

Classification

Physics Abstracts

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Depolarized light scattering studies of the nematogen pentyl cyanobiphenyl

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Résumé. — On a étudié par diffusion de la lumière dépolarisée un composé nématogène, le pentyl cyanobiphényle (5 CB), à l'état pur et en solution dans le cyclohexane. Trois domaines de concentration en 5 CB ont été observés. L'étude des milieux dilués a permis la détermination des paramètres moléculaires du 5 CB. L'importance relative des contributions isotropes et anisotropes de l'intensité diffusée en fonction de la concentration a été mise en évidence dans le domaine intermédiaire des concentrations. Enfin, les résultats obtenus par les solutions concentrées et le composé pur qui présentent la transition isotrope-nématique ont été analysés suivant la théorie de Landau-de Gennes. Les constantes phénoménologiques (a , T_c et T^*) de cette théorie ont été déterminées.

Abstract. — Depolarized light scattering has been used to study the nematogen pentyl cyanobiphenyl (5 CB) both in the pure state and in solution in cyclohexane. The results show three distinct concentration ranges. For dilute solutions, the molecular parameters have been determined. For intermediate concentrations, it has been possible to determine the relative contribution to the scattering of the isotropic and anisotropic components. For pure 5 CB and the concentrated solutions, an isotropic-nematic phase transition was observed, and the pretransitional behaviour has been analysed in terms of the Landau-de Gennes model. The phenomenological constants (a , T_c and T^*) of the theory have been determined.

1. **Introduction.** — Liquid crystals have evoked much interest in recent years, because of their use in optical displays, use in preparation of fibres, and possible biomedical implications. In general, liquid crystals can be defined as condensed fluid states with spontaneous anisotropy, and studies of such anisotropy lead to an understanding of their properties. This anisotropy, which derives from the magnetic, electrical and optical properties of the molecules, has been shown to vary strongly in the transition region between the isotropic phase and the mesomorphic (or liquid crystalline) phase. Such behaviour has been considered theoretically by de Gennes [1] and studied experimentally by a number of optical methods such as magnetic birefringence [2], static [3] and optical [4] Kerr effects and light scattering [5]. Of these methods all, except light scattering, rely on the application of an external field to induce a measurable anisotropy difference in the optically isotropic medium (i.e. induced order). In light scattering, the anisotropy fluctuations about a zero order parameter are studied in the absence of an external field and it is this method that is of interest in the current work.

Recently Gray, Harrison and Nash [6] synthesized a new family of room temperature nematics : the

cyanobiphenyls, and these materials were shown to be extremely stable to moisture, of high purity, optically transparent and excellent materials for electro-optic display devices [7].

Of these thermotropic compounds, we have chosen 4-n-pentyl-4'-cyanobiphenyl (5 CB) as a starting material, and being the first of the homologous series to exhibit an enantiotropic phase, its optical properties have been studied as a function of temperature for the isotropic phase and near to the nematic-isotropic transition temperature T_c . This has allowed an appraisal of the Landau-de Gennes model of phase transitions and a determination of the relevant phenomenological and material constants by the light scattering method. Further, by diluting the pure 5 CB in a suitable solvent (cyclohexane), we have been able to examine the transition behaviour and the evolution of the physical parameters as a function of concentration, i.e. lyotropic behaviour. At low 5 CB concentrations, the dilute solution molecular properties have been determined and at higher concentrations the evolution of structure leading to the mesophase has been examined both as a function of concentration and temperature. At high concentrations of 5 CB (i.e. $x > 0.9$ g/g) the solvent may be treated as an impurity and we have

studied this effect on the pretransitional behaviour and the phenomenological constants. In these measurements, which we believe to be the first by light scattering for 5 CB, we have measured both the absolute scattered light levels and the depolarized scattering intensities in order to interpret the results. The relevant theoretical and experimental considerations have also been given.

