Measurement of the difference in flexoelectric coefficients of nematic liquid crystals using a twisted nematic geometry

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A technique for measuring the difference between the splay and bend flexoelectric coefficients in a nematic liquid crystal is demonstrated. The method uses the flexoelectric-optic effect, but instead of a uniform lying helix structure, a TN cell geometry with an in-plane electric field is used. This has the advantage of avoiding difficulties associated with aligning the helix and can be used to measure achiral materials. The effects due to ionic screening are also taken into account.

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I. INTRODUCTION

Nematic liquid crystal molecules generally possess permanent dipole moments with components along both their long and short axes. In many situations, there will be no net polarization because of the distribution of molecular orientation within the phase. However, when an electric field is applied, the molecules are partially reoriented to align with the field, resulting in a net polarization. If the molecules also possess shape asymmetry, then this dipole reorientation will be associated with a tendency to form distorted structures. If the molecules are pear shaped, then the coupling of the electric field to the component of the polarization along the long molecular axis will tend to induce a splayed structure. Likewise, a bend deformation can be produced by banana-shaped molecules with a lateral dipole component. This coupling between dielectric and elastic properties, now known as "flexoelectricity," was presented by Meyer in 1969 [1].

This flexoelectric property of nematics has been of recent scientific interest due to the emergence of two technologies that rely on flexoelectricity for their operation. One of these is based on the "flexoelectric-optic effect" presented by Patel and Meyer in 1987 [2] and since studied by the Chalmers (Sweden) [3] and Southampton-Cambridge (UK) [4] groups. Here, an electric field is applied perpendicular to the axis of a cholesteric helix in a uniform lying helix structure. The resulting in-plane twist of the optic axis is approximately proportional to the applied electric field and, hence, moves in opposite directions for different signs of field. The other technology is the "zenithally bistable nematic device" (ZBND) [5,6]. This device has, on one surface, a topological grating structure with homeotropic anchoring, which supports two possible director configurations that are optically distinct between crossed polarizers. Again, the flexoelectric effect causes differing director reorientation for positive and negative applied electric fields; this time, it facilitates switching between the two stable ground states.

One of the problems with exploiting the flexoelectric effect in these technologies is that, unlike the elastic and dielectric constants of nematic liquid crystals, the flexoelectric coefficients are often unknown. However, it seems that since these devices depend on flexoelectricity for operation, it should be possible to obtain the relevant flexoelectric coefficients by characterizing a working device. This is, indeed, the method undertaken by Coles *et al.* [4], who compare their experimental results to the formula of Patel and Meyer [2] for the approximate change in the optic axis ϕ that will be generated by the flexoelectric-optic effect

$$\tan \phi = \frac{(e_1 - e_3)Ep}{2\pi(K_{11} + K_{33})}, \tag{1}$$

where e_1 and e_3 are the splay and bend coefficients for the flexoelectric effect, according to Meyer [1]. E is the electric field applied normal to the helical axis, p is the pitch of the material, and K_{11} and K_{33} are the splay and bend elastic coefficients, respectively. This method, therefore, generates a value for the difference of the coefficients $(e_1 - e_3)$, which is the relevant flexoelectric parameter for this device [7].

This method, however, has some disadvantages. First, it is often difficult to achieve the necessary alignment for the measurement, as a thin cell with planar alignment will generally form a Grandjean texture where the helical axis is perpendicular to the glass plates. The uniform lying helix structure (or fingerprint texture, where the helical axis is parallel to the plates) can be encouraged by a number of techniques, including the use of a hybrid alignment technique and/or shearing the glass plates after filling. However, good, uniform alignment is difficult to achieve reliably. There is the additional drawback that this method only works for chiral materials; it may be that the material to be measured is achiral, and hence, the method would not be appropriate. Also, the formula used [Eq. (1)] is only true for small tilts in the optic axis and ignores any effect due to the dielectric anisotropy. Finally, the fact that the experiment uses a dc voltage will mean that ionic drift will complicate these measurements, as is commonly the case with measurements of flexoelectric parameters [9,10].

