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Preliminary communication

Bi-mesogenic organosiloxane liquid crystal materials exhibiting antiferroelectric phases

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The first antiferroelectric low molar mass organosiloxane liquid crystal materials are presented. The molecules are bi-mesogens consisting of two chiral mesogenic units attached, via methylene spacers, symmetrically to a siloxane group. Three series of compounds with different laterally substituted halogens on the phenyl ring nearest to the chiral centre have been studied. For siloxane groups containing three silicon atoms all of the materials exhibit antiferroelectric phases over a 60°C temperature range. The tilt angle in the SmC_A^* is, within experimental uncertainties, independent of temperature and close to 45 degrees for the three series with a spontaneous polarization greater than $110\,nC\,cm^{-2}$.

Antiferroelectricity in liquid crystals has attracted much interest since its discovery by Chandani *et al.* [1]. Much work has been done to clarify the origin of the antiferroelectric order [2] and the relation between the molecular structure and the occurrence of the antiferroelectric phase [3, 4]. In this communication we present what we believe are the first antiferroelectric low molar mass organosiloxane liquid crystals. Low molar mass organosiloxane liquid crystals are a new class of materials which possess some of the robust mechanical properties of polymers and the fast electro-optic response of conventional low molar mass liquid crystals [5–7]. Because of their potential for applications in display devices, these new materials are at present the object of intense investigations [8–12]. To date most of the research effort has been concentrated on ferroelectric [13, 14] and electroclinic materials [8]. However, the electric field threshold for switching and the double hysteresis in the electro-optic response make antiferroelectric materials more suitable than ferroelectrics for certain display device applications with, in principle, grey scale capability [15]. As far as we are aware no antiferroelectric low molar mass organosiloxane liquid crystals have yet been reported in the literature.

The structure of the molecular system presented in this paper is of the ABA type illustrated in figure 1. It consists of two identical chiral mesogenic units (A) attached symmetrically by a methylene chain spacer to a siloxane group (B). The mesogenic unit is a biphenyl benzoate with a halogen *X* attached laterally to the ring closest to the chiral centre. We have synthesized homologues with different numbers of dimethyl siloxane units ($n+1=2$, 3, 4, 5, 7, 9) and different halogens ($X=$ F, Cl, Br) in the mesogenic moieties. A detailed description of the complete series will be given in a separate publication. We discuss here the materials with three dimethyl siloxane units ($n+1=3$) which display the antiferroelectric (SmC_A^*) phase irrespective of the halogen in the mesogenic unit. All the other materials in the series except the $(n+1)=5$ homologues are ferroelectric over the whole temperature range of their mesomorphism. The $(n+1)=5$ homologues in the series of fluorine and chlorine derivatives display an antiferroelectric as well as a ferroelectric phase.

The dimethyl siloxane materials with $(n+1)=3$ were obtained using the synthetic route described by Kloess *et al.* [12, 16]. The transition temperatures determined by differential scanning calorimetry and confirmed by polarized light microscopy and by the electro-optic response are given in the table.

The antiferroelectric order in the materials is evidenced by the two polarization reversal peaks in the current response to a triangular voltage waveform (figure 2) and by the three stable states in the electro-optic response (figure 3). The traces shown in these figures pertain to the material with fluorine in each mesogenic unit.

The response of the bromine and chlorine derivatives is identical to that shown in figures 2 and 3. The data

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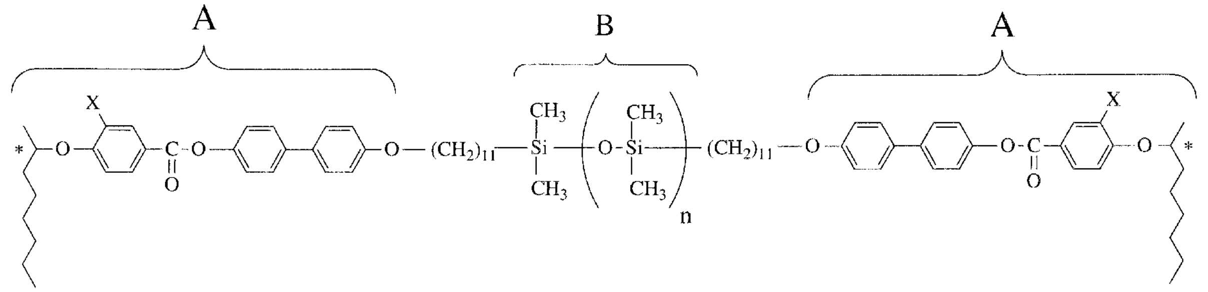

Figure 1. The structure of the ABA type molecule: two identical chiral mesogenic units (A) attached symmetrically by a methylene chain spacer to a siloxane group (B). The terminal chiral alkyl chains are 2-octyl.

