Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Y. Suzuki[a]; T. Hagiwara[a]; I. Kawamura[a]; N. Okamura[b]; T. Kitazume[b]; M. Kakimoto[c]; Y. Imai[c]; Y. Ouchi[c]; H. Takezoe[c]; A. Fukuda[c]
[a] Central Research and Development Laboratory, Showa Shell Sekiyu Co. Ltd., Kanagawa-ken, Japan [b] Department of Bioengineering, Tokyo Institute of Technology, Tokyo, Japan [c] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan

To cite this Article Suzuki, Y. , Hagiwara, T. , Kawamura, I. , Okamura, N. , Kitazume, T. , Kakimoto, M. , Imai, Y. , Ouchi, Y. , Takezoe, H. and Fukuda, A.(1989) 'New fluorine-containing ferroelectric liquid crystal compounds showing tristable switching', Liquid Crystals, 6: 2, 167 — 174

To link to this Article: DOI: 10.1080/02678298908033211

URL: http://dx.doi.org/10.1080/02678298908033211

LIQUID CRYSTALS, 1989, VOL. 6, NO. 2, 167–174

New fluorine-containing ferroelectric liquid crystal compounds showing tristable switching

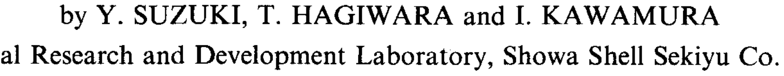
by Y. SUZUKI, T. HAGIWARA and I. KAWAMURA
Central Research and Development Laboratory, Showa Shell Sekiyu Co. Ltd., 123-1 Shimokawairi, Atsugi-shi, Kanagawa-ken 243-02, Japan

N. OKAMURA and T. KITAZUME
Department of Bioengineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

M. KAKIMOTO, Y. IMAI, Y. OUCHI, H. TAKEZOE and A. FUKUDA
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

(*Received 13 December 1988; accepted 2 March 1989*)

To understand the real cause of stabilization of the third state and to assure the possible application of the tristable switching, we have studied the effect of chiral centers on the appearance of the third state, synthesizing (*R*)-(+)- and (*S*)-(−)-4-(1-trifluoromethylalkoxy(*n*)carbonyl) phenyl 4′-alkoxy(*m*)biphenyl-4-carboxylate



where m = 8, 9, 10, or 12 and n = 6 or 8; note that the chiral centre has a trifluoromethyl group. By observing light transmittance and switching current responses to a triangular voltage wave and by taking stroboscopic micrographs, we have confirmed that all the materials synthesized show the tristable switching in wide temperature ranges; in particular, the materials with m = 10 or 12 and n = 6 have the stabilized third state even at temperatures below 30°C.

Significant advances in the surface stabilized ferroelectric liquid crystal displays (SSFLCDs) of Clark–Lagerwall type [1] have been presented at several conferences. However, it appears to be still annoyed with the selective pretilting of C-directors [2] due to the smectic layer bending (the chevron structure) and with the twisted states. The selective pretilting remarkably reduces the apparent tilt angle, i.e. the angle between the projections onto the substrate plate of the smectic layer normal and the director in the uniform states, and seriously deteriorates display contrast and/or brightness. In many FLCDs manufactured for trial, moreover, bistable switching not between the uniform states but between the twisted states appears to have been used; hence the situation concerning display contrast and/or brightness may become even more unsatisfactory. The existence of the stable twisted states may also make worse the memory effect, particularly its threshold characteristics, in the switching between the uniform states.

The SSFLCDs of Clark–Lagerwall type are really attractive, but the attraction is slightly diminished by the requirement for cell thickness to be less than 2 μm and by the chevron structure and the twisted states mentioned above [3]. On the other hand,