In this work, we present a method of measurement related to that described above, but which overcomes these difficul-

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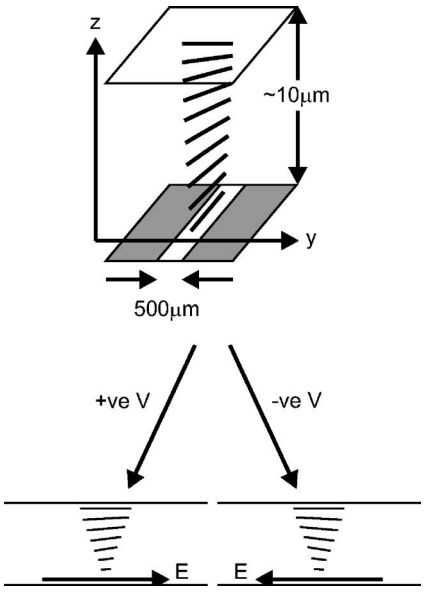

FIG. 1. Illustration of the geometry of the proposed experimental arrangement. An in-plane electric field is applied to a twisted nematic device, and the flexoelectric effect causes the director profile to tilt out of the plane of the device, in opposite directions for opposite directions of applied field.

ties. It is clear that the alignment difficulties can be removed by using a Grandjean (planar) texture with an electric field applied parallel to the glass plates, by means of in-plane electrodes. In addition, we note that by using a twisted nematic (TN) geometry, we can effectively create a quarter pitch of a cholesteric helix, even with a material that is achiral. This proposed geometry is illustrated in Fig. 1. With an in-plane electric field, a purely dielectric effect would cause the director profile to change in terms of in-plane twist, with the director remaining in the plane of the glass plates. A flexoelectric effect, however, will cause the director to tilt out of the plane of the device, in a direction that depends on the sign of the applied electric field. By probing the device with light that is obliquely incident on the cell, the response will be highly sensitive to these changes, and hence, a measurement of the flexoelectric parameter will be possible. It is interesting to note [see Eq. (1)] that the amount of change in the optic axis induced by the flexoelectric-optic effect is greater for materials with longer pitches. It is therefore expected that larger deformations will occur in this TN geometry, where the pitch will be some tens of microns, than in a system with a very tightly wound pitch of a micron or less. Finally, our method will take account of both dielectric and flexoelectric effects, by comparing the experimental results to predictions from a theoretical model that includes both effects. Our comparison will also take into account any cancellation of the local electric field due to ionic drift.

II. EXPERIMENTAL ARRANGEMENT

The experiment was carried out on TN devices of thickness 10–15 μm. The inner surface of one of the plates was coated with indium-tin-oxide (ITO), whereas the other plate was uncoated. An electrode gap of 500 μm (as shown in Fig. 1) was etched into the ITO-coated plate, in order to apply an in-plane electric field. Low pretilt ($<1°$) homogeneous alignment was achieved at both surfaces using rubbed poly-vinyl-acetate (PVA) layers. The substrate with the electrodes was rubbed in a direction parallel to the electrode edges, and the other substrate at 90° to this. One of the assembled devices was filled with achiral liquid crystal mixture E7, and the other with a mixture of E70A and 0.06% CB15, a chiral dopant. A weakly chiral mixture such as this is often used in TN devices in order to avoid the formation of domains of opposite twist. The device filled with E7 was cooled slowly from the isotropic phase in order to encourage single domain formation; this was verified by checking the cell under a polarizing microscope both before and after the quantitative measurements were taken.

Figure 2 shows the experimental arrangement in schematic form. Light of wavelength 543.5 nm, produced by a green HeNe laser, is normally incident on a beam splitter. This creates two beams of similar intensity diverging at 90° to each other. The beams are reflected by two mirrors, which cause them to cross again in the same plane. The device is

