Comparative X-ray and Dielectric Studies on Some Structurally Related Smectogenic Compounds

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In continuation of our earlier work on smectogenic compounds exhibiting large bilayer spacings, we report in this paper a comparative study of several compounds with lateral methyl or methoxy substituent. Some of the compounds do not have any strongly polar end groups while others have a cyano end group. The dielectric (both static and relaxation studies up to 13 MHz) and X-ray investigations on these compounds enable us to elucidate the physical mechanisms responsible for the observed differences in the properties of the compounds. We also discuss the possible origin of the often observed reduction of the activation energy corresponding to the $\epsilon_{\parallel}$-relaxation in the smectic A phase compared to that in the nematic phase.

1. INTRODUCTION

Recently we reported X-ray and static dielectric constant measurements on a number of smectogenic compounds having large bilayer spacings.[1-3] The compounds have a lateral methyl or methoxy substituent and a strongly polar cyano or nitro end group. The compounds also have two ester groups whose dipole moments oppose that of the terminal polar group. All the compounds exhibited a large thermal contraction of the bilayer spacing, and in many cases, a reversal of the static dielectric anisotropy which becomes negative at low temperatures. We could give a physical explanation for these observations on the basis of a structure in which the neighbouring molecules would favour an antiparallel correlation[4] such that only the polar end groups overlap in a pair. Such a structure is obviously
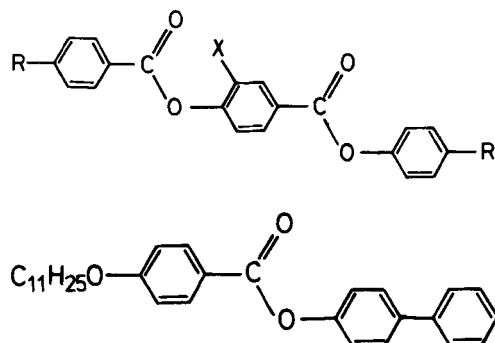
FIGURE 1   (a) General structure of the laterally substituted compounds studied in this paper. (b) Structural formula of biphenyl-4-*p*-*n*-undecyloxybenzoate.

fragile and would break up as the temperature is raised, leading to an explanation of the observed trends. If the dipole moments of the ester groups are parallel to that of the terminal cyano group and the lateral substituent is a methyl group, the compounds have a bilayer spacing $\simeq 1.4$ l (l is the molecular length), and some of them exhibit the reentrant nematic phase.[5]

In the present paper, we report our investigations on the layer spacings, static dielectric constants and dielectric dispersion studies (up to 13 MHz) on a number of structurally related smectogenic compounds. The basic structural formulas of the compounds are shown in Figure 1. The names of the compounds along with transition temperatures and enthalpies are listed in Table I.

2. EXPERIMENTAL

All the compounds used in this study were synthesized in our Chemistry Laboratory. The details of synthesis are reported elsewhere.[6-8]

The transition temperatures were determined using a Mettler FP52 hot stage in conjunction with a polarizing microscope. The enthalpies were determined using a Perkin Elmer DSC-2. X-ray photographs were taken using magnetically aligned samples. The static dielectric constants (at 1592 Hz) were determined using a Wayne Kerr B642 bridge. The experimental details are given in our earlier paper.[3] The dielectric relaxation studies were made on magnetically aligned samples taken between two glass plates coated with aluminium, using a Hewlett-Packard LF impedance analyser, model 4192A.

TABLE I

X	R	R'					
[Structural formula as in Figure 1(a)]	Symbol	K	N_R	A	N	I	
CH_3 C_nH_{2n+1} CN 4-cyanophenyl-3'-methyl-4-(4'-n-alkylbenzoyloxy)benzoate	11 CPMBB[a]	103	(78.5)	127 [0.0154]	152.5 [0.0147]	·	
	12 CPMBB	102	(59.8) [0.0464]	138.5 [0.0255]	148	·	
CH_3 CN C_nH_{2n+1} 4-n-alkylphenyl-3'-methyl-4'-(4''-cyanobenzoyloxy)benzoate	9 PMCBB[b]	64.4	—	119.6	175	·	
OCH_3 C_nH_{2n+1} CN 4-cyanophenyl-3'-methoxy-4-(4'-n-alkylbenzoyloxy)benzoate	11 CPMeOBB[c]	121 [41.2]	—	130.1 [0.17]	133.3 [1.6]	·	
	12 CPMeOBB	122.8 [43.5]	—	131.7	132.2 [3.13]	·	
OCH_3 CN C_nH_{2n+1} 4-n-alkylphenyl-3'-methoxy-4'-(4''-cyanobenzoyloxy)benzoate	11 PMeOCBB[c]	105 [35.1]	—	122 [—]	136 [1.8]	·	
	12 PMeOCBB	101.7 [28.8]	—	130.3 [0.035]	133.2 [1.7]	·	
OCH_3 Br C_nH_{2n+1} 4-alkylphenyl-3'-methoxy-4'-(4''-bromobenzoyloxy)benzoate	11 PMeOBrBB[c]	102.5	—	(85.3) [0.26]	(95.6) [1.46]	·	
	12 PMeOBrBB	93.0 [40.9]	—	(88.7) [0.29]	93.7 [1.43]	·	
Biphenyl-4-p-n-undecyloxybenzoate [Structural formula as in Figure 1b]	BO 11	100.5 [53.2]	—	109.5 [1.4]	124.5 [0.9]	·	

The numbers in square brackets indicate enthalpies in kJ/mole.
[a] see ref. 5
[b] see ref. 6
[c] see ref. 7
( ) indicate monotropic transitions.

