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The influence of pretransitional phenomena on blue phase range

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The particular phase in which a liquid crystal system will exist is that which has the lowest free energy at a certain temperature. The free energy may depend on variables such as temperature, pressure, chirality, etc. One way in which the stability of a particular thermodynamic phase, relative to its neighbours, would be manifest is in its temperature range. The effect of chirality, in particular, on the temperature range or stability of blue phases has been well-studied both experimentally and theoretically. To date these studies assume that chirality is the only parameter which will influence the existence of blue phases. However, blue phases with relatively low chirality and broad range, which should in principle only show very narrow blue phases, have been reported. This suggests that factors other than chirality are involved in blue phase stability. In this paper we investigate the phase stability of various blue phase mixtures containing equal amounts of a chiral dopant, via their blue phase temperature range. Correlation between blue phase stability and the elastic constants k_2 and k_{22}, molecular length of the nematic host, and the order parameter at the blue phase to cholesteric transition is discussed. We have confirmed that for our mixtures the total blue phase temperature range may be related equally to the elastic constant k_{22} and the chirality. We also present the first data displaying an odd–even effect in blue phases. Finally, we have found an apparent correlation between the stability of the blue phases and the magnitude of the orientational order parameter of the cholesteric phase at the cholesteric to blue phase transition.

1. Introduction

Blue phases are a group of narrow (~ 1 K) thermodynamically distinct mesophases which appear just below the clearing point of certain chiral liquid crystals. At present there are seven reported blue phases of which the best known appear in conditions of zero electric field. These are denoted, in order of increasing temperature, blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII), also known as the fog phase. The BPI and BPII are generally thought to have body centred and simple cubic symmetry, respectively, whereas the structure of BPIII has as yet defied satisfactory explanation.

It is now generally accepted that the degree of chirality is the dominant factor influencing the stability of the blue phases [1]. Apart from chirality, another important feature of blue phases is that the structures are frustrated [2]. In a frustrated system, different terms in the free energy equation compete requiring different structures for individual terms to be minimized. The competition between these different terms generally results in a structure more complex than the individual terms would require. In the case of the blue phases, the lowest energy local director configuration is a 'double-twist' structure, such as that shown in figure 1, where the director rotates about any axis perpendicular to the central axis of a cylinder. Fitting this double-twist

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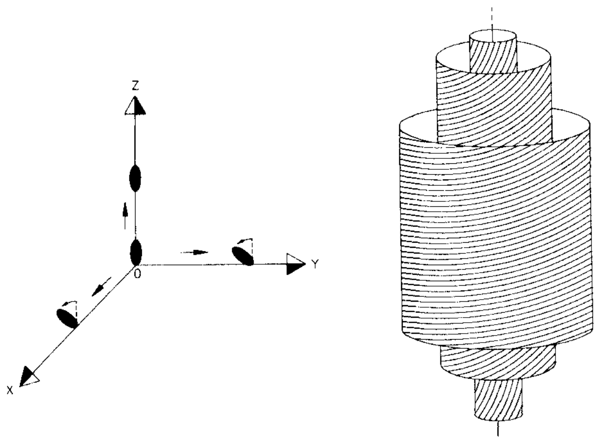

(a) (b)

Figure 1. Molecular interpretation of local free energy minimization via a double-twist configuration (*a*); this leads to a cylindrical structure on the larger scale (*b*), where lines on the surfaces of the cylinders represent director orientation. (From [2].)

structure into three dimensional space is topologically impossible, so disclinations, defects in the director field, are necessary to relieve the elastic strain energy. This was first noted by Sethna [3] who found, interestingly, that the double twist criterion could be satisfied completely in four dimensions. Figure 2 shows how these double twist cylinders fit into three dimensional space to produce cubic structures.