2. Experimental. — 2.1 SAMPLE AND TECHNIQUES.

— The pentyl cyanobiphenyl was a gift from B.D.H. Ltd (Poole, Dorset, U.K.) which is gratefully acknowledged. It has been used without further purification; the nematic-isotropic transition temperature T_c being within 0.05 °C of that accepted for 5 CB (i.e. $T_c = 35.1$ °C). In the solution measurements, gravimetric dissolutions were made using doubly distilled cyclohexane and concentrations x are expressed in weight of 5 CB per total weight of the solution, i.e. g/g. For the very dilute solutions, and in order to exploit the results, concentrations c in grams of solute per volume of solution are used, i.e. g/ml.

In the range of low concentrations or intermediate concentrations of 5 CB, the solutions have been clarified by centrifugation at 25 000 g for one hour. For the concentrated solutions, i.e. $x > 0.9$ g/g, the solvent was filtered and then added directly into the light scattering cell containing the solute. These measures, which are common practice in light scattering, were purely a precaution to eliminate any possibility of atmospheric dust being included in the solutions.

The measurements have been carried out using a Fica 50 apparatus at $\lambda_0 = 546$ nm (green light) normally with vertically polarized incident light. The scattered intensity I_{V_u} is given in arbitrary units relative to the intensity of light scattered by benzene (at $\theta = 90^\circ$) as reference. I_{V_u} can be converted [8] into absolute units *via* the Rayleigh ratio R_{V_u} :

$$R_{V_u} = I_{V_u} \left[\frac{R_{V_u}}{I_{V_u}} \right]_{bz} \frac{n^2}{n_{bz}^2} \quad (1)$$

where n and n_{bz} are respectively the refractive indices of the solution (or pure compound) and benzene, R_{V_u} is the Rayleigh ratio of benzene :

$$(R_{V_u})_{bz} = 22.5 \times 10^{-6} \text{ cm}^{-1}.$$

When the scattered intensity becomes very high (in the case of solutions near T_c), a neutral filter of controlled optical density ($O.D. = 0.5$ or 1) is placed in the scattered beam. We have also determined the depolarization factors such as ρ_u , ρ_v and ρ_H by analysing the polarized components of the incident and scattered beams :

$$\rho_u = \frac{H_u}{V_u}, \quad \rho_v = \frac{h_v}{v_v} \quad \text{and} \quad \rho_H = \frac{h_H}{v_H} \quad (2)$$

where H and V are the horizontally and vertically polarized incident components and h and v are the same polarized components for the scattered beam (u indicates an unpolarized scattered beam).

The variations in the scattered intensity as a function of temperature near T_c have been observed by decreasing the temperature at a rate of about 1° per minute; the temperature was measured *via* a thermocouple immersed in the scattering cell and connected to a voltmeter or a recorder.

2.2 RESULTS. — Measurements in solution. —

In order to interpret the results obtained from the scattering of the anisotropic molecules in solution, it is preferable to choose a solvent which is itself isotropic and does not scatter strongly. In the current work, we have found that cyclohexane fulfils these criteria. Further it is of a similar density to 5 CB and thus good mixing and rapid stabilization is obtained. The binary system 5 CB-cyclohexane has been studied over a wide concentration range : i.e. $5 \times 10^{-2} \leq x \leq 0.925$ g/g. The two important parameters for light scattered from the anisotropic solutions are respectively the total scattered intensity I_{V_u} (determined here with vertically polarized incident light) and the depolarization factor ρ_u . The variations of both parameters as a function of the concentration x are given in figure 1. From these results it is clear that there are three principal regions : *a) dilute solutions* ($x < 0.25$) where the scattered intensity increases rapidly and the depolarization factor ρ_u varies slowly, *b) intermediate concentrations* ($0.25 < x < 0.80$), in which range I_{V_u} increases slowly while ρ_u varies rapidly and *c) concentrated solutions* ($x > 0.80$) where the scattered light increases dramatically and ρ_u varies only slowly tending towards a value of $\rho_u = 0.87$ for $x \rightarrow 1$.