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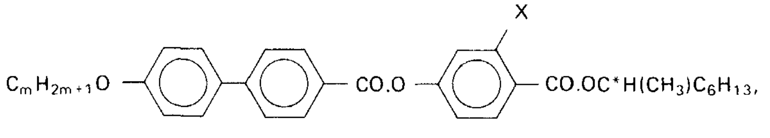
the structure and properties of FLCs are so abundant in novelty that there exist great possibilities of using FLCs as functional materials, particularly for displays. Hence it is worth while searching for other switchings which can be used practically. In fact, several novel switchings have been proposed, such as tristable switching [4, 5, 6] switching via helicoidal structure [7], etc. [8, 9]. Among these the tristable switching [4, 5, 6] is particularly interesting because of the following characteristic features: (1) The so-called third state is spontaneously stabilized remarkably; a sharp DC threshold exists. (2) The extinction direction of this state is along the layer normal. (3) This state appears even in thick cells; the surface stabilization does not directly cause the third state. (4) The switchings from and to the third state occur at different voltages, showing hysteresis.

The third state was found in (*R*)-(+)- and (*S*)-(−)-4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC). Hiji *et al.* [4] and Chandani *et al.* [5, 6] attributed the origin of the third state to the largeness of spontaneous polarization and the resulting electrostatic interaction of polarization charges $\varrho = -\mathrm{div}\, P_s$, [10, 11] but this explanation is not correct at least in this simplest statement because an almost racemic mixture of (*R*)-(+)- and (*S*)-(−)-MHPOBC also shows the third state at lower temperatures [12, 13], though the possibility that the highly hindered rotation around the molecular long axis plays an important role cannot be denied. Furukawa *et al.* [14] also noticed, though not clearly realized the stabilization of the third state, that switching between the uniform states exhibits a DC threshold. They considered the DC threshold to be a property of unknown phase, S_Y^*, which is not miscible to S_C^*, S_I^* and S_F^*. Furukawa *et al.* confirmed the S_Y^* phase in the homologous materials,



$$X = \begin{cases} \mathrm{H} & \text{for } m = 8 \text{ (MHPOBC)} \\ \mathrm{F} & \text{for } m = 7, 8, 10 \\ \mathrm{Cl} & \text{for } m = 8 \end{cases}$$

and observed the transition enthalpy, though very small. Goodby and Chin [15] reported that the optically active isomers appear to exhibit a different mesophase morphology from the racemate; at least one of the two extra ferroelectric liquid crystal phases, X_1, that the chiral compounds apparently possess may be similar to the S_Y^* phase. Anyway the real cause of the third state is not clear at present.

The purpose of this paper is to study the effect of chiral centers on the appearance of the third state. Since the number of compounds which show the third state is rather restricted at present, an increase in the number must be effective in clarifying the real cause of the third state and in assuring the possible application of tristable switching to a wide variety of optical devices. As a first step, we replaced the methyl group in the chiral centre of MHPOBC by the trifluoromethyl group and synthesized the homologous compounds shown in figure 1. Preliminary studies on branches of the trifluoromethyl type was made by Goodby and Leslie [16]. A few FLC compounds having the trifluoromethyl group in the chiral center were reported by Yoshino *et al.* [17, 18]. So long as the authors are aware of, however, no one reported the tristability in these compounds.

