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PRELIMINARY COMMUNICATION

Ferroelectrically switchable columnar liquid crystal

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The synthesis of a new disc-like mesogenic compound permitted, for the first time, ferroelectric electrooptical switching in a tilted columnar liquid crystal. The spontaneous molecular dipole moment is induced by the bend between the dibenzopyrene core and part of the eight O-hexyllactic acid chains attached to it. Two similar new compounds displayed a weak electrooptical effect in the columnar phase.

Although the electrooptical switching of nematic and smectic liquid crystals has been known for many years, no such effects have as yet been reported for the third of the three liquid crystal classes, the columnar phases. It was recognized at an early stage that tilted columnar phases of chiral disc-like molecules can be ferroelectric [1]. More recently, the possible ferroelectricity has been discussed on the basis of X-ray diffraction data of such a material [2]. However, since the rotation of columns about their long axes should be strongly hindered by the two dimensional lattice of the columns, ferroelectric switching was regarded as "no doubt impossible" [2]. In an attempt to overcome the supposed impasse, we have synthesized new chiral mesogens. The disc-like molecules were designed to make the electric dipole moment induced by the tilt as large as possible. Two of the new columnar liquid crystals displayed a weak and very fast electrooptical effect, the samples returning to the original state after the voltage was turned off. A third columnar material permitted full ferroelectric switching as it could change between two preferred states differing in the direction of the optical axes. Here, we outline the physical background of columnar ferroelectricity and give a preliminary account of the new mesogens and their electrooptical effects in the columnar phase.

The molecules which we have synthesized were of a type known to form tilted columnar phases: six or eight equal, mostly hydrocarbon chains attached by ester bonds to an aromatic core comprising four or six rings. Apart from one molecule, which was known and served as a standard [2], we placed the centre of chirality as near as possible to the core. The time averaged electric dipole moment of a disc-like molecule with chiral chains vanishes when the molecule is single or in a stack without tilt. However, when the molecules or, more precisely, the normals to their cores make an angle with the axis of the stack, they may acquire net dipole moments. This is due to the fact that the tilt, resulting from repulsion between chains and attraction between cores [3], is essentially restricted to the aromatic cores [2]. Therefore, part of the

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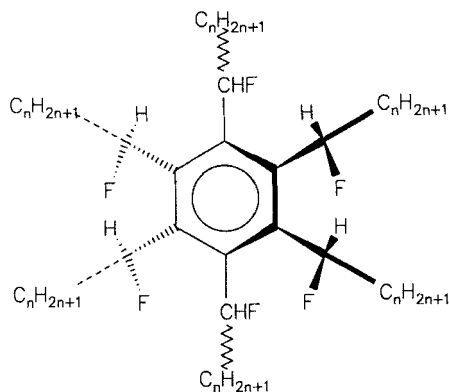


Figure 1. Schematic view of a molecule consisting of a tilted aromatic core and six equal chains lying parallel to the plane of the drawing. In this especially simple model molecule, which is hexa-(*S*-1-fluoralkyl)-benzene, a dipolar group (C–F) is linked directly to each chiral centre. The deflection between the core plane and the chain orients four of the centres so that on average their dipole moments have equal upward components. As the two vertical chains are not affected by the tilt their average contributions to the molecular dipole moment are vertical and cancel each other. This argument can be extended to the molecules synthesized by us where the polar groups are not directly at the chiral centres.

