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Ferroelectric and antiferroelectric low molar mass organosiloxane liquid crystals

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The present paper is a study of the ferroelectric and antiferroelectric behaviour in low molar mass organosiloxane liquid crystal materials classed as mono-mesogens (AB type) and bi-mesogens (ABA type). A systematic study of series of materials all based on the same chiral mesogenic moiety is presented. The mesogen is a biphenylyl benzoate with a halogen *X* attached laterally to the benzoate ring which is closest to the chiral centre. Three homologous series, where the halogen is either fluorine, chlorine or bromine, are investigated. The number of silicon atoms in the linkage or end group is varied between two and nine. It is found that the materials have a broad (~40°C) ferroelectric or antiferroelectric phase with a high $\mathbf{P}_s$ (~90 nC cm^{-2}). The siloxane moiety forces the tilt angle to a temperature independent value close to 45°. The antiferroelectric order is observed only in bi-mesogens with an odd number of silicon atoms in the siloxane link. The antiferroelectric order is attributed to the conformation of the molecule rather than to antiferroelectric interactions between layers.

1. Introduction

In a low molar mass organosiloxane liquid crystal material the molecules consist of one or more mesogenic moieties attached via an alkyl chain spacer to a short siloxane group. The siloxane chain which contains typically less than eleven silicon atoms is an integral part of the mesogenic molecule. In the liquid crystal phases the siloxane groups microseparate and form what could be regarded as an effective polymer backbone [1–3]. This molecular arrangement confers on the materials some of the robust mechanical properties of polymers but retains the fast electro-optic response of the low molar mass liquid crystal moiety. Because of their potential for applications, low molar mass organosiloxane liquid crystals are at present the object of intense investigations [4–10].

In order to gain a complete understanding of the mechanisms that determine, at the molecular level, the characteristics of low molar mass organosiloxane materials, we have undertaken the systematic study of series of materials all based on the same chiral mesogenic moiety illustrated in figure 1. The mesogenic unit is a biphenylyl benzoate with a halogen *X* attached laterally to the ring lying closest to the chiral centre. Three homologous series where the halogen is either fluorine, chlorine or bromine have been synthesized. In each series we have, in a first step, investigated the role of the siloxane moiety by varying the number of silicon atoms in the linkage or end group and keeping constant (11 carbon atoms) the length of the alkyl chain spacer.

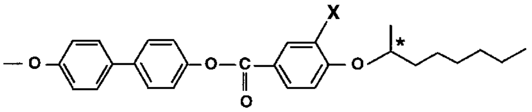

Figure 1. A schematic diagram of the mesogenic moiety.

The present paper is a study of the ferroelectric and antiferroelectric phases in the mono-mesogenic (AB type) and the bi-mesogenic (ABA type) materials. A more detailed description of the synthesis and of the properties of the materials in these series is given in separate publications [5, 11, 12]. In the AB molecules a single mesogen unit A is attached to the siloxy group B and in the ABA molecules two mesogen units are attached symmetrically to the siloxy group. As a reference base to assess the effects of the siloxy group on the behaviour of the materials, we have also characterized the vinyl terminated mesogenic precursors.

We use the notation *Xm-n* and *Xm-n-mX* to denote, respectively, the AB and the ABA type molecules; *n* indicates the number of silicon atoms in the siloxane group, *m* the number of carbon atoms in the alkyl chain spacer (*m*=11 in the present paper) and *X* refers to the halogen. In this notation the molecule illustrated in

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figure 2(*a*) is F11-3 and the molecule in figure 2(*b*) is Br11-2-11Br. The vinyl terminated precursors are denoted by *Xm* where again *X* refers to the halogen and *m* to the number of carbon atoms in the alkyl chain.

2. Experimental

The materials were synthesized following the route outlined in references [5, 11]. The phase sequences and transition temperatures were determined by differential scanning calorimetry (DSC), by polarized light microscopy and by observing the electro-optic response of the materials. All the materials display a broad smectic C* phase with a high spontaneous polarization, of the order of 100 nC cm^{-2}, and a high tilt, close to 45° in most materials.

