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Pretransitional Behavior of 8–12 CB

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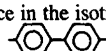
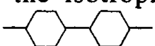
The magnetic birefringence in the isotropic phase *vs* temperature for the liquid crystals alkyl cyanobiphenyls (C_nH_{2n+1}  CN), $n = 8$–12, has been measured. The inverse of the Cotton-Mouton coefficient, R, *vs* temperature T were plotted. The shape and the influence of the smectic phase on the "bending down" in the R *vs* T curve near the clearing point T_c are discussed. The so-called "odd-even effect" are observed. In our experiments, in 9 CB and 11 CB, the "inflection" or "saturation" in the "bending down" region mentioned in the work of Coles and Strazielle, and Pouligny *et al.*, respectively, are not observed.

INTRODUCTION

The departure from the $(T - T_c^*)$ dependence in the curve of the inverse of the Cotton-Mouton coefficient or the ratio between the intensity of scattered light and temperature R *vs* temperature T near the clearing point T_c in the isotropic phase of the liquid crystal MBBA, found first by Stinson and Litster,[1] indicates the inadequacy of the mean-field approximation[2] in describing the N–I transition, where T_c^* is the maximum supercooling temperature (defined as the intercept of the straight line from the high temperature part with the T axis). This departure is shown in the graph of R *vs* T as a "bending down" as the temperature approaches T_c from above. The departure for MBBA has also been confirmed by Keyes and Shane[3] and by Zhang *et al.*[4] As for the pretransitional behavior in a homologous series of mesomorphic compounds, such as alkyl or alkoxy cyanobiphenyls (n CB or n OCB), many works have been reported.[4–9] They all observed the "bending down" effect. Moreover, "inflection" and "saturation" in the "bending down" region were observed by Coles and Strazielle,[6] and by Pouligny *et al.*,[16] respectively. But these novel pretransitional phenomena are in need of verification by more experiments.

After the mean-field theory of Landau-de Gennes was found to be inadequate in the region near T_c, the pretransitional behavior has been widely studied by different theoretical approaches.[10–15,18] Lin Lei is the first to obtain a theoretical result which is in good agreement with the experiments.[1,3,4] But generally speaking, there are still many disagreements between theories and experiments. Senbetu and Woo[15] have pointed out that the inconsistencies in the experimental data have caused difficulty in the theoretical work. Therefore, more accurate studies on the pretransitional behavior by different techniques are needed.

In this work we give results of a magnetic birefringence experiment in the isotropic phase for the alkyl cyanobiphenyl family (C_nH_{2n+1}  CN) from n = 8–12, which are, except for n = 8, the first ones to be reported, as far as we know. The purposes of our work are: first, to examine the effect of the nematic and the smectic phase on the pretransitional behavior; second, to study the effect of the lengths of liquid crystal molecules and some pretransitional phenomena for 9 and 11 CB as mentioned above.[6,16]

EXPERIMENTAL

The liquid crystals 8–12 CB series have been chosen as the samples because they exhibit a smectic phase (see Table I). The materials were provided by BDH Ltd., with the aid of Jebsen & Co. Ltd. They were degassed in vacuum (2 × 10^{-5}mmHg) at a temperature above clearing point for more than two hours before being used. Sample preparation was made in an atmosphere of N_2 or Ar. The clearing point T_c was determined by a method similar to that in Ref. 5 and the accuracy of T_c is better than ±0.05°C.

TABLE I

Transition Temperature for *n* CB

n − CB	T_{kn} or T_{ka}	T_{an}	T_{ni} or T_{ai}	$T_{ni} - T_{an}$
5	24	—	35.3	—
6	14.5	—	29	—
7	30	—	42.8	—
8	21.5	33.5	40.5	7.0
9	42	48	49.5	1.5
10	44	—	50.5	0
11	53	57	57.5	0.5
12	48	—	58.5	0

The temperature units are in °C. *k* = crystal, *n* = nematic, *a* = smectic, *i* = isotropic. The data are from the product information of BDH.

The measuring equipments for magnetic birefringence are similar to those used in our previous work[4] but some improvements have been made. The length of the sample cell was increased to 30 mm more in order to increase the amount of phase shift. In order to eliminate man-made error, a BX-21 type digital phasemeter was used in place of the usual lock-in amplifier in our previous work. Adopting the two steps mentioned above and using the method of repeated measurements, the accuracy of R has been made to be better than ten percent in the region near T_c. The temperature stability of the sample has been improved to ± 1 mK.