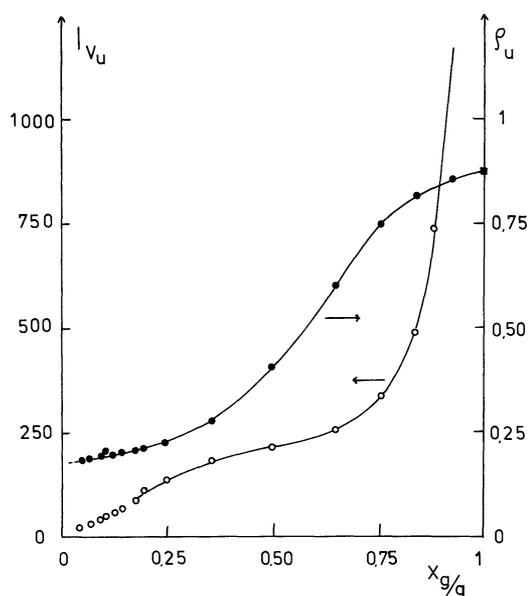


Fig. 1. — Variation of the scattered light intensity (I_{V_u}) and the depolarization ratio (ρ_u) as a function of the concentration of 5 CB in cyclohexane.

All the measurements have been carried out at $T = 25^\circ\text{C}$ which would be below the nematic-isotropic transition ($T_c = 35.1^\circ$) for $x = 1$. Consequently, the value of ρ_u for $x = 1$ given in figure 1 is obtained using the isotropic phase : $\rho_u = 0.87$ for $T = 40^\circ\text{C}$.

The dependence of the scattered intensity on the temperature in the three concentration ranges is shown in figure 2. For high concentrations (i.e. $x = 0.929$), the solutions are very near to the nematic phase and exhibit a marked pretransitional behaviour : I_{V_u} increases rapidly when the temperature decreases. For the intermediate and dilute solutions, this behaviour is not observed in the studied temperature range.

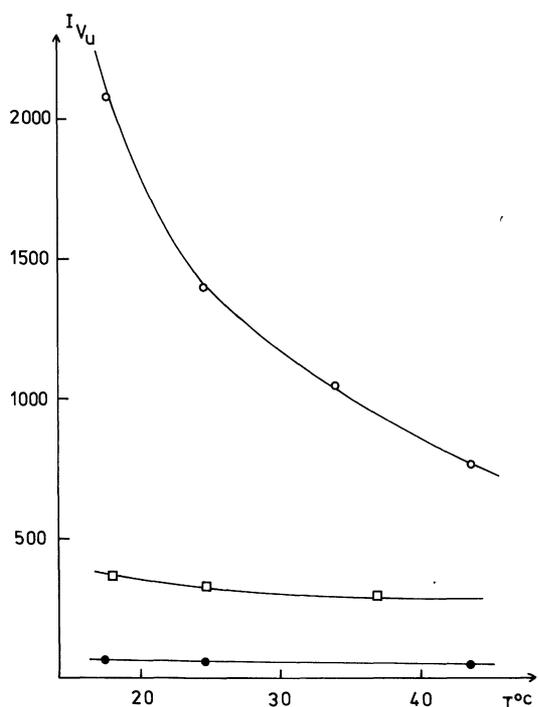


Fig. 2. — Temperature dependence of the scattered light intensity for three typical 5 CB/cyclohexane solutions : $x = 0.929$ g/g (○), $x = 0.762$ g/g (□) and $x = 0.112$ g/g (●).

Nematic-isotropic transition and isotropic phase. — The nematic-isotropic transition has been observed by light scattering with the pure compound 5 CB and also several concentrated solutions (addition of between 2 and 8 % of solvent). For these experiments, the determination of scattered intensity has been achieved by using two neutral density optical filters ($O.D. = 0.5$ and $O.D. = 1$) because of the high scattered intensity. In figure 3, we give the variations of the scattered light intensity at $\theta = 90^\circ$ as a function of temperature from the isotropic phase through the transition and into the nematic phase. These variations are obtained for the pure 5 CB (curve a) and a concentrated solution, i.e. $x = 0.985$ (curve b). These measurements are reproducible on heating.