The measurements of the tilt angle and the spontaneous polarization were made on 5 μm thick specimens contained in glass cells treated with rubbed polyimide. The tilt angle was determined by optical microscopy, as half the angle between two positions of optical extinction when the sample is switched between crossed polarizers. The spontaneous polarization was evaluated within an accuracy of ± 3 nC cm^{-2} using the current pulse technique. The measurements of the layer spacing by powder X-ray diffraction have been the object of a separate publication [13]. For completeness, a summary of the measurements is given in table 1. The layer spacings are only very weakly dependent on temperature.

3. Results

3.1. *The vinyl terminated precursors*

A summary of the relevant characteristics of the vinyl terminated precursors is given in table 2. On heating from the crystal phase all the materials display a broad ferroelectric phase and then a narrow range chiral nematic phase before clearing to the isotropic state. The tilt angle in the ferroelectric phase increases significantly with the atomic mass of the halogen. In the fluorine and the chlorine substituted materials there is a small but measurable variation of the tilt angle with temperature. The change in the tilt angle across the temperature range of the phase is of the order of four degrees 'two standard deviations in the measurements'. In the bromine substituted material the tilt angle is, within experimental uncertainties independent of the temperature.

In the bromine derivative, DSC measurements reveal a transition at about 60°C. This transition is also observed in the corresponding siloxane derivatives [11]. The phases on both sides of the transition are ferroelectric, and the spontaneous polarization and tilt angle are not affected at the transition. The nature of this transition is still being investigated and will be discussed in a separate publication.

3.2. *The siloxane materials*

All the siloxane materials with less than six silicon atoms in the siloxy group are pure monodisperse materials.

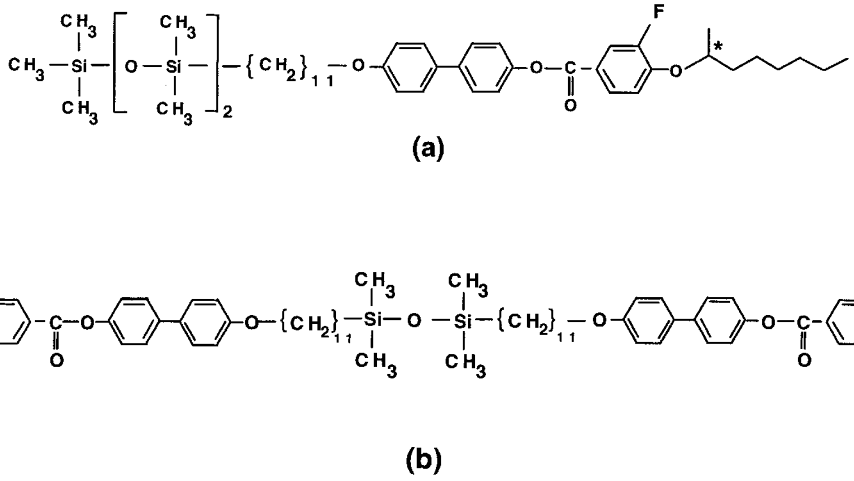


Figure 2. A schematic diagram of the F11-3 molecule (*a*) and the Br11-2-11Br molecule (*b*).

Table 1. The smectic layer spacing in Å from Corsellis *et al.* [13].

X	*X*11-2	*X*11-3	*X*11-2-11*X*	*X*11-3-11*X*	*X*11-4-11*X*	*X*11-5-11*X*
F	38·0	40·3	—	34·4	—	39·1
Br	35·0	39·0	36·0	33·2	33·9	35·6