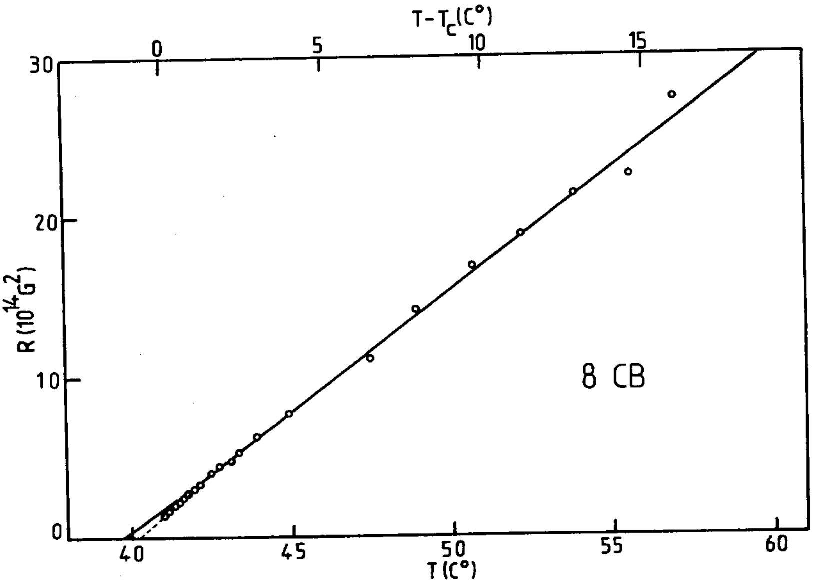
RESULTS

The inverse of the Cotton-Mouton coefficient R *vs* temperature T for 8–12 CB is shown in Figure 1. The T_b at which departure from the $(T - T_c^*)$ behavior begins, the maximum supercooling temperature T_c^* and the supercooling temperature T_{cl}^* have been determined from Figure 1. We define T_{cl}^* as the intersection of the bending down part of the R *vs* T curve with the T axis. The temperature regions separating T_b, T_c^*, and T_{cl}^* from T_c, namely, $(T_b - T_c)$, $(T_c - T_{cl}^*)$ and $(T_c - T_c^*)$, have been calculated. All these temperature regions are listed in Table II. In Table II, we list the calculated slopes of R *vs* T, $\Delta R/\Delta T$, from Figure 1 and for 5–7 CB from Muta *et al.*[5]

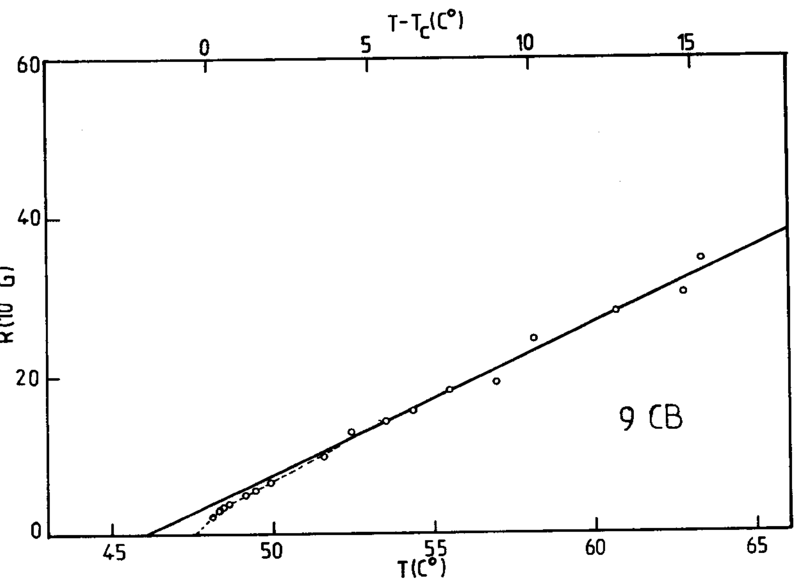
In Figure 2 we have plotted $\log_{10}R'$ *vs* $\log_{10}(T - T_{cl}^*)$ for 8–12 CB, where $R' = R/(10^{14}G^2)$ is the reduced inverse of the Cotton-Mouton coefficient and $(T - T_{cl}^*)' \equiv (T - T_{cl}^*)/(T_c - T_{cl}^*)$ is the reduced temperature. The slope of the linear fit for a given temperature range gives the apparent exponent for that temperature range.[17] γ_w and γ_c are introduced to represent the apparent exponents for the whole temperature range above T_c and the small temperature range near T_c, respectively. The values of γ_w and γ_c from Figure 2 are listed in Table II.