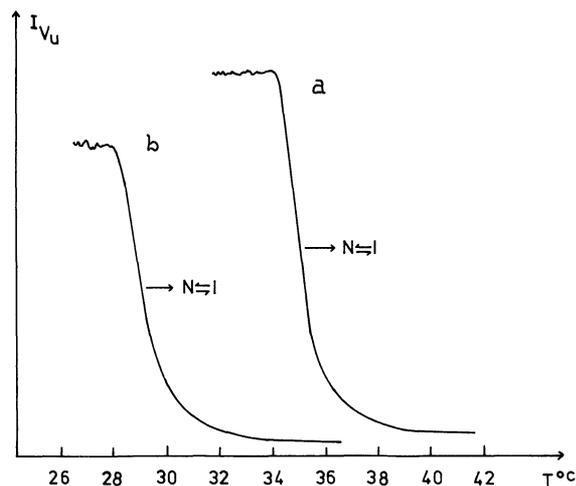


Fig. 3. — Variation of the scattered light intensity from the isotropic phase into the nematic phase for (a) pure 5 CB and (b) a nematic solution at $x = 0.985$ g/g of 5 CB in cyclohexane.

From these variations of scattered light intensity, we can determine T_c , where T_c is defined as the temperature at which the scattered intensity attains a value half way between those for the isotropic and nematic phases (see Fig. 3). The values of T_c are respectively equal to 35.1° for $x = 1$ and 29.1° for $x = 0.985$. The dependence of the transition temperature T^* on the concentration is shown in figure 4.

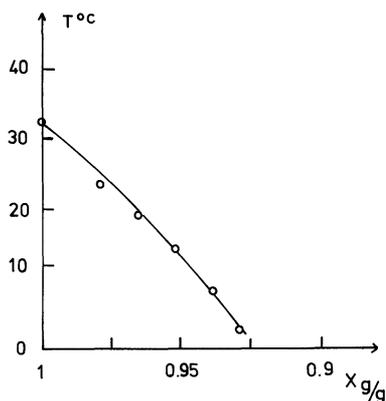


Fig. 4. — Variation of the isotropic-nematic transition temperature (T^*) as a function of concentration.

We have also determined the different depolarization factors ρ_u , ρ_v and ρ_h throughout the transition. In the isotropic phase and near to the transition, we find both ρ_h and ρ_v constant at 1 and 0.75 respectively except in the nematic phase, where ρ_h becomes greater than 1 (i.e. $\rho_h = 1.06-1.08$).

In order to determine the behaviour near the transition, the variations of the scattered intensity have been carefully determined using the isotropic phase for a temperature range of 15 to 20°C before the transition. The results given in absolute units

(i.e. the variations of the Rayleigh ratio R_{V_u} calculated from relation (1)) are shown in figure 5 for 5 CB and some of the concentrated solutions of 5 CB in cyclohexane. These curves show clearly the influence of the small amounts of added solvent on the behaviour of 5 CB in the region of the nematic-isotropic transition.

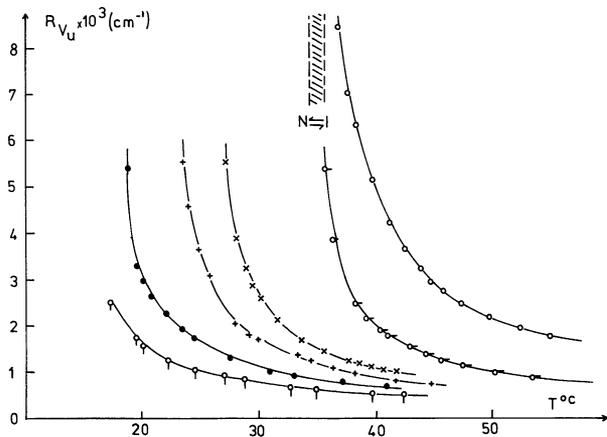


Fig. 5. — Pretransitional behaviour of the scattered light of the pure compound (O) and the concentrated solutions where $x = 0.938$ (○); 0.951 (●); 0.965 (+); 0.979 (×) in g/g and for a trace amount of cyclohexane (O—).

3. Discussion. — 3.1 DILUTE SOLUTIONS AND INTERMEDIATE CONCENTRATIONS. — We can consider the intensity of scattered light to be a result of several contributions [8] : the first R^{iso} due to the fluctuations in density (or in density and concentration for binary systems) and the second R^{ani} due to the fluctuations in orientation :

$$R_{V_u} = R_{V_u}^{iso} + R_{V_u}^{anis}$$

or

$$R_{V_u} = R_{V_u}^{iso} \frac{6}{6-7\rho_u} \quad (3)$$

where ρ_u is the depolarization factor in unpolarized incident light and $R_{V_u}^{iso}$ the isotropic contribution to the scattered light if measured with vertically polarized incident light.