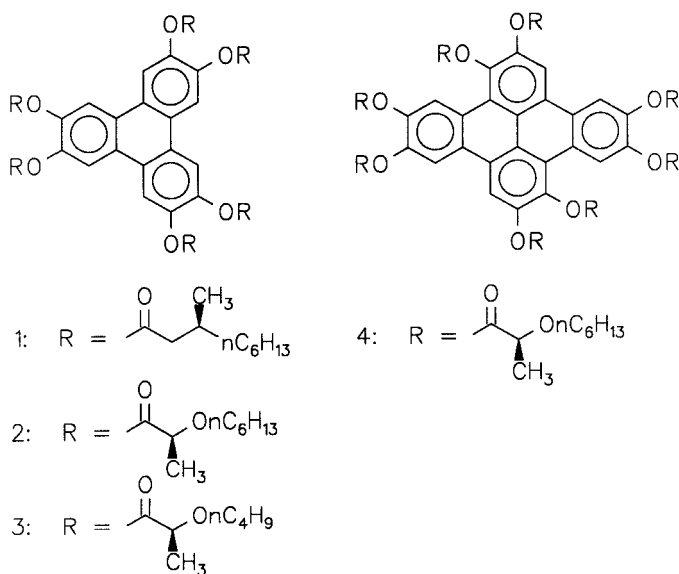
hydrocarbon chains will make an angle with the plane of the core. If the centre of chirality is where the chain deflects, nearby bonds with an electric dipole moment can give rise to a non-zero time averaged molecular dipole moment. A model showing four nearly parallel contributions to the total molecular moment is sketched in figure 1. For reasons of symmetry, the total dipole moment must be perpendicular to both the axis of the column and the tilt direction, thus being parallel to the axis about which the disc rotates when it tilts.

Columnar phases with tilt-induced molecular dipole moments are ferroelectric if the tilt direction is the same for all columns or alternates in such a way that the columnar polarizations do not cancel out. In a hexagonal lattice of columns there should be six equally preferred tilt directions. Actually, tilt is known to break the hexagonal symmetry, resulting in two types of rectangular lattices with two columns per unit cell [4]. One ($C2/m$) is an array of columns of equally oriented elliptic cross-sections corresponding to a single tilt direction, while the other ($P2_1$) forms a herringbone pattern of elliptic cross sections representing two different tilt directions. In both cases each column can assume only two opposite tilt directions that are compatible with the lattice. Accordingly, for a given rectangular lattice of columns we may expect two equivalent ground states differing by a 180° rotation of each column about its axis. The chances of ferroelectric switching between the ground states should be best if in a typical sample cell the columns are parallel to the glass plates and the ferroelectric polarization is more or less normal to the conducting glasses. The switching between the two equivalent columnar ground states by applying positive and negative voltages is, of course, similar to the ferroelectric switching of tilted chiral smectic liquid crystals. In particular, the angle made by the axis of maximum refractive index and the direction normal to the columns (which replace the smectic layers) changes its sign when the voltage is reversed.

The first molecule which we have synthesized was 2,3,6,7,10,11-hexa-(3-methylnonanoyloxy-)triphenylene **1**. Its two columnar phases have been examined with X-ray

diffraction and optically by Levelut *et al.* [2]. We studied the high-temperature phase in sample cells of the kind commonly used in electrooptical experiments. In agreement with the statement of Levelut *et al.* we found no electrooptical effect, having searched for it up to the columnar–isotropic transition at 97°C and up to electric breakdown at $c. 2 \times 10^5 \text{ V cm}^{-1}$. This failure is perhaps no surprise as the orienting effect on the carbonyl group of the asymmetric carbon in the β position should be rather weak. After that we proceeded to the synthesis of unknown disc-like compounds, testing new chains and cores. First, we linked (*S*)-*O*-hexyllactic acid to the triphenylene core, an α -chiral chain which is known to produce high spontaneous polarization in tilted smectic phases [5]. Upon purifying the compound **2** by column chromatography, we found a columnar phase below a clearing point at $c. 156^\circ\text{C}$. Cooling in a sample cell through the clearing point resulted in extended regions of low birefringence where the columns were apparently normal to the glass slides. Fortunately, we also obtained some of the flower-like particles which were seen first by Chandrasekhar *et al.* [6] who checked that in their liquid crystals the columns formed circles around the flower centres. The extinction brushes of the Maltese crosses seen between crossed polarizers were strictly parallel to the directions of polarization and remained so when the samples were annealed in the columnar phase for up to 2 days. This seems to suggest the absence of tilt, in conflict with the expected behaviour of the molecule. However, applying rectangular voltage pulses of nearly 200 V to 10 μm thick sample cells, we noticed an instantaneous rotation of the Maltese crosses of the order of one degree.

