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The Order-Disorder Phase Transition in Liquid Crystals as a Function of Molecular Structure. I. The Alkyl Cyanobiphenyls

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The pretransitional behaviour of a homologous series of mesomorphic compounds, the alkyl cyanobiphenyls ($CN\phi\phi C_nH_{2n+1}$) for $n = 5-12$, has been studied as a function of temperature by light scattering in the isotropic phase. The higher homologues, $n = 8-12$, exhibit a smectic *A* phase that becomes increasingly important at the expense of the nematic phase for increasing n and for $n = 10$ and 12 no nematic phase is observed. We have shown from light scattering and differential scanning calorimetry measurements that the presence of the smectic *A* phase changes markedly the pretransitional behaviour, and gives rise to two distinct pretransitional regions. The first region is for temperatures greater than ~3°C above the clearing temperature T_c where the systems exhibit a typical pretransitional behaviour adequately described by the phenomenological Landau–de Gennes model of a second order phase transition with an intervering first order transition at T_c. The constants of this model for this region are given and show a distinct odd-even effect. The second region is close to T_c where a strong divergence from the already critical behaviour is observed. This secondary divergence is observed to be a function of the alkyl chain length and its conformation, and is attributed to coupling between smectic *A* like layers and the orientational order parameter in the isotropic phase.

INTRODUCTION

Above the "isotropic-nematic" transition temperature liquid crystals exhibit a variety of anomalous effects due to strong orientational correlations (or short range order) existing in the isotropic phase. These anomalous effects which have been observed by a variety of methods[1] are essentially precursors of the mesomorphic phase that may be formed below the clearing

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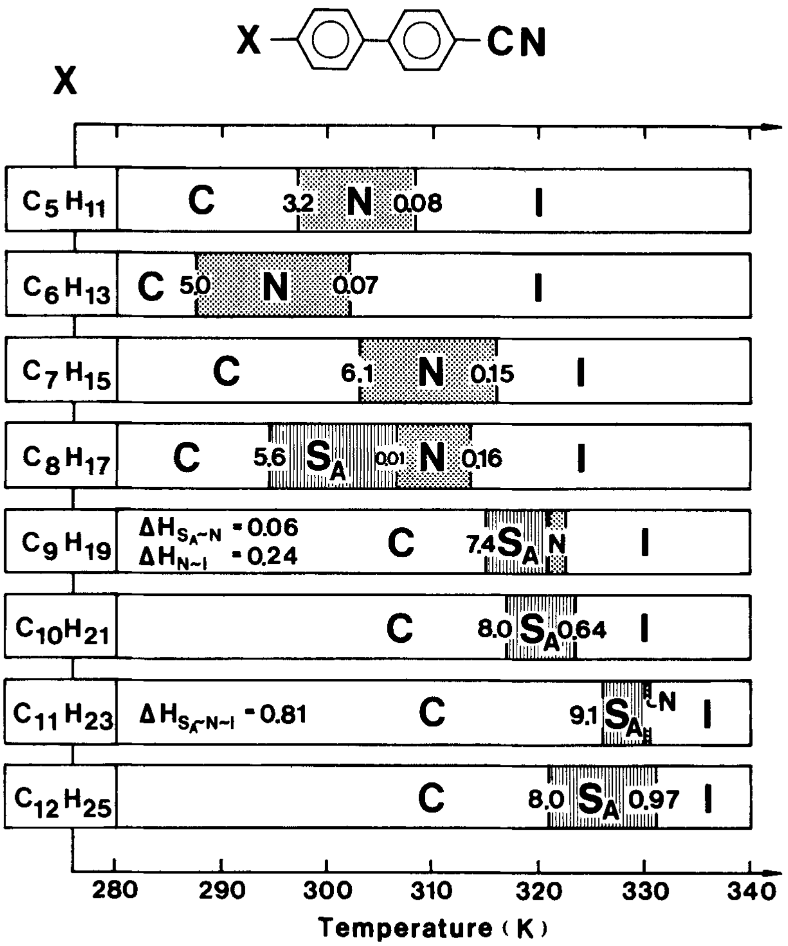

FIGURE 1 Transition temperatures and heats of transition (kcal. mol^{-1}) for the cyanobiphenyl homologues from the DSC measurements.

temperature T_c. Indeed it has been shown, using the Landau–de Gennes phenomenological model,[2] how the behaviour in the isotropic phase is related to that in the nematic phase just below T_c^3. Whilst recent literature shows that this theory is applicable to a variety of liquid crystal species very few systematic studies have been carried out within a homologous family[4,5] to examine how changing the molecular structure might affect the pretransitional characteristics and therefore be related to the behaviour in, or type of, mesophase formed.