In the case of very dilute solutions, we have analysed the results according to the classical method of measuring the variations of the ratio $K \cdot \frac{c}{\Delta I^{iso}}$ as a function of the concentration c (in $\text{g} \cdot \text{ml}^{-1}$); K is the optical constant which is a function of the wavelength λ_0^{-4} , the refractive index increment dn/dc (for this system, dn/dc was measured using a Brice-Phoenix refractometer and a value of $0.161 \text{ ml} \cdot \text{g}^{-1}$ was determined for $\lambda_0 = 546 \text{ nm}$), and also of the Rayleigh ratio of benzene, because $(\Delta I)^{iso}$ which represents the isotropic part of the intensity scattered by the solute is given in arbitrary units (see relation (1)).

In very dilute solutions, we can write :

$$K \frac{c}{\Delta I^{iso}} = \frac{1}{M} + 2 A_2 c + \dots$$

where M is the molecular weight of the solute (5 CB) and A the second virial coefficient of the osmotic pressure. The variations of $K \frac{c}{\Delta I^{iso}}$ versus concentration are given in figure 6 and lead (after extrapolation to $c \rightarrow 0$) to a molecular weight of 230 while the

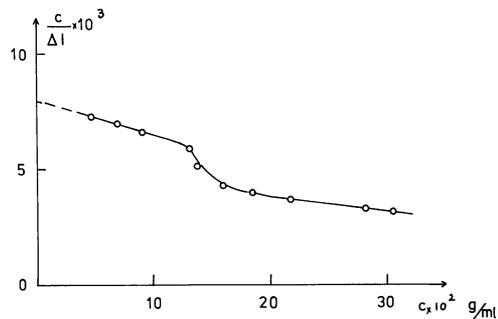


Fig. 6. — Variation of $c/\Delta I$ for dilute solutions of 5 CB in cyclohexane.

calculated molecular weight is 237. From the initial slope of this curve, a value of

$$A_2 \sim -4 \times 10^{-3} \text{ mol} \cdot \text{ml} \cdot \text{g}^{-2}$$

is obtained. The negative sign indicates a preference of the liquid crystal molecules for their own kind, and it is presumably this that gives rise to the discontinuity at $c = 13 \times 10^{-2} \text{ g} \cdot \text{ml}^{-1}$. This concentration probably marks the onset of correlation [5b] or association between the 5 CB molecules in solution.

For all the concentrations, we have also determined both contributions to the scattering, i.e. $R_{V_u}^{iso}$ and $R_{V_u}^{ani}$ as a function of the concentration x in g/g (Fig. 7). $R_{V_u}^{iso}$ presents a maximum for $x = 0.35$ then decreases rapidly to attain very low values ($\sim 10^{-5} \text{ cm}^{-1}$) for the very concentrated solutions and for pure 5 CB. This behaviour is typical of binary systems of small molecules [9]. The dotted line in figure 7 connecting the values of $R_{V_u}^{iso}$ obtained respectively for cyclohexane and 5 CB represents, to a first approximation, the contribution of the density fluctuations to the scattering. Consequently it is possible to determine the contributions due to concentration fluctuations and to calculate, in principle, the thermodynamical properties (chemical potential and free energy of the system).

The behaviour of the anisotropic scattering $R_{V_u}^{ani}$ is very different : $R_{V_u}^{ani}$ increases continuously to attain very high values for the concentrated solutions. This result is noteworthy, because as is shown in figure 7, the isotropic part $R_{V_u}^{iso}$ can be neglected relative to $R_{V_u}^{ani}$ in the macroscopically isotropic

phase near the transition, and then specifically ρ_v should be equal to 0.75. This point was experimentally verified.