3. RESULTS AND DISCUSSION

(a) X-ray studies

The temperature variations of layer spacings (d) in the smectic A phase of 11 CPMeOBB and 12 CPMeOBB are shown in Figures 2 and 3 respectively. In both the cases, the layer contracts by 1–2 Å as the temperature is raised by $\sim 70°$, the rate of contraction levelling off close to T_{AN}, the smectic A–nematic transition temperature. The molecular length (l) of 11 CPMeOBB calculated using Dreiding models is $\simeq 33.6$ Å and that of 12 CPMeOBB is $\simeq 35$ Å. Thus the measured spacings indicate interdigitated bilayers in both the cases, the aromatic cores of neighbouring molecules overlapping (as in Figure 10a of ref. 3). In the case of 11 PMeOCBB, which is obtained by interchanging the cyano and alkyl end groups of 11 CPMeOBB, the bilayer spacing is $\simeq 1.7l$ at low temperatures (Figure 4), and contracts by a large amount (~ 7 Å) as the temperature is raised to T_{AN}. The trend is similar to that observed by us[3] on other homologues of this compound. In this compound the ester dipoles oppose that of the cyano end group and consequently the structure of the bilayer at low temperatures can be expected to be as shown in Figure 10c of ref. 3. In this structure, neighbouring molecules will have antiparallel orientations with an overlap only near the terminal polar groups. As discussed earlier,[3] such a structure is fragile and breaks up to form a configuration in which the entire aromatic cores overlap as in Figure 10b of ref. 3, and/or the individual molecules can even become
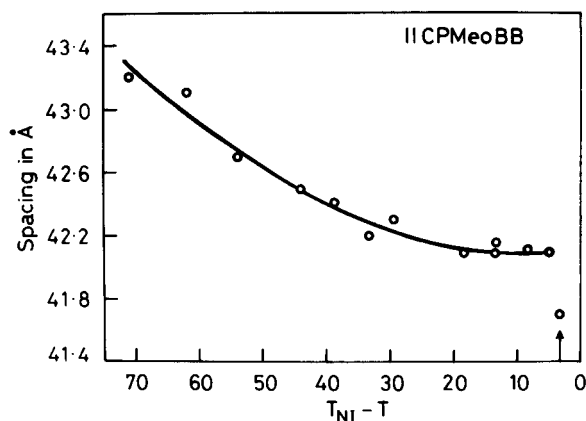

FIGURE 2   Temperature variation of layer spacing of 11 CPMeOBB. The arrow mark in this and subsequent diagrams indicates T_{AN}, the nematic–smectic A transition point.
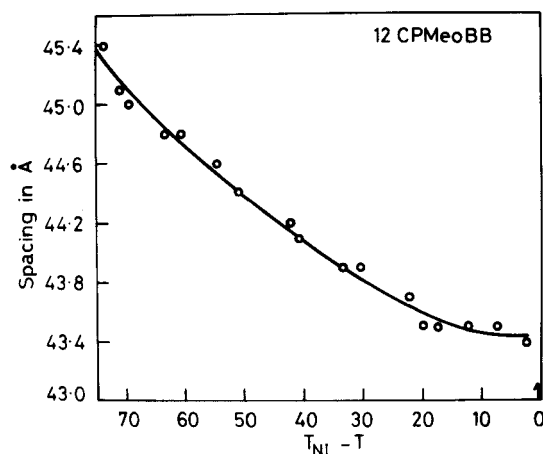
FIGURE 3   Temperature variation of layer spacing of 12 CPMeOBB.
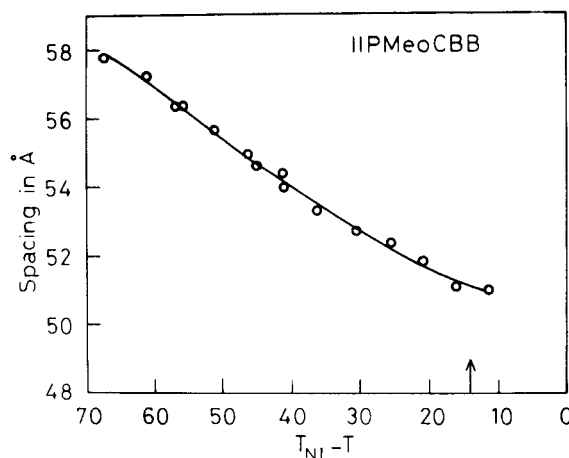
FIGURE 4   Temperature variation of layer spacing of 11 PMeOCBB.

independent (as in a monolayer). This causes large thermal contraction of d seen in Figure 4. 9 PMCBB which has only a methyl lateral group (Table I) also shows a similar behaviour except that the rate of contraction increases with increase of temperature (Figure 5). The latter trend agrees with our earlier observations[3] on the higher homologues of 9 PMCBB.