It is the purpose of the present work to examine the pretransitional behaviour in the alkyl cyanobiphenyl (*n* CB) family[6] of liquid crystals as a function of the alkyl chain length, and in terms of the Landau–de Gennes model. We have studied the series from $n = 5$ to 12 by both light scattering and differential scanning calorimetry. The results for 12CB are essentially those reported in a preliminary note on this work.[7] With these materials a smectic A phase is observed[8] for 8CB and higher homologues, and generally as the length of the alkyl chain is increased the range of the nematic phase is reduced as shown in Figure 1, and for 10 and 12CB a direct smectic A—isotropic phase transition is observed. The influence of this smectic A phase on the pretransitional behaviour has been examined in detail and leads us to the conclusion that smectic A type *cybotactic* groups do exist in the isotropic phase, and that their creation is marked by a rapid divergence, in their light scattering properties, from that observed for the isotropic-nematic transition.

EXPERIMENTAL

The cyanobiphenyls used in these studies were provided by BDH Ltd. (Poole, Dorset, U.K.). Samples were used directly from their sealed containers and their transition temperatures measured herein, see Figure 1, agree well with those accepted for these products.[9] Thus no further purification was attempted.

The light scattering measurements were carried out using a FICA 50 light scattering apparatus at $\lambda_0 = 546$ nm and with vertically polarised incident light. The calibration procedure, utilisation of the apparatus and method of exploitation of results for liquid crystals have been given in greater detail elsewhere.[10] Measurements reported herein are given directly in absolute units i.e. via the Rayleigh Ratio R_{V_u} where V refers to vertically polarised incident light and u to unpolarised scattered light. The scattered light levels recorded were generally of the order of 10 to 10^2 times that scattered from pure benzene as reference and thus in our range of measurements effects due to turbidity were negligible. Temperature measurements were carried out using a calibrated thermistor immersed in the liquid crystal in the scattering cell, and the transition temperatures are given in Figure 1. Refractive index measurements were carried out in the isotropic phase using an Abbe refractometer with a thermostated sample stage. The heats of transition were measured using a Perkin Elmer DSC 2 differential scanning calorimeter and the results standardised against Indium.

RESULTS

The mesomorphic-isotropic transition has been observed by light scattering for the pure compounds from pentyl to dodecyl cyanobiphenyl (i.e. 5 to 12CB). The light intensities were measured at a scattering angle $\theta = 90°$ as a function of temperature in the isotropic phase through to the mesomorphic phase. Very close to the transition at T_c, i.e. $T - T_c \sim 0.2°C$ the scattered light levels become extremely large and it is difficult to give absolute values of R_{V_u} without taking into account multiple scattering or turbidity. Thus we have not given values determined in this range. For the maximum values of R_{V_u} reported the turbidity effect contributes approximately 1% and its effect has been neglected herein. The results have been expressed directly as T/R_{V_u} as a function of temperature and are given in Figure 2. Over our range of measurement it was verified also that the depolarised scattering factors ρ_h and ρ_V were equal to 1 and 0.75 respectively (see later) for each material. In order to exploit further the results we have measured the mean refractive indices in the isotropic phase (at $T - T_c \sim 5°C$) at the scattering wavelength and these are given in Table 1. The heats of transition are given in Figure 1 as a function of the alkyl tail length.

DISCUSSION

I Isotropic-nematic phase transition

Before discussing in detail the results it is necessary to consider the possible contributions to the intensity of scattered light. These can be considered in two classes; that arising from the fluctuations in density namely the isotropic scattering and that arising from the fluctuations in orientation or the anisotropic scattering. As was shown in detail for 5CB,[10] for the pure material, only the anisotropic scattering is important over the temperature ranges considered (i.e. $T - T_c \sim 10$–$20°C$), and it is this that gives rise to the depolarisation factors ρ_h and ρ_V equal to 1 and 0.75 respectively. Thus for all materials studied herein the scattering in the pretransitional region comes from the spontaneous orientational fluctuations about a zero order parameter for the optically isotropic media and this justifies the use of the Landau–de Gennes model[2] in characterising the transition.