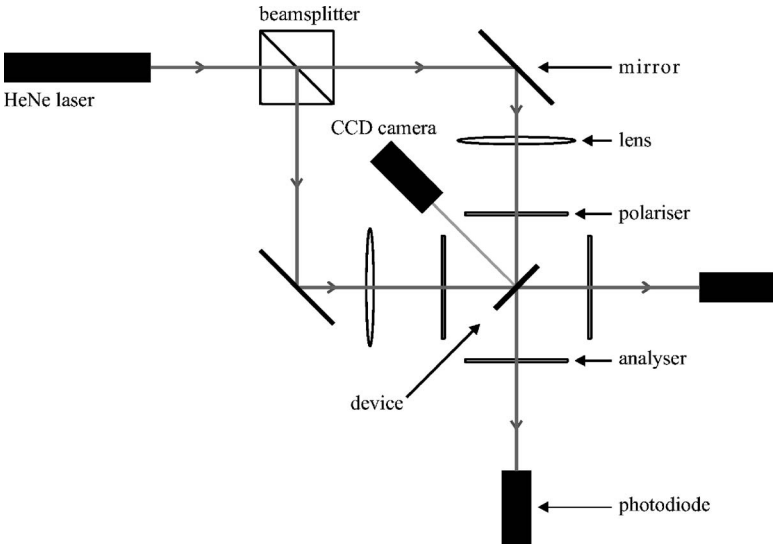

FIG. 2. Experimental arrangement used to detect the change in tilt angle caused by the applied in-plane electric field. A pair of laser beams are crossed and weakly focused onto a small ($\approx$100 μm) spot inside the (500 μm) electrode gap. The transmission through the device is monitored between crossed polarizers at these two angles of incidence and as a function of the applied voltage.

placed at the crossing point so that the two beams are incident on the cell at ±45° to the cell normal. Before reaching the cell, each beam passes through a lens (which weakly focuses the light into a spot of ≈100 μm) and a polarizer (which polarizes the light perpendicular to the plane of incidence). A charge-coupled-device (CCD) camera with a zoom lens is used to view the reflection of the focused laser beams on the cell in order to be sure that both beams are probing the same part of the liquid crystal device, and that this is inside the electrode gap. The sample is mounted so that the rubbing directions are at ±45° to the plane of incidence and such that, as the director twists from one surface to the other, the director passes through the plane of incidence. There are two analyzers that are set perpendicular to the input polarizers, and two identical photodetectors. The transmission of the device between crossed polarizers is therefore measured simultaneously for two angles of incidence (i.e., ±45°). The measurements are made as a function of applied voltage, where the applied wave form is a slow (0.2 Hz) square wave. Any ionic drift that occurs during this time in the material will be taken into account, as described in greater detail below.

III. EXPERIMENTAL RESULTS

The experimental results obtained and shown in Fig. 3(a) are for the E7 device, and Fig. 3(b) are for the E70A/CB15 device. The graphs show the variation in the transmission of the device (between crossed polarizers) for the two directions of incident light as a function of the applied voltage. The graphs show that the response of the cell to positive and negative applied voltages is highly asymmetric. This is entirely due to the tilting of the molecules in opposite directions for oppositely applied fields, which we attribute to the flexoelectric effect. If there were no such effect, then the applied field would merely twist the director in the plane of the surfaces and the signals would be symmetric about 0 V. The signals recorded by the two detectors are not exact mirror images of each other because the transmittance recorded at 0 V is not the same for the two detectors. A finite surface pretilt will cause this effect, but so would a small misalignment of the cell such that the angles of incidence of the laser beams are (perhaps) 44° and 46°, rather than both exactly 45°. This effect is discussed in greater detail below. In order to extract the flexoelectric coefficients from the experimental data, we need to compare it to theoretical predictions.

IV. THEORETICAL MODELING

The geometry of our theoretical model is shown in Fig. 1. Since the electrode gap is 500 μm, and the cell thickness is ~10 μm, the aspect ratio of the active area is approximately 1:50, and hence, it is a good approximation to say that the electric field is only in the y direction, with no component in the z direction. This is particularly true in the center of the electrode gap, where the measurements were taken. We also assume that, for the area of the device observed (a circle of diameter roughly 100 μm, i.e., considerably smaller than the

