Class Specific Physical Properties of Liquid Crystals and Correlations with Molecular Structure and Static Electrooptical Performance in Twist Cells

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For the 65th anniversary of Professor Walter Boguth

We made measurements of the temperature dependence of the static dielectric constants, the optical anisotropy and the three elastic constants of binary mixtures belonging to twelve structurally and physically markedly different liquid crystal classes. The class-specific material properties were quantitatively correlated with molecular structural elements. The changes of material properties occurring when different LC-classes are combined were investigated. Analytical approximations are presented which are shown to reproduce the static transmission characteristics of twisted nematic cells and their dependence on material constants and temperature with an accuracy comparable to exact numerical calculations. Strong smectic pretransitional effects are shown to influence not only $k_{22}$ and $k_{33}$ but also $k_{11}$, thus suggesting that not only twist and bend but also splay deformations may be prohibitive in smectics. We show that the elastic ratio $k_{33}/k_{11}$ of different liquid crystal classes increases with increasing dielectric anisotropy thus leading to a decrease of the slope of transmission characteristics of twist cells. Furthermore, it is shown that $k_{33}/k_{11}$ decreases for molecules comprising heterocyclic rings whereas hydrogenation of an aromatic ring causes $k_{33}/k_{11}$ to increase.

1. Introduction

Some macroscopic liquid crystal (LC) material parameters such as the refractive indices or the dielectric constants may be related via appropriate models with molecular properties such as conjugated π-electron systems or permanent dipole moments. Based on structural considerations predictions for these material constants are possible especially for the optical properties. As a consequence molecular structures may be designed with specific optical and dielectric properties, for instance for applications in liquid crystal displays.

All electro-optical effects known in the field of nematic liquid crystals are based in one way or another on deformations of the nematic director under the influence of an applied voltage. The extent to which a liquid crystal layer can visibly be deformed depends not only on its dielectric and optical material constants but essentially also on its elastic properties giving rise to restoring forces. In general the elastic restoring forces can be described by three elastic constants, namely those for splay ($k_{11}$), twist ($k_{22}$) and bend ($k_{33}$) deformation.

Because of experimental difficulties and the rather extensive numerical data evaluation required, it was not until recently that reliable and complete measurements of all three elastic constants could be made. Perhaps due to the lack of data physical models do not exist that could be used to correlate the macroscopic elastic properties of liquid crystals with molecular structure. Therefore, molecular engineering of specific elastic properties based on experimental data or even semiquantitative models is not yet possible. Thus, the next step, namely the elaboration of correlations between LC-class specific material properties and their specific influence on the macroscopic electro-optical performance of field effects could hardly be made either. Furthermore, calculations describing the performance of electro-optical effects of liquid crystals quantitatively — which necessarily require complete sets of relevant material parameters — could be verified only for a few LC-materials. It was not until recently that efforts were made to investigate, besides negative dielectric liquid crystals [1, 2], complete sets of material parameters of positive dielectric substances also [3—7].

To our knowledge only one attempt has been made to determine and compare the relevant material properties of different positive dielectric
liquid crystal classes [7] and to relate them with some aspects of the electro-optical performance of the twisted nematic effect. Investigations into the interactions that occur when different classes of substances are combined, the consequent changes of the material properties of such mixtures and their effects on the electro-optical performance of field-effects have not yet been reported. In the attempt to study such interactions, to make qualitative correlations with molecular structures and to relate the class specific material properties quantitatively with the static electro-optical performance of twisted nematic displays (TN-LCDs) [8], we have complemented and extended our previous measurements [7] to new LC-classes as well as to combinations of components belonging to twelve different classes which differ markedly, both with respect to molecular structure as well as with respect to their dielectric, optical and elastic properties. The influence of different structural elements and/or combinations of different structures on the measured temperature dependence of the dielectric, optical and all three elastic constants was investigated. To correlate the class specific material properties with a macroscopic electro-optical effect, measurements of the static transmission characteristic of the TN-LCDs were made. Analytical approximations describing the transmission characteristics of TN-LCDs as functions of LC-material constants were derived. They were shown to reproduce essential aspects of the experimentally determined characteristics with a high degree of accuracy comparable to that obtained from complex numerical calculations. Measurements of the class specific influence on the dynamics of TN-LCDs will be presented in a following article.

