

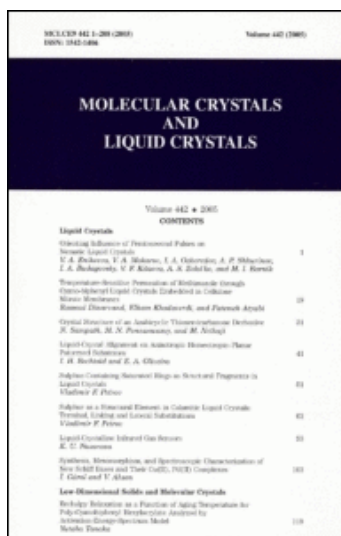
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Studies on Some Smectogenic Compounds with Large Bilayer Spacings

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Studies on Some Smectogenic Compounds with Large Bilayer Spacings[†]

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In mesomorphic compounds with strongly polar end groups, near neighbor molecules have antiparallel correlations. This results in a bilayer structure which in turn leads to several interesting phenomena like reentrance and smectic polymorphism. After a brief review of the development of this subject, we report some unusual properties in several compounds with relatively large bilayer spacings (≥ 1.6 times the molecular length). For example, 4-*n*-decylphenyl-3'-methyl-4'-(4"-nitrobenzoyloxy)benzoate (10 PMNBB) shows a remarkably large expansion (~20%) of the bilayer spacing on cooling in the S_A phase, the rate of expansion *increasing* with decrease of temperature. Further, the dielectric anisotropy reverses sign, becoming negative at lower temperatures. When the nitro group is replaced by a cyano group (10 PMCBB), (a) the rate of expansion of the bilayer spacing *decreases* with decrease of temperature, and (b) an $S_A - S_A$ transition takes place with a jump of ~ 0.4 Å in the layer spacing at $T_{AN} - T \approx 15^\circ$. We present results on several homologues of both the compounds as also on compounds with a lateral methoxy substituent.

I. INTRODUCTION

The importance of the longitudinal components of the permanent dipolar groups of mesogenic molecules in determining the stability of the nematic and smectic A phases has become clear only recently (see, for example, Ref. 1). About a decade ago, such dipolar groups were thought to play only a minor role, especially after the inadequacy of Born's theory² of the

[†]Invited paper, presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.

nematic phase was recognized.³ It is hence worthwhile recalling the development of this subject over the past few years. Even though Vorlander and his group synthesized several mesogenic compounds with the strongly polar cyano end group (see, for example, Ref. 4), no detailed physical measurements appear to have been made on those compounds. A strong motivation to synthesize and study such compounds came from the discovery of the twisted nematic device. Schadt⁵ found that the average dielectric constant ($\bar{\epsilon}$) of such compounds exhibits a positive jump at the nematic-isotropic transition point. This observation was interpreted⁶ to mean that near neighbor molecules of such compounds have antiparallel correlations, the positive jump in $\bar{\epsilon}$ being caused by a discontinuous decrease in the antiferroelectric short range order at T_{NI} . Direct evidence for the antiparallel correlations between such molecules was soon found when X-ray studies⁷⁻⁸ showed that the smectic A phases formed by such compounds have a layer spacing ≈ 1.4 times the molecular length. Even compounds which do not exhibit the smectic A phase have short range ordered cybotactic groups with a similar layer spacing. This arises from an overlap of the aromatic cores of neighboring molecules such that they are antiparallel. The structure of the bilayer is an extra degree of freedom available to such systems and gives rise to some remarkable phenomena. The first of these to be discovered was the occurrence of the reentrant nematic phase which is stable at temperatures below the range of existence of the A phase, in a binary mixture of two compounds with cyano end groups.⁹ Subsequently, reentrant phases were found in pure compounds¹⁰⁻¹² as well. In the mean time, Meyer and Lubensky¹³ developed a mean field theory of the A phase with a coupling between first and second translational order parameters. They could use this theory to explain the first order nature of the A-N transition in 4-*n*-pentylphenyl-4'-(4''-cyanobenzoyloxy)benzoate (DB5), even though this compound has a nematic range of 110°C, and should have had only a second order A-N transition according to the McMillan criterion.¹⁴ Indeed DB5 and its homologues have been found to possess a bilayer spacing which is close to twice the molecular length and a rather rich variety of smectic A polymorphism has been discovered in compounds with basically similar structures by the Bordeaux group.¹ In the present paper, we report our studies on several compounds whose molecular cores are similar to that of DB5, except for the presence of a lateral substituent.

II. EXPERIMENTAL

All the compounds were synthesized in our chemistry laboratory. The details of the synthesis are given elsewhere.^{15,16} The transition temperatures

were determined by using a Mettler hot stage (model FP52) in conjunction with a polarizing microscope, as well as a differential scanning calorimeter (Perkin Elmer, Model II). The X-ray studies were made using the flat film technique, with $\text{CuK}\alpha$ radiation from a bent quartz crystal monochromator. The sample was taken in a sealed Lindemann capillary tube, and aligned by slowly cooling in a magnetic field of strength ≈ 4 KGauss. The dielectric constants were measured using a Wayne-Kerr bridge (Model B642) operating at 1592 Hz. 100 micron thick samples were taken between tin oxide coated glass plates and were aligned in a 14 KGauss magnetic field by a slow cooling of the sample in the field. Both ϵ_{\parallel} and ϵ_{\perp} were measured on the same sample by rotating the cell to the appropriate configuration. The principal conductivities (σ_{\parallel} and σ_{\perp}) could also be measured on the Wayne-Kerr bridge. σ_{\parallel} depends strongly on the frequency of measurement at low temperatures. Hence we have also measured σ_{\parallel} and σ_{\perp} at 300 Hz by using the Wayne-Kerr bridge in conjunction with an external AC source and a PAR 186 lock in amplifier as the detector.

III. RESULTS AND DISCUSSION

(a) Thermodynamic properties

The structural formulae and acronyms of the compounds of interest are shown in Figure 1. The molecules of n CPMBB have two ester groups whose dipole moments are parallel to that of the end cyano group. The eleventh and twelfth members of this series exhibit A and reentrant nematic phases.¹¹ We were interested in studying the effect of interchanging the two end groups so that the longitudinal components of the two ester groups are now antiparallel with the terminal cyano group. It is interesting to note that the molecular cores of the resulting n PMCBB compounds are very similar to that of the DB-5 compound whose homologues have been extensively studied by the Bordeaux group, except that a lateral methyl substituent is now attached to the core. We have also studied some compounds with two structural variations: (a) replacement of the terminal cyano group with a nitro group (n PMNBB) and (b) substitution of the lateral methyl group with a methoxy group (n PMeOCBB). We have studied only a few higher homologues in each series, since our main interest was to investigate the smectic A phase. The transition temperatures and where available, the heats of transition are given in Table I.

Comparing n CPMBB and n PMCBB series of compounds, first we notice that (a) n PMCBB compounds melt at much lower temperatures than the corresponding n CPMBB compounds, (b) an enantiotropic smectic A phase appears at the ninth member of n PMCBB¹⁵ while 11 CPMBB is the lowest

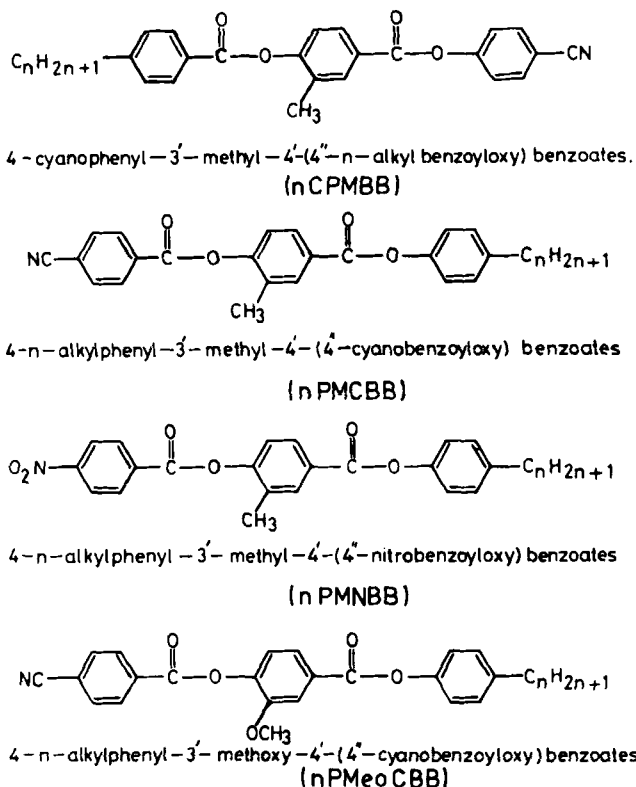


FIGURE 1 Structural formulae and acronyms of various compounds used in the present investigation.

homologue which exhibits the A phase, (c) both the *AN* and *NI* transition temperatures of 12 PMCBB are higher than the corresponding temperatures of 12 CPMBB, (d) while *n*CPMBB with $n = 11$ and 12 exhibit a re-entrant nematic phase, there is no such phase in the case of *n*PMCBB and (e) the DSC run of 10 PMCBB shows a slope change at 124.5°C, indicative of a phase transition at that temperature. However, observations under a polarizing microscope did not show any change in the texture, which corresponds to that of the smectic A phase, both above and below 124.5°C.