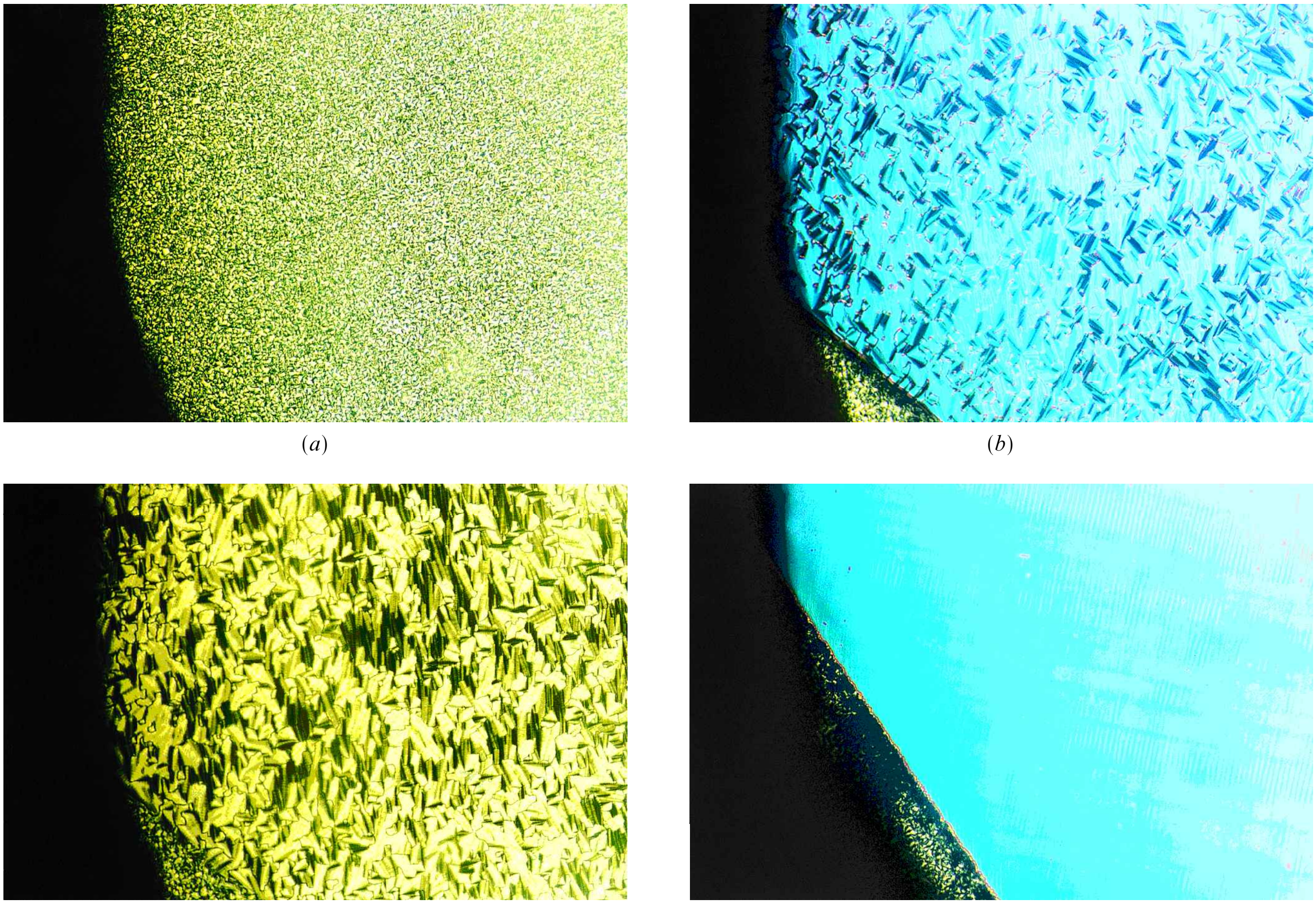
Table 2. The characteristics of the vinyl terminated precursors. The tilt angle and the spontaneous polarization were measured at the reduced temperature of −20°C.

	Transition temperatures/°C				
Compound	I/N*	N*/ferro	ferro/Cr	θ/ degrees	$\mathbf{P}_s$/ nC cm^{-2}
F11	106	101	62	22	70
Cl11	91·5	90	42	39	135
Br11	84	81	44	43	130

The materials with seven and nine silicon atoms had some degree of polydispersity ranging from two to eighteen repeat units.

When cooled in thin cells from the isotropic phase, all the siloxane materials adopt the fine sanded texture shown in figure 3(*a*). A focal-conic texture typical of the SmC* phase (figure 3(*b*)) can be induced by applying an electric field. This texture is stable and remains after the applied field is removed (figure 3(*c*)). A uniformly aligned texture (figure 3(*d*)) can be obtained by slowly cooling the specimen from the isotropic phase in the presence of a low frequency (1 Hz) triangular wave.