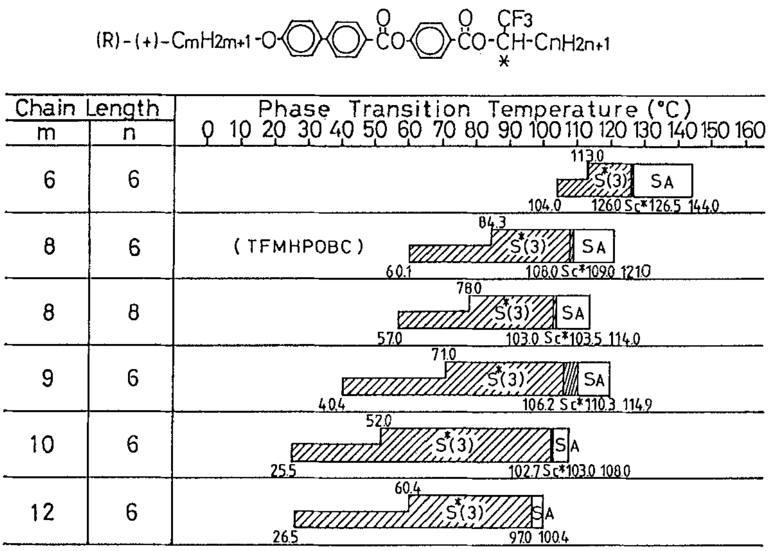
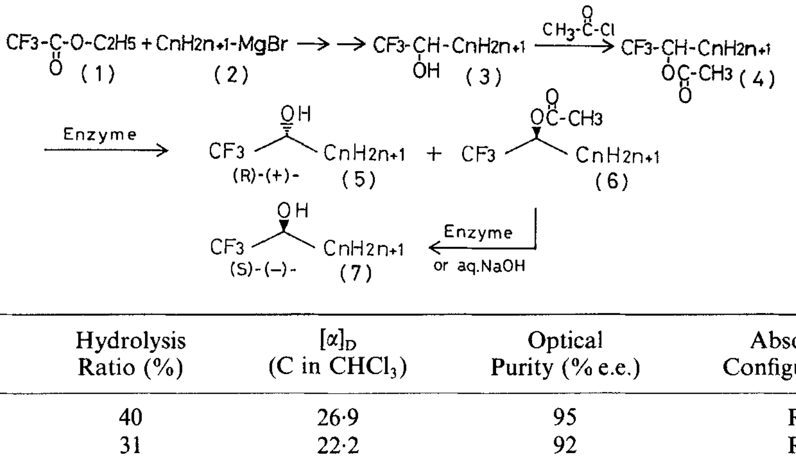


Figure 1. Phase sequences and transition temperatures of (*R*)-(+)-4-(1-trifluoromethylalkoxy(*n*)carbonyl) phenyl 4′-alkoxy(*m*)biphenyl-4-carboxylate.



C_nH_{2n+1}	Hydrolysis Ratio (%)	$[\alpha]_D$ (C in $CHCl_3$)	Optical Purity (% e.e.)	Absolute Configuration
C_6H_{13}	40	26·9	95	R
C_8H_{17}	31	22·2	92	R

Figure 2. Synthetic route of optical active compounds.

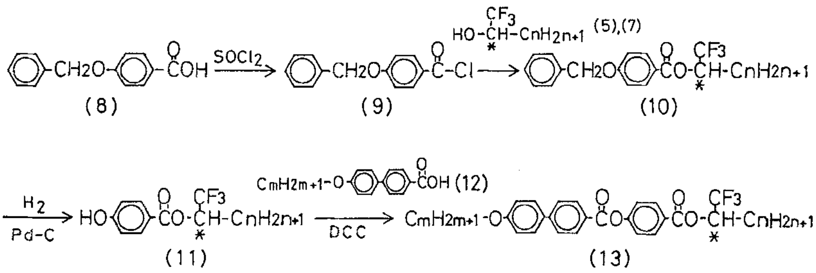


Figure 3. Synthetic route of FLC compounds.

The synthetic route is given in figures 2 and 3. Optically active 1-(trifluoromethyl)-alkanols **5**, **7** were prepared by the Grignard reaction of ethyl trifluoroacetate **1** with appropriate alkylmagnesium bromides **2**, followed by the asymmetric hydrolysis of the corresponding ester derivatives **4** with enzymes of microbial or animal origin [19]. Ethyl trifluoroacetate **1** was added dropwise to a solution of the Grignard reagents at a temperature below − 50°C. The hydrolysis was carried to less than 45 per cent with Lipase MY (Candida cylindracea) to obtain the alcohols with high optical purity greatly enriched in the (*R*)-enantiomers **5**. The (*S*)-enantiomers **7** were prepared from recovered acetates **6** by hydrolysis using a Cellulase (Tricoderuma viride) and/or by the chemical method. The optical purity was determined by ^{19}F-N.M.R. signal intensities of the diastereomers which were derived from (*R*)-α-methoxy-α-(trifluoromethyl) phenylacetic acid chloride and optically active 1-(trifluoromethyl)-alkanols **5**, **7**.