Comparing the transition temperatures of *n*PMNBB with those of *n*PMCBB, the former have higher melting points but lower *A-N* and *N-I* transition points. Replacement of the lateral methyl substituent of *n*PMCBB by the bulkier methoxy group results in higher melting points of *n*PMeOCBB, but considerably lower *A-N* and *N-I* transition points than even those of *n*CPMBB. This can be attributed to the weakening of the intermolecular interactions resulting from the bulkier side group of *n*PMeOCBB.

TABLE I
Transition temperatures in °C and heats of transition of the compounds
used in the present investigation.

<i>n</i>	<i>K</i>	<i>N_R</i>	<i>A_d</i>	<i>N</i>	<i>l</i>
<i>n CPMBB</i>					
11	• 103	(• 78.5)	• 127	• 152.5	•
		[0.0154]	[0.0147]		
12	• 102	(• 59.8)	• 138.5	• 148	•
		[0.0464]	[0.0255]		
<i>n</i>	<i>K</i>	<i>A₂</i>	<i>A_d</i>	<i>N</i>	<i>l</i>
<i>n PMCBB</i>					
10	• 58	• 124.5	• 139.5	• 169.5	•
	[14.1]		[0.06]	[1.38]	
12	• 67.5	• 77.1(?)	• 155.3	• 159.3	•
	[16.8]		[0.42]	[1.48]	
<i>n</i>	<i>K</i>	<i>A_d</i>	<i>N</i>	<i>l</i>	
<i>n PMNBB</i>					
9	•	75.9 (• 66.1)	• 156.5	•	
		[16.3]	[0.019]	[1.11]	
10	•	77.0 • 108.5	• 150.0	•	
		[21.6]	[0.062]	[1.13]	
12	•	73.3 • 141.3	• 146.9	•	
		[20.0]	[0.165]	[1.28]	
<i>n</i>	<i>K</i>	<i>A_d</i>	<i>N</i>	<i>l</i>	
<i>n PMeOCBB</i>					
10	•	97.8 (• 94.4)	• 135.4	•	
		[33.7]	[1.56]		
12	•	101.7 • 130.3	• 133.2	•	
		[28.8]	[0.21]	[1.7]	

(•) indicate monotropic transitions

Numbers written inside square brackets are the heats of transitions expressed in KJ/mole.

(b) X-ray studies

The temperature variation of the layer spacing in 10 PMCBB is shown in Figure 2. There is a large expansion of the layer as the temperature is *decreased*, the rate of expansion decreasing at lower temperatures.¹⁷ The molecular length *l* of 10 PMCBB calculated with Dreiding models is $\approx 33 \text{ \AA}$. The measured layer spacing thus corresponds to that of a bilayer whose spacing $d \approx 1.6l$ close to T_{AN} and increases to $d \approx 1.85l$ at the lowest temperature before crystallization takes place. Further there is a clear jump of $\sim 0.4 \text{ \AA}$ in the layer spacing at $\sim 15^\circ$ below T_{AN} . The rate of increase of spacing slows down somewhat as the sample is cooled to this

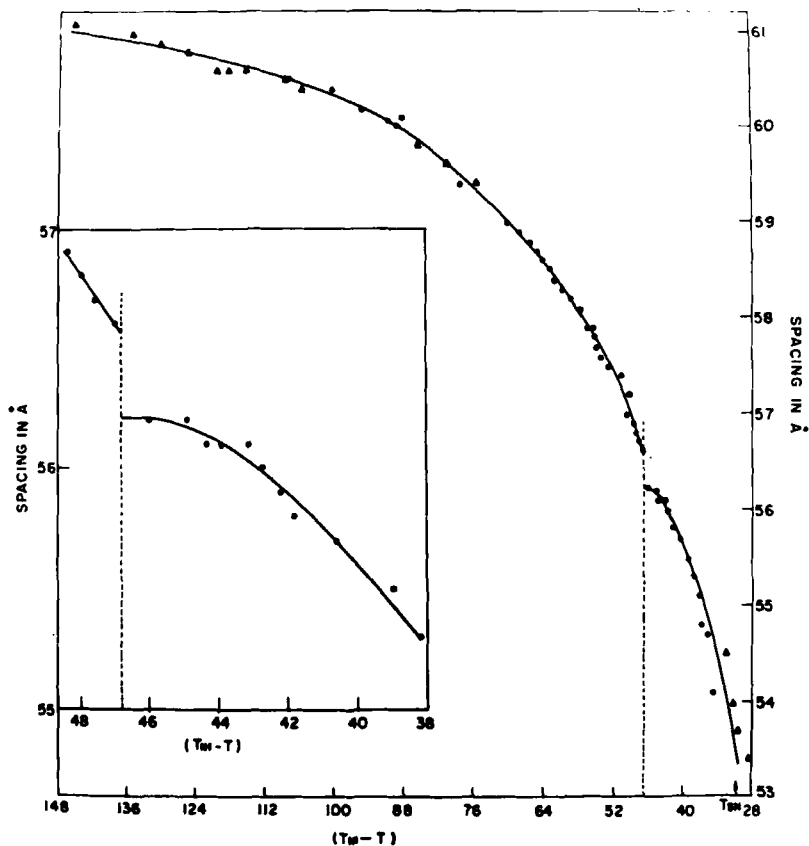


FIGURE 2 Temperature variation of the layer spacing of 10 PMCB. ● and ▲ represent measurements accurate to $\pm 0.1 \text{ \AA}$ and $\pm 0.3 \text{ \AA}$ respectively. An A_1-A_2 transition occurs with a jump in the layer spacing at the temperature corresponding to the dashed line. The region around this transition point is shown on a magnified scale in the inset. In this and all subsequent figures, the vertical arrow on the temperature axis represents the AN transition point.

temperature, before the jump occurs (see inset of Figure 2). The jump was confirmed by three independent experiments. This corresponds to an $A-A$ transition of the type found by the Bordeaux group in several cases.¹ The jump in the layer spacing is from ~ 1.71 to $\sim 1.72l$. The lower temperature A phase gives rise to a relatively strong second order reflection, whose intensity increases with decrease of temperature. This transition corresponds to an A_1-A_2 transition according to the nomenclature of the Bordeaux group.¹

Figure 3 shows the layer spacing in the case of 12 PMCB. The general features are similar to those of 10 PMCB. There is a change of slope in

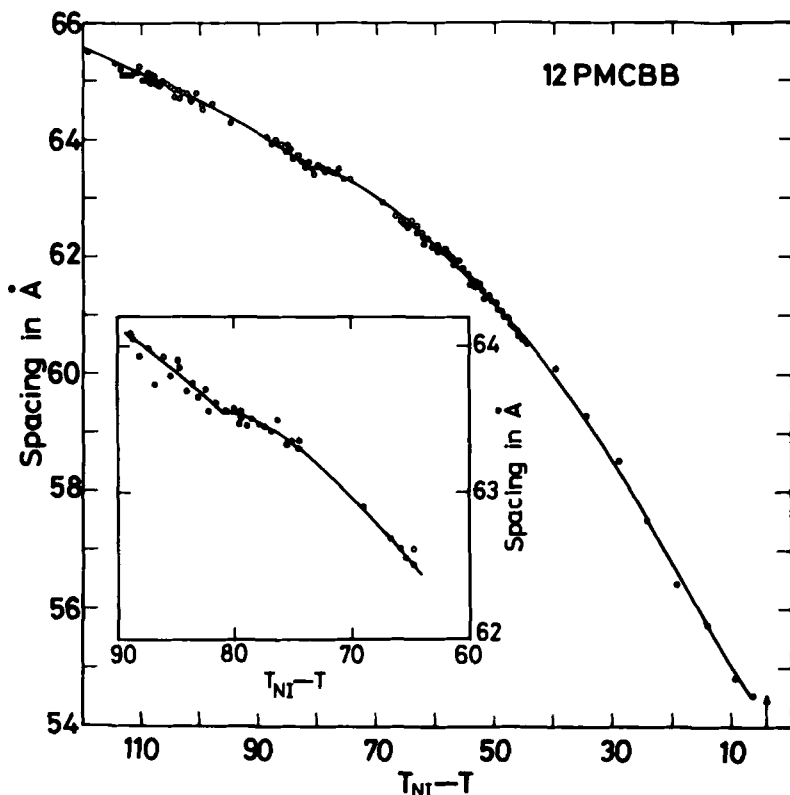


FIGURE 3 Temperature variation of the layer spacing of 12 PMCBB. The inset shows on a magnified scale the region around the temperature at which a slope change occurs.

the thermal evolution of the layer spacing at $T_{NI}-T \approx 82^\circ$, with a lowering of the rate of expansion as the temperature is lowered to that temperature and a faster expansion at lower temperatures. The second order reflection is strong at lower temperatures. This trend is reminiscent of that shown by 10 PMCBB (see Figure 2), but without any jump in the layer spacing. It most probably represents a second order A_d-A_2 transition.