Apart from the higher order ferroelectric phase mentioned in the previous section the SmC* and SmC$_A^*$ are


(*a*) (*b*)

(*c*) (*d*)

Figure 3. The textures of Cl11-3-11Cl at 70°C viewed between crossed polarizers. (*a*) shows the texture on cooling from the isotropic phase. (*b*) shows the same area of the specimen in the presence of a d.c. electric field above threshold; the edge of the electrode can be seen at the left-hand bottom corner. In (*c*) the field has been switched off; notice the 45 degree rotation of the optic axis of the large domain in the centre of the picture. (*d*) is the same area of the specimen after alignment as described in the text.

the only mesophases observed; all the materials display a transition from the isotropic phase into the smectic C* phase and from the smectic C* into a glass.

The phase transition temperatures on heating are given in table 3 together with the spontaneous polarizations and the tilt angles measured at a fixed reduced temperature of -20°C. The response times are typically in the range of 100 to 300 μs in a field of 7 V μm^{-1}. Since the materials with nominally seven or nine silicon atoms are polydisperse, the data for these materials given in the table should be regarded only as indications and not as the true values for the monodisperse materials. The antiferroelectric order in the X11-3-11X and the X11-5-11X materials was evidenced by the three stable states in the electro-optic response (figure 4(*a*)) and by the two polarization-reversal peaks in the current response to a triangular voltage waveform, figure 4(*b*).

The temperature dependence of the tilt angle, the spontaneous polarization and the response time is very much the same in the fluorine, the chlorine and the bromine substituted series. For clarity we show only the data for the chlorine substituted series in figures 5(*a*), 5(*b*) and 5(*c*). In the figures the temperature dependence of the tilt angle, the spontaneous polarization and the response time measured for the mono-mesogenic and bi-mesogenic siloxane materials is compared with that measured for the vinyl terminated material.

4. Discussion

Three observations can be made from a glance at the data in table 3 and figure 5. The grafting of the siloxane group suppresses the chiral nematic phase, the tilt angle in the smectic C phase is always close to 45° and antiferroelectric phases are observed only with bi-mesogenic molecules containing an odd number of silicon atoms.

4.1. *Stabilization of the smectic phase*

The suppression of the chiral nematic phase in the siloxane material is expected because of the microseparation of the aromatic, paraffinic and siloxane moieties [2]. When, as in the present case, the siloxane moiety is an open chain, the siloxane moieties tend to aggregate in planes. This segregation at the molecular level strongly favours the formation of smectic phases and therefore suppresses any nematic phases. Similar observations have been made on organosiloxane materials based on cyanobiphenylyl mesogenic moieties [14].

4.2. *The tilt angle*

The definition of the molecular axis and therefore of the tilt angle for the low molar mass organosiloxane molecules is not trivial, and the direction of the average axis of the siloxane moiety can be quite different from that of the mesogenic moiety. Because it is the long axis of the mesogen that determines the electro-optic properties of the material, we define the tilt angle as the angle between the long axis of the mesogen and the normal to the plane of the smectic layers. It is clear from the data in tables 1 and 2 that the grafting of the siloxane moiety tends to impose a tilt of 45 degrees on the mesogens. This is most noticeable for the fluorine

Table 3. Physical properties of the organosiloxane materials at a fixed reduced temperature of -20°C below the clearing point.

Compound	Clearing temp./ °C	Mesophase	Melting temp. °C	$\mathbf{P}_s$/ /nC cm^{-2}	Tilt angle/ degrees
F 11-2	86·8	SmC*	34·8	61	43·8
F 11-3	81	SmC*	27·1	46	43·6
Cl 11-2	91·5	SmC*	42	111	43·4
Cl 11-3	92·5	SmC*	41	100	42
Br 11-2	82	SmC*	45	95	44
Br 11-3	88	SmC*	46	87	45
F11-2-11F	82	SmC*	36·5	20	39
F11-3-11F	121	$\mathrm{SmC_A^*}$	51·2	101	40·4
F11-4-11F	96	SmC*	38·0	30	40·5
F11-5-11F	115	SmC*/$\mathrm{SmC_A^*}$	46·9	87	40
F11-7-11F	84	SmC*	37·5	67	38
F11-9-11F	111·3	SmC*	46·3	61	36
Cl11-3-11Cl	110	$\mathrm{SmC_A^*}$	55·2	119	41·7
Cl11-5-11Cl	128	$\mathrm{SmC_A^*}$	52	106	41·2
Br11-3-11Br	106	$\mathrm{SmC_A^*}$	50	135	43·5
Br11-5-11Br	100	SmC*	41	100	43

