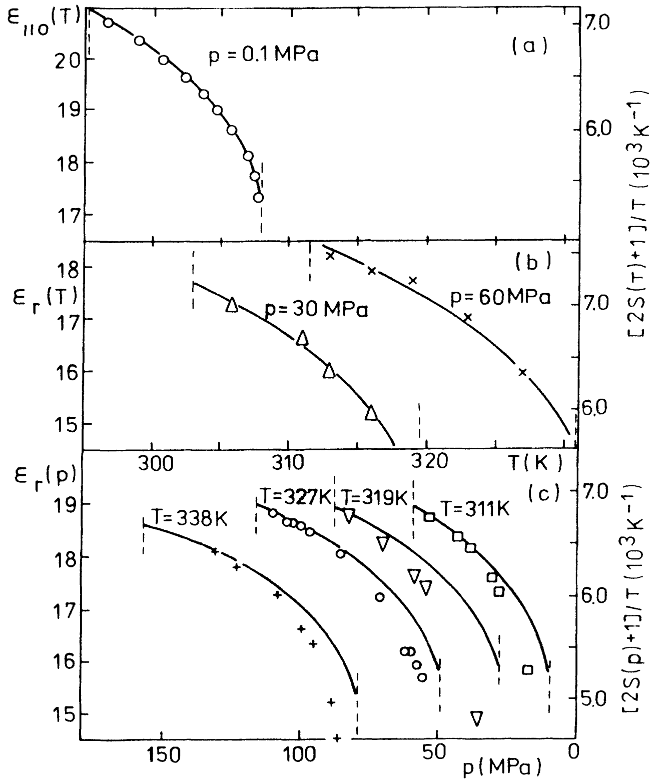

FIG. 6. Comparison of the temperature and pressure dependences of the static permittivity with the curves corresponding to formula (2). Results of $\epsilon_{\parallel 0}$ in (a) are taken from [18]. In (b) and (c) the right-hand scale corresponds strictly to the left-hand curves only. The vertical dotted lines mark the range of the nematic phase of 5CB.

More light can be cast on this phenomenon by comparison of the dielectric properties of 5CB with the analogous properties of a substance that does not show dipole-dipole correlations in the nematic phase. Such studies were recently carried out and the preliminary analysis of the results seems to support the above conclusions [26].

T = const case. As one can see in Fig. 4, the pressure significantly influences the lf relaxation process in the nematic phase of 5CB. The relaxation times $\tau_{\parallel}$ calculated from the spectra measured on particular "temperature levels" (compare Fig. 1) are shown in Fig. 7 in the form of $\ln\tau_{\parallel}$-versus-p plots. The lines drawn through the points correspond to the average behavior. The relaxation times used in further discussions in this paper are taken from this figure.

From Fig. 7 one can notice that $\tau_{\parallel}$ is not a strictly exponential function of pressure. In spite of this fact, we have calculated the slopes $(\partial \ln\tau_{\parallel}/\partial p)_T$ by means of a linear regression. They are listed in Table II, together with the values of the activation volume,

$$\Delta V_{\parallel} = RT\left[\frac{\partial \ln\tau_{\parallel}}{\partial p}\right]_T \tag{3}$$

(R is the gas constant). According to the rate theory of chemical reactions, the activation volume is the difference between the volume indispensable for a molecule in the excited (top of the energy barrier) state and the volume needed in the relaxed (minimum of energy) state. Thus, $\Delta V_{\parallel}$ characterizes—to some extent—a rotational freedom of molecules in a substance. Its change with temperature and/or pressure elicits additional information about a real dynamical situation of molecules in the nematic phase of 5CB. One can see in Table II and Fig. 9 that $\Delta V_{\parallel}$ decreases significantly with an increase in temperature. According to the phase diagram (Fig. 1), it corresponds to a situation in which the pressure is higher. Such effects have been found to exist in plastic crystals as well, but to a much smaller extent [11]. It can be expected that a molecule linked in a dimer needs more room for rotation than a single one, as dimerization introduces an additional anisotropy in the surroundings of a molecule.