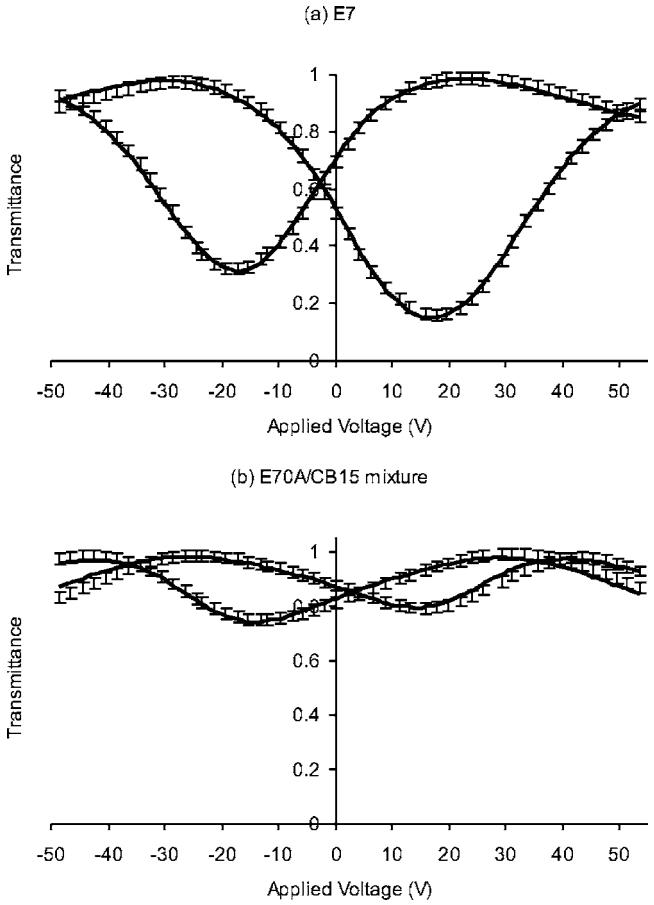

FIG. 3. Example of the experimental results obtained for both liquid crystal materials studied: (a) is for achiral nematic mixture E7 and (b) is for a weakly chiral mixture of E70A and CB15. The experimental data points are shown as solid points with error bars, and the continuous lines show the best fit theoretical predictions for the case of infinitely strong anchoring conditions.

electrode gap), the electric field is uniform. We can therefore model the device in only one dimension, along the z axis.

We describe the bulk free energy of the liquid crystal as follows:

$$F = \frac{K_{11}}{2}(\nabla\cdot\mathbf{n})^2 + \frac{K_{22}}{2}\left((\nabla\times\mathbf{n})\cdot\mathbf{n} - \frac{2\pi}{p}\right)^2 + \frac{K_{33}}{2}\left((\nabla\times\mathbf{n})\times\mathbf{n}\right)^2 - \frac{1}{2}\epsilon_0\Delta\epsilon(\mathbf{n}\cdot\mathbf{E})^2 - \{e_1(\nabla\cdot\mathbf{n})\mathbf{n} + e_3\left((\nabla\times\mathbf{n})\times\mathbf{n}\right)\}\cdot\mathbf{E}. \quad (2)$$

The first three terms correspond to the Frank elastic energy, with splay, twist, and bend elastic coefficients K_{11}, K_{22}, and K_{33}, respectively. The fourth term is the dielectric energy (anisotropy $\Delta\epsilon$), and the final term is the flexoelectric energy, where e_1 and e_3 are the splay and bend flexoelectric coefficients, respectively, as defined by Meyer [1]. The Euler-Lagrange equations for the three components of the director $\mathbf{n}$ are solved numerically to find the equilibrium director profiles as a function of applied electric field. In this case, where the electric field is assumed to be uniform, only one flexoelectric parameter $(e_1 - e_3)$ appears in the Euler-Lagrange equations [11]; this is why our method probes the difference

TABLE I. The fixed parameter values used in the model in this work for both liquid crystal materials.

	E7	E70A/CB15
K_{11}	11.1 pN	10.0 pN
K_{22}	6.5 pN	5.8 pN
K_{33}	17.1 pN	10.4 pN
$\Delta\epsilon$	14.3	10.4
Δn	0.232	0.181
p	∞	250 μm

in the flexoelectric coefficients rather than the sum. The resulting director profiles for a range of positive and negative applied fields are then used as an input to a 4×4 Berreman optics routine to find the transmittance of the device at the two angles of incidence of ±45°.

The material parameters for both liquid crystal mixtures shown in Table I are kept constant throughout the process of fitting the theory to the experimental data. These values are a combination of measurements made by the manufacturer, Merck, and our own in-house measurements.

At the surfaces, the pretilt (known to be very low for the PVA alignment material used) was set to zero. The reason for doing this was that the effect of changing the surface pretilt on the electro-optic characteristic was found to be almost identical to a small misalignment in the cell orientation within the laser beam. Since the true values of the pretilt and the cell orientation were both unknown, it made sense to set the pretilt to zero, and use the cell orientation as a fitting parameter, as the two cannot meaningfully be separated. Finite surface anchoring (both zenithal and azimuthal) was considered within the range of reported values for the anchoring coefficients (10^{-3}–10^{-5} Jm^{-2}). The effect of a finite zenithal anchoring coefficient (compared to infinitely strong boundary conditions) on the predicted electro-optic characteristic was found to be minimal, whereas a weak azimuthal anchoring coefficient of 10^{-5} Jm^{-2} had a significant effect on the transmittance predicted at any particular voltage. Since the azimuthal anchoring energy was unknown, theoretical predictions were generated for a range of values of this coefficient and the effect on the measured flexoelectric coefficient determined.