Table. The transition temperatures of the $(n+1)=3$ dimethyl siloxane bi-mesogenic compounds.

	Transition temperatures/°C	
Halogen	I–SmC$_A^*$	Melting point
F	121·2	51·2
Cl	122	55·2
Br	105	45

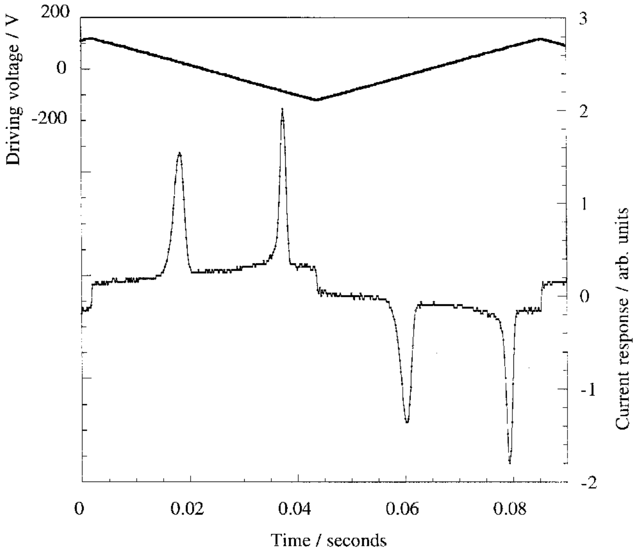

Figure 2. The current response to a triangular voltage waveform. The two peaks correspond respectively to the transition from the ferroelectric up state to the antiferroelectric and from the antiferroelectric state to the ferroelectric down state.

were taken at a temperature of 75°C with a 12 Hz triangular wave as the driving voltage. The samples were contained in 5 μm thick cells treated with rubbed polyimide to give a homogeneous alignment.

Figure 4 shows the temperature dependence of the spontaneous polarization and of the tilt angle. The spontaneous polarization was calculated from the sum of the areas under the two polarization reversal peaks [17]. The tilt angle was determined by optical microscopy as half the angle between the two positions of optical extinction when the sample is switched between crossed polarizers. For clarity only the data from the fluorine derivative are given in figure 4. The temperature dependence of the spontaneous polarization and the tilt angle are approximately the same for the fluorine, chlorine and bromine materials. The values for the tilt angle and the maximum spontaneous polarization are, respectively, 43·5 degrees and 135 nC cm^{-2} for the ABA bromine derivative and 42 degrees and 115 nC cm^{-2} for the ABA chlorine derivative. Note that the tilt angle is independent of temperature and close to 45 degrees, the ideal value for antiferroelectric electro-optic device applications.

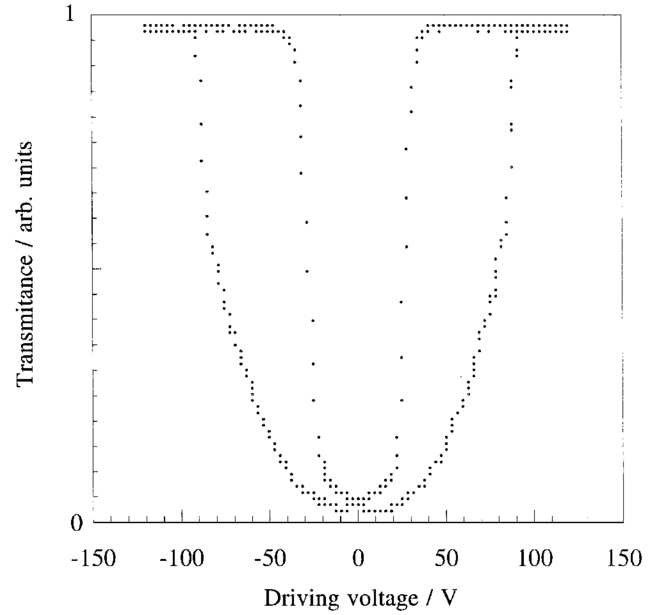

Figure 3. The three stable states in the electro-optic response. The orientation of the aligned specimen between the crossed polarizers is such that the antiferroelectric phase appears dark.

In the three materials studied ($X=$ F, Cl, Br) the SmC$_A^*$ phase is the only mesomorphic phase present.