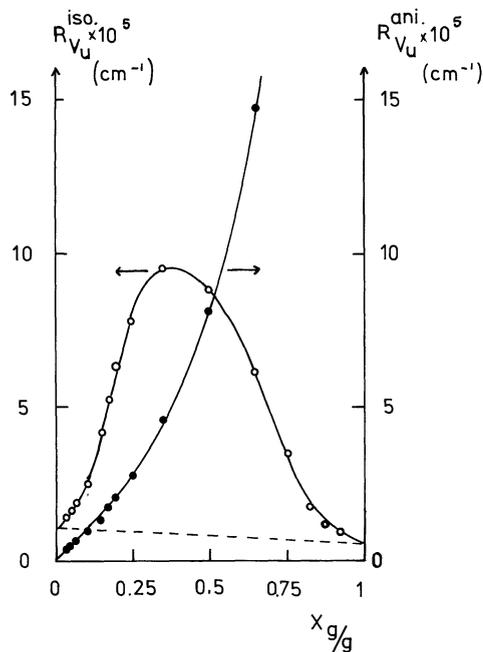


Fig. 7. — Variation of the isotropic and anisotropic contributions to the light scattering as a function of concentration.

3.2 ISOTROPIC PHASE NEAR THE NEMATIC-ISOTROPIC TRANSITION. — The results previously presented for pure 5 CB and concentrated solutions ($x \geq 0.93$ g/g), figure 5, have been analysed using the phenomenological de Gennes theory [1] of the isotropic-nematic transition. This theory, based on cooperative pre-transitional effects dominated by short range order, expands to the excess free energy F as a function of the scalar order parameter Q such that :

$$F = \frac{1}{2} a(T - T^*) Q^2 - \frac{b}{3} Q^3 + \frac{c}{4} Q^4 + \dots$$

where a , b and c are phenomenological constants characteristic of the transition. T^* is the second order transition temperature that the system would have in the absence of the intervening weak first order transition that occurs at the clearing temperature T_c .

In the case of light scattering the value of Q in the isotropic phase is zero. However fluctuations about this zero order parameter give rise to the anomalous scattering of light in the pretransitional region and it can be shown for vertically polarized scattered light and vertically polarized incident light that :

$$R_{Vv} = \frac{8 \pi^2}{27 \lambda_0^4} \frac{(\Delta\epsilon)_0^2}{a} \frac{kT}{(T - T^*)}$$

and for the horizontally polarized scattered light and vertically polarized incident light that :

$$R_{Vh} = \frac{4 \pi^2}{18 \lambda_0^4} \frac{(\Delta\epsilon)_0^2}{a} \frac{kT}{(T - T^*)}$$

Consequently :

$$R_{Vu} = \frac{14 \pi^2}{27 \lambda_0^4} \frac{(\Delta\epsilon)_0^2}{a} \frac{kT}{(T - T^*)} = \frac{T}{p_{Vu}(T - T^*)}$$

where k is the Boltzmann constant and $(\Delta\epsilon)_0$ is the dielectric anisotropy of optical frequencies for a fully aligned system. Note also from the above and previous definition that $\rho_v = 0.75$.

From the relationship for R_{Vu} , and if the mean field theory is applicable, a graph of T/R_{Vu} versus T should be linear and allow T^* (from the intercept) and a (from the slope p_{Vu}) to be determined. Figure 8

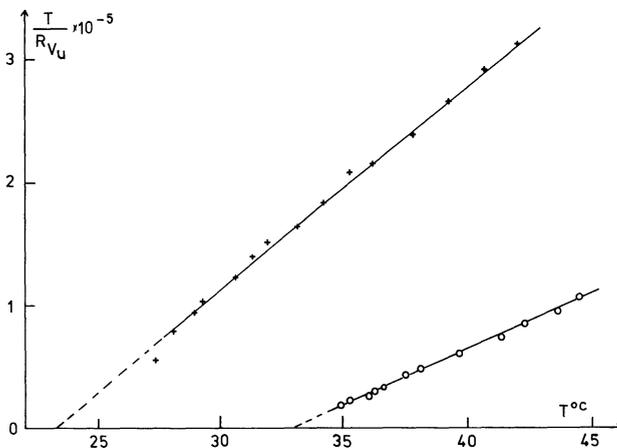


Fig. 8. — Variation of the ratio T/R_{Vu} as a function of temperature for pure 5 CB (O) and $x = 0.965$ g/g (+).

gives this representation, i.e. T/R_{Vu} versus T for the pure 5 CB and for a typical solution with

$$x = 0.965 \text{ g/g,}$$

and as can be seen from this figure the de Gennes theory was upheld. This was true not only for the pure compound, but also for all of the concentrated solutions for $x \geq 0.93$ g/g, and thus T^* and the

Table I. — Summary of results for 5 CB ($x = 1$) and concentrated 5 CB solutions.