2. LC-Classes and Experimental Procedure

The liquid crystals chosen cover a wide range of dielectric and optical anisotropies \((-1 \leq \Delta \varepsilon \leq 25; 0.07 \leq \Delta n \leq 0.25\) i.e. ranges into which most substances fall that can be made today. Table 1 shows their molecular structures. With one exception the rigid part of the molecules contains two rings which are either linked directly or via different linking bonds. Furthermore, molecules with

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Table 1. Nomenclature, composition and chemical structures of the pure class-specific binary mixtures (upper 10) and of binaries comprising components belonging to different LC-classes (bottom 8); R = pentyl or hexyl respectively.
polar and nonpolar end groups as well as with aromatic, hydrogenated or heterocyclic rings are used. The different structural elements are chosen such that the physical changes occurring in the material- and electro-optical properties can hopefully be related with them.

As some of the LC-components investigated exhibit rather narrow non-overlapping mesomorphic ranges or are even monotropic, binary mixtures were made to enlarge the mesomorphic ranges. Except for binaries containing components which do not belong to the same LC-class, all positive dielectric mixtures contained a pentyl and a heptyl component in molar proportions (40%, 60%). Thus, effects on the material properties due to unequal proportions or unequal chain lengths which affect the dielectric [15] as well as the elastic [2] properties within homologous series could be omitted. The abbreviations and the corresponding compositions of the binary mixtures are depicted in Table 1 where \( R \) and \( R' \) designate alkyl chains. For example E5 stands for pentyl cyano ester. Their mesomorphic properties including melting \( (T_m) \), smectic A-nematic \( (T_{sn}) \) and nematic-isotropic \( (T_c) \) transition temperatures are depicted in Table 3 below.

The lower part of Table 1 shows 8 binary mixtures consisting of components which belong to different LC-classes and are combined in different molar proportions. Most of these mixtures contain a 2-paracyanophenyl-heptylpyrimidine as one component designated by a capital P in the respective mixture denomination. These two-class binaries are used to show the effects of one LC-class — namely pyrimidines — on the material parameters of other classes or vice versa.

The experimental details or references to the methods used to determine the static dielectric constants, the optical anisotropies, the static electro-optical transmission characteristics of TN-LCDs and the cell preparation were described earlier [3]. The three elastic constants were determined by optically detecting the magnetic-field-induced deformations of the nematic director of homogeneously aligned LC-layers. Numerical fitting procedures were used to evaluate the results. The twist elastic constants were measured by means of a recently described method [17]. A detailed description of the accurate (±3%) measuring techniques used to determine \( k_{11}, k_{22} \) and \( k_{33} \) were described recently [17].

### 3. Class-Specific Material Properties

#### 3.1. Dielectric Constants

Figure 1 shows measurements of the temperature dependence of the static dielectric anisotropy \( \Delta \varepsilon = (\varepsilon_|| - \varepsilon_\perp) \) of those binary mixtures in Table 1 for which the respective data were not yet published in reference [7]. Except for mixture EC all others exhibit a positive dielectric anisotropy (Figure 1). Table 2 summarizes the dielectric data of all mixtures measured at constant temperature \( (T_c - 10 \, ^{\circ}C) / T_c \approx 0.97 = \text{constant} \).

Among the 10 single-class mixtures in Table 1 P and E exhibit \( +20 \) — the largest positive dielectric anisotropies, followed by a number of mixtures with \( \Delta \varepsilon \approx +10 \) and the barely positive anisotropic mixture PDO, whereas \( \Delta \varepsilon \) of EC is slightly negative (Fig. 1, Table 2). From \( \Delta \varepsilon (PD) \approx 13 \) and \( \Delta \varepsilon (PDO) \approx 0 \) in Table 2 follows...
that the large dielectric anisotropy of PDs is essentially due to their longitudinal permanent dipole moments of the cyano end groups.

At first it is astonishing to note the considerable difference between the values of \( \varepsilon_\perp \) and \( \Delta \varepsilon \) of the structurally similar esters E and PE in Table 2. From the dielectric theory of Maier and Meier [18] the differences have to be explained either by a smaller dipole moment of PE compared with E which in addition lies off the long molecular axis or by markedly different reaction field- and cavity factors. Considering the electron affinity of cyano- and ester groups and the ability of aromatic rings to release electrons, the first explanation appears quite plausible. Accordingly, mesomeric interactions in the aromatic esters E which cause the displacement of \( \pi \)-electrons from the left aromatic ring of E (Table 1) towards the electron-acceptor oxygen double bond in the ester linkage lead to cumulative dipole moments in E’s; whereas in PE’s — due to the single aromatic ring — induced electron shifts lead to oppositely polarized dipole moments, thus causing \( \Delta \varepsilon \) of PE to decrease.