To date, attention has been focused almost exclusively on the dependence of the stability of blue phases upon the chirality of the system. However, recent studies by Coles and Gleeson [4] have found blue phases with total ranges of the order of 2·5 K for systems with relatively low chirality. In other systems of comparable chirality, blue phase ranges are typically 0·2 K. This suggests that there may be factors other than chirality involved in determining blue phase range. Also the stability of any phase will depend on the free energy of the structure, and for blue phases the elastic free energy equation, as given by Meiboom *et al.* [5], involves the so-called splay, twist, bend and saddle-splay elastic constants, k_{11}, k_{22}, k_{33} and k_{24}, respectively, as well as the chirality factor, q_0. The relationship between q_0 and the elastic constants k_2 and k_{22} may be seen when we consider two alternative descriptions of the elastic free energy density in cholesterics. The chiral term in the free energy equation as given by Meiboom *et al.* is $\frac{1}{2}k_{22}(\mathbf{n}\nabla\wedge\mathbf{n}+q_0)^2$. Expanding this and ignoring the constant term, which is unimportant, we obtain $k_{22}q_0(\mathbf{n}\cdot\nabla\wedge\mathbf{n})+\frac{1}{2}k_{22}(\mathbf{n}\cdot\nabla\wedge\mathbf{n})^2$, where, comparing this to the elastic free energy equation as given by Chandrasekhar [6], we may equate the factor $k_{22}q_0$ with the elastic constant k_2 which in non-chiral systems is zero. Finally, we have noted that blue phases have frustrated structures; here the energetic disadvantage of forming disclinations, influenced by the factors k_{22} and k_{24} in the free energy equation, is played off against the energetic advantage of the double-twist structure, influenced by the factors k_{22} and q_0 where $q_0=k_2/k_{22}$.

Hence, it may be expected that the stability and therefore the temperature range of the blue phases depend upon factors other than just the chirality q_0. These factors include the Frank elastic constants k_2, k_{22} and k_{24} and also the orientational order parameter S in the cholesteric phase. In this paper we present new results from which we investigate the correlation between the blue phase temperature range, which was

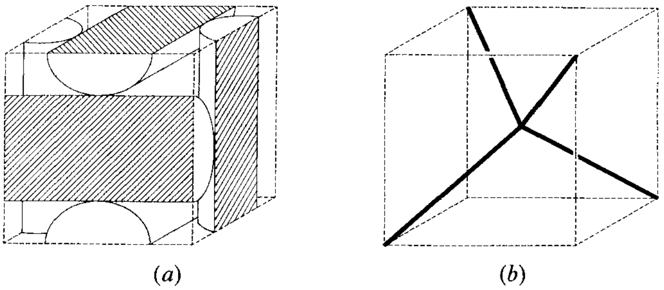

Figure 2. One of the simplest cubic arrangements of infinite double-twist cylinders (a) and its corresponding network of $s=-\frac{1}{2}$ disclination lines (b). Its symmetry space group is $0^2=P4_232$. (From [2].)

Summary of mixtures used in the experiments; their compositions are given, with the approximate twist elastic constants two degrees below the nematic to isotropic transition for the nematic hosts [7,8].

Nematic component	Mol fraction of CE2/%	Twist elastic constant in nematics at $T-T_{NI}=-2K$/pN
4CB	20·1 ± 0·2	—†
5CB	20·0 ± 0·1	2·3
6CB	20·0 ± 0·1	1·9
7CB	20·0 ± 0·1	2·7
PCH4	20·1 ± 0·2	1·8
PCH5	19·8 ± 0·4	2·6

† 4CB does not display any liquid crystalline phases under normal conditions.

taken as a measure of the phase stability, the twist elastic constants k_{22}, k_2, and the order parameter. All the physical properties were measured for the cholesteric phase close to the cholesteric to blue phase transition.

2. Materials

In order to carry out our aims, a series of mixtures were made up which included a constant proportion of a chiral liquid crystal, CE2 (Merck Ltd. U.K.), in a range of nematic host materials, thereby hoping to produce a range of mixtures of equal chirality. CE2 was chosen because (i) it is highly chiral (pitch $\sim 0{\cdot}10\,\mu m$) and (ii) its clearing temperature is higher than room temperature which makes measurement of the physical properties easier.

A range of six nematic materials was chosen as the hosts in this experiment. The nematic materials were chosen as they represented host materials with well-defined elastic constants (measured by Bancroft [7] and Sefton [8]). Also these nematic hosts displayed a reasonable spread in values of their twist elastic constants. The table shows a summary of the nematic materials used and their approximate twist elastic constants close to the nematic to isotropic phase transition. The nematic materials chosen included an homologous series. Figure 3 shows the chemical structures of the materials chosen.