For the sake of comparison we have also studied the temperature variations of layer spacings of 11 PMeOBrBB and 12 PMeOBrBB in which the cyano end group of nPMeOCBB is replaced by a bromine

FIGURE 5 Temperature variation of layer spacing of 9 PMCBB.

atom leading to a large decrease in polarity of the terminal group. As shown in Figures 6 and 7, the layer spacing now corresponds to one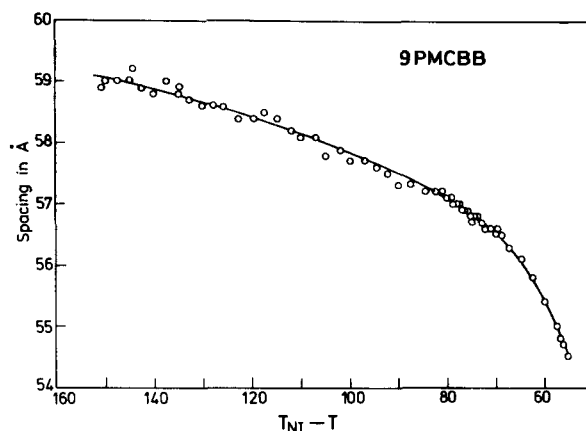 molecular length, i.e., the bromine compounds form a monolayer smectic A phase. Further, the layer spacing *expands* by ~ 1–2 Å as the temperature is raised by ~ 30–40°C, and the layer expansion coefficient increases as T_{AN} is approached. This expansion appears to be much larger than that observed in earlier studies on monolayer smectics[9,10] which were made on compounds without any lateral substituent. Our own measurements on the monolayer spacing of B0 11 (see Table I) which does not have any lateral substituent is shown in Figure 8 and this compound also exhibits only a very weak layer expansion with temperature. The layer expansion coefficient $(\Delta d/d\Delta T) \simeq 20 \times 10^{-4}$ in nPMeOBrBB near T_{AN} while it is about 10 times smaller in B0 11. We believe that this difference is due to the presence of a bulky methoxy substituent in the former compounds, leading to a much weaker attractive interaction between the aromatic moeities. Thus the layer expansion coefficient is of the order of volume expansion coefficient observed near A-N transition points of several compounds.[11] On the other hand, the attractive forces between the aromatic parts of molecules like B0 11 are much stronger and the layer expansion coefficient is weak and in such cases the volume expansion should therefore be accounted for by the creation of voids in the plane of the layers. Indeed as de Vries[10] has noted the average lateral spacing in such a system increases with temperature more rapidly in the A phase compared to that in the isotropic phase. The thermal contraction of the bilayer in the A phase of nCPMeOBB means that the molecular pairs with interdigitation of the aromatic
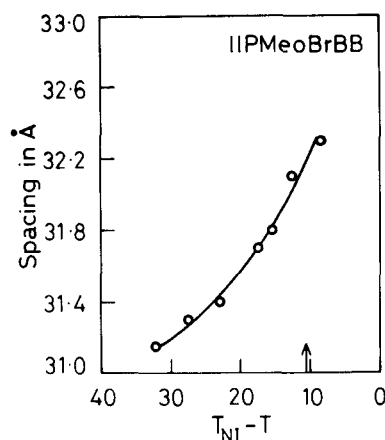
FIGURE 6   Temperature variation of layer spacing of 11 PMeOBrBB.
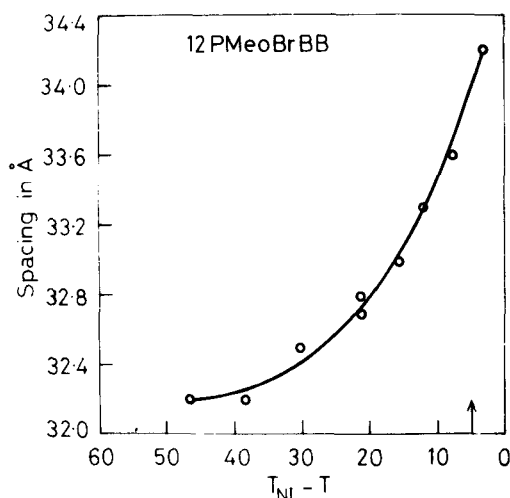
FIGURE 7   Temperature variation of layer spacing of 12 PMeOBrBB.

parts are also not strongly bound in these compounds. As we discussed earlier in the case of nPMeOBrBB, the mutual interactions are not very strong due to the presence of the lateral methoxy group and as the temperature is raised, the pairs can break up, giving rise to the layer contraction. However, there should also be an opposing trend, since, as in the case of nPMeOBrBB, the volume expansion should lead to a layer expansion. At lower temperatures, the latter effect is much smaller than the contraction effect due to the breaking up of

FIGURE 8 Temperature variation of layer spacing of BO 11.