The parameters that were allowed to vary for the purposes of fitting the theoretical results to the experimental ones are as follows:

Cell thickness. Although both cells were known to be around 10–15 μm in thickness, the exact thickness at the point where the laser beams cross was treated as an unknown parameter and allowed to vary in order to match the transmittance recorded at zero volts. The results are shown in Table II.

Cell orientation. Again, although the cells were nominally aligned at 45°, there could be a small misalignment that would affect the exact angles of incidence of the laser beams with respect to the cell normal, which, in turn, would affect the electro-optic characteristic. The exact cell orientation is therefore used as a fitting parameter to obtain a good match between theory and experiment, but does not influence the value of the flexoelectric coefficient measured. The values obtained were all within a degree or two of the nominal orientation. This method also takes into account the small (but unknown) surface pretilt, which has an almost identical effect on the electro-optic characteristic as a small misalignment of the cell orientation from 45°.

Ratio of electric field to applied voltage. In a device with in-plane electrodes of gap g, the relationship between the applied voltage and the electric field is not simply $E=V/g$. If the liquid crystal had the same dielectric permittivity as the surrounding glass, then in the middle of the gap, the electric field would be $E=2V/\pi g\approx0.64V/g$. In reality, however, the fact that the liquid crystal has a higher dielectric permittivity than the glass means that the electric field is concentrated within the liquid crystal layer, so the coefficient can be somewhat higher than 0.64. In addition, the electric field depends weakly on position within the gap, so that, although it is a good approximation to assume that it is uniform within the region of observation (about one-fifth of the electrode gap), the value of the electric field can be higher than it would be at the exact center. Furthermore, we know that the application of slowly varying voltage waves can lead to ionic migration in most liquid crystal materials (including E7 and E70A), which leads to partial cancellation of the electric field. For a certain applied voltage, therefore, the electric field experienced by the liquid crystal is unknown, even if the electrode gap has been carefully measured. In order to resolve this issue, we define a parameter α as

$$E=\alpha\frac{V}{g} \tag{3}$$

and use it as a further fitting parameter when matching the theoretical predictions to the experimental data. The effect of varying α is merely to scale the x axis of the theory curves as shown in Fig. 3, and hence, it is very clear when the correct value has been obtained. The values obtained were close to 1, as shown in Table II.

TABLE II. The parameters obtained by fitting theoretical results to experimental data.

Cell	Material	Azimuthal anchoring coefficient (Jm^{-2})	d (μm)	α	(e_1-e_3) (Cm^{-1})
1	E7	infinite ($>10^{-3}$)	14.56	1.01	9.0×10^{-12}
1	E7	finite (10^{-5})	14.60	0.91	9.6×10^{-12}
2	E70A	infinite ($>10^{-3}$)	12.44	1.21	3.3×10^{-12}
2	E70A	finite (10^{-5})	12.47	1.07	3.7×10^{-12}