The temperature variation of the layer spacing in 9 PMNBB, 10 PMNBB and 12 PMNBB are shown in Figures 4–6 respectively. In 9 PMNBB (Figure 4), the curvature appears to change sign at T_{AN} , the rate of expansion becoming larger at lower temperatures in the A-phase. The latter trend is particularly obvious in 10 PMNBB (Figure 5).¹⁸ Indeed from a comparison with the data on 10 PMCBB (Figure 2), some striking differences are seen when the cyano end group is replaced by the nitro end group: (a) the curvature of the thermal dependence of the layer spacing changes sign; and (b) A_d-A_2 transition is absent in the nitro compound. Since the

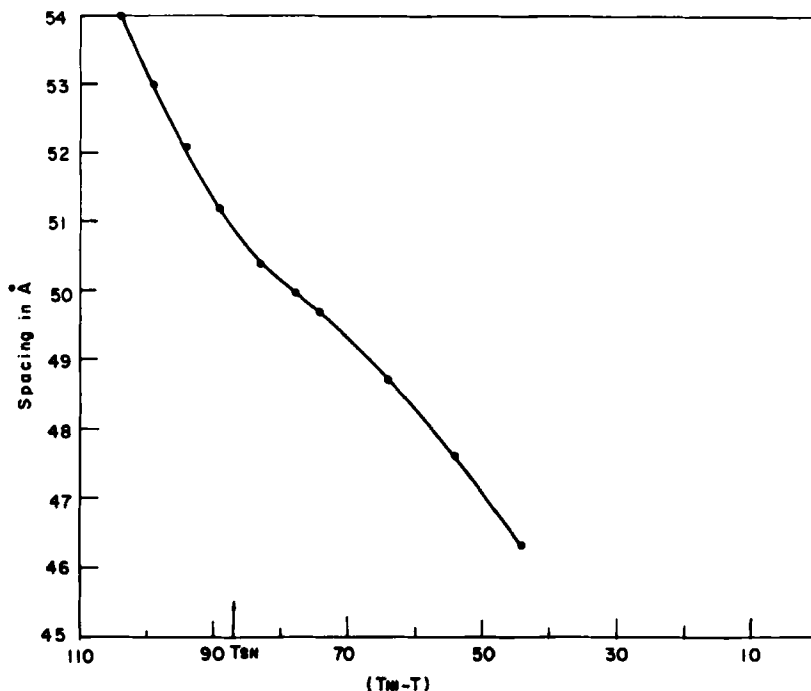


FIGURE 4 Temperature variation of the layer spacing of 9 PMNBB.

molecular lengths in the two cases are practically same, it is also clear that the bilayer spacing in the nitro compound is somewhat lower than in the cyano compound. In the case of 12 PMNBB (Figure 6), the curvature changes sign in the A phase, the rate of expansion becoming lower at the lowest temperatures for which measurements could be taken. In all these cases, the second order reflection is seen only at very low temperatures and perhaps all of them exhibit only the A_d phase.

Figures 7 and 8 show the results on 10 PMeOCBB and 12 PMeOCBB respectively. Again there is a fairly large expansion in the layer spacing as the temperature is lowered, without any indication of jump or change of slope. The second order reflection was very difficult to get even at the lowest temperatures and the A phase exhibited by these compounds also most probably belong to the A_d class.

Thus all the compounds studied by us show (i) a relatively large bilayer spacing $d \approx 1.6l$ and (ii) a fairly large expansion of the spacing as the temperature is lowered in the smectic A phase. Though the temperature variation of d is by no means linear, it is interesting to compare the average

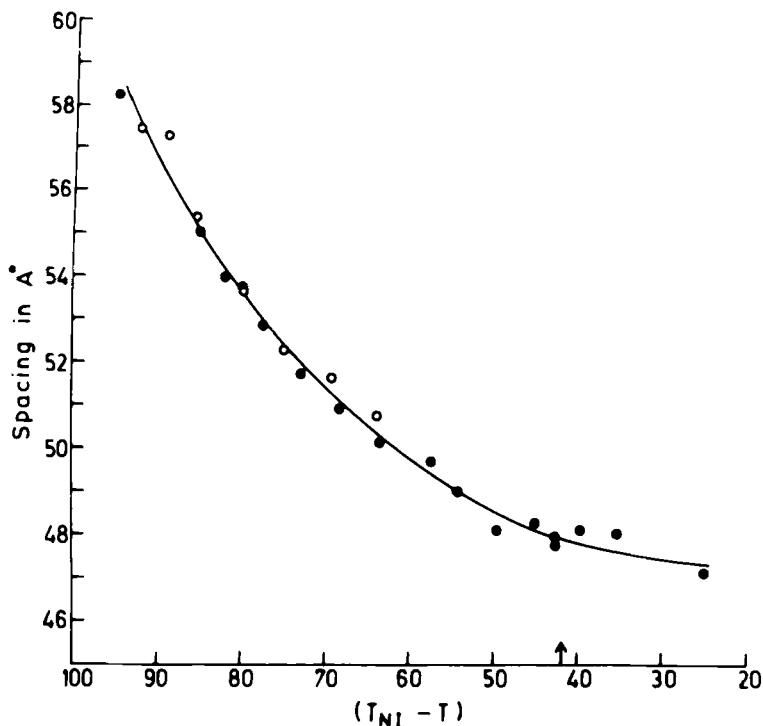


FIGURE 5 Temperature variation of the layer spacing of 10 PMNBB.

values of $(\Delta d/\Delta T)$ over the entire range of measurement in all the cases. The results are shown in Table II. The values increase for the higher homologues. This trend is similar to that found earlier by Cladis, *et al.*,¹⁹ in the case of 4-*n*-alkoxyphenyl-4'-cyano benzoates which have one ester linkage group whose longitudinal component of the dipole moment opposes that of the cyano end group. When the compound has two ester linkage groups (as in the compounds that we have studied), but without any lateral substituent, one finds $A-A$ transitions in many homologues of both the cyano and nitro compounds,¹ and further the layer spacing does not appear to be strongly temperature dependent. However, when one of these compounds is mixed with octyloxycyanobiphenyl, the A_d-A_2 transition becomes weaker as the 8 OCB concentration is increased, and the layer spacing also becomes strongly temperature dependent.²⁰

We can also compare the X-ray results on the *n*PMCB_B compounds with those on *n*CPMB_B compounds. As mentioned earlier, the latter compounds with $n = 11$ and 12 exhibit a re-entrant nematic phase. The layer spacing in the A-phase is $d \approx 1.25l$ and the temperature dependence of d is quite weak.²¹

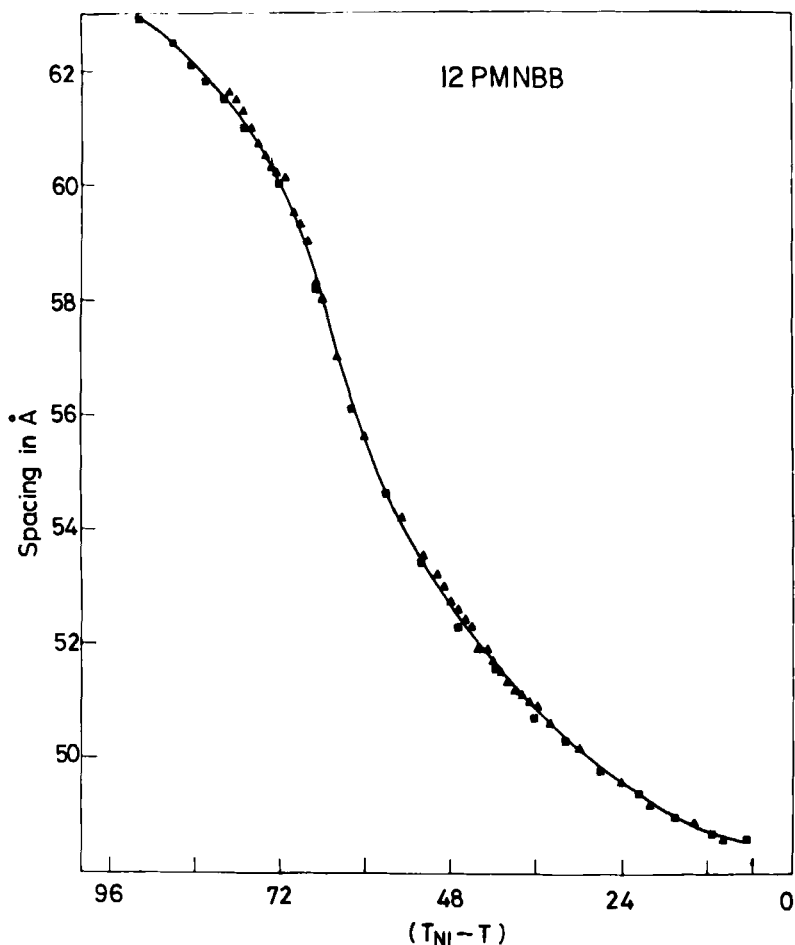


FIGURE 6 Temperature variation of the layer spacing of 12 PMNBB.