pairs. As the temperature approaches T_{AN}, the two effects appear to balance each other leading to a levelling off in the layer spacing (Figures 2 and 3). On the other hand, in the case of nPMeOCBB, the breaking up effect on the large bilayer spacing is so strong that the volume expansion hardly affects the trend in the thermal evolution of layer spacing (Figure 4).
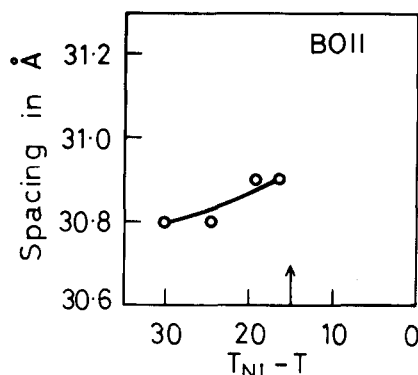
It is interesting at this point to refer to an earlier study[12] on some nCPMBB compounds (Table I), which exhibit the reentrant nematic phase. These have a lateral methyl group which is smaller than the methoxy group of nCPMeOBB compounds. The 11th and 12th homologues of the former series exhibit layer contraction as the temperature is raised from T_{AN_R}, and with further increase of temperature exhibit a broad minimum, and then an *expansion* of the bilayer spacing. Probably the breaking up of pairs is responsible for the low temperature behaviour and the large volume expansion as T approaches T_{AN} leads to the high temperature behaviour.

(b) Low frequency dielectric constants

The dielectric constants of 11 CPMeOBB and 12 CPMeOBB are shown in Figures 9 and 10 respectively. Both show relatively large positive dielectric anisotropy. The average dielectric constant $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ increases with increase of temperature in the smectic A and nematic phases, and show a considerable positive jump at T_{NI}. ϵ_{is} exhibits a broad maximum as the temperature is increased in the isotropic phase. These observations indicate a strong antiparallel correlation between the neighbouring molecules. $\epsilon_{\parallel}$ decreases as the temperature is lowered in the smectic A phase. As we have already
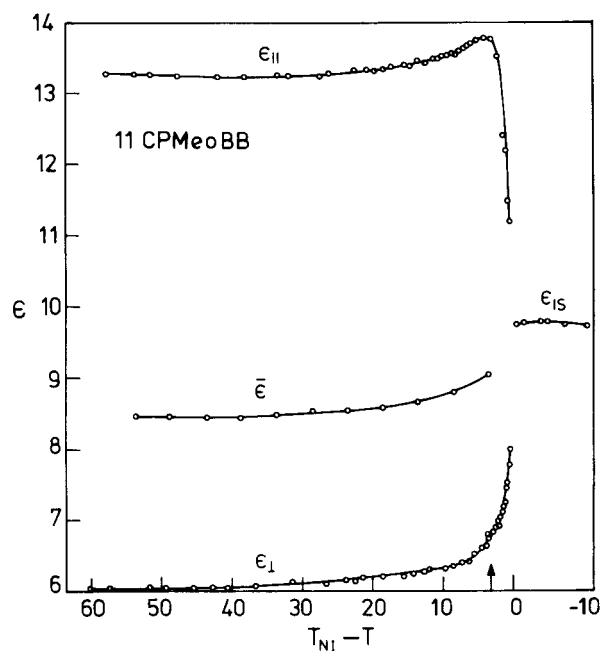
FIGURE 9 Temperature variations of low frequency dielectric constants of 11 CPMeOBB (measured at 1592 Hz).
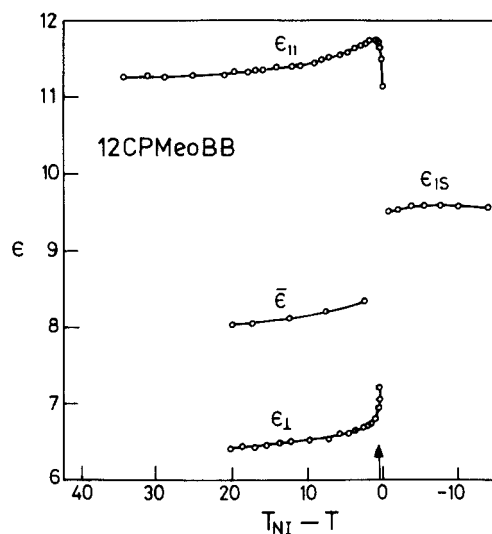

FIGURE 10 Temperature variations of low frequency dielectric constants of 12 CPMeOBB (measured at 1592 Hz).
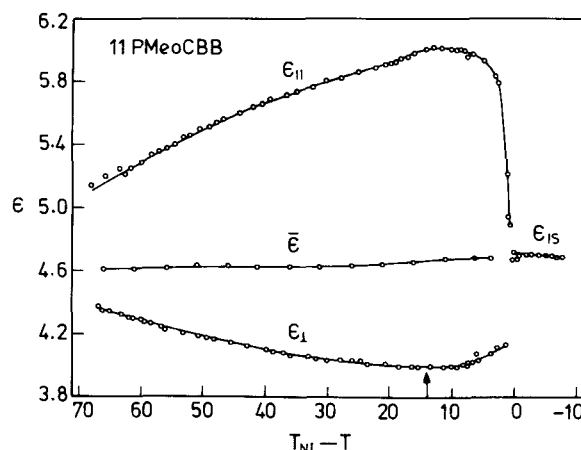
FIGURE 11　Temperature variations of low frequency dielectric constants of 11 PMeOCBB (measured at 1592 Hz).