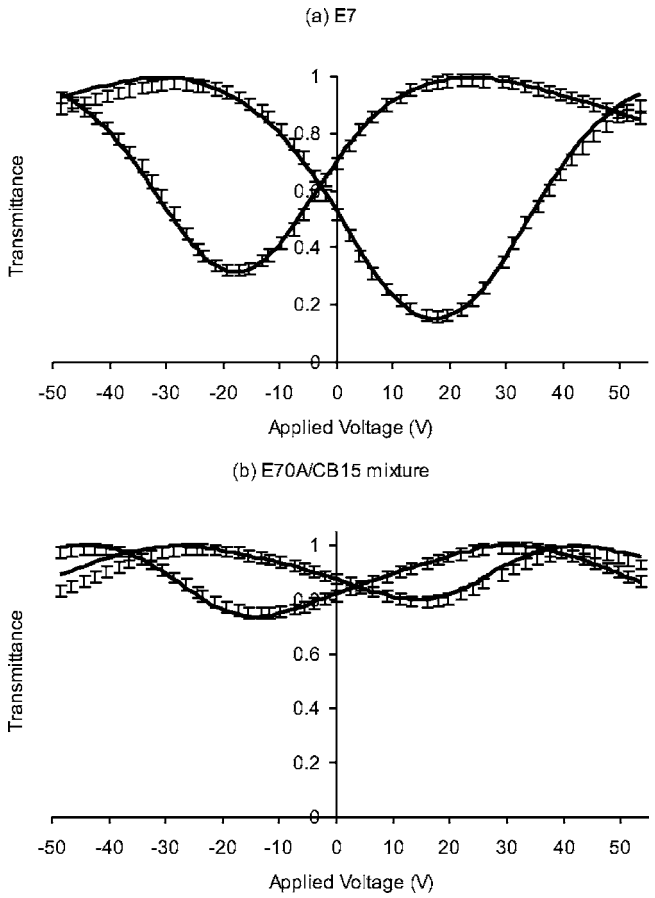

FIG. 4. Example of the experimental results obtained for both liquid crystal materials studied: (a) is for achiral nematic mixture E7 and (b) is for a weakly chiral mixture of E70A and CB15. The experimental data points are shown as solid points with error bars, and the continuous lines show the best fit theoretical predictions for the case of a finite azimuthal anchoring coefficient of 10^{-5} Jm^{-2}.

Flexoelectric parameter (e_1-e_3). This was allowed to vary freely for fitting theoretical data to the experimental data for different cells, since this is the parameter we wish to measure. Note that the effect of changing the flexoelectric parameter is to vary the maximum and minimum values of the transmittance and, hence, is orthogonal to changing parameter α.

The results of the fitting procedure (for infinitely strong surface anchoring) are shown by the solid lines in Fig. 3; it can be seen that the fitting between theory and experiment is extremely good. The values obtained for all the adjustable parameters for each cell are summarized in Table II. For the case of infinite boundary conditions, the flexoelectric parameter (e_1-e_3) in E7 was found to be $+9.0\times10^{-12}$ Cm^{-1}, and $+3.3\times10^{-12}$ Cm^{-1} in E70A/CB15. Note that this method determines both the magnitude and sign of the flexoelectric parameter. The theoretical predictions in the case of a somewhat weaker azimuthal anchoring strength (10^{-5} Jm^{-2}) were also fitted to the experimental data, and the results are shown in Fig. 4. As shown in Table II, the values obtained for the flexoelectric parameters for the two materials were slightly higher: $+9.6\times10^{-12}$ Cm^{-1} in E7, and $+3.7\times10^{-12}$ Cm^{-1} in E70A/CB15. We therefore use this range of possible values for the flexoelectric coefficients (determined by uncertainty in the azimuthal anchoring strength) to define the error on the measurement, as this is the principle source of error. A future modification of the experiment will be to repeat the experiment at high frequency, matching theoretical results generated with no flexoelectricity to these results. This will enable an independent measurement of the azimuthal anchoring strength to be made, and hence, the flexoelectric coefficients will then be determined to an even greater level of accuracy.

V. CONCLUSIONS

In this work, we have demonstrated a highly effective and accurate technique for measuring the magnitude and sign of the difference of the flexoelectric coefficients (e_1-e_3) in nematic liquid crystals. The method is inspired by the flexoelectric-optic effect, but uses a TN cell with an in-plane electric field so that achiral and weakly chiral materials can be studied. The method could also be extended to highly chiral materials by using multiple pitches in the device and would be preferable to trying to achieve a uniform lying helix texture. Perhaps most importantly, our technique takes into account the effect of ionic drift on the measurements. The technique has been used to obtain the flexoelectric parameter (e_1-e_3) in E7 and a weakly chiral mixture of E70A with CB15, to a good degree of accuracy. The results are $(+9.3\pm0.3)\times10^{-12}$ Cm^{-1} for E7 and $(+3.5\pm0.2)\times10^{-12}$ Cm^{-1} for E70A/CB15. The accuracy of the measurement could be improved by making an independent measurement of the azimuthal anchoring energy.

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[7] Following the convention of the Chalmers group [8], it has become common among those working on the flexoelectric-optic effect to substitute e_s for e_1 and $-e_b$ for e_3, so that $(e_1 - e_3) = (e_s + e_b)$. In much of the literature on the flexoelectric-optic effect, therefore, the relevant flexoelectric coefficient is expressed as a sum of two coefficients rather than a difference. Since this convention seems, at the moment, to be confined mainly to two groups, we therefore persist with the definition given by Meyer [1], particularly as our studies of flexoelectricity are not restricted to the flexoelectric-optic effect.

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