A possible interpretation of the strong temperature dependence of d in all the cases reported in this paper is that the interdigitation in the bilayer varies continuously with temperature (Figure 9). A more plausible interpretation can, however, be obtained by considering the mutual interactions between a pair of molecules. For the sake of comparison, we shall first consider a pair of n CPMBB molecules (Figure 10a). Since the longitudinal components of both ester groups are aligned parallel to the dipole moment of the

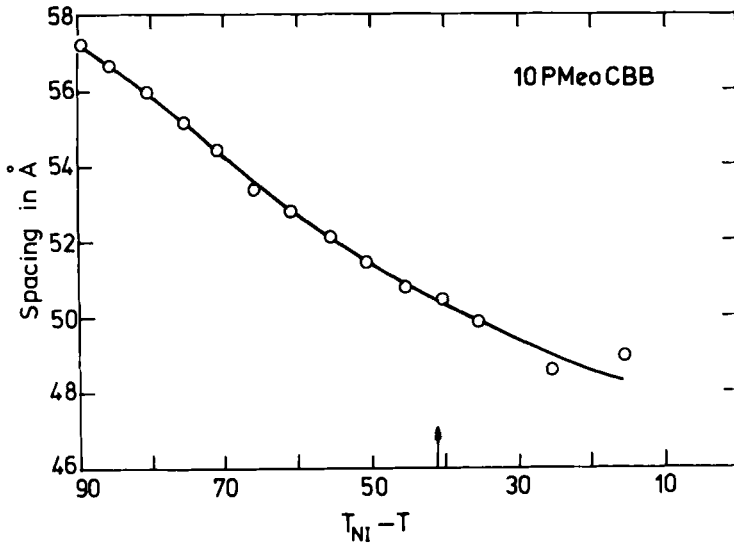


FIGURE 7 Temperature variation of the layer spacing of 10 PMeOCBB.

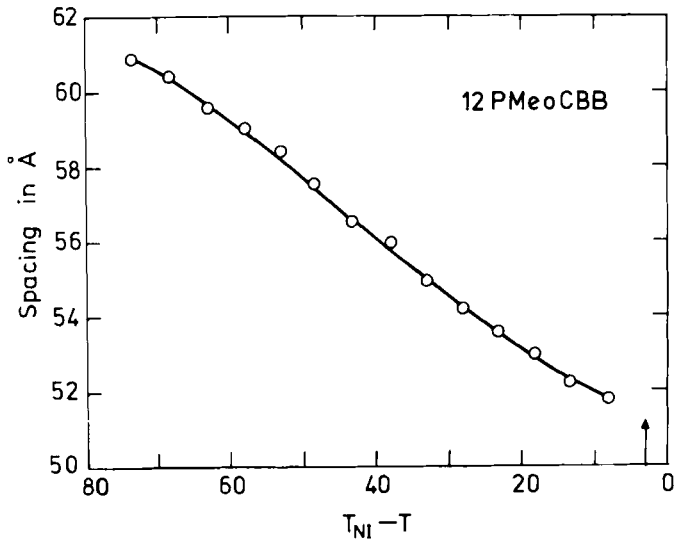


FIGURE 8 Temperature variation of the layer spacing of 12 PMeOCBB.

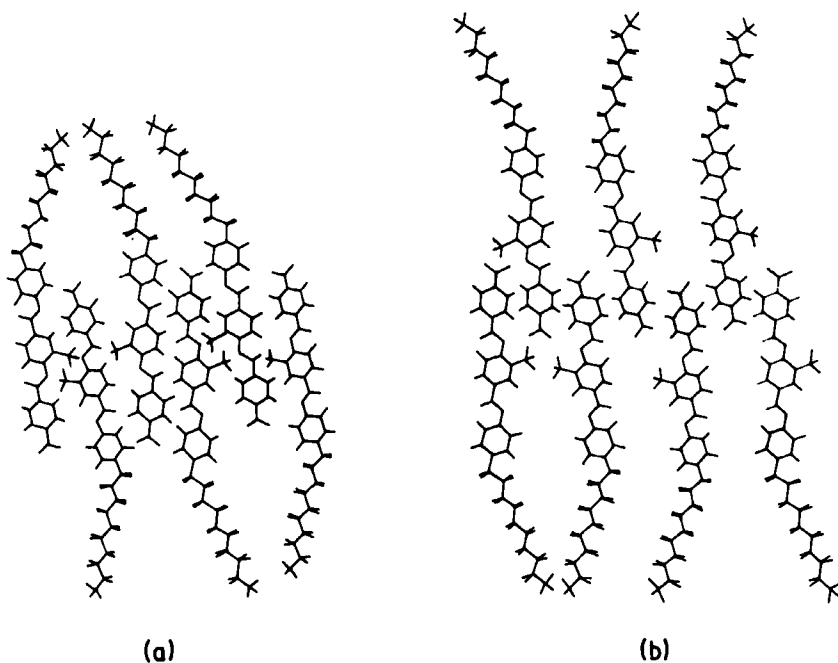


FIGURE 9 Schematic drawings of a possible structure of the bilayer in (a) higher temperature range, and (b) lower temperature range of the A phase. Actually, the three phenyl rings are *not* likely to be coplanar.

cyano group, the interaction energy can be minimized by a complete overlap of the aromatic cores as shown in Figure 10a. On the other hand, in *n*PMcBB compounds a similar overlap of the aromatic cores (Figure 10b) would result in strong repulsive interactions between the dipole moment of the cyano group and that of one of the ester groups. The dipolar contribution to the interaction energy would be minimized by an overlap of the two molecules only near the cyano end groups as shown in Figure 10c. Since the dipole moment of the cyano end group is $\approx 4D$, the dipolar interaction energy ($\sim \mu^2/r^3$) is a few times the thermal energy $k_B T$. Further, since this interaction is confined to one end of the molecule, it is clear that the structure as shown in Figure 10c should be rather fragile. As the temperature is raised, the structure can easily break up. This physical model can easily explain the rapid decrease in the layer spacing as the temperature is raised. As the molecules become heavier with longer chains, the structure shown in Figure 10c can be expected to become more fragile accounting for the larger coefficients of thermal contraction of the layer spacing (Table II). The lateral substituent also makes the molecules bulkier

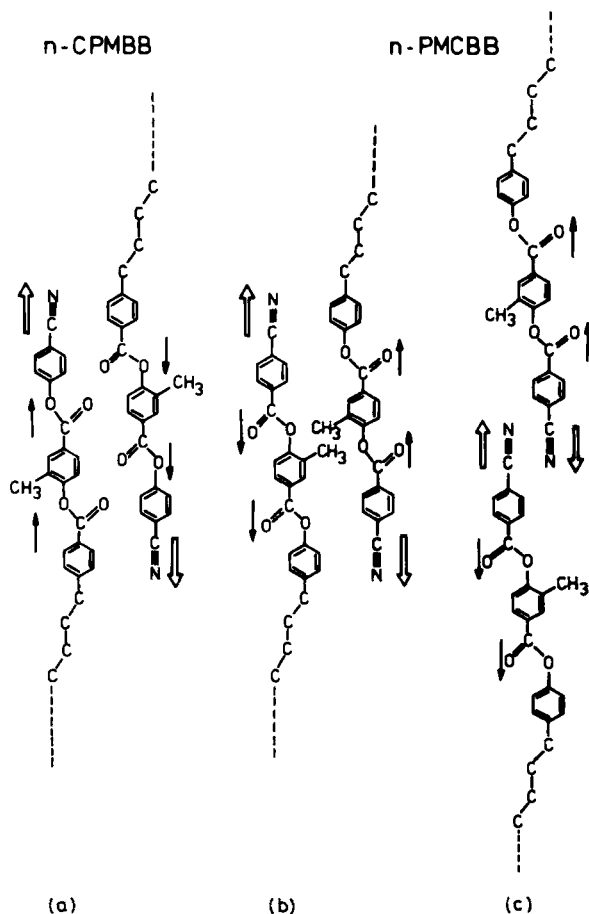


FIGURE 10 Schematic diagrams showing the disposition of various dipolar groups of a pair of (a) *n*-CPMBB, (b) *n*-PMCBB molecules with an overlap of the aromatic cores and (c) a pair of *n*-PMCBB molecules with an overlap of the polar end groups.

adding to the fragility of the structure. Further, the intermolecular repulsions of the single molecules which break away from the structure shown in Figure 10c would be smaller than in compounds without the lateral substituent. This may account for the relatively stronger thermal contraction observed in compounds with the lateral substituents than in the compounds without lateral substituents. Further, this interpretation accounts for the somewhat larger thermal contraction of *n*PMEOCBB compounds compared to those of *n*PMCBB compounds. *n*PMNBB compounds have the largest thermal contraction of the layer spacings, even though the

TABLE II

Average rate of thermal expansion of the layers.

	$\Delta d/\Delta T$ in $\text{\AA}/^\circ\text{C}$		
	$n = 9$	$n = 10$	$n = 12$
n PMCBB	—	-0.07	-0.1
n PMNBB	-0.13	-0.16	-0.17
n PMeOCBB	—	-0.12	-0.14

longitudinal dipole moment of the NO_2 group is almost the same as that of the cyano group. Obviously the interactions between the lateral components of the dipole moments of the NO bonds would be repulsive on the average and would contribute to a reduction in the attractive interactions between the end groups. A quantitative formulation of these physical ideas is underway and will be published elsewhere.

(c) Dielectric studies

The principal dielectric constants ϵ_{\parallel} and ϵ_{\perp} (parallel and perpendicular to the director respectively), the average value $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ and the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ are shown in Figure 11 for 12 PMCBB. We note several interesting points: (a) ϵ_{\parallel} increases with the decrease of temperature in the N phase but starts *decreasing* fairly rapidly as the temperature is lowered in the smectic phase. The rate of decrease goes down at lower temperatures. (b) ϵ_{\perp} has exactly the opposite trend, though the rate of variation is somewhat smaller than that of ϵ_{\parallel} . (c) The two curves cross at $T_{NI} - T \approx 30^\circ$ so that $\Delta\epsilon$ changes sign from positive to negative at the temperature. (d) $\bar{\epsilon}$ increases as the temperature is lowered in the isotropic phase and decreases in the mesophases. There appears to be a cusp in $\bar{\epsilon}$ at T_{NI} .