p = const case. Figure 8 presents activation plots based on the results shown in Fig. 7. (A few immediate experimental $\tau_{\parallel}$ values are shown for comparison.) The slopes of straight lines drawn by means of a linear regression give activation enthalpies according to the Arrhenius equation,

$$\tau_{\parallel} = \tau_{\parallel 0}\exp(\Delta H_{\parallel}/RT)_p \; . \tag{4}$$

The calculated values of $\Delta H_{\parallel}$ are listed in Table II and are shown in Fig. 9. It is evident that the activation enthapy decreases with increasing pressure. This effect is again consistent with the suggestion that the dipole-dipole correlations become weaker at elevated pressures. The molecules forming dimers must also overcome the dissociation energy apart from the nematic potential. It is characteristic that the observed reduction of $\Delta H_{\parallel}$ within the nematic phase of 5CB (approximately 12 kJ/mol, Table II, Fig. 9) coincides well with the value of association energy (9±4 kJ/mol) estimated for nCB homologous series ($n = 5 \div 8$) on the basis of dielectric

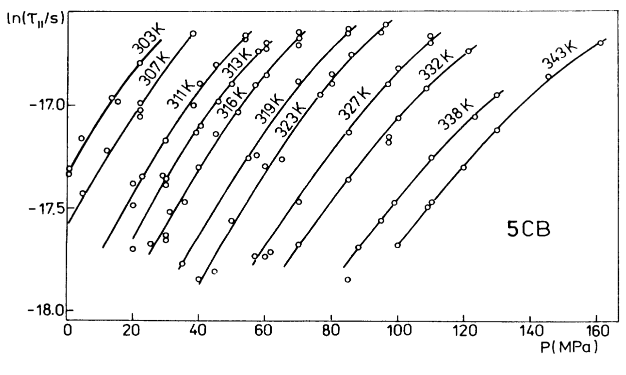

FIG. 7. $\ln(\tau_{\parallel})_p$-vs-p plots for the nematic phase of 5CB at different temperatures.

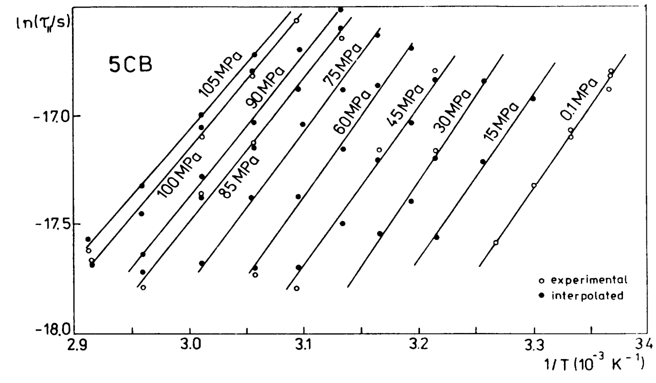

FIG. 8. $\ln(\tau_{\parallel})_p$-vs-$1/T$ plots for the nematic phase of 5CB at different pressures.

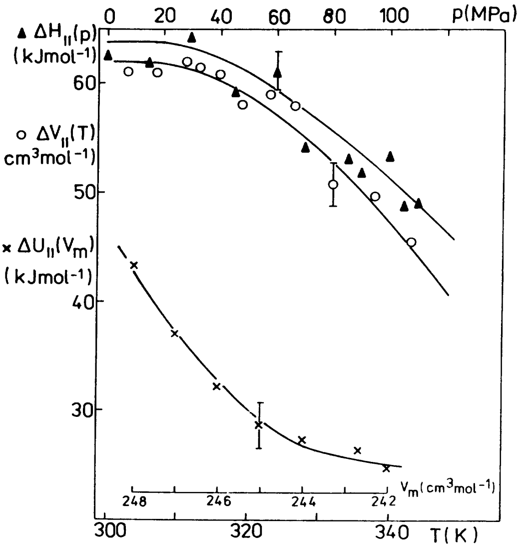

FIG. 9. Comparison of the activation parameters characterizing the molecular reorientations around the short axes in the nematic phase of 5CB: enthapy $\Delta H_{\parallel}$ as a function of pressure, volume $\Delta V_{\parallel}$ as a function of temperature, and energy $\Delta U_{\parallel}$ as a function of molar volume. The lengths of the units on the abscissae correspond roughly to the pressure scale. The lines are drawn as guides for the eye only.