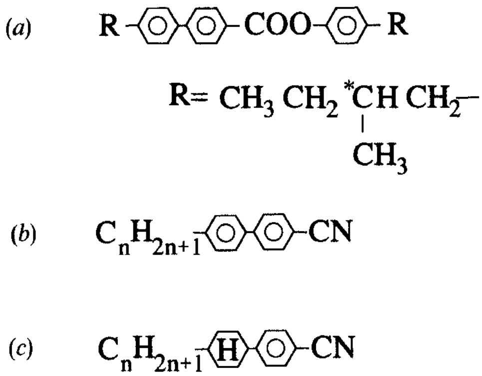

Figure 3. Structures of materials chosen to make up the mixtures: (*a*) CE2; (*b*) *n*CB; (*c*) PCH*n*.

The optimum concentration of CE2 in the nematic host was found by making a range of mixtures of CE2 and 6CB, and examining the blue phase temperature range. Using this method, a mole fraction of 0·2 of CE2 was chosen which gave blue phase temperature ranges of the order of 0·5 K. It was considered important to maintain the mol fraction of chiral material constant, rather than the weight percentage.

3. Experiment

In order to characterize the blue phase stability fully in terms of the parameters suggested, we needed to determine (i) the total blue phase temperature range, (ii) the twist elastic constant k_{22}, (iii) the elastic constant k_2, (iv) the order parameter and (v) a measure of the order of the phase transition.

3.1. *Phase transition temperatures*

The phase transition temperatures of the mixtures were measured using a Linkam TMS91 hot stage which quotes an accuracy of 0·1°C and a polarizing microscope upon which the samples were observed in reflection.

3.2. *Elastic constants*

The elastic constants were measured from the field-induced cholesteric to nematic phase transition. The critical field required for this transition may be derived from the elastic free energy density equation in an electric field [9]

$$f=\frac{k_{11}}{2}(\nabla\cdot\mathbf{n})^2+\frac{k_{22}}{2}(\mathbf{n}\cdot\nabla\wedge\mathbf{n}+q_0)^2+\frac{k_{33}}{2}(\mathbf{n}\wedge\nabla\wedge\mathbf{n})^2-\varepsilon_0\Delta\varepsilon(\mathbf{E}\cdot\mathbf{n})^2, \tag{1}$$

where the terms are as before, with $\Delta\varepsilon$ equal to the dielectric anisotropy of the liquid crystal and $\mathbf{E}$ the applied electric field. For the case of an undistorted cholesteric with helical axis along the z axis, the director field is given by $\mathbf{n}=(\cos q_0z, \sin q_0z, 0)$ and the elastic free energy density for zero electric field is zero. However, if we consider the same liquid crystal induced into a nematic structure by an electric field applied along the z axis, the director field becomes $\mathbf{n}=(0,0,1)$ and the electric field is $\mathbf{E}=(0,0,E)$; then the elastic free energy density for this structure is given by

$$f=\frac{k_{22}q_0^2}{2}-\frac{\varepsilon_0\Delta\varepsilon}{2}E^2. \tag{2}$$

Hence, since the structure formed by a liquid crystal is given by that which minimizes the free energy, there will be a transition from the undistorted cholesteric phase to a nematic one when the free energy of the field-induced nematic is less than that of the cholesteric. The critical field is given by

$$E_c^2 = q_0^2 \frac{k_{22}}{\varepsilon_0 \Delta\varepsilon}. \tag{3}$$

However, the chirality factor q_0 as defined here is equal to $2\pi/p_0$, where p_0 is the pitch of the cholesteric structure. Hence,

$$E_c = \frac{2\pi}{p_0} \sqrt{\left(\frac{k_{22}}{\varepsilon_0 \Delta\varepsilon}\right)}, \tag{4}$$

which gives a method for measuring the elastic constant k_{22}. Note that equation (4) has no real solutions for materials with negative dielectric anisotropy.