DISCUSSION

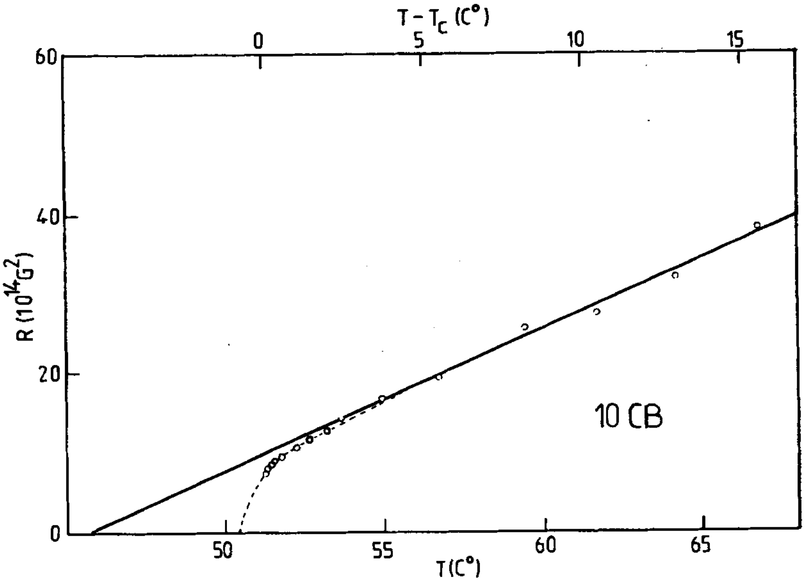
1. First, let us consider the departure from $(T - T_c^*)$ for the R *vs* T curve in Figure 1. For 8 CB, the departure increases slowly and fairly linearly as the temperature approaches the transition point T_c, which is similar to the result for 8 CB of Muta *et al.*,[5] and also similar to that for 5–7 CB.[5] For 9–12 CB, it seems that at first most of the departures still follow a departure shape similar to 8 CB but when the temperature approaches T_c, about 1°C from T_c, the departures increase rapidly and the curves bend down faster


T - T_c (C°)
0
5
10
15
30
20
10
0
R (10^14 G^2)
8 CB
40
45
50
55
60
T (C°)

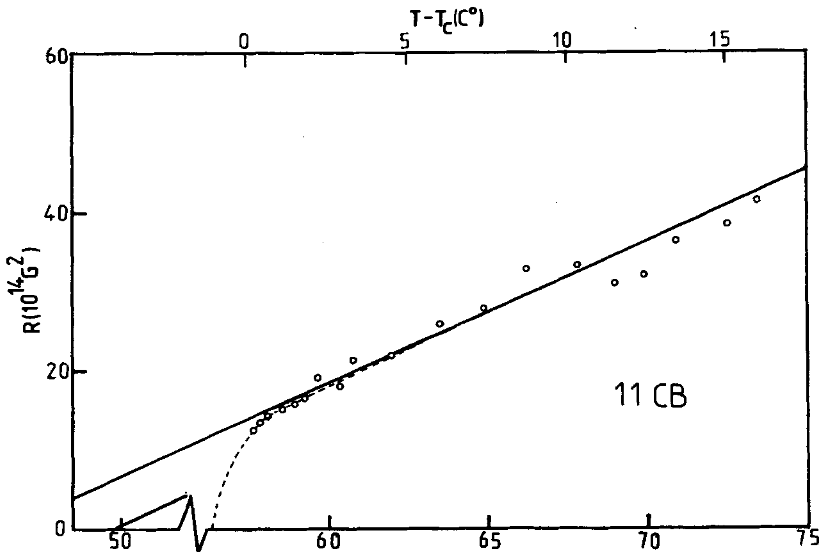
(*a*)


T - T_c (C°)
0
5
10
15
60
40
20
0
R (10^14 G^2)
9 CB
45
50
55
60
65
T (C°)

(*b*)



(*c*)



(*d*)

FIGURE 1 The inverses of the Cotton-Mouton coefficient *R* *vs* temperature *T* for 8–12 CB.