The above findings show that predictions of the dielectric properties of the liquid crystalline state based on structural considerations may in some cases be rather difficult. However, if the dielectric properties of an LC-class are experimentally verified, predictions with respect to the changes that occur upon blending different classes are possible. From the measurements in Fig. 1 and Table 2 follows that the dielectric anisotropy \( \Delta \varepsilon_{a,b} \) of a mixture containing components a and b that belong to different LC-classes is given in a first approximation by

\[
\Delta \varepsilon_{a,b} \approx m_a \Delta \varepsilon_a + m_b \Delta \varepsilon_b; \quad m_a + m_b = 1. \quad (1)
\]

\( m_a \) and \( m_b \) are the respective molar proportions and \( \Delta \varepsilon_a \) and \( \Delta \varepsilon_b \) the dielectric anisotropies of the single-class mixtures a and b. The measurements in Table 2 show that a relation analogous to (1) holds for \( \varepsilon_\perp \).

As an example the dependence of \( \Delta \varepsilon \) on different blending ratios made among mixtures P and EC is shown in Figure 2. The normalized measuring points (circles) follow from the respective values of \( \Delta \varepsilon \) of mixtures P, P8, P64, P88 and EC in Table 2. The deviations of the measured \( \Delta \varepsilon \)-values for large concentrations of P37 in mixtures (P37, 5EH03) from the linear solid line in Fig. 2 are probably due to the lower \( \Delta \varepsilon \)-values of P37 compared with those of P5 [15] used in the normalizing mixture P = (P5, P37).

3.2. Refractive Indices

Figure 3 shows measurements of the temperature dependence of the ordinary and extraordinary refractive indices \( n_0 \) and \( n_\perp \) of those binary mixtures not investigated in reference [7]. Table 2 contains data of the birefringence \( \Delta n = (n_\perp - n_0) \) and of \( n_0 \).
Fig. 2. Plot of the normalized dielectric anisotropy $\Delta \varepsilon = \Delta \varepsilon(P, EC)/\Delta \varepsilon(P)$ for different molar proportions following from the respective measurements of $\Delta \varepsilon$ in Table 2 for mixtures $P$, $P_{82}$, $P_{64}$, $P_{38}$ and $EC$ (solid line). The dashed graph shows the analogous dependence for the respective optical anisotropies $\Delta n$.

of all mixtures measured at $(T_c - 10{\degree}C) = constant$. The largest optical anisotropies in Table 2 correspond to compounds with elongated and highly conjugated $\pi$-electron systems such as Schiff's bases $S$. Shorter or less conjugated molecules such as biphenyls $K$ or aromatic esters $E$ exhibit lower values of $\Delta n$; whereas the lowest optical anisotropies correspond as expected to the partially hydrogenated compounds $PC$, $PE$, $EC$, $PD$ and $PDO$ (Table 2). Thus, the optical anisotropies of all LC-classes investigated can at least qualitatively be predicted based on individual molecular properties.

In analogy to (1) the resulting birefringence of mixtures comprising components belonging to different LC-classes can rather accurately be determined for a given mixing ratio. This is illustrated by the dashed graph in Fig. 2 where the measurements were taken from Table 2.

3.3. Elastic Constants $k_{11}$, $k_{22}$ and $k_{33}$

In the following, measurements of the temperature dependence of the splay ($k_{11}$), twist ($k_{22}$) and bend ($k_{33}$) elastic constants are reported. Figure 4 shows measurements of $k_{11}(T)$, whereas those for $k_{22}(T)$ and $k_{33}(T)$ are depicted in Figs. 5 and 6 respectively. Except for $T_{28}$ (Table 1) all binaries in Figs. 4—6 belong to the single-class type, whereas the measurements depicted in Figs. 7 and 8 were made — except for PDO and $EC$ — with binaries containing components belonging to different classes; i.e. with two-class mixtures. For reference purposes the data for mixture $P$ are included in Figs. 7 and 8. For a few of the mixtures measurements were reported earlier using electric-field realignment and a capacitive detection method to determine $k_{11}$ and $k_{33}$ [7]. Since then numerical evaluation methods and improved measuring tech-
Fig. 4. Measurements of the splay elastic constants $k_{11}$ versus reduced temperature $T/T_c$.

Fig. 5. Measurements of the twist elastic constants $k_{22}$ versus reduced temperature $T/T_c$.