For measuring the elastic constant k_{22}, an alternating electric field of frequency 1 kHz (sine wave) was applied to the samples; this produced a cholesteric to nematic transition with increasing electric field according to equation (4). The measurements were taken at two degrees below the cholesteric to blue phase transition in order to avoid a divergence in errors close to the transition. This divergence in the errors is caused by the limit on the temperature stability and the strong dependence of the parameters on temperature close to the transition. The electric field, E, in this equation is taken as the rms voltage divided by the cell thickness. In order to obtain a value for the elastic constant k_{22}, using equation (4), several other variables must be measured.

3.3.1. *Cell thickness*

The cell thickness, d, was determined by measuring the interference peaks in the reflection spectrum from the empty cell. This gave the cell thickness typically to an error of 0·2 μm.

3.3.2. *Dielectric anisotropy*

The dielectric anisotropy of the liquid crystal, $\Delta\varepsilon$, was determined by measuring the capacitance of a cell when empty and when filled. In the experiment, care was taken to account for stray capacitances and capacitances of the leads, and the measurements were taken at the frequency of the applied electric field (1 kHz). The relative permittivity is then given by the ratio of the capacitance of the filled cell to that of the empty cell. Planar alignment was used in the cells, identifying this measurement with the dielectric permittivity perpendicular to the molecules, $\varepsilon_\perp$. Isotropic values of the relative permittivity were extrapolated into the cholesteric phase and identified with a mean relative permittivity given by $\bar{\varepsilon} = \frac{1}{3}(\varepsilon_\parallel + 2\varepsilon_\perp)$ to deduce a value for $\varepsilon_\parallel$. This allowed the dielectric anisotropy to be measured with a typical accuracy of 2 per cent.

3.3.3. *Cholesteric pitch*

The final variable needed in equation (4) is the undistorted pitch, p_0, in the cholesteric phase. This can be found from the relation

$$p_0 = \frac{\lambda_p}{\bar{n}_s}, \tag{5}$$

where λ_p is the peak wavelength of selectively reflected light and $\bar{n}_s$, is the mean refractive index. λ_p was measured using a computer controlled scanning monochromator with the sample held in a reflection microscope. The wavelength resolution of this method is of the order of 2 nm. $\bar{n}_s$ was calculated from measurements of the bulk refractive indices made on an Abbé refractometer at a wavelength of 589 nm. In the bulk cholesteric phase, the two refractive indices measured, n_o and n_e, are given by

$$\begin{aligned} n_o &= n_\perp, \\ n_e^2 &= \tfrac{1}{2}(n_\parallel^2 + n_\perp^2), \end{aligned} \tag{6}$$

where $n_\parallel$ and $n_\perp$ are the refractive indices parallel and perpendicular to the cholesteric molecules respectively. The mean refractive index $\bar{n}_s$ is then given by

$$\bar{n}_s = \tfrac{1}{2}(n_\parallel + n_\perp). \tag{7}$$

The refractive index data may also be used to calculate the order parameter in the cholesteric phase.

3.4. *Order parameter*

The order parameters for the mixtures in the cholesteric phase were calculated from the refractive index data according to the Haller method. Vuks [10] gives the relation between the refractive indices and the order parameter as

$$S = \left(\frac{n_\parallel^2 - n_\perp^2}{\bar{n}^2 - 1}\right) f(\alpha), \tag{8}$$

where S is the order parameter, $n_\parallel$ is the refractive index parallel to the molecules, $n_\perp$ is the refractive index perpendicular to the molecules, $f(\alpha)$ is a function of the molecular polarizabilities, and the mean refractive index $\bar{n}$ is given by $\bar{n}^2 = \tfrac{1}{3}(n_\parallel^2 + 2n_\perp^2)$. Haller [11] also postulates an equation of the form

$$S = \left(1 - \frac{T}{T^*}\right)^\beta, \tag{9}$$

where T is the temperature in Kelvins and T^* and β are fitting parameters. These two parameters and the value of the function $f(\alpha)$ may then be found by fitting equations (8) and (9) to the refractive index data. Hence the order parameter may be calculated. It is important to note that care must be taken in the selection of the fitting procedure used since the measure of the fit, χ^2, has a shallow minimum with respect to T^*.