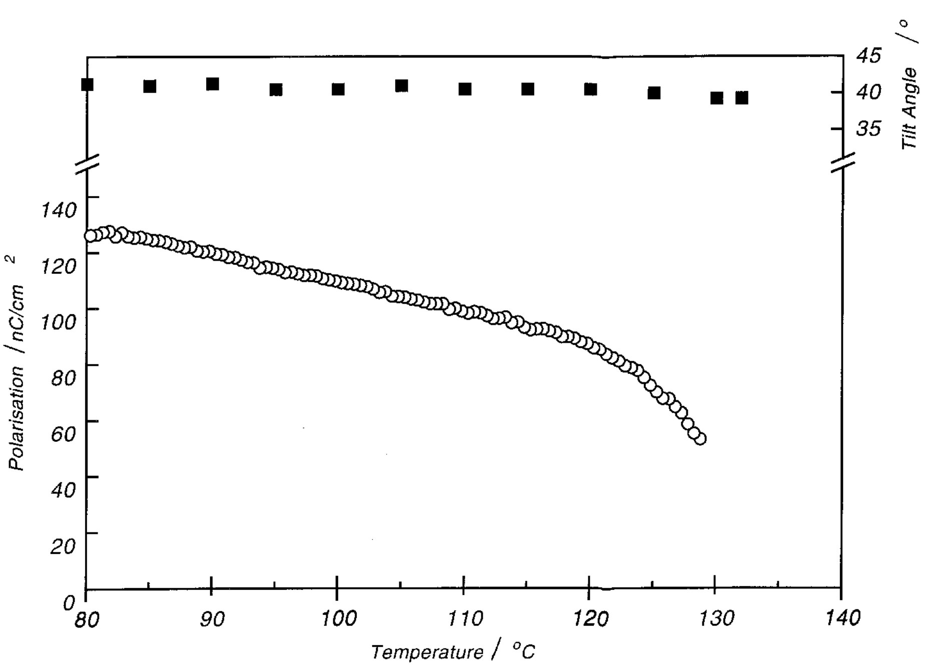

Figure 4. The temperature dependence of the tilt angle (■) and of the spontaneous polarization (○) in the fluorine substituted material.

The materials have therefore an unusual transition from the isotropic into the antiferroelectric phase. Sužuki *et al.* [18] have made similar observations on materials with dimer molecules consisting of two mesogenic units attached to each other by a methylene chain. They observed an isotropic to SmC$_A^*$ transition in the materials with molecules having either an odd number of units in the methylene chain or a long spacer chain. From their observations they inferred that the antiferroelectricity is due to an antiparallel alignment of the electric dipoles in the two mesogenic units within the dimer. The details of the molecular arrangement in our materials are still being investigated. A conformation of the molecule of the type proposed by Susuki *et al.* is not excluded. We note however a significant difference between the behaviour of our materials and those of Susuki *et al.* In our case, a long siloxane spacer chain or one that contains an even number of dimethyl siloxane units favours the ferroelectric and not the antiferroelectric phase. Some of our observations [19] indicate that the three-siloxane group favours the bent conformation illustrated in figure 5. In that conformation the long axes of the two mesogenic units are roughly perpendicular to each other with the two dipole moments in an antiferroelectric alignment. It would therefore appear that the antiferroelectric order in the material is the result of a delicate balance between intramolecular interactions favouring the antiferroelectric conformation of the molecule and co-operative interactions favouring the ferroelectric order. These observations are consistent for each of the three series of compounds $X = \mathrm{F}$, Cl, Br. This work is currently being extended to two phenyl ring systems [6] in order to reduce the operating temperature to room temperature. The highly significant observation is that

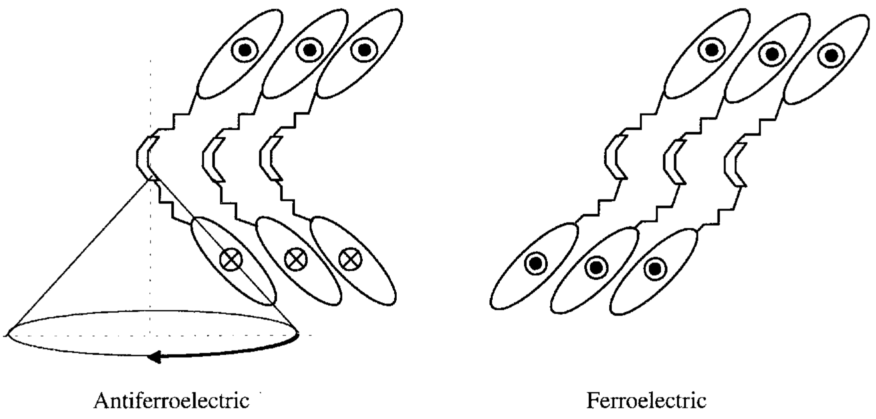

Figure 5. The model for antiferroelectric order with bi-mesogen molecules. The switching between the antiferroelectric and the ferroelectric states involves a change of conformation of the molecule.

by using the same mesogenic unit and a different siloxane content, one can change from ferroelectric to antiferroelectric behaviour; this opens up a new field of molecular design control.

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