Series of FLC compounds were synthesized by the esterification of 1-(trifluoromethyl)alkyl 4-hydroxybenzoates **11** and 4-alkoxybiphenyl-4′-carboxylic acids **12** using a dehydrating reagent such as dicyclohexylcarbodiimide. 1-(Trifluoromethyl)-alkyl 4-hydroxybenzoates **11** were obtained by the reaction of 4-benzyloxybenzoyl chloride **9** and (*R*)-(+)-1-(trifluoromethyl)alkanol **5** in pyridine at room temperature. 1-(Trifluoromethyl)alkyl 4-benzyloxybenzoates **10** were converted to 1-(trifluoromethyl)alkyl 4-hydroxybenzoates **11** by the reduction using Pd-carbon catalyst in methanol. The obtained ferroelectric liquid crystal compounds were purified by recrystalizing from absolute ethanol several times. The structure was confirmed by means of I.R., ^{1}H-N.M.R. and ^{19}F-N.M.R. spectroscopy.

All the synthesized compounds have the phase sequence of Iso $\leftrightarrow S_A \leftrightarrow S_C^*$; the temperature range of the ordinary S_C^* phase is rather narrow and is followed by the range designated $S^*(3)$ where the third state appears. The $S^*(3)$ range is very wide particularly in the cooling process when the supercooling is observed; a compound with $m = 10$ or 12 and $n = 6$ shows the tristability even at temperatures below 30°C. These results are summarized in figure 1. The melting point was measured by a DSC (Seiko DSC-20) and the phase sequence was determined by a polarizing optical microscope with a hot stage (Metler FP-82).

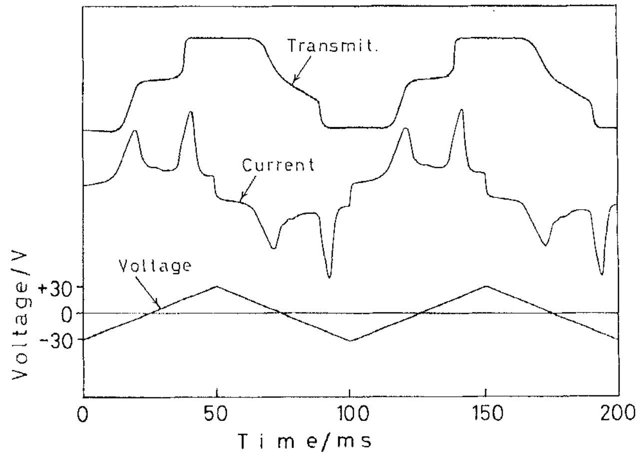


Figure 4. Light transmittance and switching current responses to a triangular voltage wave observed at 90°C in the $S^*(3)$ temperature range of (*R*)-(+)-TFMHPOBC ($m = 8$ and $n = 6$).

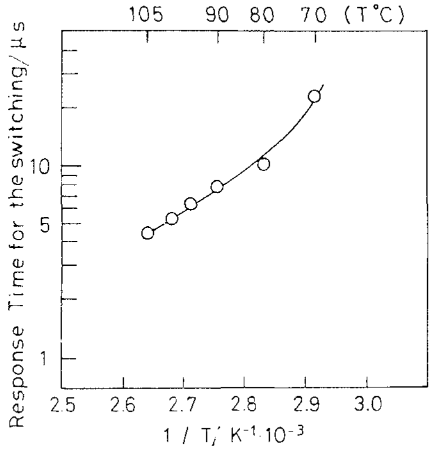


Figure 5. Temperature dependence of switching time between uniform states measured by reversing the applied voltage from +30 V to −30 V in (*R*)-(+)-TFMHPOBC.

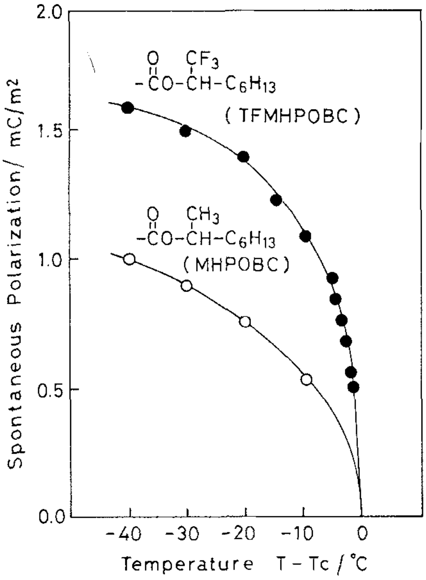


Figure 6. Temperature dependence of spontaneous polarization in (*R*)-(+)-TFMHPOBC and (*R*)-(+)-MHPOBC.