4. Results and discussion

4.1. *Influence of orientational order parameter*

Figure 4 shows the measured total blue phase temperature range for the mixtures containing the four cyanobiphenyl (*n*CB) and the two phenylcyclohexane (PCH*n*) based nematic hosts. An odd-even effect can clearly be seen in the mixtures containing the *n*CB homologues. The existence of this odd-even effect is supported by the data in figure 5 which show the orientational order parameters in the cholesteric phase, measured at the cholesteric to blue phase transition, for each of these mixtures. From these data, we may also note the following

(i) The orientational order parameters at the Ch→BP phase transition are lower than may be expected. This can be attributed to the measurement technique: determining order parameters from birefringence measurements is difficult as there is no rigorous way of correcting for the effects of polarization field in the medium [6], though approximate methods have been proposed, including that used here, determined by Haller [11].

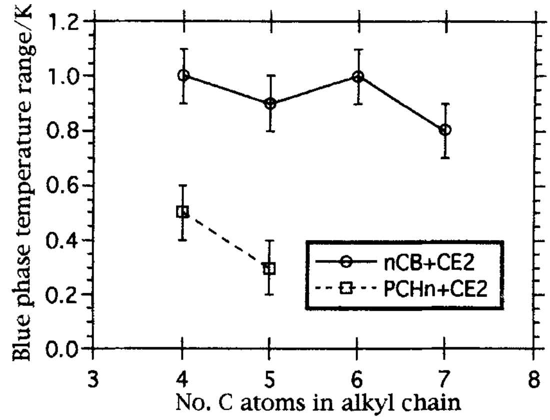

Figure 4. Graph showing the total blue phase temperature ranges plotted against the number of carbon atoms in the alkyl chain of the nematic components.

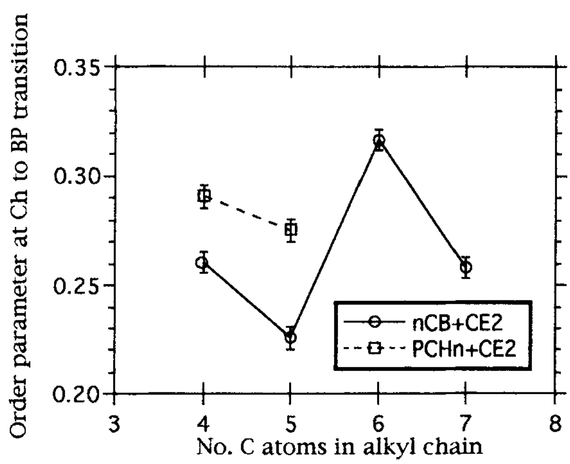

Figure 5. Graph showing the order parameters of the mixtures plotted against the number of carbon atoms in the alkyl chain of the nematic components at the cholesteric to blue phase transition. These values were calculated from equation (9) using the fitted parameters (see text).

(ii) The order parameters of the PCH*n* materials, at the transition, are measured as higher than those of comparable *n*CB materials. It is tempting to draw a conclusion from this regarding the influence of the absolute value of the orientational order parameter at the transition on the phase temperature range. However, it should be noted that the difficulty in allowing for the local field corrections adequately makes it difficult to justify direct comparisons between materials with very different polarizabilities, i.e. the *n*CB and the PCH*n* based materials, though comparisons between members of the same homologous series would appear to be reasonable.

(iii) Within an homologous series the higher order parameters at the phase transition (even members) appear to correspond to more stable blue phases.

Figure 6 shows the variation in the parameter $T^{*}-T_{CB}$ plotted against the total blue phase range. The value of the parameter T^{*}, obtained when calculating the order

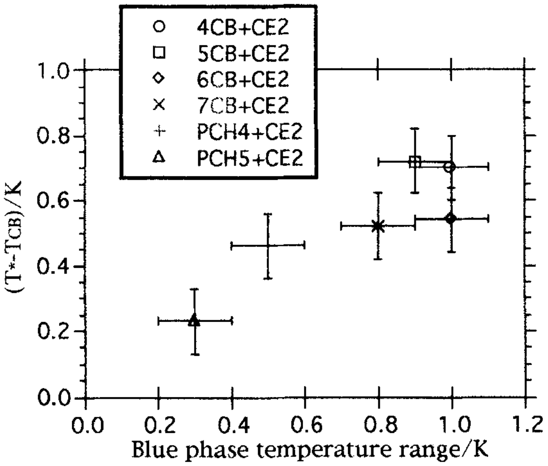

Figure 6. Graph showing the parameter (T^*-T_{CB}), (where T^* is the highest temperature to which the cholesteric phase may be superheated and T_{CB}, is the cholesteric to blue phase transition temperature) plotted against total blue phase temperature range of the various mixtures.