We have shown the significant dipole moments (taken from Ref. 22) of an n PMCBB molecule in Figure 12. The conformation of the molecule is not known but the three phenyl rings are very unlikely to be coplanar. The values of μ_{\parallel} and μ_{\perp} , the components parallel and perpendicular to the long axis of the molecule of the net dipole μ depend on the molecular conformation. According to the theory of Maier and Meier,²³ the dipolar contribution to ϵ_{\parallel} of a nematic liquid crystal is proportional to $\mu^2/T[1 - (1 - 3 \cos^2 \beta)S]$ while that to ϵ_{\perp} is proportional to $\mu^2/T[1 + \frac{1}{2}(1 - 3 \cos^2 \beta)S]$. If β , the angle made by μ with the long axis of the molecule exceeds 54.7° , the dipolar contribution to $\Delta\epsilon$ will be negative. On the other

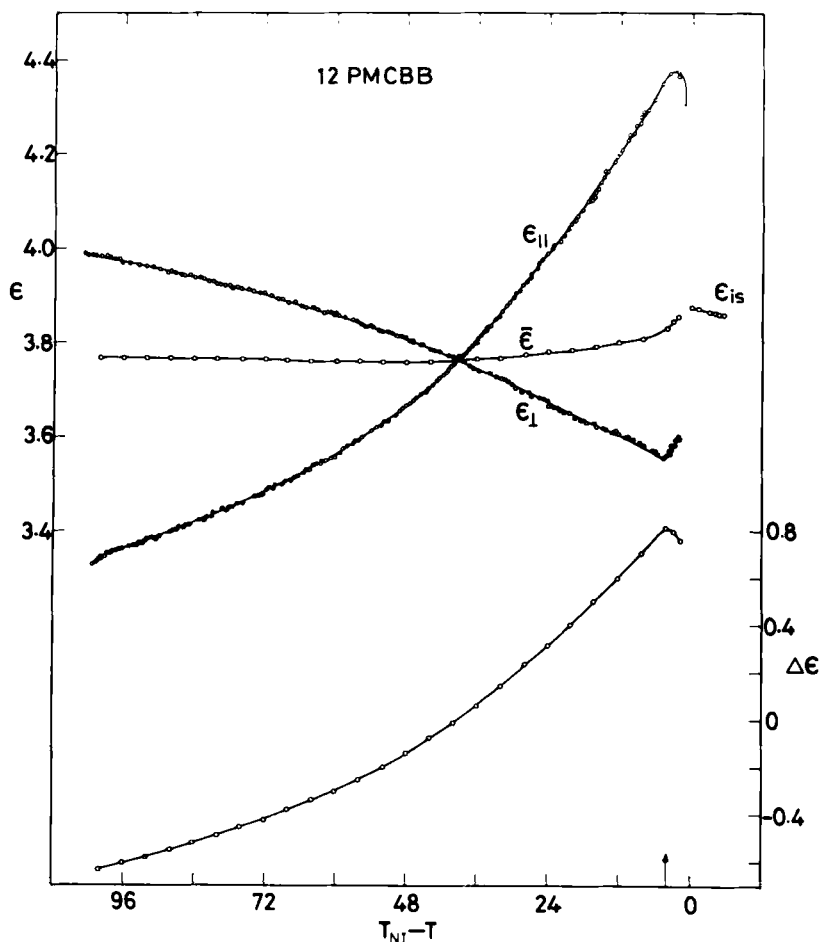


FIGURE 11 Temperature variations of the dielectric constants (upper section) and the dielectric anisotropy (lower section) of 12 PMCB.

hand, the contribution from the polarizability anisotropy $\Delta\alpha$ is always positive. If the two contributions are of similar magnitude, the dielectric anisotropy can be very small and can even change sign at some temperature, becoming positive at higher temperatures.²⁴ This mechanism could indeed be contributing to the reversal of the sign of $\Delta\epsilon$ in 12 PMCB, but we must note some additional points: if it is the only mechanism, $\bar{\epsilon}$ should have *decreased* with increase of temperature. Since $\bar{\epsilon}$ actually varies in the opposite manner, we could think of an increasing

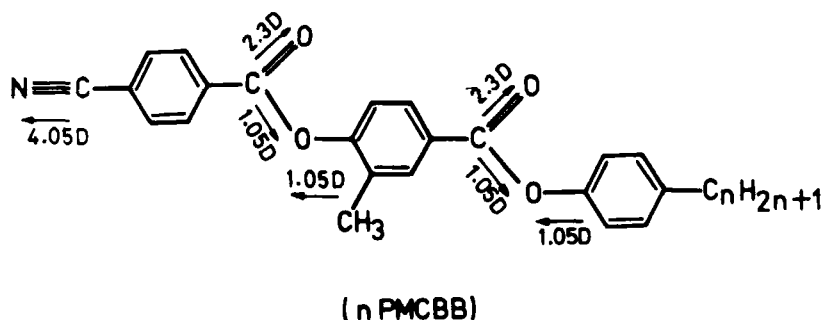


FIGURE 12 The most important dipole moments of an *n*-PMcBB molecule.

antiparallel short range order between neighboring molecules at lower temperatures.⁶ In addition, the reversal occurs in the smectic A phase, which has a layered structure. In such a case, the dipole correlation factors for μ_{\parallel} and μ_{\perp} will be such as to lower ϵ_{\parallel} and enhance ϵ_{\perp} .²⁵

We get a natural explanation for the observed temperature variation of $\bar{\epsilon}$ on the basis of the model shown in Figure 10c. At lower temperatures, a larger number of molecules are associated, and the dipole moment of the cyano end group is more effectively reduced. This gives rise to a faster reduction of ϵ_{\parallel} as the temperature is lowered, compared to the increase of ϵ_{\perp} . Thus $\bar{\epsilon}$ decreases with decrease of temperature.

The dielectric properties of 10 PMeOCBB are shown in Figure 13. ϵ_{\parallel} increases with decrease of temperature, attains a broad maximum a few degrees above T_{AN} and then continuously decreases. On the other hand, as the temperature is lowered ϵ_{\perp} starts increasing at a relatively high temperature in the N phase, and shows a small cusp-like peak at T_{AN} . This may be caused by a misalignment close to T_{AN} which is observed in some other compounds also^{26,27} that favor a homeotropic alignment. $\bar{\epsilon}$ shows a positive jump at T_{NI} but increases slightly as the temperature is lowered. $\Delta\epsilon$ shows a broad maximum. ϵ_{\parallel} , ϵ_{\perp} and $\bar{\epsilon}$ have somewhat higher values than in the case of 12 PMcBB because of the additional oxygen atom which has a high polarizability.

The dielectric constants of 9 PMNBB, 10 PMNBB and 12 PMNBB are shown in Figures 14–16 respectively. Though the dielectric properties of 9 PMNBB (Figure 14) are broadly similar to those of 10 PMeOCBB (Figure 13), there are some differences. As the temperature is lowered, ϵ_{\perp} starts increasing at a fairly high temperature far above T_{AN} . ϵ_{\parallel} starts decreasing at a somewhat lower temperature, though still above T_{AN} . The decrease of ϵ_{\parallel} becomes very rapid at T_{AN} . These trends may be a reflection of (a) short range order effects near T_{AN} and (b) the strong variation of local

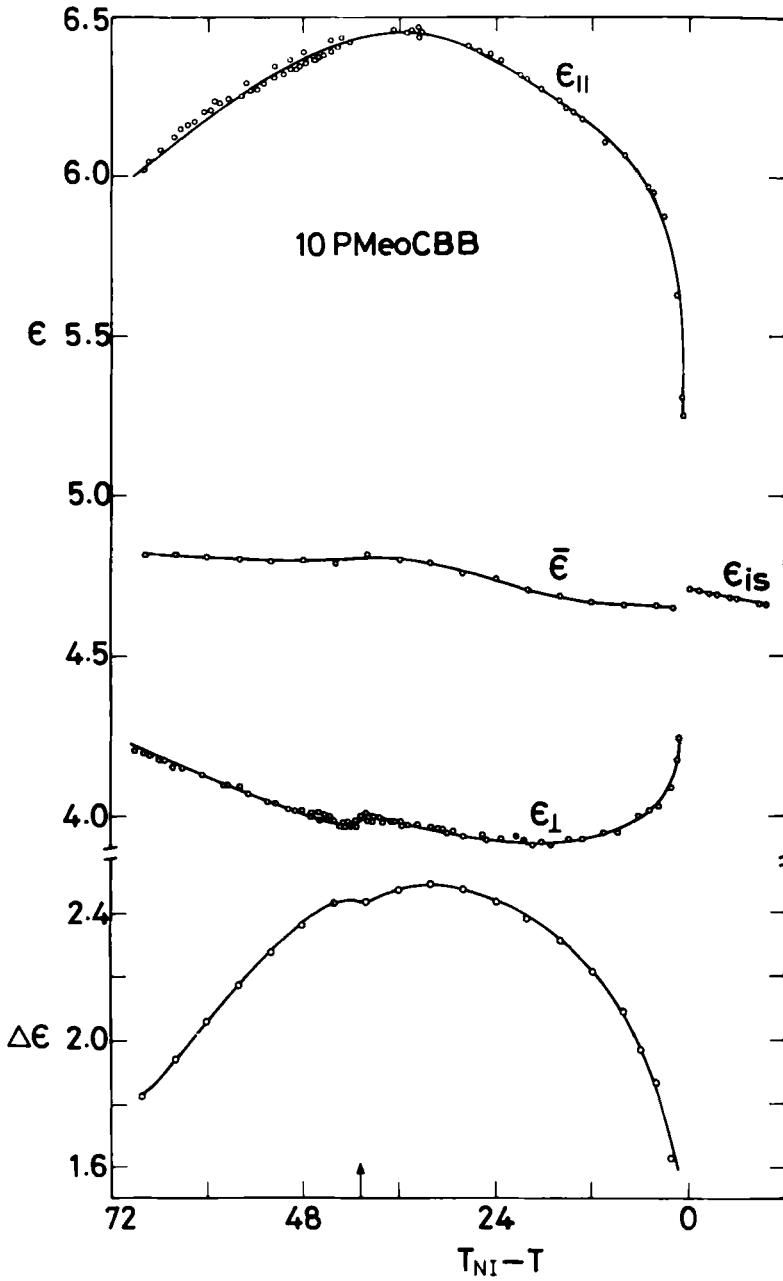


FIGURE 13 Temperature variations of the dielectric constants and anisotropy of 10 PMeOCBB.