Fig. 6. Measurements of the bend elastic constants $k_{33}$ versus reduced temperature $T/T_c$.

When looking at the temperature dependence $k_{tt}(T/T_c)$ depicted in Figs. 4—6 one gets the impression that the variations among $k_{11}(T/T_c)$ and $k_{22}(T/T_c)$ are small for the single-class mixtures. Even the graphs of $k_{33}$ which exhibit the largest variations appear to fit onto each other when scaled appropriately. In contrast to this finding Figs. 7 and 8 show that the two-class mixtures exhibit a much larger variety of the shape of $k_{tt}(T/T_c)$ despite they all consist of 60% $P_{37}$. This different behaviour offers potentially the possibility to design mixtures exhibiting a relatively weak temperature dependence of the elastic constants which is desirable for many electro-optical applications.

The measurements depicted in Fig. 9 show the influence of temperature on the elastic ratios $k_{33}/k_{11}$ and $k_{22}/k_{11}$ for some binaries. Evidently the temperature dependence of $k_{33}/k_{11}$ is low for all substances investigated. A similarly low temperature dependence was found for $k_{22}/k_{11}$ for most compounds except for those with smectic phases and to some extent also for the phenyl dioxanes PD and PDO (Figure 9). Besides, the measurements in Fig. 9 show large LC-material specific variations of
Fig. 7. Measurements of the splay and twist elastic constants versus reduced temperature made mainly with non-class-specific mixtures.

$k_{33}/k_{11}$ covering a range from $\sim 0.7$ to $\sim 2.0$. Therefore, if one assumes that the variations of $k_{33}/k_{11}$ reported for two homologous series [2, 4] are typical for nematics, it seems possible to achieve ratios of $k_{33}/k_{11}$ ranging from $\sim 0.7$ to $\sim 3.0$ by properly combining different LC-classes and homologues.

3.4. Smectic Pretransitional Effects

Because of the incompatibility of elastic twist-and bend deformations with smectic structures [19] the elastic constants $k_{22}$ and $k_{33}$ are expected to increase in the nematic phase of liquid crystals when approaching a smectic-nematic transition temperature $T_{sn}$. Our measurements made with mixtures $P_{28}$ and $T_{28}$ (Figures 5—8) show as a surprise that not only $k_{22}$ and $k_{33}$ but also $k_{11}$ exhibits a pretransitional behaviour. Because splay deformations were so far thought to be compatible with the layer structure of smectic A phases it was generally expected that $k_{11}$ should not show such a pretransitional behaviour. The astonishingly strong increase of $k_{11}(T \to T_{sn})$ which we found in $P_{28}$ and $T_{28}$ can best be seen in the representation of $k_{33}/k_{11}$ and $k_{22}/k_{11}$ versus temperature in Figure 9. $k_{22}/k_{11}$ steadily decreases for $T \to T_{sn}$ without any evidence of a pretransitional upward bending which one would expect if only $k_{22}(T \to T_{sn})$ would diverge; whereas $k_{33}/k_{11}$ shows a rather minor increase very close to $T_{sn}$. Thus, if the pretransitional behaviour of $k_{22}$ and $k_{33}$ should differ from that of $k_{11}$ the difference would have to occur in a very narrow temperature interval near $T_{sn}$. Therefore, our measurements suggest that pretransitional smectic tendencies affect all three elastic deformations similarly.
3.5. Structural and Blending Effects on $k_{33}$

Table 2 summarizes all elastic data measured at constant temperature ($T_c - 10^\circ C$); i.e. far from any smectic-nematic transition temperature of the mixtures used (Table 1, Table 3). The elastic ratios $k_{22}/k_{11}$ show only minor variations of $\pm 10\%$ among different liquid crystal materials (Table 2). Therefore, we shall concentrate our discussion of structural effects on the ratio $k_{33}/k_{11}$ which was found to vary appreciably and in a significant manner (Table 2).