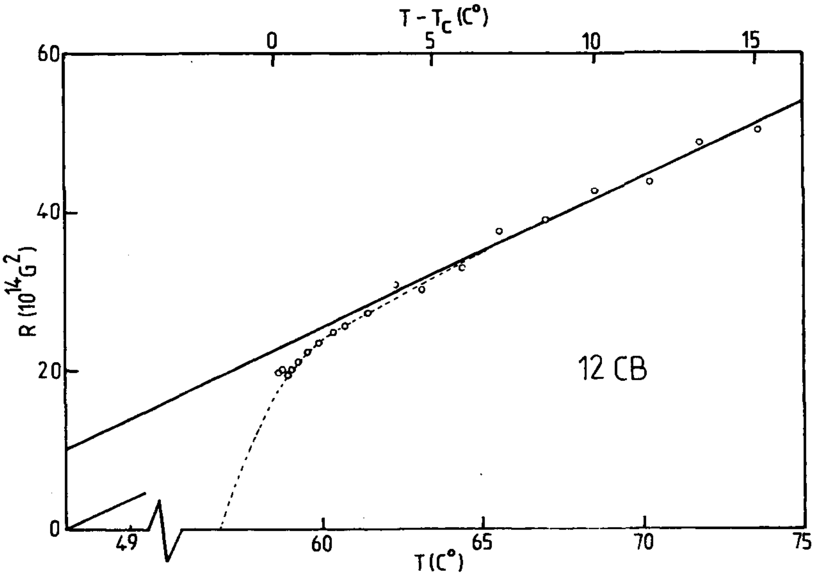


Figure 1 (continued) (*e*)

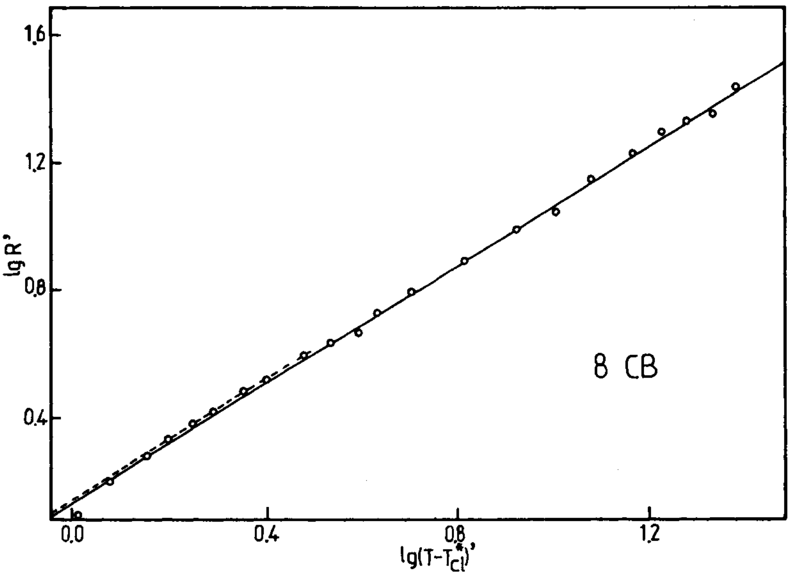
and faster. If one looks at Figure 1 carefully, one can see that the extent of the departure very close to T_c for 10 CB and 12 CB seems larger than that for 9 CB and 11 CB. In the above discussion, the last two points near T_c for 12 CB, are not considered because we believe they are due to instability of the measurements. The pattern of departure just mentioned seems to be verified by the values of γ_c (see Table II).