Homogeneously aligned cells of 2·1 μm thickness were prepared by rubbing thin polyimide films coated on the substrate plates. The spontaneous polarization was measured by the triangular wave voltage method [20]. The frequency was 10 Hz and the amplitude was ±30 V. Figure 4 shows an example of the current response in (*S*)-(+)-TFMHPOBC ($m = 8$ and $n = 6$), where the light transmittance response is also plotted; the crossed polarizers were set for one of the uniform states to be dark. The transmittance changes occur by two steps from one uniform state to the other. Switching current peaks appear at each instant of the transmittance changes. As was already pointed out by Chandani *et al.* [5, 6] and Furukawa *et al.* [13, 14] a DC threshold is clearly observed in the switching from the third state to the uniform state.

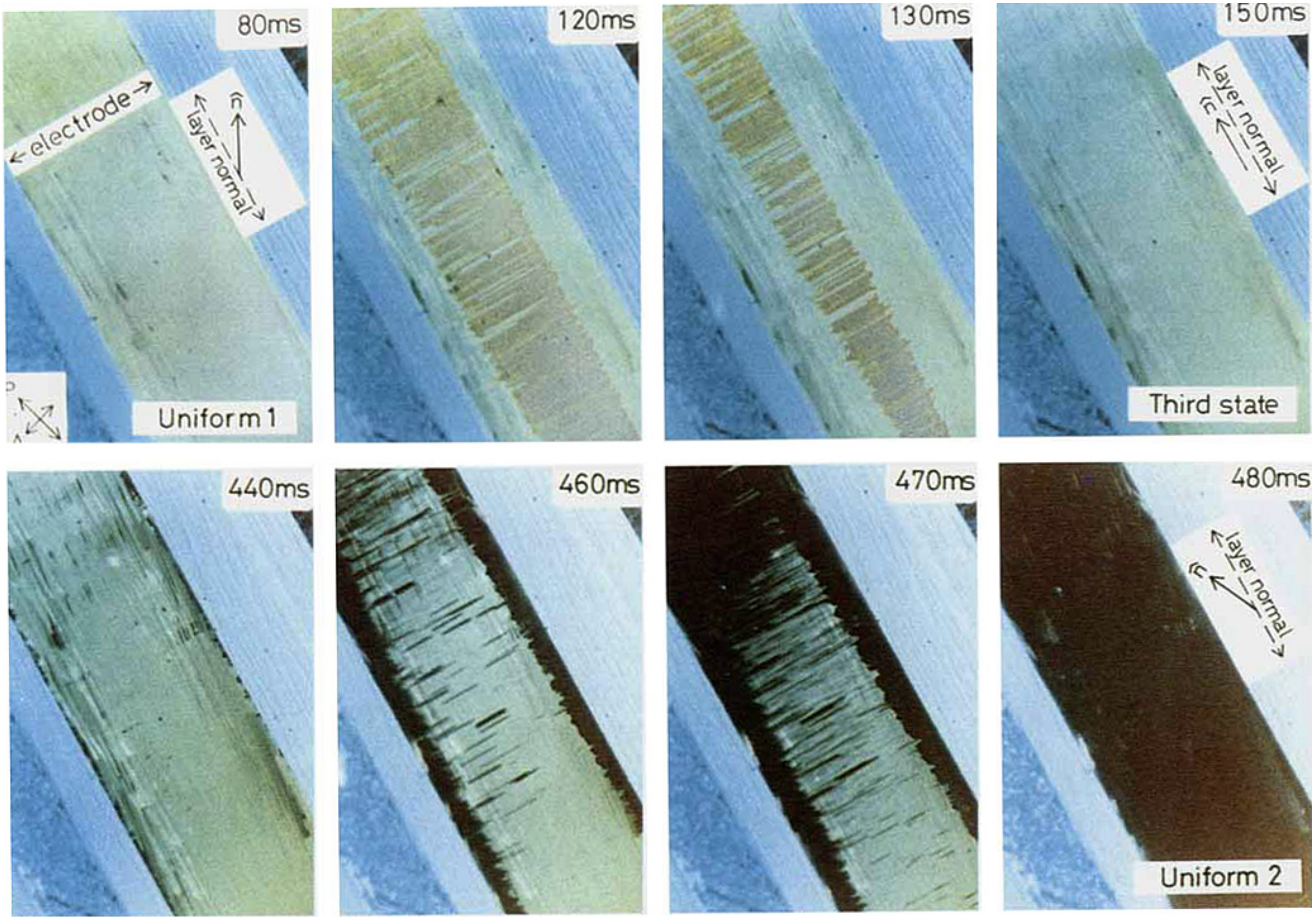


Figure 7. A series of micrographs taken stroboscopically during the switching from one of the uniform state to the other via the third state at 90°C in the $S^*(3)$ temperature range of (*R*)-(+)-TFMHPOBC. The applied voltage changes from -30 V at 0 ms to $+30$ V at 500 ms, becoming 0 V at 250 ms.

In spite of the DC threshold, the switching time from one uniform state to the other is rather fast when measured by reversing the applied voltage from +30 V to −30 V as illustrated for (*S*)-(+)-TFMHPOBC in figure 5. Figure 6 summarizes the temperature dependence of the spontaneous polarization of (*R*)-(+)-TFMHPOBC together with that of the corresponding non-fluorinated compound, (*R*)-(+)-MHPOBC. The spontaneous polarization increases monotonically as a function of $T_{AC} - T$ without showing any irregularities even at the temperature where the third state begins to appear [5, 6, 14]. The negative sign and the value observed in *R*-(+)-TFMHPOBC appear to indicate that the dipole moments on the carbonyl group and the chiral centre are not fully constructive in producing the spontaneous polarization. If both of the dipole moments were on the same plane, the resulted spontaneous polarization would be expected much larger.