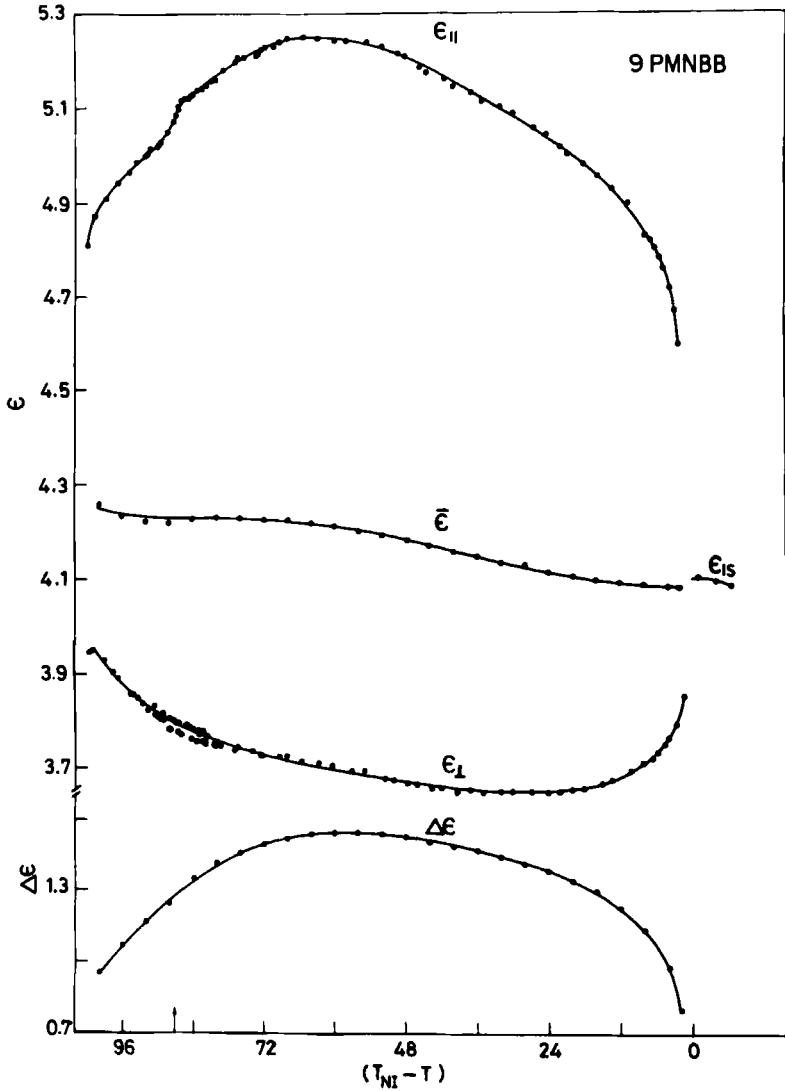


FIGURE 14 Temperature variations of the dielectric constants and anisotropy of 9 PMNBB.

field with temperature which depends on the relative number of associated molecules and single molecules (see the discussion in connection with the X-ray results). In the case of 10 PMNBB (Figure 15), $\epsilon_{||}$ exhibits a clear negative jump while ϵ_{\perp} shows a less prominent increase as the sample is

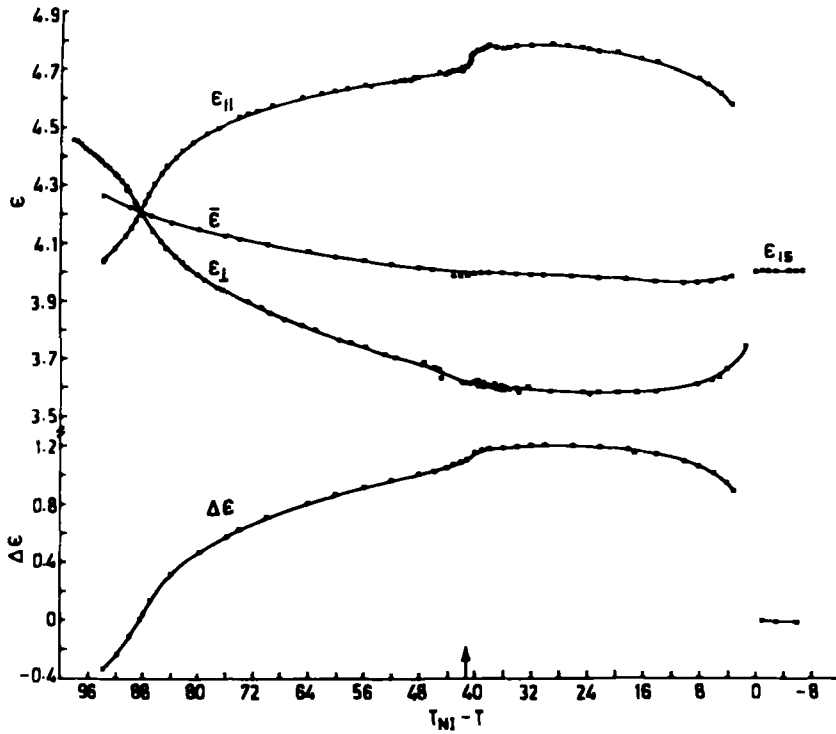


FIGURE 15 Temperature variations of the dielectric constants and anisotropy of 10 PMNBB.

cooled across T_{AN} . The rates of decrease of $\epsilon_{||}$ and increase of ϵ_{\perp} as the temperature is lowered in the A phase are somewhat similar. $\Delta\epsilon$ decreases continuously in the A phase and changes sign becoming negative at $T_{NI} - T = 90^{\circ}$. $\bar{\epsilon}$ shows a general increase with decrease of temperature. This result most probably means that the cancellation of the longitudinal components of the NO_2 dipole moments of two associated molecules (see Figure 10c) is not as effective as in the case of cyano compounds for reasons discussed earlier.

In the case of 12 PMNBB (Figure 16), the temperature variations of $\epsilon_{||}$ and ϵ_{\perp} change sign as the sample is cooled across T_{AN} . The rate of variations become somewhat stronger at $T_{NI} - T \approx 70^{\circ}$ at which temperature $\Delta\epsilon$ itself changes sign. At still lower temperature, the rates of variation level off. $\bar{\epsilon}$ increases with decrease of temperature in the A phase, the increase being somewhat larger than in the case of 10 PMNBB.

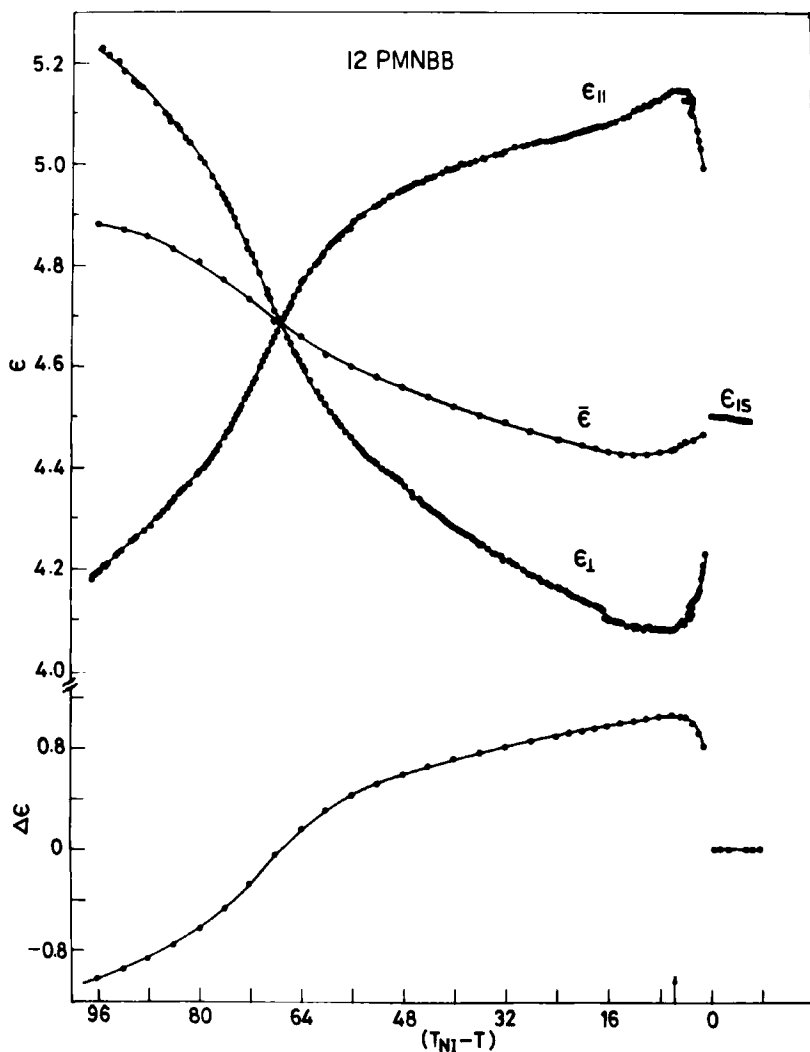


FIGURE 16 Temperature variations of the dielectric constants and anisotropy of 12 PMNBB.