The mixtures were chosen such that effects due to different alkyl chain lengths can be expected to be very similar in all of them. Variations of material parameters among different binaries can therefore be attributed to other molecular structural elements. We deduce from the measurements of $k_{33}/k_{11}$ in Table 2 the following interpretation of the dependence of $k_{33}/k_{11}$ on molecular structure and polarity: (i) $k_{33}/k_{11}$ is closely correlated with the polarity of the molecules; i.e. with $\Delta \varepsilon$, (ii) hydrogenation of one ring causes $k_{33}/k_{11}$ of the hydrogenated compound to increase by $\delta_1 \approx 0.41$ compared with its aromatic counterpart and (iii) the introduction of two heteroatoms into a hydrogenated ring (oxygen in the cyclohexyl rings of phenyldioxanes PD and PDO) or in an aromatic ring (nitrogens in pyrimidines P) causes $k_{33}/k_{11}$ of the heterocyclic compound to decrease by $\delta_2 \approx -0.45$ compared with its non-heterocyclic aromatic counterpart. These findings are visualized in Fig. 10 where measured $k_{33}/k_{11}$-data from Table 2 — reduced if structurally required by the postulated corrections $\delta_1$ and $\delta_2$ — are plotted against the respective dielectric anisotropies of the binaries. The reduced elastic ratios are denominated by $x$ to distinguish them from the actually measured $k_{33}/k_{11}$-data in Table 2. The upper straight line in Fig. 10 shows the excellent correlation obtained for the single-class mixtures.

Our measurements made with the two-class mixtures in Table 2 show that mixing components of different liquid crystal classes leads to a depression of $k_{33}/k_{11}$ compared with the values one would expect from a linear interpolation of $k_{33}/k_{11}$ of the respective single-class data (compare for instance $k_{33}/k_{11}$ of the two-class mixture $P_{28}$ with $k_{33}/k_{11}$ of the respective single-class mixtures $P$ and $EC$ in Table 2 which are both larger than $k_{33}/k_{11}$ of $P_{28}$). The corrected and weighted values of $k_{33}/k_{11}$ of the two-class mixtures lead to the $x$-values depicted in Figure 10. $x$ was determined by correcting each of the components $X$ and $Y$ with the corresponding structural factors $\delta$ (if required) and by weighting the amounts of the components used in the mixture with the respective molar proportions $m$ according to the following equation:

$$x = x_{X,Y} = \frac{k_{33}/k_{11} - m_x \delta_x - m_y \delta_y}{m_x + m_y};$$

$$m_x + m_y = 1.$$  \hspace{1cm} (2)

Equation (2) not only holds for two-class mixtures but is applicable to single-class mixtures also if one inserts $m_x = 1$ and $m_y = 0$.

Figure 10 shows that the $x$-values of the two-class mixtures — like those of the single-class mixtures — fit well on a straight line, thus indicating that the assumed correlations between $k_{33}/k_{11}$, structural- and dielectric properties apply also in the two-class binaries investigated. The increased
The static electro-optical characteristics of a TN-LCD can be defined by a driving voltage $V_{50}$ at which the transmission has reached 50% and by a parameter $p$ characterizing its (linear) slope. $p$ is defined as

$$p = (V_{50} - V_{10})/V_{10},$$

where $V_{10}$ is the driving voltage for 10% transmission. In the following we assume vertical incidence of light onto the display at wavelength $\lambda$ and zero bias tilt angles of the LC-molecules at the electrode boundaries.

It was shown by Berreman [20] that elaborate numerical calculations are required to determine the field-induced deformation of the director pattern and the electro-optical transmission characteristics of twisted nematic cells. Due to the complex non-analytical calculations the influence of specific LC-material parameters such as dielectric, elastic and optical constants on the transmission characteristics of TN-LCDs is rather difficult to elaborate. Based on numerical calculations [21] we have therefore made an attempt to derive analytical approximations reproducing the main features of the dependence of the static transmission characteristics of TN-LCDs on LC-material and display parameters. In these calculations for which a computer programme from Berreman was used, the dependence of the parameter $p$ in (3) on $d/\lambda$ was investigated for systematically varying elastic and dielectric constants; $d =$ display spacing. The graphical representation of the results suggested that a parabolic approximation can be used to describe the function $p(\ln (d/\lambda))$. By means of least mean square fitting we obtain the following approximation $p^+$ for the parameter $p$

$$p^+ = 0.1330 + 0.0266 \left( \frac{k_{33}}{k_{11}} - 1 \right) + 0.443 \left( \ln \frac{\Delta n d}{2\lambda} \right)^2.$$  

(4)

It will be shown in Sect. 5 that the dependencies of $p^+$ on the dielectric constants as well as on $k_{22}/k_{11}$ which were disregarded when deriving equation (4) can indeed be neglected. Equation (4) suggests that the slope of the transmission characteristics of TN-LCDs depends essentially only on the elastic ratio $k_{33}/k_{11}$ and on the optical path difference $\Delta n d/\lambda$. It was shown before [21] that the lowest $p$-values, i.e. the steepest slopes are obtained if the display spacing and/or the optical anisotropy
of the LC-material are chosen such that
\[ \Delta n d/2 \lambda = 1 \] is fulfilled. This corresponds to the minimum of the parabola (4).