TABLE II

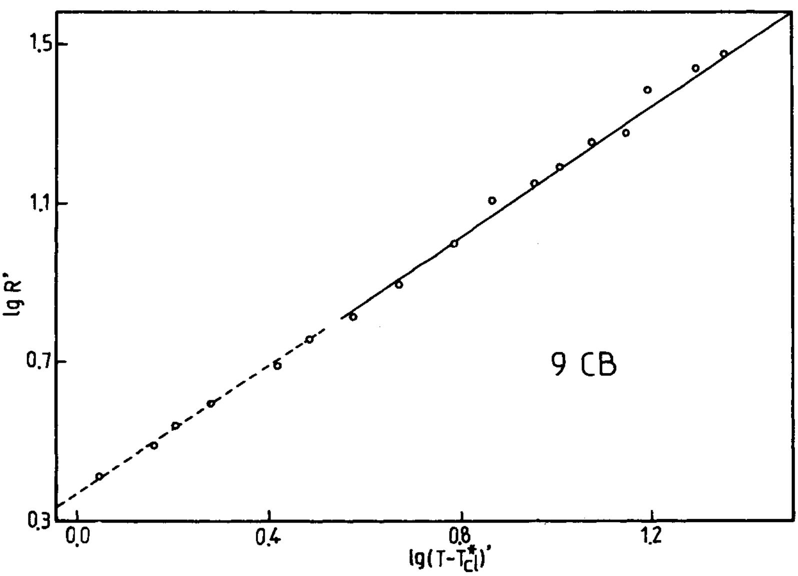
Temperature Parameters about Pretransitional Behavior, Apparent Exponents and Slopes of Inverse of the Cotton-Mouton Coefficient *vs* Temperature for *n* CB

$n-$CB	T_c	T_b	T_c^*	T_{cl}^*	T_b-T_c	$T_c-T_c^*$	$T_c-T_{cl}^*$	γ_c	γ_w	R/T ($10^{14}G^2/°C$)
5	35.9	36.7	33.35	34.45	0.8	2.55	1.45			0.77
6	30.1	31.5	27.98	29.05	1.4	2.12	1.05			0.73
7	43.4	44.0	41.82	42.38	0.6	1.58	1.02			1.56
8	41.0	42.4	39.8	40.3	1.4	1.2	0.7	0.93	0.93	1.51
9	48.02	51.2	46.0	47.3	3.2	2.0	0.7	0.80	0.80	1.90
10	51.12	55.5	45.7	50.4	4.4	5.4	0.7	0.44	0.50	1.76
11	57.56	63.0	49.8	56.0	5.4	7.8	1.6	0.46	0.48	1.82
12	58.59	65.2	47.0	56.7	6.6	11.6	1.9	0.43	0.46	1.89

The temperature units are in °C. The data for 5–7 CB are from Muta *et al.*[5]

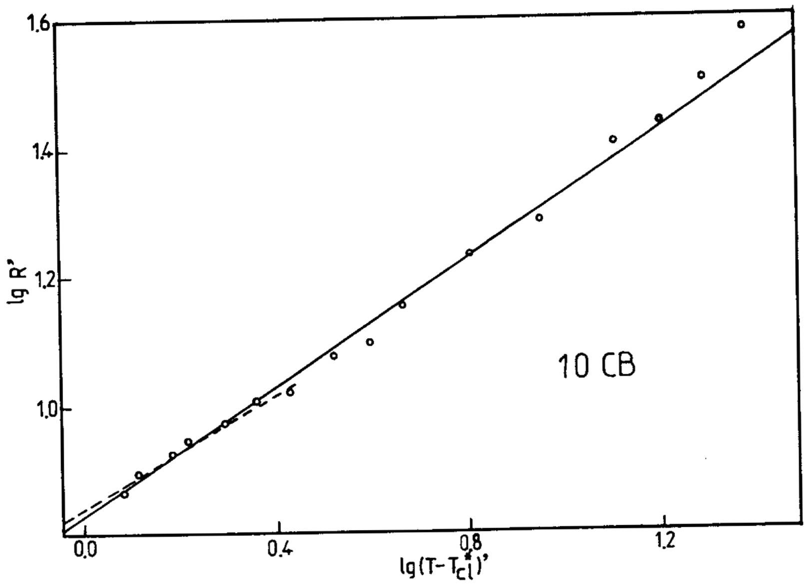


(*a*)