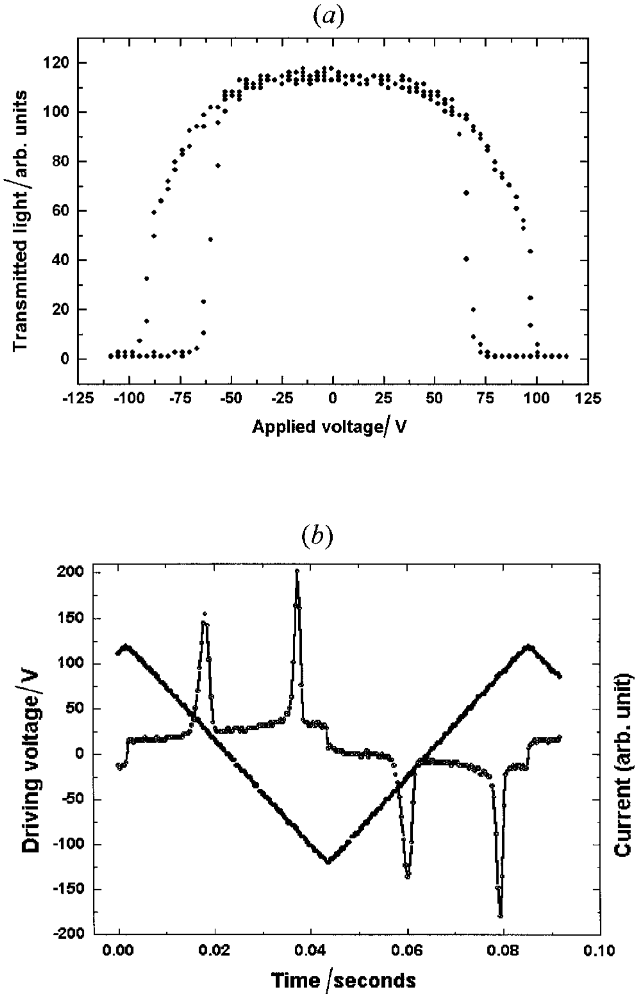


Figure 4. The three stable states in the electro-optic response (*a*). The two polarization-reversal peaks in the current response to a triangular voltage waveform (*b*). The measurements were taken on Cl11-3-11Cl at the reduced temperature of −20°C.