In this model, based on cooperative pretransitional effects dominated by short range order, the excess free energy F is expanded as a function of the scaler order parameter Q such that:

$$F = \frac{a}{2}(T - T^*)Q^2 - \frac{b}{3}Q^3 + \frac{c}{4}Q^4 + O(Q^5) \tag{1}$$

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

TABLE I

Molecular parameters and phenomenological constants for the cyanobiphenyl homologues, as determined by light scattering.

n − CB	Units	5	6	7	8	9	10	11	12
$T_c(N,S_A - \mathrm{I})$	°C(±0.2)	34.3	30.1	42.6	40.2	49.2	50.5	59.0	58.2
$T^*(N - I)$	°C(±0.2)	32.9	28.7	41.5	38.2	48.7	45.7	55.1	49.7
$L(N,S_A - I)$	J.kg^{-1}(±2%)	1.42	1.11	2.30	2.45	3.43	8.78	10.6	12.1
n	—	1.5828	1.5748	1.5668	1.5638	1.5545	1.5500	1.5432	1.5400
Δn	—	0.402	0.378	0.363	0.336	0.316	0.295	0.274	0.253
$(\Delta\varepsilon)_0^2$	—	1.619	1.417	1.277	1.104	0.965	0.836	0.715	0.607
P_{V_u}	$\times 10^{+2}$m(±3%)	0.92	1.70	2.39	2.14	3.33	2.80	4.35	4.20
a	$\times 10^4$Jm^{-3}K^{-1}(±1)	12	19	24	19	26	19	25	20
Q_c^p	(±0.02)	0.28	0.20	0.25	0.29	0.29	0.54	0.50	0.61
Q_c^m	—	0.27	0.25	0.27	0.30	—	—	—	—

temperature T_c. Further evidence of the weakness of this first order effect is given by the relatively small values of ΔH recorded for the isotropic-mesomorphic transition in comparison with those recorded for the mesomorphic-crystal transition, Figure 1. From the original derivations[2] the latent heat ΔH of the nematic-isotropic transition is given by:

$$\Delta H = \frac{a}{2} T_c \cdot Q_c^2 \tag{2}$$

where Q_c is the order parameter at T_c. The above development also assumes the mean field theory is applicable, a fact that was verified by both the laser and electric field Kerr effects for 5 to 8CB.[5]

As noted above the value of Q is zero in the isotropic phase and it is fluctuations about this zero order parameter that gives rise to the anomalous scattering of light in the pretransitional region. This anomalous scattering increases as the transition is approached and following the Landau-de Gennes model this behaviour may be expressed via the Rayleigh ratio R_{V_u} where:

$$R_{V_u} = \frac{14}{27} \frac{\pi^2}{\lambda_0^4} \frac{(\Delta\varepsilon)_0^2 kT}{a(T - T^*)} = \frac{T}{P_{V_u}(T - T^*)} \tag{3}$$

k is the Boltzmanns constant, and $(\Delta\varepsilon)_0$ is the dielectric anisotropy at optical frequencies for a fully aligned system. Thus a graph of T/R_{V_u} should be a linear function of T the intercept defining T^* and the slope P_{V_u} giving the sharpness of the transition as a function of temperature and also allowing $a/(\Delta\varepsilon)_0^2$ to be determined. Thus knowing $(\Delta\varepsilon)_0$ a can be directly determined.

From Figure 2 and for the homologues 5–7CB the Landau-de Gennes model can be seen to be upheld over the temperature range studied. However starting with 8CB and progressing up to 12CB a marked departure from linearity is observed near to the transition, this departure being the most marked for 11 and 12CB. At temperatures sufficiently elevated the theory is upheld, which also implies the applicability of the mean field theory. The departure from linearity will be discussed below. From the slope of the linear region $a/(\Delta\varepsilon)_0^2$ has been determined as a function of n, Figure 3, from which it is clear that the odd-even effect observed in the transition temperatures T_c and T^*, and the viscosity coefficient ν for the homologues 5–8CB[5] is also seen in $a/(\Delta\varepsilon)_0^2$. This latter parameter essentially describes the rapidity (as a function of temperature) with which the light scattering varies near to the transition. Thus for the higher homologues the transition is more abrupt than for the lower members. This feature could be useful for improving display services that rely on a smectic A to isotropic phase transition by heating to change the optical properties of the device.[11]