Concentration x (g.g ⁻¹)	T_c (K)	T^* (K)	$p_{Vu} \times 10^4$	$\frac{a}{(\Delta\epsilon)_0^2}$	
				$\times 10^5 \text{ cm}^{-3} \text{ erg.K}^{-1}$	
—	—	—	—	7.28	12
1	307.4	306	0.92	7.28	12
0.979	300.1	296.2	1.72	13.67	22.5
0.965	294	292.2	1.67	13.24	21.8
0.951	—	287.4	1.76	14.0	23
0.938	—	283.0	1.76	13.9	22.9

slope p_{vu} were determined. These values, together with those for T_c and the calculated values of $\frac{a}{(\Delta\epsilon)_0^2}$ and a are listed as a function of concentration in table I. In calculating a we have used a value of $(\Delta\epsilon)_0^2 = 1.648$ deduced from refractive index measurements [10], and used the relationship $\Delta\epsilon_0 = 2n\Delta n$ for $\lambda_0 = 546$ nm. $(\Delta\epsilon)_0$ was assumed constant for the concentrated solutions.)

From these results, it would appear that the addition of small amounts of impurity rapidly reduces the transition temperature T_c and theoretical second order transition temperature T^* and, as shown in figure 4, leads to a limited phase diagram for the 5 CB-cyclohexane system. Further the rate of transition as indicated by p_{vu} near the transition temperature T_c increases on addition of the cyclohexane. Far from T_c , i.e. $T - T_c > 20$ °C, a departure from linearity might be expected as the liquid crystal or concentrated solution behaves more like a classical liquid. Although not studied in the current work, we have observed such behaviour with heptyl cyanobiphenyl, a closely related system, and similar results with Nematel 105 were obtained by the optical Kerr effect [11] far from the transition.

Finally the value of $a = 12 \times 10^5 \text{ cm}^{-3} \text{ erg} \cdot \text{K}^{-1}$ is in good agreement with a value of

$$13 \times 10^5 \text{ cm}^{-3} \text{ erg} \cdot \text{K}^{-1}$$

determined by the electrical and optical Kerr effect [12] and of between 10 and $14 \times 10^5 \text{ cm}^{-3} \text{ erg} \cdot \text{K}^{-1}$ determined from viscosity [13] and acoustical absorption methods [14]. Thus the method, despite its inherent simplicity, leads to a reliable determination of the static pretransitional characteristics of liquid crystalline phase transitions.

4. Conclusion. — The nematogen 5 CB has been studied both in solution in cyclohexane and in the pure state by light scattering, and this has allowed three principal regions of study to be established: dilute solution, intermediate concentrations and concentrated solutions. Absolute light scattering values *via* the Rayleigh ratios and depolarized scattering ratios were determined.

For the dilute solutions, it was possible to determine both the molecular weight of 5 CB and the second virial coefficient A_2 . After a critical concentration ($x \sim 0.13$ g/g), aggregation or association phenomena were observed and the depolarized light scattering increased rapidly, while the total light scattering varied only slowly. Finally for concentrated solutions sufficient structure exists in the solutions for a nematic phase to be exhibited in cooling the solutions. The Landau-de Gennes phenomenological theory was found to be applicable for both pure 5 CB and concentrated solutions and the constants of this theory were evaluated. From the variations of T^* with concentration, a phase diagram was established to illustrate the influence of small amounts of solvent on the transition characterization. The phenomenological constant a was invariant for all the highly concentrated solutions but different from that value found for pure 5 CB. In the Landau-de Gennes theory, the constant a has no apparent molecular significance other than to describe the free energy characteristics of the transition. However, only 2% of cyclohexane markedly changed its absolute value, and as Kerr effect measurements [12] recently established that the constant a is a function of molecular structure for the cyanobiphenyls, we propose to examine this behaviour further for concentrated solutions and as a function of molecular structure.

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