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HIGH PRESSURE MEASUREMENTS OF THE REFRACTIVE INDICES OF TWO NEMATIC LIQUID CRYSTALS

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Abstract. — The refractive indices of two nematogens, 4-methoxy-benzylidene-4'-n-butylaniline (MBBA) and 4-n-pentyl-4'-cyanobiphenyl (5CB), have been measured throughout their nematic ranges at pressures up to 2 kbar and temperatures up to 70 °C in the first substance and up to 5 kbar and 145 °C in the second. Measurements were made at \( \lambda = 5890 \, \text{Å} \), using a sensitive interference fringe technique. Results are presented in the form of functions \( n_e(P, T) \) for the extraordinary index and \( n_o(P, T) \) for the ordinary index, obtained by least squares fits to the experimental data.

1. Introduction. — The orientational order parameter in nematic liquid crystals, S, has generally been measured as a function of temperature at constant (atmospheric) pressure. The present work was inspired by the belief that, in order to check the various theories of nematic order which exist, it is highly desirable to establish the temperature dependence of S at constant volume, and also to find how S varies with volume at constant temperature. To this end, we have made measurements inside a pressure vessel of the two principal refractive indices, \( n_e \) and \( n_o \), for the two nematogens 4-methoxy-benzylidene-4'-n-butylaniline (MBBA) and 4-n-pentyl-4'-cyanobiphenyl (5CB). From \( n_e \) and \( n_o \), it is possible to estimate not only S but also the density, and to know how the density varies with pressure and temperature is essential for our purposes. There have been three previous attempts to measure the order parameter inside a pressure vessel [1-3] but in only one of these [2] was density measured at the same time; the subject of that investigation was p-azoxyanisole (PAA).

The problems that have to be overcome before S can be extracted from refractive index data have been discussed elsewhere [4]. These problems may for the moment be set aside, since this paper is concerned only with description of the experimental method and presentation of the results obtained. A further paper, concerned with the analysis of the results, is in course of preparation.

2. The high-pressure vessel. — The specimen was compressed inside a beryllium-copper cylinder, of external diameter 76 mm, by means of a beryllium-copper piston, of diameter 9.5 mm, the cylinder and piston being squeezed together in a hydraulic press. The specimen was observed through a sapphire window set in a transverse hole through the middle of the cylinder. To fill the vessel completely, 4.5 ml of the nematogen was required.

Pressure and temperature were measured by means of a manganin resistance gauge and a chromel/alumel thermocouple mounted in the lower part of the vessel. Electrical connections were made by the method of Cornish and Ruoff [5]: two lengths of stainless-steel-sheathed mineral-insulated cable, one carrying a pair of copper wires and the other a chromel/alumel pair, were silver-soldered into holes through a sealing plug.

Changes in resistance of the manganin gauge were determined by measuring the out-of-balance signal of a nearly-balanced Wheatstone bridge. The pressure coefficient of resistance of the gauge was measured at room temperature using a dead-weight tester at the Department of Mechanical Engineering, Imperial
College, London. During the experiments the whole vessel was heated, so it was also necessary to know the change of manganin resistance with temperature; this was measured at atmospheric pressure. It was assumed, following the results of Wang [6], that the pressure coefficient of resistance was independent of temperature. Cheng, Allen and Lazarus [7] have shown that thermocouple voltage is hardly affected by pressure. For the chromel/alumel thermocouple the correction would correspond to less than 0.5 °C at the highest temperature and pressure attained in these experiments; this correction was not applied.

Near room temperature, errors of up to about 0.6 % may have occurred in each pressure measurement, due to uncertainties in the calibration and measurement of the gauge resistance. At higher temperatures there were additional uncertainties in the measurement of the gauge temperature, the temperature variation of the gauge resistance, and the temperature variation of the pressure coefficient. These effects were reckoned to contribute an uncertainty of ± 50 bar to pressures measured at 150 °C. However, changes in pressure could always be measured with an accuracy of ± 2 bar.

The operational temperature of the vessel was limited by the silk coating of the manganin wire, which began to char at 150 °C. To cover the whole nematic range of the room-temperature nematogens studied here up to 150 °C it was necessary to increase the pressure to 5 kbar, which the vessel was well able to withstand.