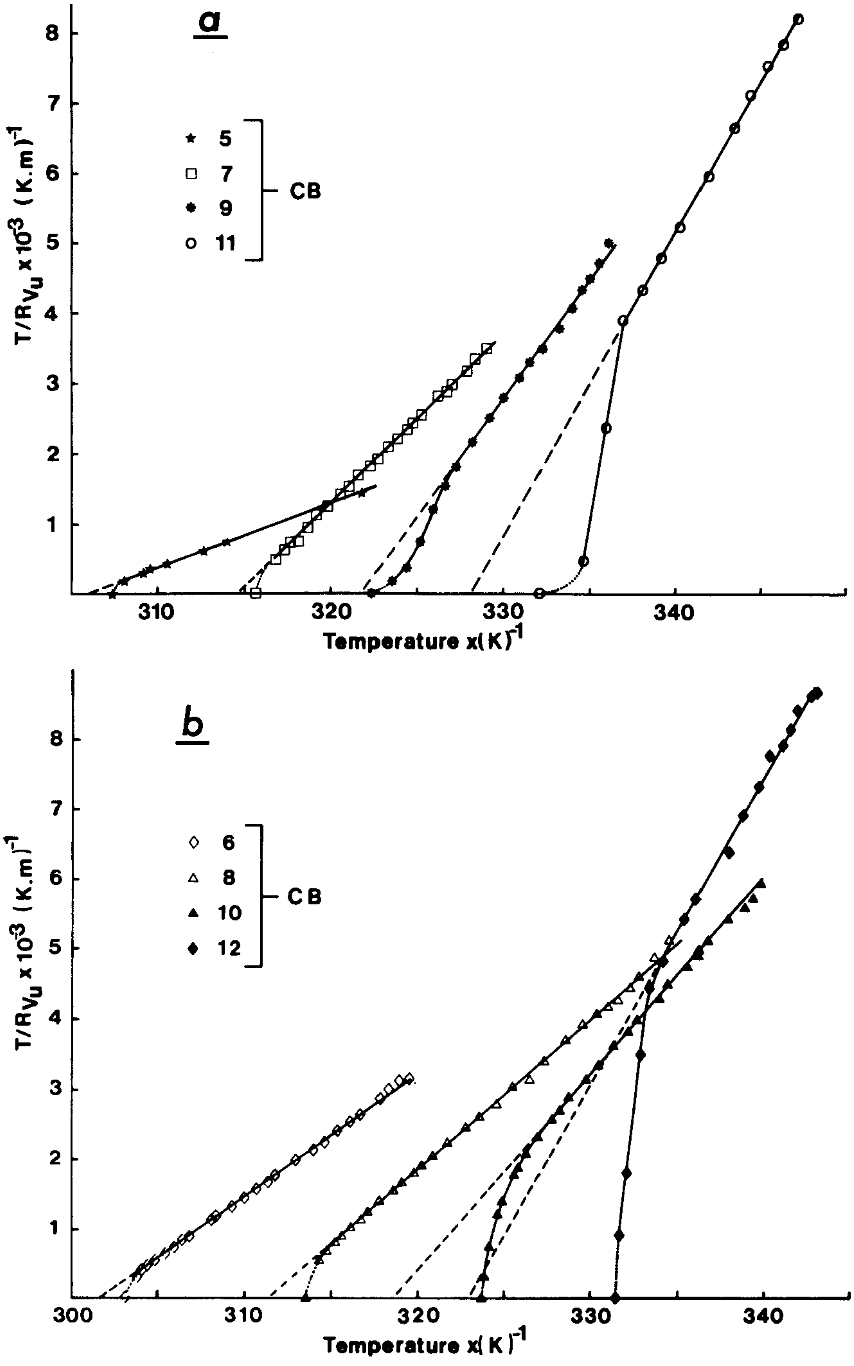

FIGURE 2 Inverse light scattering as a function of temperature for the odd (a) and even (b) homologues. The dotted curves represent the extrapolation from the measured values to the transition temperatures (T_c).