discussed, pair formation is more effective at lower temperatures, and this leads to an effective lowering of the dipole moment along the long axis of the molecules, and hence to the observed reduction in $\epsilon_{\parallel}$. The dielectric constants of 11 PMeOCBB are shown in Figure 11. The dielectric anisotropy and $\bar{\epsilon}$ are much smaller than in 11 CPMeOBB as is to be expected (see Table I). In the smectic A phase $\epsilon_{\parallel}$ decreases and $\epsilon_{\perp}$ increases as the temperature is lowered due to the formation of pairs with an overlap of the polar ends, as discussed in our earlier paper.[3]

The dielectric constants of 11 PMeOBrBB are shown in Figure 12. The compound exhibits a negative dielectric anisotropy, $\bar{\epsilon}$ *decreasing* with increase of temperature as is to be expected in the absence of any associations between strongly polar groups. Further, $\bar{\epsilon}$ has a positive jump of 1% at T_{NI}.

(c)　Dielectric relaxation

As is well known, if the molecules have a long axis component of the dipole moment, $\epsilon_{\parallel}$ relaxes at relatively low frequencies.[13] The long axis of the molecules have two potential energy minima in the nematic and smectic A phases and the molecules have to overcome a potential barrier to reorient under the action of an external oscillating field along the director. Thus, in 11 CPMeOBB, $\epsilon_{\parallel}$ relaxes at a frequency of $\simeq$ 90 KHz at the lowest temperature of measurement in the smectic A phase ($\sim$ 80°C), the frequency shifting to higher values at higher
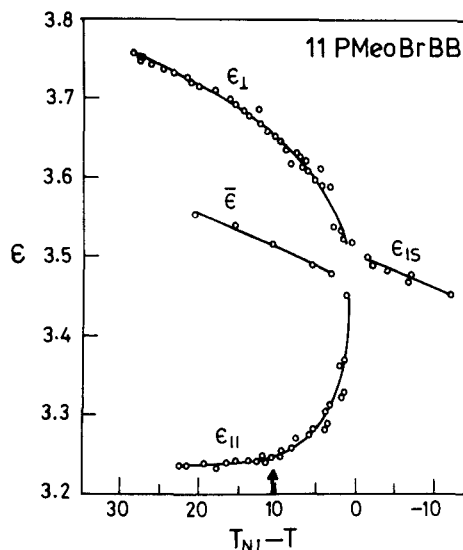
FIGURE 12 Temperature variations of low frequency dielectric constants of 11 PMeOBrBB (measured at 1592 Hz).

temperatures. One of the curious trends noted for the compound is that the peak of $\epsilon_{\parallel}''$ (imaginary part of the dielectric constant) has practically the same *level* at all temperatures. One would normally expect a progressive reduction in this level as the temperature is increased since the orientation polarization which determines the height of this peak is reduced at higher temperatures. As was discussed in an earlier section, 11 CPMeOBB molecules tend to break off from the bilayer structure at higher temperatures. This means that the effective dipole moment per molecule *increases* with increasing temperature and thus the orientation polarization does not have the normal decreasing trend. Indeed the Cole–Cole plot which is a good semicircle (Figure 13) is practically identical at all temperatures in the smectic A phase. The same trend is observed in 12 CPMeOBB also. The $\epsilon_{\parallel}''$ peak in this case is 3.8 compared to 4.9 of 11 CPMeOBB as the effective dipole moment per unit volume is lower for the higher homologue. As in the X-ray studies, the effect of the breaking up of the bilayer structure is even more spectacular in the case of 11 PMeOCBB. The $\epsilon_{\parallel}''$ peak actually *increases* with increase of temperature from ~ 1.16 at 80°C to ~ 1.36 at 114°C in the smectic A phase (Figure 14). On the other hand, in the nematic phase, there is a slight reduction in the peak value of $\epsilon_{\parallel}''$ with increase of temperature. As we have discussed earlier, the bilayer structure in this case is very fragile
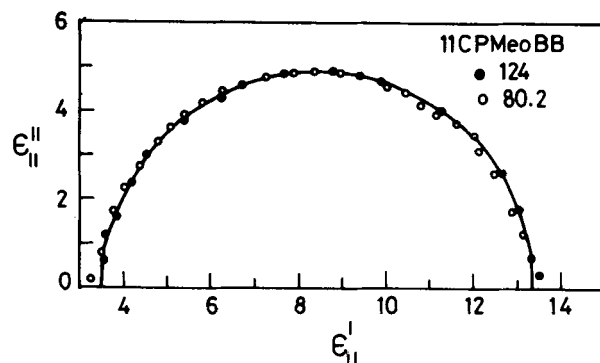
FIGURE 13   Cole–Cole plot for $\epsilon_{||}$ relaxation in the case of 11 CPMeOBB. The centre of the semicircle lies on the ϵ' axis indicating that the relaxation is of Debye type. In this and subsequent diagrams, the numbers against the symbols indicate the temperatures in °C.
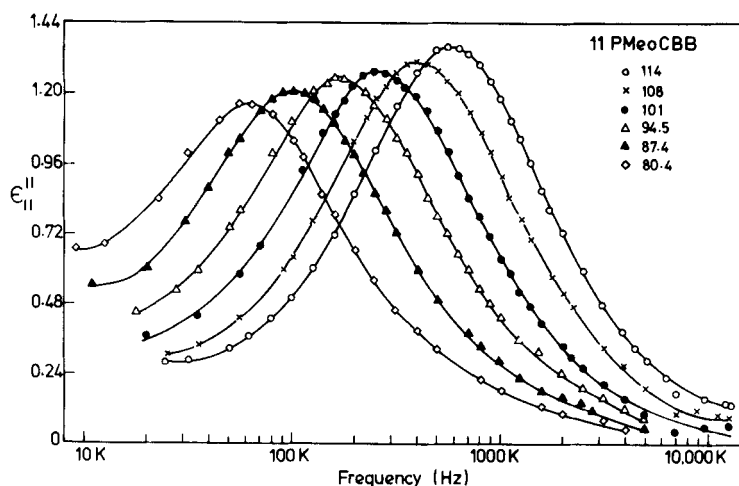
FIGURE 14   Frequency dependence of $\epsilon_{||}^{||}$ at various temperatures in the smectic A phase of 11 PMeOCBB.