3. Method of measuring refractive indices. — Refractive indices were measured by monitoring the change in the interference pattern seen in a thin film of oriented nematic sample as its pressure or temperature (or both) were changed. In a sample of thickness \( d \) a dark fringe appears in reflection whenever

\[
\frac{m \lambda}{2} = n d,
\]

where \( m \) is an integer, \( \lambda \) the wavelength of the light used, and \( n \) the refractive index. The change in optical thickness \( nd \) over a certain interval of pressure or temperature was obtained by counting the number of fringes which appeared in that interval, and the change in refractive index was found after allowing for compression and thermal expansion of the spacers which determined the thickness \( d \). The absolute value of the index at any point was obtained by measuring its change along a path from a point where it had already been determined by other methods, for example at atmospheric pressure.

The method is sensitive: for typical values of \( \lambda = 5890 \text{ Å} \) and \( d = 0.25 \text{ mm} \), one fringe corresponds to a change in \( n \) of 0.001 2, and it was generally possible to estimate a change of 0.1 fringe. It is also particularly good for exploring the region near the clearing transition because it is sensitive to changes in \( n \) and therefore collects most data where the refractive index is changing most rapidly with temperature or pressure (see Figs. 3 and 4).

Fringes were observed in sodium light (\( \lambda = 5890 \text{ Å} \)), and were counted in two polarisations to determine the two refractive indices \( n_p \) and \( n_s \) for light polarised parallel and perpendicular to the optic axis respectively. A similar experiment has been performed by Balzarini [8] on MBBA at atmospheric pressure, although by placing his sample between crossed polars, he determined only the birefringence \( \Delta n = n_p - n_s \). The method has also been used to measure the refractive index of certain solids and isotropic liquids as a function of pressure [9]. It is well-suited for use in a pressure vessel because it avoids any problems caused by distortion of the light beam in the pressure windows. In the experiments quoted [8, 9] a parallel-sided sample was used, and the periodic changes in transmitted or reflected intensity due to interference were counted automatically using a photocell. In the present study the sample was in the shape of a very narrow wedge with an angle of about \( 10^{-2} \text{ radians} \) between the two surfaces, so that an interference pattern of parallel lines was formed with a typical spacing of 5 lines/mm. The fringes were observed by eye as they moved across the wedge when the optical thickness changed, being counted as they passed a particular point in the wedge. Thus any change in the direction of movement was apparent, which was important in this experiment because it was found that the ordinary index \( n_s \) passes through a minimum as pressure is varied (see Fig. 4).

The wedge was formed between the inner surface of a sapphire pressure window and a glass disc held against it by a spring. Its thickness \( d \) was determined by two spacers of pure molybdenum wire, the compressibility and thermal expansivity of which are known. The two faces of the wedge were coated to enhance the sharpness and contrast of the fringes, and to promote uniform alignment of the sample. Fringes were observed in reflection, so the back surface (the glass disc) was made highly reflecting and the front surface (sapphire) partially reflecting by evaporation of thin gold films. Layers of silicon monoxide were then evaporated onto both surfaces at an angle of \( 60^\circ \) to the normal to give parallel alignment of the sample [10] as well as protection for the reflecting films. Although a magnetic field was available to align the sample, it was found that the effect of the silicon monoxide coatings alone was always enough to produce excellent alignment throughout the wedge.

The sapphire window was cut with its optic axis along the viewing direction; any strain birefringence induced at high pressures was not enough to affect the visibility of the fringe pattern in either polarisation. It was also noted that the fringes remained straight at all pressures, indicating that the inner face of the pressure window remained very flat.
4. Experimental procedure. — The signals from the manganin gauge and the thermocouple which characterised pressure and temperature were recorded automatically by pressing a switch whenever a fringe was counted as it passed a particular point in the wedge, or whenever any other noteworthy event occurred. For example, the melting and clearing transitions were easily observed and recorded in this way, so that the phase diagrams could be investigated.

Experiments on MBBA were continued up to 73 °C, and a least-squares fit to the collection of measured clearing points gave

\[ T_c = 40.9 + 34.0 P - 1.78 P^2 \]  

(2)

where \( T_c \) is the clearing temperature in °C and \( P \) the pressure in kbar, which is in good agreement with previous measurements on this substance [11, 12]. The melting curve was not investigated. Figure 1 shows the clearing curve (2) and experimental clearing points for MBBA, with the melting curve taken from Keyes et al. [12]. MBBA is notoriously unstable, and the clearing temperature at atmospheric pressure was observed to decline from 40.9 °C at the start of the experiment to about 36 °C at the end. Each point in figure 1 incorporates a drift correction for this deterioration; the corrections were estimated assuming the decrease in \( T_c \) to be linear with time and independent of pressure.