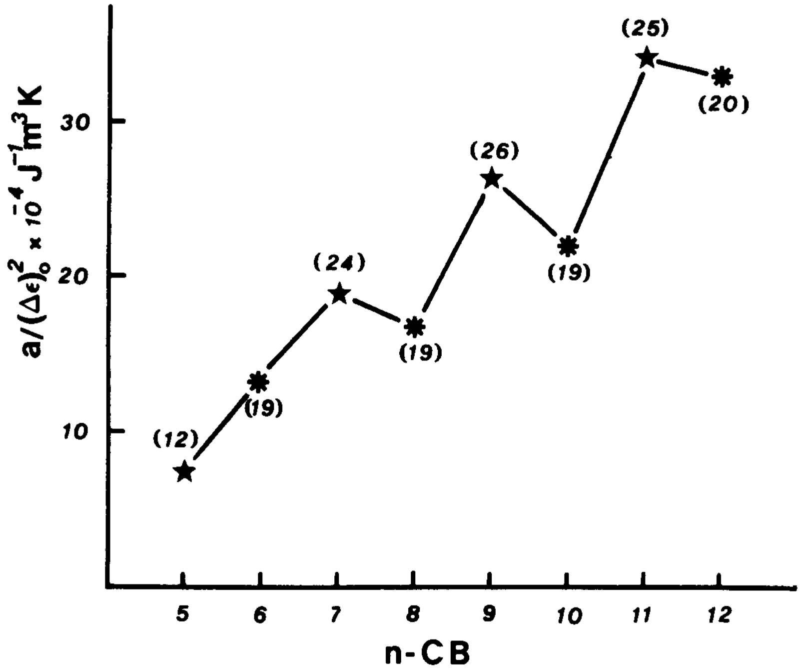

FIGURE 3 Dependence of $a/(\Delta\varepsilon)_0^2$ on the alkyl chain length. Figures in brackets represent the calculated values of *a*.

In order to determine *a* we have used the values of $(\Delta\varepsilon)_0^2$ given in Table 1. These values have been determined assuming $(\Delta\varepsilon)_0^2 = 4n^2\Delta n^2$ where *n* is the mean refractive index and Δn the refractive index anisotropy for a perfectly ordered system. The values of *n* have been determined herein and the values of Δn have been taken from existing refractive index anisotropy and order parameter data[12] for 5–8CB at the measuring wavelength of $\lambda_0 = 546$ nm. Following the linear dependence, within the experimental uncertainty, of Δn on the number carbon atoms in the alkyl tail we have extrapolated Δn for 9–12CB. From Table 1 the values of *a* can be seen to be approximately constant but different for the odd and even series with the exception of 5CB. These values are in good agreement with those determined by the electric field Kerr effect[5] for 5–8CB. In the case of 5CB which is the first of the alkyl cyanobiphenyls to show a stable mesophase the value of *a* is also in good accord with that of between 10 and 14 × 10^4 $Jm^{-3}K^{-1}$ determined by viscosity[13] and acoustical absorption[14] methods respectively. The value of 7CB is however higher than that recorded independently by magnetic and electric field birefringence[15] where a value of 19 × 10^4 $Jm^{-3}K^{-1}$ was recorded. However given the different approximations used in these authors' calculations and those above the agreement between the two methods is reasonable. In the current work the assumptions and approximations made in the calculations are consistent for all members of the series and thus while an overall uncertainty of up to 10% is possible in the absolute value the comparison between members of the same family should be valid. The constancy of, but the difference between the *a* values for the odd and even members suggests that above a certain number of carbon atoms in the alkyl chain it is not the length that characterises the isotropic to nematic like pretransitional behaviour but the conformation of the terminal links. Because of the phenomenological nature of the model it is difficult to take this analysis further as *a* is a mathematical constant describing the characteristics of the transition and would appear to have no physical meaning. Nonetheless the model does allow the resolution of a clear odd-even effect in the constant *a* as a function of alkyl chain length.