In analogy to the least mean square fitting procedure used to derive the above approximation for \( p \) we also derived an analytical approximation \( V_{50}^+ \) for the driving voltage \( V_{50} \) using the results of the numerical calculations of \( V_{50}/V_c \) versus \( \ln(d/\lambda) \) in [21]:
\[ V_{50}^+ = V_c \times \left[ 2.044 - \frac{1.044}{1 + k_{33}/k_{11}} \right] \times \left( 1 + 0.123 \left( \frac{\Delta \varepsilon}{\varepsilon_\perp} \right)^{0.6} - 1 \right) \times \left( 1 + 0.132 \ln \frac{\Delta n d}{2 \lambda} \right). \] (6)

\( V_c \) is the threshold voltage for the mechanical deformation of the helical structure in a TN-LCD. \( V_c \) can accurately be determined for instance from capacitance measurements [3]. In a TN-LCD with twist angle \( \varphi \) comprising a nematic LC-material doped with an optically active additive, \( V_c \) is given by
\[ V_c = \frac{1}{\varepsilon_0 \Delta \varepsilon} \left[ k_{11} + (k_{33} - 2 k_{22}) \left( \frac{\varphi}{\pi} \right)^2 \right] + 2 k_{22} \left( \frac{\varphi}{\pi} \right) \left( \frac{2 d}{\varphi} \right)^{1/2}. \] (7)

In (7) \( \varphi \) is the natural pitch of the doped nematic. From (6) and (7) one obtains for a 90° twisted TN-LCD comprising a purely nematic LC-material, i.e. \( \varphi = \infty \).
\[ V_{50}^+ = \pi \left[ \frac{k_{11}}{\varepsilon_0 \Delta \varepsilon} + \frac{k_{33}/k_{11} - 2 k_{22}/k_{11}}{4} \right]^{1/2} \times \left[ 2.044 - \frac{1.044}{1 + k_{33}/k_{11}} \right] \times \left( 1 + 0.123 \left( \frac{\Delta \varepsilon}{\varepsilon_\perp} \right)^{0.6} - 1 \right) \times \left( 1 + 0.132 \ln \frac{\Delta n d}{2 \lambda} \right). \] (8)

The analytical approximation (8) suggests that unlike the slope of the transmission, \( V_{50} \) depends not only on \( k_{33}/k_{11} \) and on \( \Delta n \cdot d \) but also on \( k_{22}/k_{11} \) as well as strongly on \( k_{11} \) and on the dielectric properties of the LC-material.

We will show in the next chapter that the above analytical approximation for \( p \) and \( V_{50} \) hold for all LC-classes investigated.

5. Material Constants and Electro-Optical Performance

5.1. Comparison Between Calculated and Measured TN-LCD Transmission

In the following measurements of the transmission characteristics of TN-LCDs are compared with those calculated by means of the analytical approximations of the preceding paragraph as well as with exact numerical calculations. The material parameters of Chapt. 3 obtained from measurements independent from those of the transmission characteristics of TN-LCDs are used in the calculations. TN-LCDs with 90° twist, zero bias tilt and spacings \( d = 10 \mu m \) were used (\( \lambda = 550 \text{ nm} \)).

Figure 11 shows measured transmission characteristics of TN-LCDs comprising four different binary mixtures which cover a wide range of optical, dielectric and elastic properties (Table 2). The dashed graphs in Fig. 11 are those of the numerically calculated transmission characteristics using the material constants depicted in Table 2. Figure 11 shows that the agreement between calculated and measured transmission is better than 10% for all voltages and LC-materials; or vice versa: the driving voltage required for a given transmission

![Fig. 11. Measured and numerically calculated transmission characteristics of TN-LCDs comprising the binary mixtures P, K, PE and P28 respectively. The recordings were made at \( (T_c - 10 ^\circ C) = \text{constant.} \)]
agrees within 4% between measurement and calculation. Thus, considering the experimental accuracy (3%) with which the transmission characteristics and the elastic constants could be determined, the overall agreement between calculation and experiment following from Fig. 11 is very good.