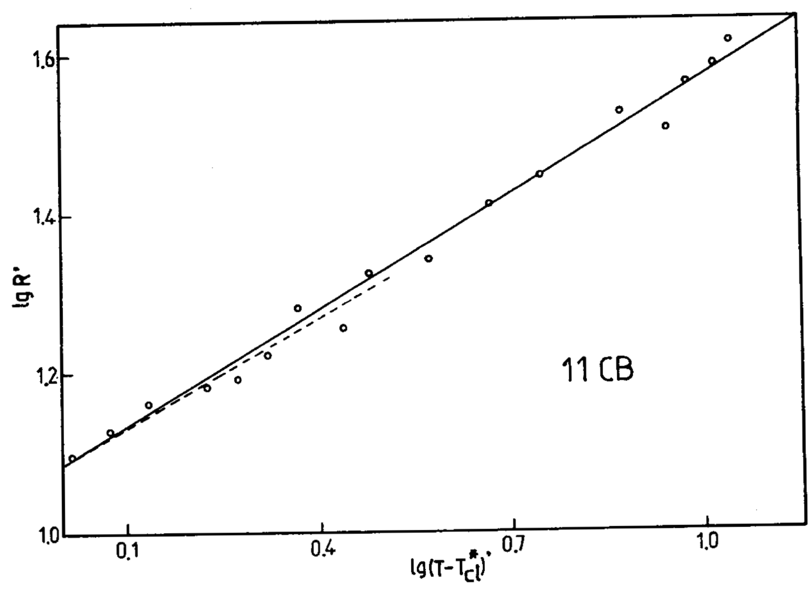


(*b*)

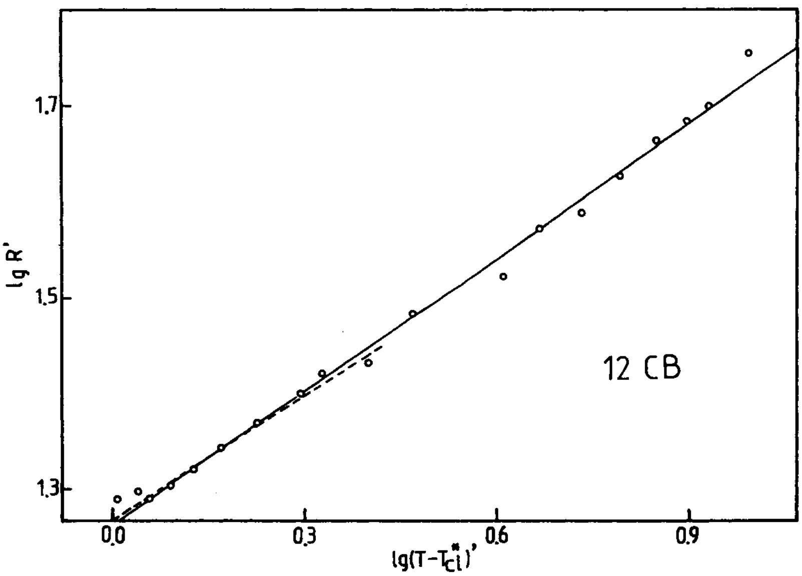
FIGURE 2 Common logarithmic R', lgR', *vs* common logarithmic $(T - T^*_{cl})'$, lg$(T - T^*_{cl})'$, for 8–12 CB. The slope of the linear fit (solid and dashed lines) gives the apparent exponent γ_w or γ_c. The solid lines correspond to γ_w. The dashed lines correspond to γ_c.


1.6
1.4
1.2
1.0
lg R'
10 CB
0.0
0.4
0.8
1.2
lg(T−T*cl)'

(c)


1.6
1.4
1.2
1.0
lg R'
11 CB
0.1
0.4
0.7
1.0
lg(T−T*cl)'

(d)

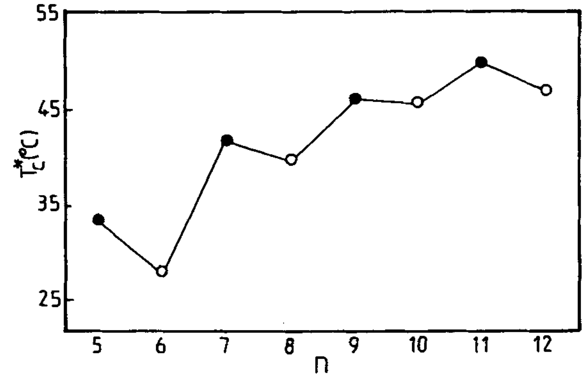


(*e*)