II Influence of the smectic A phase on the isotropic-nematic phase transition

However, and much more importantly, where the alkyl chain length and the odd even effects are critical is in the type of mesomorphic structure observed, the existence of different types of mesophase, their transition temperatures and influence on the pretransitional behaviour. For the alkyl cyanobiphenyls the former properties i.e., mesophase type, transition temperatures and latent heats are summarised in Figure 1, and the influence of the smectic *A* phase on the pretransitional behaviour in the isotropic phase very close to the transition is clearly demonstrated in Figure 2. As the smectic *A* phase progresses in temperature towards the nematic-isotropic transition temperature the divergence from the Landau–de Gennes model becomes more and more marked for both the odd and even series. For the 11 and 12CB members the divergence is so abrupt as to appear as a critical temperature within the isotropic phase several degrees above T_c. As noted above far enough away from the transition the phenomenological constant *a* is invariant within the odd or even series and the transition behaves as though it were typically isotropic-nematic like. Following the Landau–de Gennes model the ordering is one dimensional for the isotropic-nematic transition and can be used to predict the order parameter Q_c at the clearing temperature from the latent heat of transition ΔH and the constants *a*, and T_c, see Eq. (2). These predicted values Q_c^p are given with those extrapolated from the temperature dependence[12] of Q for 5–8CB in Table I (i.e. Q_c^m). The agreement is in general good and justifies the predictions for 9–12CB. However for 10–12CB the predicted order parameter approximately doubles in magnitude and we believe this is in fact a reflection on the two dimensional order that exists in the smectic *A* phase and that these order parameters are fictitious. They are also higher than those observed in the smectic *A* phase for 8 and 9CB by Dunmur *et al.*[4] Thus the extra transition energy is being used not to produce a higher one dimensional order but a two dimensional or layer like structure in the pretransitional region. This observation is confirmed by our preliminary X-ray measurements[7] carried out in the smectic *A* and isotropic phases for 12CB, and by those carried out in the nematic phase for the smectic A-nematic transition in 8CB and 8 OCB.[15]

The appearance of a two dimensional order in the nematic phase for a smectic *A*–nematic transition was considered by de Gennes[16] who postulated a smectic *A* order parameter (ψ) related to a density wave perpendicular to the smectic layers. A free energy expansion of the Landau type was then proposed as a function of this parameter ψ. The periodicity of this function ψ is the layer thickness which we have measured by X-ray scattering to be 38.5 Å in the smectic *A* phase and 37.7 Å in the isotropic phase.[7] Such dimensions are normally too small to be observed directly by light scattering at a wavelength of 5460 Å. However as was recently pointed out[17] coupling between fluctuations in the orientational (nematic) and smectic order parameters (i.e. Q and ψ respectively) should allow the indirect observation of the smectic *A* characteristics in the pretransitional behaviour by light scattering in the isotropic phase. This indeed was observed[17] for the direct smectic *C*-isotropic transition with the undecyl member of the dialkoxybenzenes. We believe the results reported herein are the first observations of this behaviour for the direct smectic *A*-isotropic transition for which the theory was originally developed. Further in the current work this has been studied as a function of the alkyl chain length for the complete range of alkyl cyanobiphenyls available. Following Ref. 17 and allowing for the cross coupling then for our experimental conditions it can be shown that:

$$\frac{T}{R_{V_u}} = \frac{27\lambda_0^4}{14\pi^2 k(\Delta\varepsilon)_0^2}\left[a(T - T^*) - \frac{\gamma k T}{\alpha_0(T - T_s^*)}\right] \tag{4}$$

where a and T^* are as previously defined, α_0 and γ are phenomenological constants related to the smectic *A* order parameter and the cross coupling respectively. Based on the Landau–de Gennes model and the mean field theory T_s^* is an assumed critical temperature of the smectic *A* second order phase transition. Thus α_0 and T_s^* are analogous to a and T^* but allow for the two dimensionality of the model.

By comparison between the equations presented above it can be seen that the pretransitional behaviour can be considered as being composed of two independent terms in the light scattering, one due to the nematic characteristics of the transition and the other due to short range smectic order parameter fluctuations and the coupling characteristics. Within the odd or even homologous series it was shown above that a is constant and thus for each of the series 7, 9, 11CB and 6, 8, 10, 12CB the nematic characteristics are identical (i.e. $a(T - T^*)$). Therefore subtraction of the nematic contribution from the scattering (when normalised by the $(\Delta\varepsilon)_0^2$ term) for the odd and even series indicates the evolution of the influence of the smectic A phase on the pretransitional behaviour. This has been shown in Figure 4 as a function of $T - T^*$.

From Figure 4 it is evident that as the alkyl tail length is increased the influence of the smectic A phase becomes more important for the pretransitional behaviour. As indicated by the temperatures given by the intersection of the curves with the $T - T^*$ axis the point of departure from a nematic-isotropic type behaviour moves regularly away from T^*. Further for the higher homologues $\Delta[T/R_{V_u}]$. $(\Delta\varepsilon)_0^2$ varies sharply both in magnitude and as a function of temperature and it is this that gives the appearance of a critical temperature for the onset of the influence of the smectic A phase in the isotropic phase. This region also corresponds, from the X-ray scattering