As we have indicated, the results of dielectric studies can be understood in terms of the model of associated pairs breaking up with increase of temperature. It is interesting to note that the decrease of $\Delta\epsilon$ in the smectic phase in all the five compounds for which we have measured the dielectric properties, is somewhat similar in shape to the increase of the layer spacing in the corresponding cases.

(d) Conductivity studies

The principal conductivities of 12 PMCBP measured at 1592 Hz are shown in Figure 17. The conductivity anisotropy which is positive in the nematic phase changes sign and becomes negative in the smectic A phase, as is to be expected.²⁸ As the temperature is lowered in the A phase, the negative $\Delta\sigma$ increases further, both σ_{\parallel} and σ_{\perp} decreasing initially. However, at $T_{NI} - T \approx 80^{\circ}$, σ_{\parallel} attains a broad minimum, and starts *increasing* slightly as the temperature is further lowered. This is caused by the effect of the relaxation of ϵ_{\parallel} on σ_{\parallel} . As the temperature is lowered, the relaxation frequency decreases rapidly and thus it has an influence on the measured value of σ_{\parallel} . According to the theory of Schadt and Van Planta,²⁹

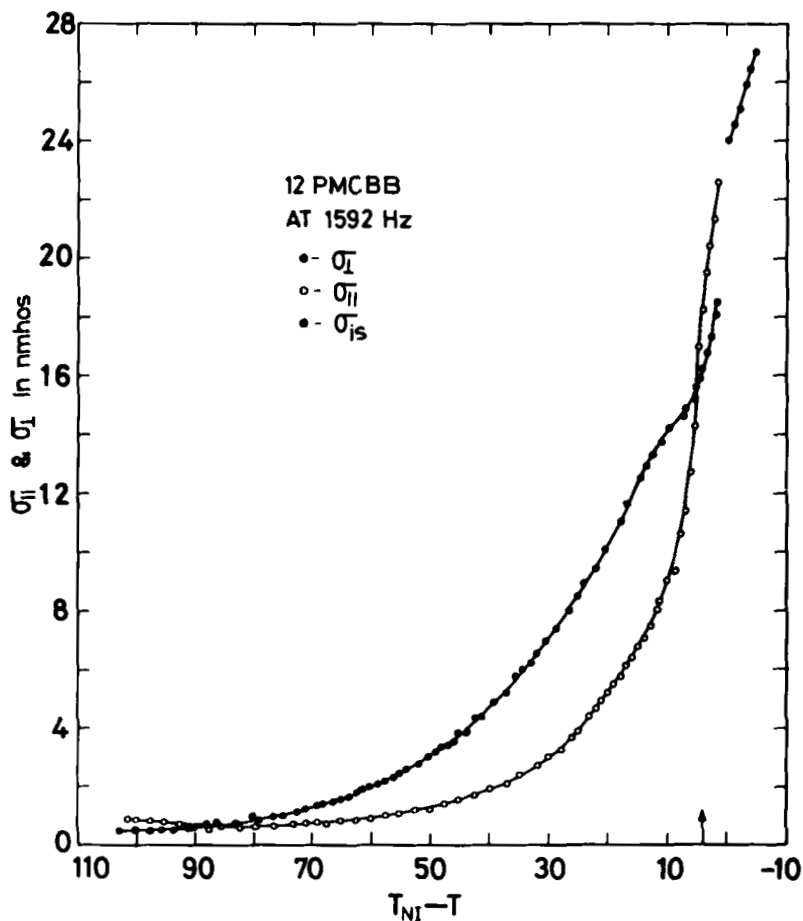


FIGURE 17 Temperature variations of the conductivities of 12 PMCBP at 1592 Hz.

$$\sigma(\omega) = \sigma(dc) + \frac{\epsilon_0(\epsilon - 1)}{1 + \omega^2\tau^2} \tau\omega^2$$

where τ is the relaxation time. If $\omega\tau \ll 1$,

$$\sigma(\omega) = \sigma(dc) + \epsilon_0(\epsilon - 1)\tau\omega^2.$$

The relaxation of ϵ_{\parallel} thus causes $\Delta\sigma$ at 1592 Hz to reverse sign again, becoming positive at very low temperatures. If we reduce the frequency of measurement to 300 Hz, however, σ_{\parallel} monotonically decreases with lowering of temperature (Figure 18) and there is no reversal of the sign of $\Delta\sigma$.

The trends in the conductivities of 10 PMEOCBB and 9 PMNBB are similar at 1592 Hz. $\sigma_R = \sigma_{\parallel}/\sigma_{\perp}$ does not become <1 , but tends to increase at low temperatures because of the relaxation effect of ϵ_{\parallel} as discussed above (Figure 19).

In the case of 10 PMNBB, as the temperature is lowered, the conductivity ratio at 1592 Hz becomes less than one at $\sim 15^\circ$ above T_{AN} , but does not go to a very low value and starts increasing as the temperature is lowered below $\sim T_{AN} - 15^\circ$ (Figure 20). In 12 PMNBB (Figure 21), the conductivity ratio σ_R at 1592 Hz takes a value considerably less than 1 before it starts increasing as the sample is cooled in the smectic phase. At 300 Hz (Figure 22), the conductivity ratio takes lower values as can be expected, but the relaxation effect is felt even at this frequency at low

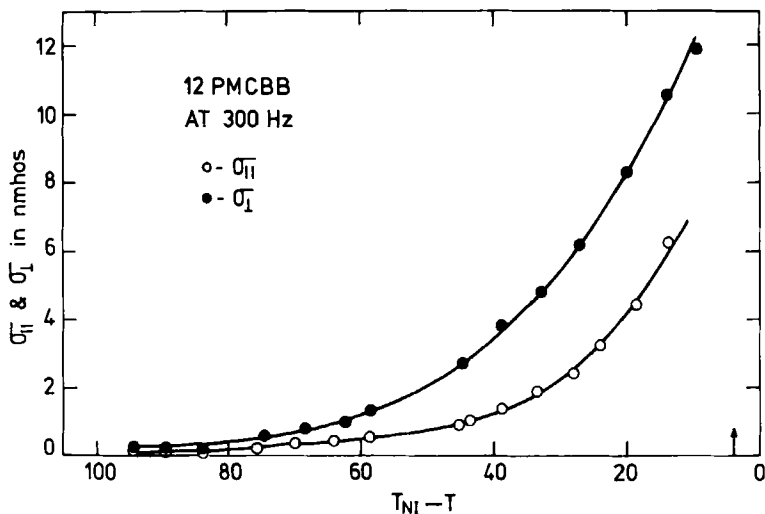


FIGURE 18 Temperature variations of the conductivities of 12 PMCBB at 300 Hz.

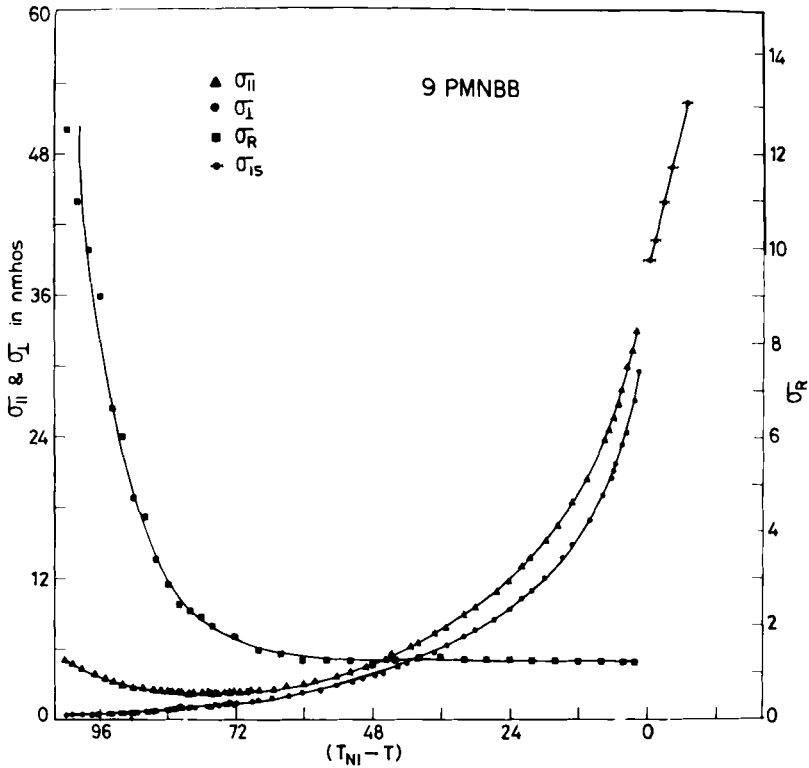


FIGURE 19 Temperature variations of σ_{\parallel} (triangles), σ_{\perp} (circles) and σ_R (squares) of 9 PMNBB at 1592 Hz.

temperatures. The progressive decrease in the minimum value of σ_R at 1592 Hz, as we increase n from 9 to 12 in n PMNBB is most probably connected with the progressively increasing smectic order of the higher homologues.