parameters using equation (9) in the Haller procedure, corresponds to the maximum temperature to which the cholesteric phase could be superheated. Figure 6 shows a strong linear relationship between T^*–T_{CB} and the total blue phase temperature range. The difficulties in drawing direct comparisons between the absolute values of the orientational order parameters for the *n*CB and PCH*n* series of materials do not apply to the parameter T^*, as in each case, a curve is extrapolated to the temperature axis giving an intercept which is independent of any local field correction. It would therefore seem that the parameter T^*–T_{CB} is related to the blue phase range.

4.2. *Influence of elastic constants*

Figure 7 shows the twist elastic constants, k_{22}, calculated from the data. These values are also at two degrees below the cholesteric to blue phase transition. It is interesting to note that there appears to be virtually no correlation between these values and the values of the twist elastic constants for the nematic host materials on which basis the materials were chosen.

The next two graphs show the total blue phase temperature range plotted against the cholesteric pitch (see figure 8) and the twist elastic constant (see figure 9) both at two degrees below the cholesteric to blue phase transition. Firstly, it is noted that in figure 8, contrary to expectation, the mixtures with the longest pitch, and hence lower chirality, display the widest blue phases. Secondly, the degree of scatter on both graphs is of the same order, which would suggest, at least on the basis of these data, that there is as much dependence of the blue phase temperature range on the twist elastic constant on its own as there is on the chirality.

Thirdly, if we look at these two graphs more closely, we can see that the points for the various mixtures appear in similar relative positions on the graphs. We interpret this as due to the fact the twist elastic constant, k_{22}, and the pitch, p_0, are related via the elastic constant, k_2, where

$$p_0=\frac{2\pi k_{22}}{k_2}. \tag{10}$$

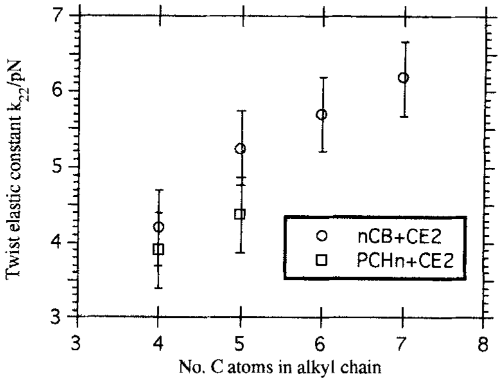

Figure 7. Graph showing the twist elastic constant, k_{22}, for the various mixtures in the cholesteric phase two degrees below the cholesteric to blue phase transition plotted against the number of carbon atoms in the alkyl chain of the nematic component.

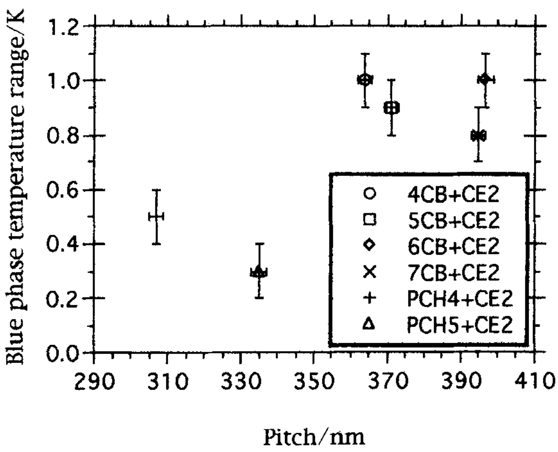

Figure 8. Graph showing the total blue phase temperature range plotted against the pitch in the cholesteric phase two degrees below the cholesteric to blue phase transition.