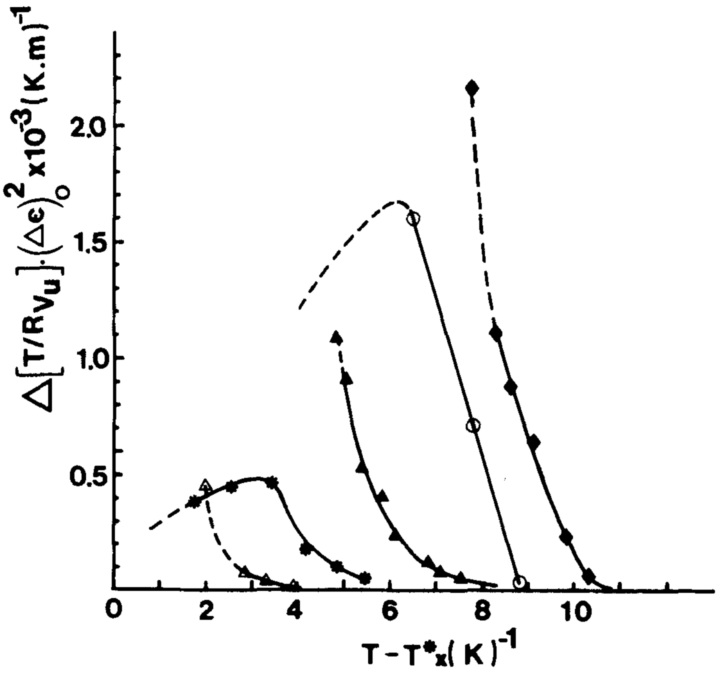

FIGURE 4 Contribution to the scattering in the pretransitional region due to the presence of the smectic A phase for : 8(△), 9(✱), 10(▲), 11(○) and 12CB(◆). The dashed lines correspond to the extrapolations indicated in Figure 2.

on 12 CB[7] to a relatively sharp increase of 10% in the interlayer spacing with decreasing temperature. Thus the range of the ψ order parameter fluctuations must also increase and this is in accord with the light scattering observations. However following reference 2 it would be expected that the light intensity scattered would vary as the square of the coherence length and a 10% change in layer thickness alone is not sufficient to account for the large changes in light scattering in this region. Two other additional mechanisms are possible: either the number of the *cybotactic* groups increases or their size also increases due to the addition of further molecules into the groups. Light scattering alone cannot resolve this question. For 10 and 12CB, the two materials that give a direct smectic *A* to isotropic transition, the curves can be reasonably well fitted to the above theoretical formula from which the order of magnitude values of γ/α_0 and T_s^* were determined. These are listed in Table 2 with those already determined for T_c and T^*. From this table it can be seen that the theoretical second order smectic *A* transition (T_s^*) occurs at higher temperatures than the theoretical second order nematic-isotropic transition (T^*). In the cases of 9 and 11CB the curves show an inflection and the theory cannot be fitted to the results. This is presumably related to the fact that in these two cases the isotropic-smectic *A* transition is not direct but is interrupted by a nematic phase of short temperature range and thus the above expression is over simplified and should contain extra terms related to the orientational (nematic like) order parameter Q. If this were true then such terms involving the coefficients b and c of Eq. (1) would have to be included for both the even as well as the odd members of the series. That an inflection is not observed for the even series would suggest that these coefficients are smaller for the even series than for the odd members (which would also follow the behaviour in a), although this prediction remains to be verified. None the less these results also follow an odd-even effect, the 10 and 12CB's giving a direct smectic *A*-isotropic transition, whereas 9 and 11CB do not which must be linked to the orientation of the terminal links.

Finally it is worth commenting on the first and second nature of these transitions. From the pretransitional effects recorded above far from the transition the Landau-de Gennes model for nematic isotropic phase transi-

TABLE II

Experimental and theoretical transition temperatures and the phenomenological constants associated with the direct smectic *A*-isotropic phase transition.