For all binary mixtures depicted in Table 1 we have measured the display driving voltages \( V_{10} \) and \( V_{50} \) at \( T_c - 10 \, ^\circ C \) constant as well as the parameter \( p \) defined by (3). The results are depicted in Table 3. To check the agreement between measured and calculated transmission characteristics of TN-LCDs for all LC-materials investigated, \( V_{10} \), \( V_{50} \) and \( p \) were numerically calculated. The respective values in Table 3 are denominated \( V_{10}^*, V_{50}^* \) and \( p^* \). Also depicted in Table 3 are \( V_{50}^* \) and \( p^* \) following from the analytical approximations (4) and (8). The material constants of Table 2 were used for the numerical and the analytical calculations. Comparing the measured values of the parameter \( p \) in Table 3 with the corresponding calculated parameters \( p^* \) and \( p^* \) respectively shows that the maximum deviation between \( p \) and \( p^* \) is 8%, whereas \( p^* \) agrees within 11% with \( p \). The analytical approximation (4) thus leads to results whose accuracy is comparable to that of the much more complex numerical calculations.

A comparison between the numerically calculated driving voltages \( V_{10}^* \) and \( V_{50}^* \) in Table 3 with those determined experimentally shows that the agreement is better than 5% for all LC-classes investigated. Table 3 also shows that the same agreement was obtained between \( V_{50}^* \) and \( V_{50}^* \). These findings show that the electro-optical transmission characteristics of TN-LCDs at vertical light incidence can indeed be accurately determined for virtually any LC-material from the above analytical approximations and from measurements of the dielectric, optical and elastic material constants; i.e. from \( k_{33}/k_{11}, \Delta n, \Delta e/\varepsilon_\perp \) and \( V_c \) when using (4) and (6).

### 5.2. Influence of Temperature on the Transmission of TN-LCDs

In the following the analytical approximations of Chapt. 4 will be used together with the measured temperature dependence of the material constants of chapter 3 to determine the parameters influencing the temperature dependence of the transmission characteristics of TN-LCDs. The strongly different binary mixtures K and E were chosen to show the effects to temperature on the characteristics.

Table 4 contains the material constants of mixtures K and E measured at different reduced tem-
Table 4. Elastic, dielectric and optical material constants of mixtures K and E measured at different reduced temperatures $T/T_c$. $V_c$ and $V_{50}^+$ were calculated by inserting the respective material constants into (7) and (8).

<table>
<thead>
<tr>
<th>$T/T_c$</th>
<th>$k_{11}$ ($\times 10^{-12}$ N)</th>
<th>$k_{22}$ ($\times 10^{-12}$ N)</th>
<th>$k_{33}$ ($\times 10^{-12}$ N)</th>
<th>$k_{33}/k_{11}$</th>
<th>$\Delta \varepsilon$</th>
<th>$\Delta \varepsilon/\varepsilon_\infty$</th>
<th>$\Delta n$</th>
<th>$V_c$ [volts]</th>
<th>$V_{50}^+$ [volts]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99 (K)</td>
<td>4.40</td>
<td>2.50</td>
<td>5.50</td>
<td>2.25</td>
<td>9.40</td>
<td>1.382</td>
<td>0.149</td>
<td>0.733</td>
<td>1.236</td>
</tr>
<tr>
<td>0.98 (E)</td>
<td>4.35</td>
<td>2.70</td>
<td>6.50</td>
<td>2.50</td>
<td>16.90</td>
<td>1.656</td>
<td>0.125</td>
<td>0.552</td>
<td>0.933</td>
</tr>
<tr>
<td>0.97</td>
<td>5.85</td>
<td>3.06</td>
<td>7.30</td>
<td>2.50</td>
<td>10.55</td>
<td>1.661</td>
<td>0.164</td>
<td>0.806</td>
<td>1.399</td>
</tr>
<tr>
<td>0.95</td>
<td>7.35</td>
<td>3.50</td>
<td>8.70</td>
<td>1.29</td>
<td>11.30</td>
<td>1.852</td>
<td>0.174</td>
<td>0.841</td>
<td>1.495</td>
</tr>
<tr>
<td>0.94</td>
<td>8.00</td>
<td>4.28</td>
<td>11.20</td>
<td>1.40</td>
<td>12.40</td>
<td>2.175</td>
<td>0.191</td>
<td>0.882</td>
<td>1.634</td>
</tr>
<tr>
<td>0.92</td>
<td>7.25</td>
<td>4.26</td>
<td>12.50</td>
<td>1.72</td>
<td>20.95</td>
<td>2.570</td>
<td>0.162</td>
<td>0.669</td>
<td>1.303</td>
</tr>
<tr>
<td>0.90</td>
<td>8.70</td>
<td>4.60</td>
<td>12.30</td>
<td>1.41</td>
<td>12.85</td>
<td>2.315</td>
<td>0.198</td>
<td>0.907</td>
<td>1.701</td>
</tr>
<tr>
<td>0.90</td>
<td>7.80</td>
<td>4.56</td>
<td>13.70</td>
<td>1.83</td>
<td>21.50</td>
<td>2.704</td>
<td>0.168</td>
<td>0.669</td>
<td>1.303</td>
</tr>
<tr>
<td>0.90</td>
<td>8.80</td>
<td>5.21</td>
<td>14.50</td>
<td>1.48</td>
<td>13.58</td>
<td>2.562</td>
<td>0.209</td>
<td>0.942</td>
<td>1.814</td>
</tr>
<tr>
<td>0.90</td>
<td>8.60</td>
<td>5.10</td>
<td>16.10</td>
<td>1.87</td>
<td>22.40</td>
<td>2.909</td>
<td>0.176</td>
<td>0.708</td>
<td>1.403</td>
</tr>
</tbody>
</table>