and thus there are a larger number of free molecules with a corresponding enhancement of the effective dipole moment at higher temperatures. As is to be expected $\epsilon_{||}^{||}$ peak is much smaller than in 11 CPMeOBB since the effective long axis component of the permanent dipole moment is much smaller in the case of 11 PMeOCBB (see Table I). The Cole–Cole plot (Figure 15) also brings out the fact that there are additional relaxations at higher frequencies for this compound, unlike in the case of 11 CPMeOBB. This is probably caused by the
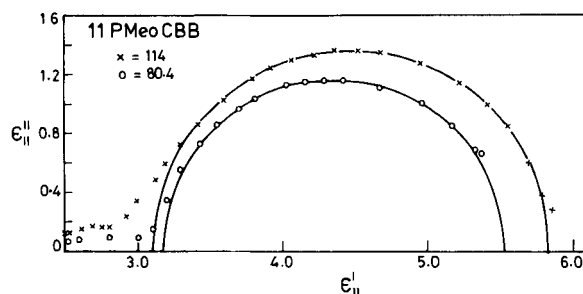
FIGURE 15   Cole–Cole plot for $\epsilon_{\|}$ relaxation in the case of 11 PMeOCBB.

relaxation of the reorientation of $\mu_\perp$, the component of the dipole moment perpendicular to the long axis. Indeed $\epsilon_\perp$ shows a very broad relaxation (Figure 16) with a broad maximum at ~ 6 MHz. This appears to be a particularly low frequency for the relaxation of $\mu_\perp$ and in contrast we did not see any indication of $\epsilon_\perp$ relaxation in 11 CPMeOBB in this frequency range. Obviously the structure characterized by a large bilayer spacing is responsible for this relaxation. If the molecular *pairs* which have an overlapping region only near the cyano end groups reorient as a *single unit*, we could expect a lowering of the relaxation frequency for the moment of inertia of the pair reorienting about an axis which is tangential to the surface of contact of the two molecules is much larger than that for a single molecule reorienting about its long axis. Further, the pair would have much greater probability of colliding against neighbouring pairs or individual molecules in the reorientation process and hence the effective friction coefficient would also be large. Thus the relaxation occurs at a fairly low frequency. Indeed measurements at higher frequencies can be expected to show another relaxation of $\epsilon_\perp$ due to the reorientations of the individual molecules about their long axis. The relaxation of the *pairs* is also reflected in the dispersion of $\epsilon_{\|}$ as we saw in Figure 15. The Cole–Cole plot corresponding to $\epsilon_\perp$ (Figure 16) also shows that
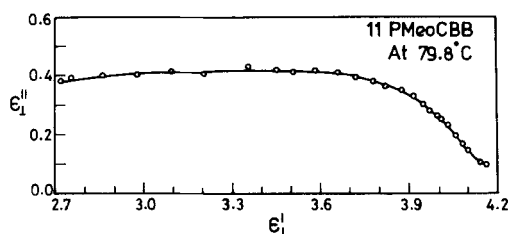
FIGURE 16   Cole–Cole plot for $\epsilon_\perp$ relaxation in the case of 11 PMeOCBB.

the dispersion is characterized by a rather broad distribution of relaxation times. A broad distribution is indeed expected for the $\epsilon_\perp$ relaxation as the libration of the molecules about the short axis contributes to this relaxation process. The molecular order and hence the local field is not well defined in this direction. The barrier height for reorientation is so small that only a distribution of relaxation times can be expected.[14] Further, in the case of 11 PMeOCBB there are more than one species (pairs which overlap at the end groups only, those with overlap of the entire aromatic core and individual molecules) which should contribute to the extremely broad distribution of relaxation times seen in Figure 16.