In conclusion, the mutual disposition of permanent dipolar groups in the molecules of mesomorphic compounds which have a strongly polar end group has a profound influence on the nature of phases exhibited by them. In order to bring home this point, in Table III we have collected together various properties of the 12th homologues of the different series studied by us.

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We are grateful to Professor S. Chandrasekhar for useful discussions. Our thanks are also due to Dr. K. A. Suresh for help in X-ray studies.

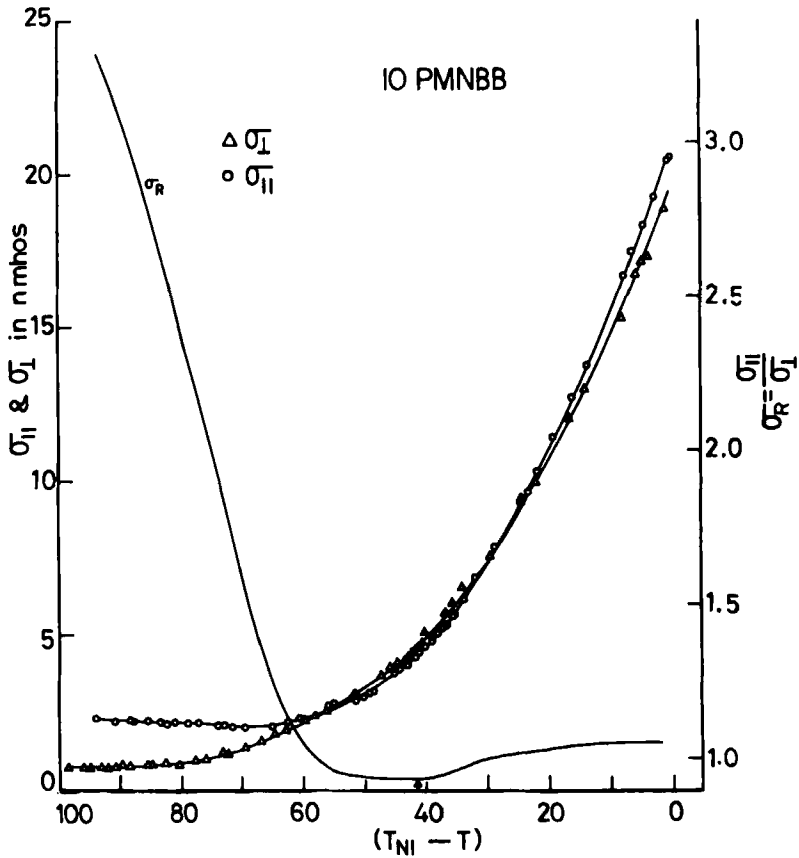


FIGURE 20 Temperature variations of $\sigma_{||}$, σ_{\perp} and σ_R of 10 PMNBB at 1592 Hz.

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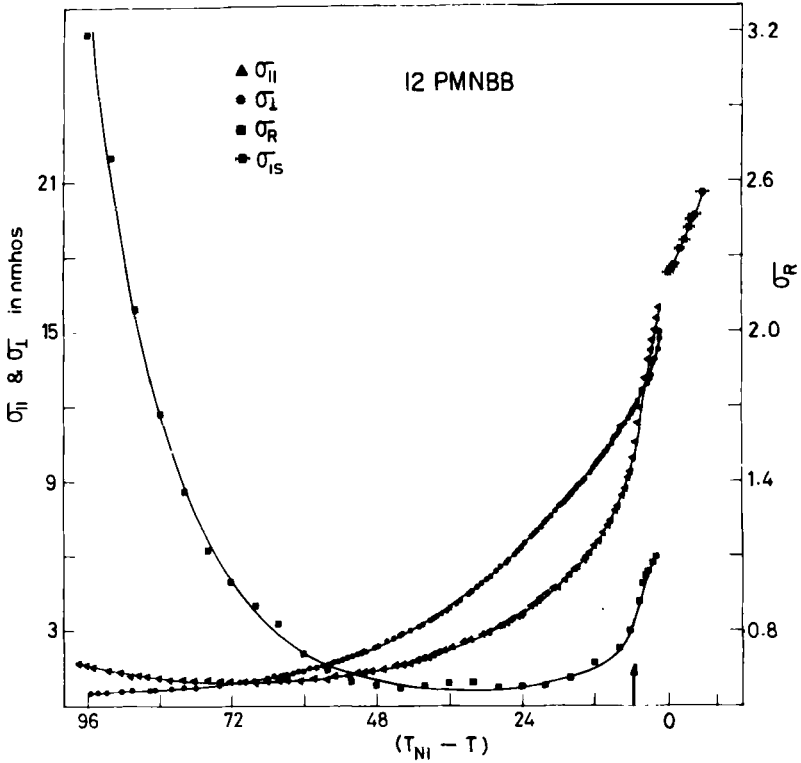


FIGURE 21 Temperature variations of $\sigma_{||}$ (triangles), σ_{\perp} (circles) and σ_R (squares) of 12 PMNBB at 1592 Hz.

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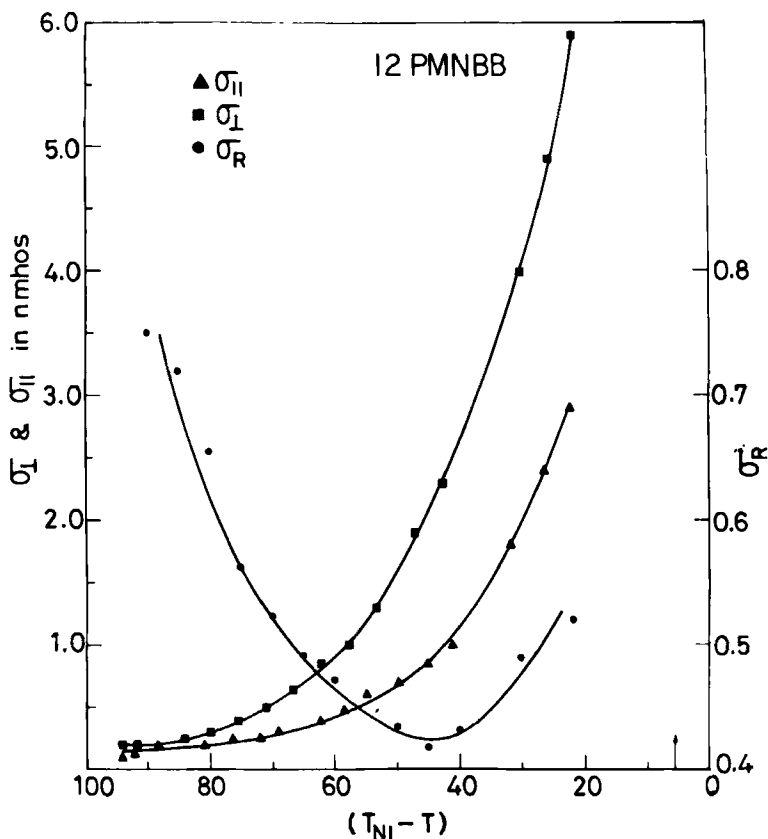


FIGURE 22 Temperature variations of σ_{\parallel} (triangles), σ_{\perp} (squares) and σ_R (circles) of 12 PMNBB at 300 Hz.

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TABLE III

Comparison of different properties of the 12th members of different series of compounds.

Compound	Transition temperatures in °C			d/l	$\Delta d/\Delta T$ Å/°C	$\bar{\epsilon}$	$ \Delta\epsilon $
12 CPMBB	$K \xrightarrow{102} A_d$	$A_d \xleftrightarrow{138} N$	$N \xleftrightarrow{148.5} I$	1.24	$\sim 0^+$	$\sim 11^+$	$\sim 11^+$
	$N_r \xleftarrow{59.8} A_d$						
12 PMCBB	$K \xrightarrow{67.5} A_2$	$A_2 \xleftrightarrow{77.1(?)} A_d$	$A_d \xleftrightarrow{155.3} N$	1.54 to 1.85	~ -0.1	~ 3.85	~ 0.8
			$I \xrightarrow{159.3} N$				
12 PMeOCBB	$K \xrightarrow{101.7} A_d$	$A_d \xleftrightarrow{130.3} N$	$I \xrightarrow{133.2} N$	1.46 to 1.72	-0.14	—	—
12 PMNBB	$K \xrightarrow{73.3} A_d$	$A_d \xleftrightarrow{141.3} N$	$I \xrightarrow{146.9} N$	1.39 to 1.8	~ -0.17	~ 4.5	~ 1

†from Ref. 21

‡from Ref. 30

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