We have presented the values for k_2, for the sake of completeness, in figure 10. These values vary little with the total blue phase temperature range and there appears to be no dependence of the blue phase stability on the elastic constant k_2 alone.

5. Conclusions

We believe that this is the first systematic study of the dependence of blue phase stability on parameters other than chirality. It is interesting to note that in the mixtures we have made the ones with lower chirality have the wider blue phases. Another point of note is that the scatter on the graphs of blue phase range against pitch and elastic constant are of the same order. From this we may conclude that there is as much dependence of the stability on the elastic constant, k_{22}, as on the chirality.

We also believe that this is the first time that a definite odd-even effect has been found for blue phases, shown by both the blue phase temperature range and the order parameter measurements. Finally, we have shown for the first time that there appears

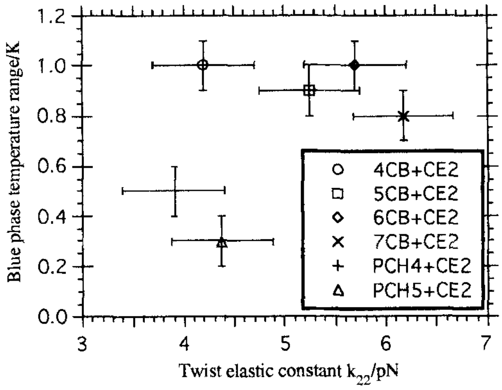

Figure 9. Graph showing the total blue phase temperature range plotted against the twist elastic constant, k_{22}, in the cholesteric phase two degrees below the cholesteric to blue phase transition.

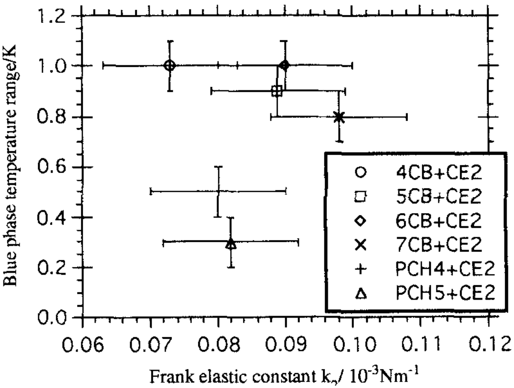

Figure 10. Graph showing the blue phase temperature range plotted against the elastic constant k_2 calculated from equation (10) for the various mixtures.

to be a positive connection between the blue phase stability and the order of the phase transition between cholesteric phase and the blue phase. This work forms a solid basis for future measurements which will be made, wherever possible, in the blue phases. The measurements were taken for the cholesteric phase, as the techniques used to deduce the physical parameters under consideration cannot be used to deduce the same constants for the blue phases. Experiments to measure the order parameter for both cholesteric and blue phases using Kossel diagram techniques are currently underway. These will allow the apparent relationship between order parameters, elastic constants and the blue phase range to be investigated more fully across the phase boundaries, and the results of these experiments will be reported at a later date.

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References

[1] Crooker, P. P., 1989, *Liq. Crystals*, **5**, 751 (review and references to earlier work).

[2] Dubois-Violette, E., and Pansu, B., *Molec. Crystals liq. Crystals*, **165**, 151.

[3] Sethna, J. P., 1983, *Phys. Rev. Lett.*, **51**, 2198.

[4] Coles, H. J., and Gleeson, H. F., 1988, *Molec. Crystals liq. Crystals*, **167**, 213.

[5] Meiboom, S., Sethna, J. P., Anderson, P. W., and Brinkman, W. F., 1981, *Phys. Rev. Lett.*, **46**, 1216.

[6] Chandrasekhar, S., 1977, *Liquid Crystals* (Cambridge University Press), Chap. 3.

[7] Bancroft, M. S., 1988, PhD Thesis, University of Manchester.

[8] Sefton, M. S., 1985, Ph.D. Thesis, University of Manchester.

[9] Sheng, P., 1975, *Introduction to Liquid Crystals*, edited by E. B. Priestley (Plenum Press), Chap. 8.

[10] Vuks, M. F., 1966, *Optics Spectrosc., N.Y.*, **20**, 644.

[11] Haller, I., 1975, *Prog. Solid St. Chem.*, **10**, 103.