We shall now return to a further discussion on the dispersion of $\epsilon_{||}$. It is interesting to note that *both* 11 PMeOCBB and 11 CPMeOBB tend to have the same value of $\epsilon_{||}$ at frequencies just greater than that of relaxation, the value being $\simeq 3$ at the lowest temperatures of measurement. This is understandable, since at these frequencies the contributions to $\epsilon_{||}$ arise from the induced dipole moment along the long axes of the molecules and induced as well as permanent dipoles perpendicular to the long axes.[15] All these contributions are eventually the same in the two compounds. However, in the case of 11 PMeOCBB as the frequency is further raised to ~ 13 MHz $\epsilon'_{||}$ begins to decrease again since the orientational polarization perpendicular to the long axes relaxes as we discussed earlier.

By plotting $\ln f_R$ against $1/T$ where f_R is the frequency corresponding to the maximum in $\epsilon''_{||}$ and T the absolute temperature, we get straight line graphs in the nematic and smectic A phases as shown in Figure 17 for 11 PMeOCBB. The slope of the line gives the activation energy, the values of which are listed in Table II for all the 3 compounds studied. It is interesting to note that the activation energy is practically the same in the A phases of both 11 CPMeOBB and 11 PMeOCBB. The activation energy is *lower* in the smectic A phase than in the nematic phase. The latter result has been found earlier in several studies[16-18] on compounds exhibiting both nematic and smectic A phases. The activation energy is a sum of both the rotational potential barrier against flipping about the short axis and the dissipation due to the friction coefficient which is effective against such a rotational diffusion. Hence the lowering of the activation energy in the smectic A phase is somewhat puzzling as one would expect that at least the orientational potential barrier would be higher due to the higher order parameter in the smectic A phase. Druon and Wacreneir[19] have tried to explain this reduction in the case of bilayer smectics by pointing out that the two neighbouring molecules have an asymmetric potential
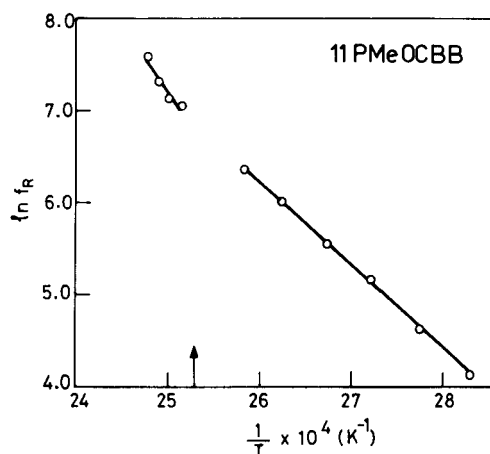
FIGURE 17 Plot of $\ln f_R$ against $1/T$ in the smectic A and nematic phases of 11 PMeOCBB.

energy curve as a function of the angle between their long axes (Figure 18). They assumed that in the nematic phase the asymmetry would disappear (i.e., $W_{SN} = W'_{SN}$). In the A phase the layering is supposed to bring in the asymmetry such that $W_{SA} > W'_{SA}$ and further that $W'_{SA} < W_{SN}$. If W_{SA} is very much greater than W'_{SA}, one can expect that the external field will not be able to disturb the molecular pairs in the antiparallel configuration (i.e., with energy W_{SA})[20] and only the molecules in the parallel configuration (with potential barrier W'_{SA}) would participate in the reorientation. As it is assumed that $W'_{SA} < W_{SN}$, the activation energy is lowered in the A phase. However, we must point out that it is unlikely that the anisotropy of the potential energy will vanish in the nematic phase. Druon and Wacreneir's argument still holds if the anisotropies in the two phases are such that $W'_{SA} < W'_{SN}$. In other words, the layering of the A phase helps to *increase* the repulsive interactions between cyano end groups of parallel molecules.

TABLE II

Activation energies in eV in the smectic A
and nematic phases

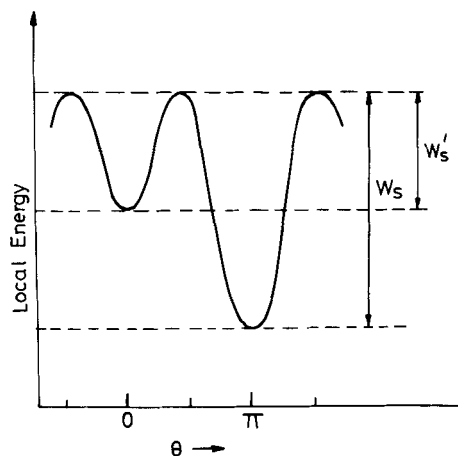| Compound	Smectic A	Nematic
11 CPMeOBB	0.75	—
12 CPMeOBB	0.70	—
11 PMeOCBB	0.78	1.27

FIGURE 18   Schematic diagram depicting the variation of local energy of a pair of highly polar molecules as a function of the angle between their long axes (according to the Ref. 19).