n − CB	$\frac{\gamma}{\alpha_0} \times 10^{-3} \mathrm{m}^{-3} \mathrm{J}$	$T_c(K)$	$T_s^*(K)$	$T_c - T_s^*(K)$	$T^*(K)$	$T_c - T^*(K)$
10CB	1	323.6	323.4	0.2	318.8	4.8
12CB	2	331.3	330.5	0.8	322.8	8.5

tions is upheld. Close to the clearing temperature, for the higher homologues, the influence of the smectic *A* phase extends over several degrees into the isotropic phase and in the case of 10 and 12CB is adequately described by the extended Landau–de Gennes model for formation of smectic *A* phases. Even for 9 and 11CB a divergence due to the presence of the smectic *A* phase is observed that also extends several degrees into the isotropic phase. Thus all the transitions involved have a strong second order nature. However as shown in Figure 1 they all have a small but measurable heat of transition. This includes the nematic-smectic *A* transitions. For 8CB ΔH_{SA-N} is extremely small and this confirms the speculation of Ref. 16 that if this transition is first order it is very weakly so. For 9CB ΔH_{SA-N} is of the same order of ΔH_{N-I} for 6CB and thus whilst it is weak it is not negligible. For the 10–12CB members ΔH_{S-I} (or ΔH_{S-N-I} for 11CB) is roughly ten times that of ΔH_{N-I} for 5 or 6CB and thus the first order nature is much more important. These heats of transition are roughly one tenth of those of the crystal-smectic *A* transition. Thus for all of the alkyl cyanobiphenyls studied the transitions exhibit a first order nature whose strength though generally weak depends markedly on the alkyl chain length. Therefore all values of T^* and T_S^* reported herein are hypothetical. Further all of the measured heats of transition show an odd even effect that illustrates yet again the importance of the conformation of the terminal links.

CONCLUSIONS

The effect of the alkyl chain length on the isotropic-mesomorphic transition has been studied for the alkyl cyanobiphenyls. From these results we conclude that the appearance of the smectic *A* phase with increasing chain length changes markedly the pretransitional behaviour and that this can be readily observed by light scattering. Two principle regions were observed: the first for temperatures relatively far from the transition where the pretransitional behaviour was typical for the isotropic-nematic transition and the Landau-de Gennes model was upheld, and the second region near to the clearing point (i.e. $T - T_c < 3°C$) where a strong divergence in the light scattering was observed. This divergence has been explained in terms of cross coupling between orientational and layer like fluctuations arising from a smectic *A* like structure in the isotropic phase. For both regions and also in the heats of transition, a strong odd-even effect was observed confirming the importance of the orientation of the terminal links.

It is not clear from our results whether the secondary divergence near to the transition is due solely to an increase in size of the *cybotactic* groups or their number and we are currently carrying out measurements both on the dynamic properties of the transition and with the alkyloxy series to try to resolve this problem and to examine whether this is typical alkyl chain behaviour.

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References

1. S. Chandrasekhar, *Liquid Crystals*, C.U.P. London (1977).
2. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971); and *The Physics of Liquid Crystals* (O.U.P., London, 1974).
3. Y. Poggi, P. Atten, and J. C. Filippini, *Mol. Cryst. Liq., Cryst.*, **37**, 1 (1976).
4. E. G. Hanson, Y. R. Shen, and G. K. L. Wong, *Phys. Rev.*, **A14**, 1281 (1976), D. Dunmur, M. R. Manterfield, W. H. Miller, and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.*, **45**, 127 (1978).
5. H. J. Coles, *Mol. Cryst. Liq. Cryst. Letts*, **49**, 67 (1978).
6. G. W. Gray, K. J. Harrison, and J. A. Nash, *Electron. Lett.* **9**, 130 (1973).
7. H. J. Coles and C. Strazielle, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 259 (1979).
8. G. W. Gray, *J. de Physique Colloque*, **36**, (Cl), 337 (1975).
9. B. D. H. Technical Publications, (Poole, Dorset, U.K.), *Liquid Crystals*, 18 (1978).
10. C. Strazielle and H. J. Coles, *J. de Physique*, **40**, 895 (1979).
11. M. Hareng and S. Le Berre, *Ann. Phys.*, **3**, 317 (1978).
12. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **36**, 51 (1976).
13. P. Martinoty, F. Kiry, S. Nagai, S. Candau, and F. Debeauvais, *J. de Physique*, **38**, 159 (1977).
14. S. Nagai, P. Martinoty, and S. Candau, *J. de Physique*, **37**, 769 (1976).
15. J. D. Litster, J. Als-Nielsen, R. J. Birgeneau, S. S. Dana, D. Davidov, F. Garcia-Golding, M. Kaplan, C. R. Safinya, and R. Schaetzing, *J. de Physique Colloque*, **40**, 339 (1979).
16. P. de Gennes, *Solid State. Comm.*, **10**, 753 (1977).
17. T. R. Steger, *Ph.D. Thesis*, Massachusetts Institute of Technology, (1974).