To confirm the occurrence of tristable switching, stroboscopic micrographs were also taken using a similar apparatus described in a previous paper [21]. The cell of 2·4 μm thickness was aligned by the method of 'epitaxial' growth from a spacer edge under a temperature gradient which assures its high quality [22]. The electrodes should be shorted during the growth because the large spontaneous polarization may deteriorate the cell quality. A series of micrographs taken at 90°C by applying ±30 V triangular wave voltage at 1 Hz is shown in figure 7. Zigzag defects [3] were observed in the cell when it is virgin, after applying voltages, however, the cell is characterized by a series of lines almost parallel to the layer normal. When the crossed polarizers are set for one of the uniform states to be dark, the lines are not conspicuous in the uniform states but become clearly observed during the switching between them; see the micrographs at +22·8 V (440 ms) and +25·2 V (460 ms).

The tristable switching occurs via the third state between the two uniform states. At −20·4 V (80 ms) the cell takes one of the uniform state. As the voltage decreases its negative value, the third state begins to appear as domains of characteristic shape mainly from both edges of the electrode; the domains are bars or elongated rectangles parallel to the smectic layer. The uniform state region is gradually squeezed into the middle part of the electrode area as illustrated in micrographs at −15·6 V (120 ms) and −14·4 V (130 ms) and finally disappears completely as shown in a micrograph at −12·0 V (150 ms). The whole electrode area is covered by the third state.

As already mentioned above, a DC threshold exists in the transition from the third state to either of the uniform state. In fact, the third state is quite stable and no change takes place until +22·8 V (440 ms), where the other uniform state begins to appear. The domain nucleation and growing processes as well as the resulted domain shape are quite similar to those described in the preceding paragraph as illustrated in micrographs at +25·2 V (460 ms) and +26·4 V (470 ms). The third state gradually squeezed into the middle part and finally disappears. The electrode area is covered with the uniform state at +27·6 V (480 ms). We are in the process of detailed studies, trying to understand the real cause of the third state†.

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† *Note added in proof.*—Recently we confirmed that the third state is a novel antiferroelectric chiral smectic phase [23].

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