Further, the lowering of the activation energy is found not only in bilayer structures but also in monolayer smectics[21] in which the potential energy anisotropy is likely to be quite small. Hence the origin of the phenomenon is to be sought in the layered arrangement of the A phase itself. In the following paragraphs, we will try to argue that two different mechanisms may be responsible for this effect.

Recently Edwards and Madden[22] have proposed a molecular theory of the dielectric permittivity of a *nematic* liquid crystal in which intermolecular dipole–dipole correlations are explicitly taken into account. Following a procedure developed earlier by Sullivan and Deutch[23] for isotropic liquids, they have given frequency dependence of the parallel and perpendicular components of the complex dielectric constant in terms of dipole correlations which are of short range and under certain simplifying approximations have derived explicit expressions for the dielectric constants. From these expressions one can write for the relaxation time parallel to the director

$$\tau_\| = \tau_D g_\| \left(\frac{\epsilon_\| - 1}{\epsilon - 1} \right) \qquad (1)$$

with a similar expression for $\tau_\perp$. Here τ_D is the usual Debye relaxation time, $g_\|$ the retardation factor caused by the nematic potential introduced by Maier and Meier.[13,14] $\epsilon_\|$ the *static* dielectric constant parallel to the director and ϵ the mean dielectric constant. The terms in

brackets are new in this theory and arise from the dipole correlations in the medium.

We assume that the relation (1) can be used in the A phase also. The layering of the A phase gives rise to increased antiparallel dipole correlations between the long axis components of dipoles. This has been found experimentally for several cases, including relatively weak polar compounds.[24-26] Indeed such correlations lead to a lowering of $\epsilon_{\parallel}$ in the smectic A phase as we can see from Figures 9–11. This means that $\tau_{\parallel}$ will be smaller in the smectic A phase than in the nematic phase even if $g_{\parallel}$ which depends only on the orientational order parameter is the same in the two phases. Thus the layering order present in the smectic A phase gives rise to a lowering of $\tau_{\parallel}$ or equivalently a higher value of the frequency of relaxation. Further, as the temperature is lowered in the smectic A phase, the smectic order parameter increases and hence this effect also increases. This is obviously equivalent to a lowering of the activation energy as can be seen, for example, from Figure 17.

We also believe that a second mechanism may operate in the smectic A phase due to packing effects. As we discussed earlier, the thermal expansion in the smectic A phase appears to be considerably anisotropic. Usually the layer spacing does not vary much with temperature in monolayer smectics. In other words, voids are pushed into the layers in the A phase, and the density per unit area of the layer appears to be smaller than the density per unit area normal to the director in a nematic of the same overall density per unit volume. Consequently the number of collisions that a molecule suffers in a reorientational motion can be smaller in the smectic A phase[27] or the relaxation time can be lower or effectively the activation energy can be lower than in the nematic phase at the same density. This effect perhaps makes a relatively important contribution in smectics formed by compounds which do not have any bulky lateral substituent. For instance, this effect may be important in 4-n-octyloxy-4-cyano-biphenyl (8 OCB) which exhibits a bilayer smectic A phase with hardly any temperature dependence of the layer spacing.[28] 8 OCB also exhibits a lower activation energy in the A phase than in the nematic phase.[29] The packing effect may also explain the earlier observation[18] of two activation energies in 11 CPMBB and 12 CPMBB. As we noted earlier, these compounds have a contraction of the layer spacing in the lower temperature range of the smectic A phase but an *expansion* at higher temperatures. The activation energy in the two regions is distinctly different, being lower in the lower temperature range. The layer expansion in the higher temperature range would imply that the

expansion is more isotropic in this range and thus the packing effects would *increase* the activation energy, compared to that of the A phase at lower temperatures even though it continues to be smaller than that of the nematic phase.

As we discussed earlier, in the case of 11 PMeOBrBB the layer spacing increases considerably with temperature. But we could not study the influence of this factor on the activation energies: the long axis component of the dipole moment is so low in 11 PMeOBrBB that no dispersion of $\epsilon_{\parallel}$ could be measured.

In conclusion, we have found that bromo compounds whose molecules do not have strongly polar end groups exhibit monolayer smectic A phase. When the bromine atom is replaced by the polar cyano group a bilayer is found. If the cyano dipole moment is parallel to the ester dipole moments, the bilayer spacing is $\simeq 1.4 \ l$. On the other hand, if the ester dipoles oppose the cyano dipole the bilayer thickness is much larger and the structure rather fragile. It tends to break up with the increase of temperature, this effect being strong enough in the case of 11 PMeOCBB to give rise to some unusual effects in the dielectric relaxation. Further, the increased antiparallel correlation in the layered A phase compared to that in the nematic phase and the anisotropy in the expansion coefficient of the layered A phase appear to lead to a lower activation energy for the low frequency dielectric relaxation of $\epsilon_{\parallel}$ in the smectic A phase compared to that in the nematic phase.

Acknowledgments

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