With a view to modifying the interaction of the columns, we also synthesized the homologous compound **3** with the hydrocarbon chains shortened by two methylene



NMR spectra (CDCl_3/TMS , 90 MHz):

- 2: $\delta = 0.90$ (t, 6 Hz, 18 H), 1.10–1.85 (m, 48 H), 1.70 (d, 6.5 Hz, 18 H), 3.30–3.95 (m, 12 H), 4.25 (q, 6.5 Hz, 6 H), 7.90 (s, 6 H);
- 3: $\delta = 1.00$ (t, 6 Hz, 18 H), 1.25–1.80 (m, 24 H), 1.70 (d, 6.5 Hz, 18 H), 3.35–3.95 (m, 12 H), 4.25 (q, 6.5 Hz, 6 H), 7.95 (s, 6 H);
- 4: $\delta = 0.70$ –1.00 (m, 24 H), 1.10–1.85 (m, 88 H), 3.30–3.95 (m, 16 H), 4.00–4.55 (m, 8 H), 8.45 (s, 2 H), 8.60 (s, 2 H), 9.05 (s, 2 H).

groups. A columnar phase was found to exist in a temperature range below *c.* 93°C. Its switching behaviour did not differ noticeably from that of the other material.

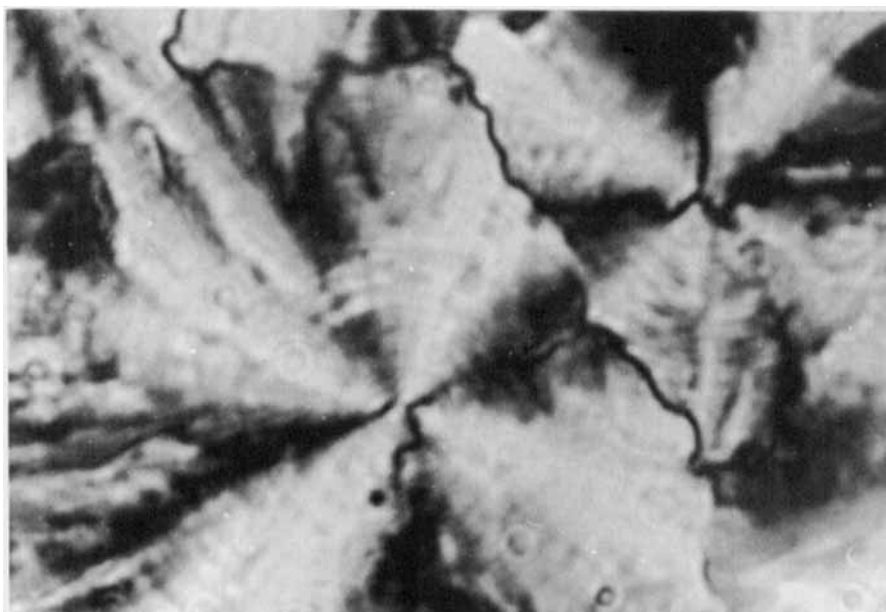
We conclude from our observations that in both materials the columns are tilted but their polarizations cancel out because the columns are arranged in a particular lattice or their tilt directions are disordered. The tilt-induced molecular dipole moment is strong enough to permit a high electric field to rotate the tilt direction of those columns slightly whose polarization is roughly perpendicular to the electric field. Any further change of the tilt direction seems to be blocked by the interaction of the columns.

Subsequently, we synthesized 2,5,6,9,12,13-hexahydroxydibenzo-[e,1]-pyrene-1,8-quinone, following a known four step procedure [7], and acylated it under conditions which lead to the derivative **4** with eight hydrocarbon chains. Although no mesogens with this aromatic core have been known so far, we considered the molecule to be particularly suitable for the present purpose. The large number of chains, a sufficient core size, and a tight oxygen ring around the core made us expect columnar mesophases even with α -branched chains. On the other hand, the rotation of the chains squeezed in positions 1 and 8 should be strongly hindered. This and the large number of chains promises a large tilt-induced dipole moment.