To separate the influence of the temperature dependence of the elastic, the dielectric and the optical material parameters on the transmission characteristics of TN-LCDs we have calculated $[V_{50}^+(T/T_c)]_x$ of mixture E from equation (8) for $x$ corresponds to the respective parameters $k_{11}(T/T_c=0.99)$, $\Delta \varepsilon(T/T_c=0.99)$ or $\Delta n(T/T_c=0.99)$ in Table 4. Thus, one obtains the three dashed-dotted graphs in the upper part of Fig. 12 for the temperature dependence $V_{50}^+(T/T_c)_x=\text{constant}$. The deviation of these graphs from the actual temperature dependence of $V_{50}$ shows the extent to which $k_{11}$, $\Delta \varepsilon$ and $\Delta n$ influence the temperature dependence of the transmission. From Fig. 12 follows that the temperature dependence of $k_{11}(T)$ influences $V_{50}^+(T)$ most, followed by $\Delta \varepsilon(T)$, whereas the influence of $\Delta n(T)$ is comparably small.

6. Conclusions

We have measured the temperature dependence of the class-specific material properties, namely the three elastic constants, the static dielectric properties and the optical anisotropies of binary mixtures belonging to twelve structurally and physically markedly different liquid crystal classes. An attempt was made qualitatively to relate material properties with molecular structure. Besides, we have investigated the changes of material properties occurring when different classes of liquid crystals are combined. The class-specific material properties and their temperature dependence were quantitatively correlated with measurements of the static electro-optical transmission characteristics of twisted nematic cells using numerical calculations. The analytical approximations derived to describe the transmission characteristics of twist cells were shown to reproduce the experimentally determined characteristics with a high degree of
From elastic measurements made in the nematic range of liquid crystals exhibiting a smectic A as well as a nematic phase we found strong smectic pretransitional effects to occur already at temperatures far above the smectic-nematic transition temperature. The pretransitional effects were found not only to affect twist and bend deformations strongly but also splay deformations. This finding is surprising considering that splay deformations have so far — in contrast to twist and bend — been supposed to be compatible with the smectic state.

We found large variations of $k_{33}/k_{11}$ varying by a factor of 3 among different LC-classes at a given reduced temperature, whereas the measured variations of $k_{22}/k_{11}$ were small. Our experiments show that hydrogenation of an aromatic ring in the core of two-ring LC-molecules causes the elastic ratio $k_{33}/k_{11}$ to increase by the amount $\delta_1 = +0.41$, whereas substitution of an aromatic- or hydrogenated ring by a 1,3-substituted heterocyclic ring leads to a decrease of $k_{33}/k_{11}$ by $\delta_2 = -0.45$. By taking the effects of different ring structures into account we have found an excellent correlation between the polarity of LC-molecules and $k_{33}/k_{11}$ in single- as well as two-class mixtures. The lowest ratios $k_{33}/k_{11}$ which lead to the steepest transmission characteristics and largest multiplexing rates in twist cells at a given temperature were found for non-polar, aromatic molecules comprising one heterocyclic ring.

By blending components belonging to different LC-classes we found that “elastic depressions” may occur leading to values of $k_{33}/k_{11}$ of the mixture which are smaller than those of either of its components. From our experiments it seems that the length/width ratio of the rigid core may not influence $k_{33}/k_{11}$ to the extent supposed so far.

**Acknowledgement**

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