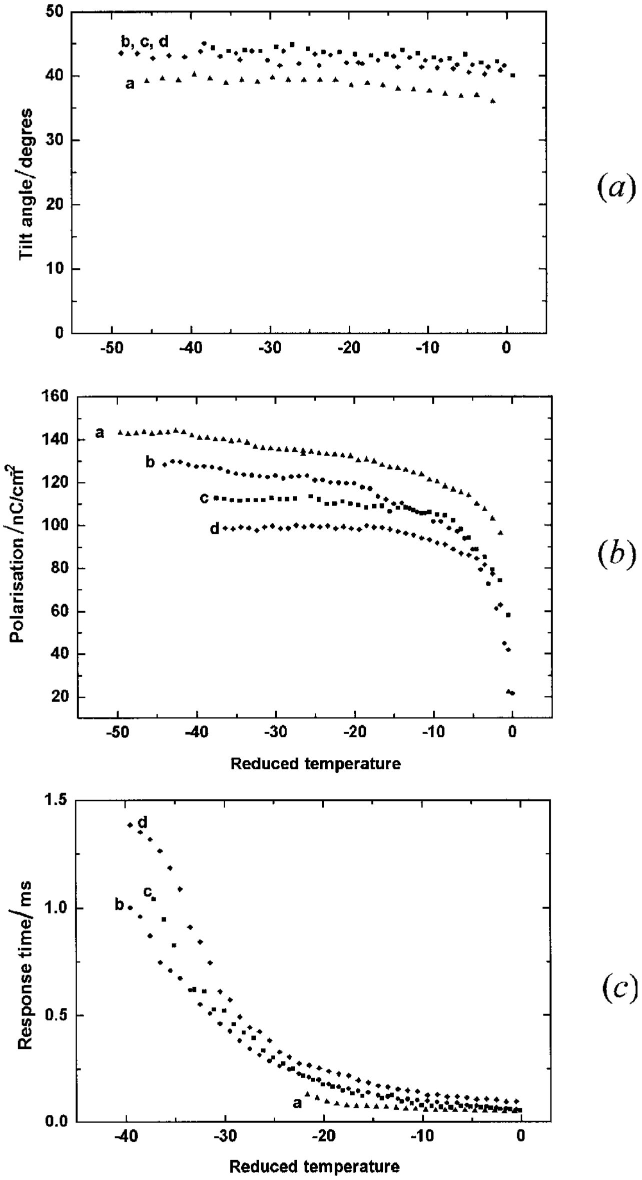


Figure 5. The temperature dependence of the tilt angle (*a*), the spontaneous polarization (*b*) and the response time (*c*) in the chlorine substituted materials. a: the precursor, b: Cl11-2, c: Cl11-3, d: Cl11-3-11Cl.

compound where the intrinsic tilt of 22° observed in the precursor is increased to almost 44 degrees in the F11-2 material. In the bromine materials the tilt in the precursor is already close to 45° and is therefore almost unaffected by the siloxane group. The tilt angle is weakly dependent on the length of the siloxane group. As the length of the siloxane chain is increased, there is only a small tendency for the tilt angle to return to the intrinsic value in the vinyl terminated compounds.

From these observations one can infer that there is a preferred relative orientation of the average axis of the alkyl spacer and the average axis of the siloxy group [figure 6(*a*)]. Because in the bi-mesogenic molecules with a bent conformation [figure 6(*b*)] symmetry requires that the axis of the siloxane chain is perpendicular to the smectic planes, one can conclude that this preferred angle is, as illustrated in figure 6(*b*), equal to the tilt angle which is 45°. In a recent work on ferrocene containing organosiloxane liquid crystals [15], we have also observed that the grafting of the siloxane group forces the tilt angle of the mesogen to a value very close to 45 degrees. Note in passing that in the mono-mesogens or bi-mesogens with straight conformations (figure 6(*c*)) the tilt angle is not necessarily equal to the angle between the axis of the siloxy group and the axis of the alkyl chain spacer [14].

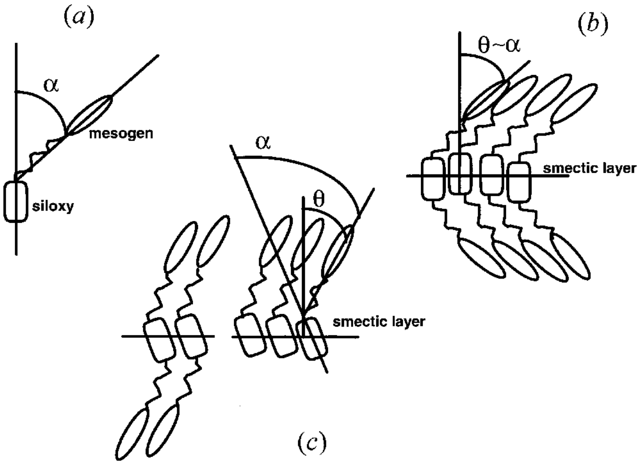


Figure 6. The preferred angle α between the axis of the siloxane chain and the axis of the alkyl chain spacer (*a*). In bi-mesogens with the bent conformation symmetry requires the tilt angle to be equal to α (*b*). In mono-mesogens the tilt angle may be different from α (*c*).

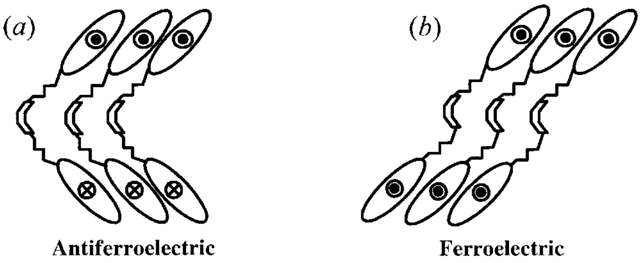


Figure 7. In the bent conformation (*a*) of the bi-mesogenic molecule the axes of two mesogenic units are forced into an anticlinic position with the two dipoles antiparallel to each other. In the straight conformation (*b*), the dipoles are parallel to each other.