The dibenzopyrene **4** with eight (*S*)-O-hexyllactic acid chains has a columnar phase which after chromatography and recrystallization ranges from a melting point at *c.* 84°C, as revealed by DSC in the first heating, to a clearing point at *c.* 124°C. Cooling the sample cells through the clearing point produces textures with many Maltese crosses. Their brushes are initially all parallel to the polarizer directions. However, the crosses become oblique as soon as the sample is exposed to a sufficient DC voltage, and when positive and negative voltage pulses are applied the material switches between two preferred states. The obvious ferroelectric switching rotates the Maltese cross between + and -20° and requires at 90°C a field strength of about $8 \times 10^4 \text{ V cm}^{-1}$. Typical textures are shown in figure 2. We checked with a phase retardation plate that it is the direction of maximal refractive index which switches between + and -20° from the radial direction in the flowers. Since the tilt angle of the aromatic cores should be well below 45° , this confirms that the columns in a flower are arranged in circles, in agreement with other columnar liquid crystals [6, 8]. If the switching voltage was applied for much less than 1 s we observed a weak rotation of the Maltese crosses of the type seen in the other two materials, the rise and decay times being *c.* 20 μs .

Simple mechanical shearing of a sample produced a rather uniform orientation of the columns parallel to the shear direction [9] with no indication of tilt, as was verified again with phase retardation. Sheared samples permitted an equally uniform switching of the direction of maximum refractive index between + and -20° from the normal to the shear plane. Two textures of a sheared sample are shown in figure 3. In the spontaneously grown textures there were always regions that were optically quasi-isotropic and did not take part in the switching. In these inactive regions the columns were probably normal to the glass slides.

While the Maltese crosses in freshly prepared samples were generally parallel to the polarizer directions, overnight annealing of such samples in the columnar phase made many of the crosses oblique, the angle varying from -20 to $+20^\circ$. The obliqueness brought about by annealing shows the ground state of the columnar phase to be ferroelectric rather than antiferroelectric. It cannot be ruled out that the ferroelectric polarization tends to be normal to the glass slides. In this case, the absence of a visible tilt in freshly prepared samples could mean that we observe a mixture of the two ground

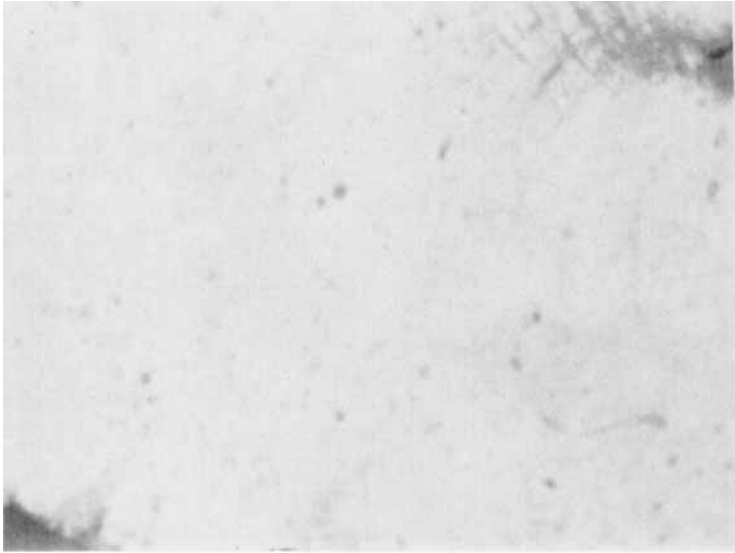


(a)