TABLE III. Relations between the activation parameters obtained for the nematic phase of 5CB.

V_m ($\mathrm{cm^3\,mol^{-1}}$)	T (K)	p (MPa)	$\Delta U_\parallel$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta V_\parallel/RT$ ($10^{-2}\ \mathrm{MPa^{-1}}$)	$(\partial p/\partial T)_V$ ($\mathrm{MPa\,K^{-1}}$)	$\Delta H_\parallel^{\mathrm{calc}}$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta H_\parallel^{\mathrm{expt}}$ ($\mathrm{kJ\,mol^{-1}}$)
247	316	32	37.0	2.31	1.48	65.5	63
245	327	64	28.6	2.14	1.60	59.2	58
243	338	100	24.8	1.76	1.71	53.5	53

studies [21].

V = const case. From optical measurements of 5CB under pressure [9], Horn and Faber [10] deduced the variation of molar volume with temperature and pressure. Their results, however, must be corrected due to a "zero error" in the pressure readings, as was explained by Wallis and Roy [16]. After doing that, we calculated a set of isochoric lines in the nematic phase of 5CB; three of them are shown in Fig. 1. Taking from Fig. 7 the $\ln\tau_\parallel$ values corresponding to the particular isochores, one can calculate the activation energies,

$$\Delta U = R\left[\frac{\partial \ln\tau_\parallel}{\partial(1/T)}\right]_V , \tag{5}$$

which are listed in Table II and shown in Fig. 9.

DISCUSSION

The analysis of the results of the dielectric studies of 5CB in the nematic phase shows that the pressure significantly influences all the parameters characterizing the molecular reorientations around the short axes. The temperature and pressure dependence of the order parameter and the dipole-dipole correlations between the molecules are the main factors determining such influence. The breaking of the dipole-dipole correlations is clearly reflected in the increase in static permittivity with increasing pressure at a constant temperature, which is markedly stronger than that caused by the change in the order parameter only. The activation parameters seem to be influenced by this effect also.

Figure 9 presents the observed changes in the activation enthapy, energy, and volume. The lengths of the units on the abscissae are roughly normalized to the same pressure (compare the phase diagram in Fig. 1). The general tendency is common for all the parameters. There are a few formulas joining these activation parameters (discussed, for example, in [27]). The accessible data for the substance under study allow us to check the following relation:

$$(\Delta H_\parallel)_p = (\Delta U_\parallel)_V + \left[\frac{\partial p}{\partial T}\right]_V T(\Delta V_\parallel)_T , \tag{6}$$

where $(\partial p/\partial T)_V = \alpha/\beta$ is the slope of an isochoric line, α is the thermal expansivity, and β is the compressibility. All these parameters can be obtained from Horn's data [9]. They depend slightly on both the pressure and temperature within the nematic phase of 5CB (see Table III). The calculations done using the slopes of different isochoric lines and the data quoted in Table II are shown in Table III. One can see that relation (6) is fulfilled well within the nematic phase of 5CB. Thus, consistency of the thermodynamic parameters characterizing the molecular reorientations around the short axes is evident in spite of a significant change in their values with increasing pressure and/or temperature.

CONCLUSIONS

We now present our conclusions.

(1) For LC substances with the dipole moments directed along the main molecular axes, the dielectric studies elicit reliable information about the lf relaxation process also in the case of an unoriented nematic sample.

(2) The pressure strongly influences the lf relaxation process in the nematic phase of 5CB.

(3) The strong increase in static permittivity ϵ_r with increasing pressure indicates that the dipole-dipole correlations between neighboring molecules become weaker at elevated pressures.

(4) The decrease in activation enthapy and volume with increase in temperature and/or pressure within the nematic phase of 5CB corroborates the conclusion (3).

(5) The activation energy distinctly decreases if the molar volume decreases.

(6) In the nematic phase of 5CB, consistency between the activation enthalpy, energy, and volume was proved.

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