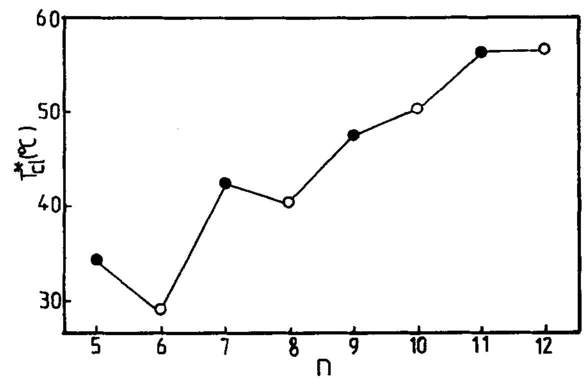
Figure 2 (continued)

The cause of the difference of the extent of the departures from $(T - T_c^*)$ for 8 CB and 9–12 CB in the *R vs T* curve very close to T_c may stem from the presence or absence of the effect of the smectic phase on pretransitional behavior. For 8 CB the difference between clearing point T_c and the smectic-nematic transition temperature, $(T_c - T_{an})$, is so large (7.0°C, see Table 1) that the smectic phase cannot effect the pretransitional behavior in the isotropic phase. It makes the departure behavior for 8 CB similar to that for 5–7 CB which have no smectic phases. $(T_c - T_{an})$ are exactly equal to zero for 10 CB and 12 CB or to only 1.5°C and 0.5°C for 9 CB and 11 CB, respectively, justifying our view that the smectic phase has an effect on the pretransitional behavior. The experiments seem to show that the effect of the smectic phase is more pronounced than the effect of the nematic phase so that the departure increases strongly as the temperature approaches T_c for 9–12 CB. For the same reason the departure for 10 CB and 12 CB, where no nematic phase exists, is sharper than that for 9 CB and 11 CB in which a small nematic temperature region exists.

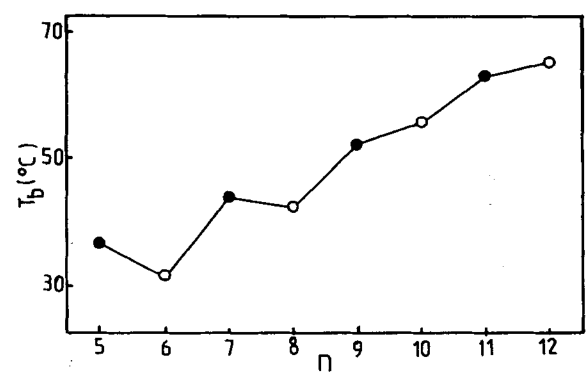
2. T_c^* T_{cl}^*, T_b and $\Delta R/\Delta T$ *vs n*, where *n* is the number of C atoms in the alkyl chains, are plotted in Figure 3 for 5–12 CB. T_c^*, T_{cl}^* and T_b clearly show the so-called "odd-even effect." As for the slope of $\Delta R/\Delta T$, the


55
45
35
25
T_c^*(°C)
5 6 7 8 9 10 11 12
n

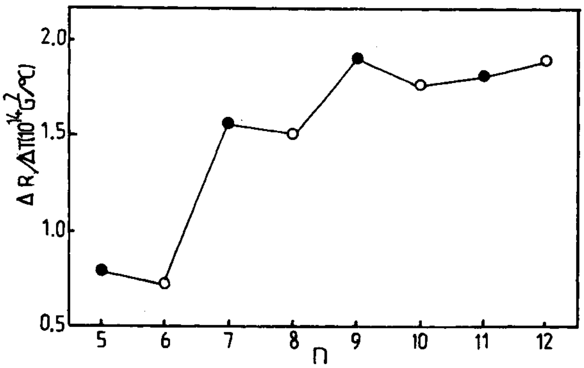
(*a*)


60
50
40
30
T_{cl}^*(°C)
5 6 7 8 9 10 11 12
n

(*b*)


70
50
30
T_b(°C)
5 6 7 8 9 10 11 12
n

(*c*)



(*d*)

FIGURE 3 The odd-even effects of T_c^*, T_{cl}^*, T_b and $\Delta R/\Delta T$ for 5–12 CB.