The second substance investigated, 5CB, is much more stable. It was found that the clearing temperature at atmospheric pressure had only decreased by 0.5 °C after a much longer set of experiments covering the range from room temperature up to 145 °C, and no drift corrections were necessary. Melting points were measured up to 110 °C and clearing points up to 145 °C, and the following least-squares fits were obtained for the melting temperature \( T_m \) and clearing temperature \( T_c \) in °C as functions of pressure \( P \) in kbar:

\[ T_m = 21.4 + 28.4 P - 1.44 P^2 \]  

(3)

\[ T_c = 34.8 + 37.2 P - 1.58 P^2 \]  

(4)

The phase diagram for 5CB is shown in figure 2.

In figure 1 there are lines labelled A, B, C which indicate the types of path along which fringes were counted, each path being followed twice to determine the two indices \( n_e \) and \( n_o \). The procedure may be illustrated using some of the results for 5CB; the MBBA results are qualitatively similar.

First, path A, the vessel was heated at atmospheric pressure. Figure 3 shows the number of fringes

![FIG. 1.](image1.png)

![FIG. 2.](image2.png)

![FIG. 3.](image3.png)

**FIG. 1.** — Phase diagram for MBBA. Circles are the experimental points, the solid line is the clearing curve (equation (2)) and the dashed line is the melting curve taken from Keyes et al. [12]. S, N and I label the solid, nematic and isotropic phases; the arrows A, B and C are discussed in the text.

**FIG. 2.** — Phase diagram for 5CB. The melting and clearing curves are given by equations (3) and (4).

**FIG. 3.** — Variation of fringe number with temperature at atmospheric pressure in 5CB. e, o and i label the extraordinary polarisation, ordinary polarisation and isotropic phase.
counted in such a run plotted against temperature. A plot of this number against the absolute value of refractive index measured at the same temperature by other methods in MBBA [13, 14] and 5CB [4] then gave the value of the thickness $d$ of the wedge at the point where the fringes were counted (from the slope) and the fringe number $m$ (from the intercept) (equation (1)). The whole range of pressure and temperature was then covered by counting fringes as pressure was released slowly at constant temperature (path B), the process being repeated at intervals of 2-3 °C. It was not necessary to keep the temperature exactly constant during such runs because it was automatically recorded at each point. By releasing pressure slowly enough it was possible to count the fringes seen in either polarisation in the nematic phase right up to the clearing transition where they suddenly disappeared, to be replaced almost immediately by a different set of fringes in the isotropic phase. Finally, fringes were counted as pressure and temperature were increased together, taking care to stay in the nematic phase (path C), thus connecting all the constant-temperature runs (paths B) with the atmospheric pressure results. It was then possible to enumerate every fringe and compute the refractive index at every point recorded, using equation (1) and taking into account the small changes in $d$ due to the compression and thermal expansion of the molybdenum spacers.

Figure 4 shows typical results of a few of the constant-temperature runs in 5CB. The curves are not as smooth as in figure 3, probably due to small variations in the temperature of the sample and of the manganin gauge.

![Figure 4](image.png)

**Figure 4.** Variation of refractive indices with pressure at various constant temperatures for 5CB: (A, 35 °C; B, 39 °C; C, 44 °C; D, 49 °C). The lines serve only as an aid to the eye.

5. Results. — The refractive indices were found by the method described above at several thousand points in the pressure-temperature plane and it would be impracticable to present all the data here. Instead, computer fits have been obtained for the functions $n_e(P, T)$ and $n_o(P, T)$ for the two nematogens studied; we will speak of refractive index surfaces above the P-T plane.

A least-squares routine was used to find the twelve parameters $a_i$ ($i = 1-12$) characterising each surface expressed as:

$$n_e(P, T) = (a_1 + a_2 P + a_3 P^2) +$$
$$+ (a_4 + a_5 P + a_6 P^2) (T^* - T)^{0.5}$$
$$+ (a_7 + a_8 P + a_9 P^2) T$$
$$+ (a_{10} + a_{11} P + a_{12} P^2) T^2$$

$(j = e, o)$ (5)

where $T^*$ is a temperature just above the clearing temperature $T_c$. This choice of function is not supposed to have any theoretical significance for the variation of $n_e$ or $n_o$ with $P$ and $T$, but simply to provide a form which gives a good computer fit to the experimental data using a reasonably small number of free parameters. The shape of the surface is very sensitive to the quantity $T^* - T_c$; the best fit was obtained with $T^* - T_c = 0.1$ °C, and $T^*$ was fixed at each pressure by reference to equations (2) or (4) for $T_c(P)$. If a particular constant-temperature run ended with a measured clearing temperature rather far from the fitted curve (2) or (4), an assumption was made that throughout that run the temperature or pressure measurements were erroneous, and all the readings were adjusted by the same amount — the amount needed to bring $T_c$ onto the fitted curve — before feeding them into the computer. This assumption seemed justified because none of the various errors that were liable to affect measurements of $T$ or $P$ were likely to change much during the short time it took to complete a single run. The adjustment described did greatly improve the fit that was obtained.