These experimental facts may appear to be somewhat paradoxical because the stable all-*trans*-conformation of the un-perturbed siloxane chain is not an extended chain. The silicon atoms define a convex polygon which closes on itself after eleven repeat units [16]. One would therefore have expected the tilt angle to vary strongly with the number of silicon atoms in the siloxane moiety. Detailed molecular modelling and systematic studies of organosiloxane molecules based on different mesogenic moieties are currently in progress in order to determine the exact conformation of the siloxane chain when the molecules are in the smectic phase.

4.3. *Antiferroelectricity*

In conventional low molar mass liquid crystal materials, antiferroelectric order is observed when short range interactions between adjacent layers cause an anticlinic alignment of the molecules in successive layers. In the present series of materials, we observe no antiferroelectric phases in the vinyl terminated materials or in the mono-mesogenic materials. This implies that there are no significant antiferroelectric interactions between the mesogens in adjacent layers and that the synclinic (ferroelectric) arrangement of the mesogens is the one with the lowest energy. The antiferroelectric behaviour observed in the *X*11-3-11*X* and the *X*11-5-11*X* materials is attributed [5, 6, 17, 18] to a bent conformation of the bi-mesogenic molecule. Because it is the conformation of the siloxane moiety that controls the conformation of the molecule in reference [5], we have called the siloxane moiety the *template*. However it is more appropriate to include the alkyl chain spacers in the *template*. In the present paper we call *template* the three-block chain consisting of the siloxane moiety and the two alkyl spacers.

The bent conformation of the template forces the axis of the two mesogenic moieties of the molecule into an anticlinic position with the two electric dipoles antiparallel to each other as shown in figure 7(*a*). The packing of the molecules in the smectic phase then results in a long range antiferroelectric ordering of the electric dipoles. However, we emphasize the fact that this order is not due to antiferroelectric interactions in the material. Switching the antiferroelectric material to the ferroelectric state requires changing the conformation of the molecule from bent [figure 7(*a*)] to straight [figure 7(*b*)].

The fact that in the bi-mesogen series only the *X*11-3-11*X* and the *X*11-5-11*X* materials are antiferroelectric can be explained if one makes the following assumptions: (i) the stable conformation of the template is straight if the siloxy group contains an even number of silicon atoms and bent if it contains an odd number of silicon atoms, (ii) the energy barrier between the straight and the bent conformations decreases with lengthening of the siloxane chain and (iii) an energy U is needed to force the mesogenic units into the anticlinic arrangement. The relative values of U and the conformational energy barrier W determine whether the molecules with an odd number of silicon atoms are bent (antiferroelectric) or straight (ferroelectric).

If W is much larger than U then the template imposes the conformation on the molecule; this is the case in the *X*11-3-11*X* materials which display a stable antiferroelectric phase. If on the other hand W is much smaller than U, then the mesogenic moieties impose the synclinic molecular arrangement on the material and this is the case for the *X*11-*n*-11*X* materials with n greater than 5. In the *X*11-5-11*X* materials, W is of the same order as U. Both W and U vary with temperature, and one expects W to decrease and U to increase with increasing temperature. There is therefore the possibility of finding, within the mesomorphic range, a temperature where W

and U are equal. At that temperature there is a cross-over from a bent (antiferroelectric) to a straight (ferroelectric) conformation of the molecules and a concurrent sudden change in the macroscopic polarization of the material. This cross-over is observed at 95°C in the F11-5-11F material. In Cl11-5-11Cl and Br11-5-11Br, the cross-over would occur at a temperature above the clearing point.

The threshold field for switching the material from antiferroelectric to ferroelectric is directly related to the quantity (W–U). The threshold field measured in the X11-3-11X materials is of the order of $12\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ and less than $0{\cdot}5\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ in the X11-5-11X materials. These figures are in agreement with our assumptions. Conclusive experimental evidence for the relative values of U and W for various values of n is given in our most recent work on mixtures of ferroelectric and antiferroelectric materials to be reported in a separate publication [19].

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