"odd-even effect" is also shown clearly for 5–10 CB. The cause of no "odd-even effect" on $\Delta R/\Delta T$ for 11 CB and 12 CB is not clear at present.

3. The differences $(T_b - T_c)$, $(T_c - T_{cl}^*)$ and $(T_c - T_c^*)$ are the parameters reflecting transition behavior. The curves of $(T_b - T_c)$, $(T_c - T_{cl}^*)$ and $(T_c - T_c^*)$ *vs n* for 5–12 CB are shown in Figure 4. From Figure 4, it can be seen that the value of the difference $(T_b - T_c)$ increases as we go from 8 CB to 12 CB. The results agree with that for *n*04 obtained by Gohin *et al.*[18] They stated that the domain in which the mean-field theory fails increases strongly when *n* increases. Now we have found that a situation similar to that for $(T_b - T_c)$ also occurs in $(T_c - T_c^*)$ for 8 CB to 12 CB. But for $(T_c - T_{cl}^*)$ the tendency just mentioned exists only for 10–12 CB.

4. The "inflection" in the "bending down" region for 9 CB and 11 CB, pointed out by Coles and Strazielle,[6] are not observed in our experiments. The so-called "saturation" for 9 CB and 11 CB, observed by Pouligny *et al.*,[16] are not found either.

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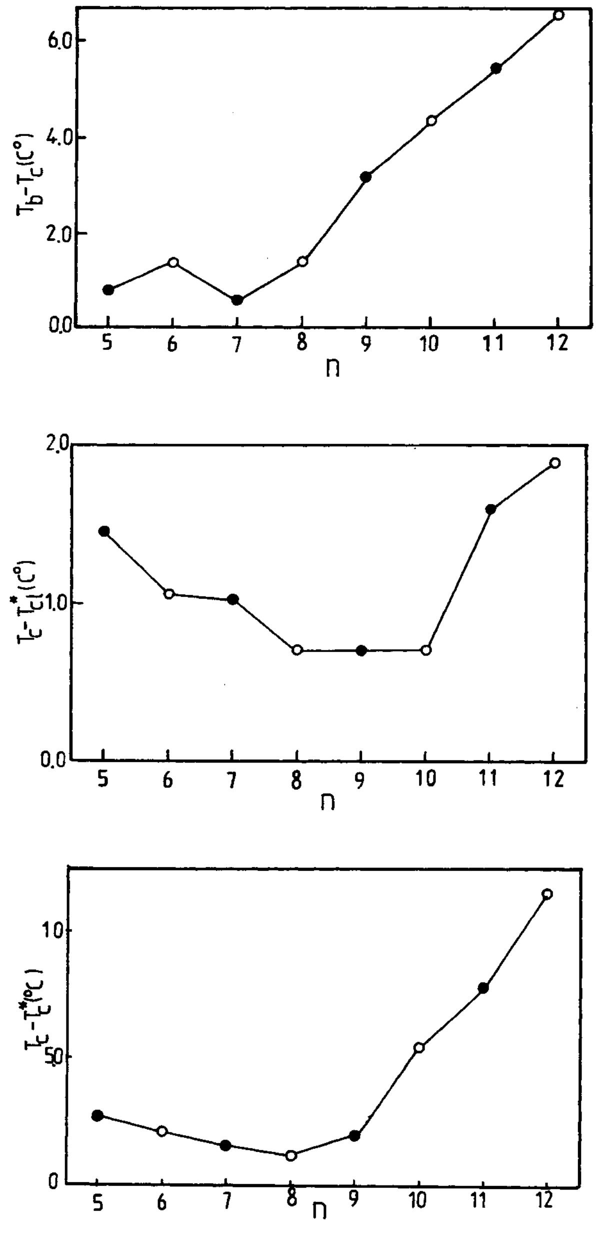

FIGURE 4 $T_b - T_c$, $T_c - T_{cl}^*$ and $T_c - T_c^*$ vs n for 5–12 CB.

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