For MBBA the data were adjusted in temperature to compensate for progressive degradation of the sample as described in section 4, and in 5CB some sets of points at high temperatures were shifted in pressure to adjust for errors in the measurement of pressure by the manganin gauge at these temperatures, as discussed in section 2.

The coefficients defining the computed surfaces $n_e(P, T)$ and $n_o(P, T)$ for MBBA and 5CB are listed in table I. Pressures are in kbar and temperatures in °C. Examination of the differences between the original experimental points (values not adjusted in pressure or temperature) and the surfaces showed that sections through the computed surfaces give a good representation of each constant-temperature run: this difference was approximately the same for all points in any particular run. The computed surfaces are least satisfactory at each extreme, high pressure and low pressure. This is partly due to greater experimental
**TABLE 1**

Coefficients defining the refractive index surfaces for 5CB and MBBA (see equation (5)). Note that only the relative values of the refractive indices have been determined to the accuracy given by these coefficients. Uncertainty in the absolute values would change the value of \(a_1\) (see text).

<table>
<thead>
<tr>
<th>(n_s) surface</th>
<th>5CB</th>
<th>MBBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>1.617 3</td>
<td>1.595 7</td>
</tr>
<tr>
<td>(a_2)</td>
<td>4.629 1 \times 10^{-3}</td>
<td>1.718 3 \times 10^{-2}</td>
</tr>
<tr>
<td>(a_3)</td>
<td>-3.677 7 \times 10^{-3}</td>
<td>3.356 7 \times 10^{-2}</td>
</tr>
<tr>
<td>(a_4)</td>
<td>2.319 6 \times 10^{-2}</td>
<td>3.064 6 \times 10^{-2}</td>
</tr>
<tr>
<td>(a_5)</td>
<td>3.025 4 \times 10^{-4}</td>
<td>1.974 6 \times 10^{-3}</td>
</tr>
<tr>
<td>(a_6)</td>
<td>-3.125 5 \times 10^{-4}</td>
<td>4.745 7 \times 10^{-3}</td>
</tr>
<tr>
<td>(a_7)</td>
<td>8.222 2 \times 10^{-4}</td>
<td>1.200 9 \times 10^{-3}</td>
</tr>
<tr>
<td>(a_8)</td>
<td>-5.558 1 \times 10^{-4}</td>
<td>1.448 0 \times 10^{-3}</td>
</tr>
<tr>
<td>(a_9)</td>
<td>1.699 5 \times 10^{-4}</td>
<td>4.504 0 \times 10^{-4}</td>
</tr>
<tr>
<td>(a_{10})</td>
<td>3.623 8 \times 10^{-6}</td>
<td>1.194 8 \times 10^{-5}</td>
</tr>
<tr>
<td>(a_{11})</td>
<td>3.392 4 \times 10^{-7}</td>
<td>4.834 9 \times 10^{-6}</td>
</tr>
<tr>
<td>(a_{12})</td>
<td>-5.655 2 \times 10^{-7}</td>
<td>7.607 1 \times 10^{-7}</td>
</tr>
</tbody>
</table>

Figure 5 shows the experimental values of the refractive indices of 5CB at the clearing point, together with values computed from the surfaces evaluated along the clearing curve (4). It can be seen that the surfaces give an excellent representation of the data even in this region where they are very steep.

6. Conclusion. — We have described measurements of the two refractive indices of MBBA and 5CB throughout their nematic phase over a range of pressure and temperature, and presented the results in the form of computer fits to the experimental data. With certain approximations, both the order parameter and the density of these nematogens can be calculated from these results, so the variation of the order parameter with both temperature and density can be obtained. A forthcoming paper [15] will present the results of such calculations, and discuss their implications about the type of intermolecular forces which are responsible for the long-range orientational order in a nematic liquid crystal.

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References

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