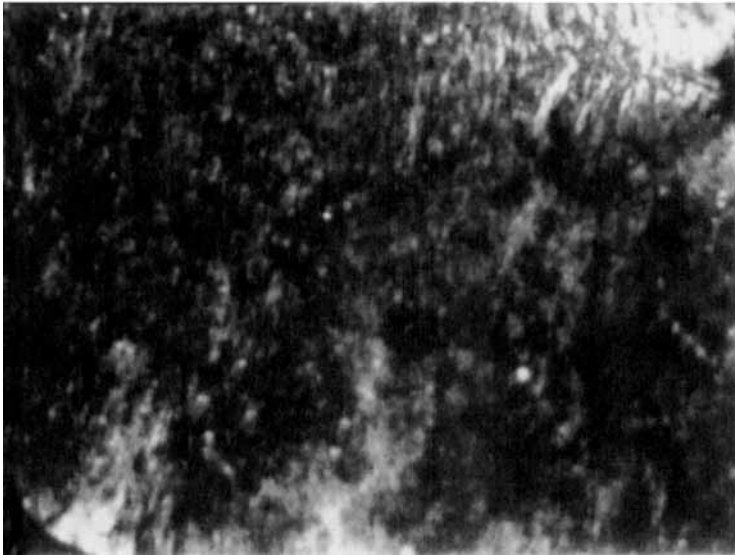


(b)

Figure 2. Maltese cross seen between crossed polarizers. The directions of polarization are vertical and horizontal. The switching voltage is $8 \times 10^{-4} \text{ V cm}^{-1}$, the temperature *c.* 90°C . Positive voltage (a) at top and (b) at bottom of sample cell viewed from above. The dark brushes turn counter-clockwise when the voltage at the top changes from negative to positive.



(a)



(b)

Figure 3. Textures of sheared sample as seen between crossed polarizers at 22.5° and -67.5° . (a) Dark state with axis of the maximum refractive index at $+20^\circ$, (b) light state with axis of the maximum refractive index at -20° . All angles refer to the vertical.

states. However, it seems more probable that an initially highly disordered lattice of parallel columns becomes ordered, during annealing, without preference for a particular orientation of the plane perpendicular to the columns. This would imply that the preferred orientation of the two dimensional lattice found in ferroelectric switching can be created by the electric field itself.

A novel feature of ferroelectric columnar switching is partial switching. As the transition from one preferred state to the other is slow, taking about 1 s at $8 \times 10^4 \text{ V cm}^{-1}$ and 90°C , we are able to watch the rotation of the Maltese crosses. By turning off the voltage, the rotation can be stopped at any angle between -20° and $+20^\circ$. The intermediate positions persist at least for several hours without noticeable alteration.

The appearance of the sample cell undergoes remarkable changes if the field strength is close to the limit of electric breakdown. The birefringence becomes stronger, as revealed by the emergence of colours, and the switching angle increases to about 45° . The return to 20° and the uniform yellow of a $10 \mu\text{m}$ thick cell takes about $\frac{1}{2}$ h. We suspect that the strongly birefringent state represents a rectangular lattice of columns with a single tilt direction while in the normal state the columns are arranged in a herringbone pattern. Prolonged exposure to the very high voltages breaks the columnar phase as seen between crossed polarizers into an irregular pattern of dark and light. These textures eventually include the otherwise inactive regions and do not return to the original state after the voltage is turned off.

Although the picture resulting from our experiments seems to be rather consistent, there remain many open questions. Obviously, the structures of the new columnar phases will have to be examined by means of X-ray diffraction. A difference in structure, especially in the deviation from hexagonal order of the columns, might explain why only one of the O-hexyllactic acid compounds can be switched between equivalent states. An especially interesting problem is the mechanism of ferroelectric switching once the two dimensional lattice is properly oriented. The tilt direction and, thus, the dipole moment of a column can be reversed either by a rotation of the column as a whole or by a collective molecular flip-flop through the untilted state. Both mechanisms will be hampered by energy barriers and the transformation may start locally in a single column. On the chemical side, we do not know the enantiomeric purity of the newly synthesized compounds.

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