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

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To cite this Article De La Fuente, M. Rosario , Martín, Enrique , Jubindo, Miguel Ángel Pérez , Artal, Carmen , Ros, Blanca and Serrano, José Luis(2001) 'Achiral diacrylate with an anticlinic smectic phase', Liquid Crystals, 28: 1, 151 — 155
To link to this Article: DOI: 10.1080/026782901462490
URL: http://dx.doi.org/10.1080/026782901462490

LIQUID CRYSTALS, 2001, VOL. 28, NO. 1, 151–155

Preliminary communication

Achiral diacrylate with an anticlinic smectic phase

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(*Received 7 March 2000; accepted 11 June 2000*)

We present an achiral diacrylate that shows a phase transition from the synclinic smectic C phase (SmC) to the anticlinic smectic C ($\mathrm{SmC_{alt}}$). This last phase has been previously reported only for swallow-tailed or dimeric compounds. Our studies using differential scanning calorimetry, X-ray diffraction, polarizing optical microscopy and broad band dielectric spectroscopy suggest the existence of this mesophase in this bifunctional smectogen.

Recently it has been shown that certain achiral swallow-tailed and dimeric materials may display an anticlinic smectic C phase ($\mathrm{SmC_{alt}}$) [1–4]. This 'antiferroelectric-like' smectic C phase (see figure 1) has an alternating tilted structure, being the non-chiral, non-helical version of the most common antiferroelectric $\mathrm{SmC_A^*}$ phase. These materials are now considered to be potentially useful as host component for antiferroelectric mixtures based on the chiral-dopant concept [4].

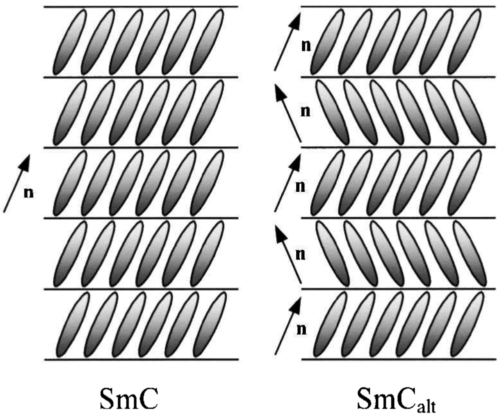
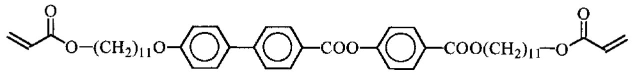


Figure 1. Structures of the SmC and $\mathrm{SmC_{alt}}$ mesophases.

In the course of a study of the effect of polymer stabilization of the antiferroelectric properties, we studied several antiferroelectric gels. These gels were obtained by *in situ* photopolymerization of a mixture of a non-chiral direactive material and an antiferroelectric compound [5]. Surprisingly, one of the synthesized diacrylates showed the $\mathrm{SmC_{alt}}$ phase. As far as we know this is the first non-swallow-tailed or non-dimeric material that forms this mesophase. In this paper we present the mesomorphic properties of this compound, as obtained from studies by DSC, XRD, polarizing optical microscopy and dielectric spectroscopy.



Due to the high reactivity of the acrylate group, prior to any study it was necessary to add a catalytic amount of an inhibitor (2,6-di-*t*-butyl-4-methylphenol) to prevent thermal polymerization. The phase sequence is:

$$\mathrm{I}\ 120°\mathrm{C}\ (6.12\,\mathrm{kJ\,mol^{-1}})\ \mathrm{SmA}\ 112°\mathrm{C}\ (0.13\,\mathrm{kJ\,mol^{-1}})$$
$$\mathrm{SmC}\ 94°\mathrm{C}\ \mathrm{SmC_{alt}}\ 74°\mathrm{C}\ (63.5\,\mathrm{kJ\,mol^{-1}})\ \mathrm{Cr}.$$

The SmC–$\mathrm{SmC_{alt}}$ phase transition was detected neither by DSC (at 20°C $\mathrm{min^{-1}}$) nor by XRD. The diffraction pattern is similar at 100°C and 85°C: a sharp ring at low angles corresponds to interlayer spacings of 45 and 44 Å, respectively; a diffuse halo at 4.5 Å, indicates the lack of order inside the layers. However, the texture in

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
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the polarizing microscope clearly undergoes an abrupt change, both on heating and on cooling, with 6°C of thermal hysteresis between cooling and heating at 1°C min^{-1}. This indicates that the phase transition is first order but with a very low (undetectable by DSC) enthalpy change. Figure 2 shows the texture at 85°C when the sample is between an untreated microscope slide and coverslip. Together with the 4-brush singularities, typical of the schlieren texture of the SmC phase, there are a number of 2-brush singularities that have been reported for antiferroelectric compounds and also for the above mentioned swallow-tailed compounds in the $\mathrm{SmC_{alt}}$ mesophase [2]. Figure 3 (*a*) shows the texture change at the transition from SmC (left) to $\mathrm{SmC_{alt}}$ (right) with the compound confined in a polyimide-coated cell (thickness 5 μm). It is interesting to remark that in the last phase, the extinction position coincides with that in the SmA phase; this is when polarizer or analyser coincides with the layer normal, figure 3 (*b*).

The dielectric studies also revealed important changes at the SmC–$\mathrm{SmC_{alt}}$ phase transition, as we shall show below. We have measured the dielectric permittivity in a broad frequency range (10^2–10^9 Hz) using two impedance analysers, the HP 4192A and the HP 4191A. The cells consist of two gold-plated brass electrodes of diameter 5 mm separated by 50 μm thick silica spacers. In the three smectic mesophases we observed two relaxations fairly well separated in the frequency domain. Figures 4 and 5 are plots of the imaginary component of the complex dielectric permittivity (fullpoints) versus the logarithm of the frequency at 100°C (SmC) and 90°C ($\mathrm{SmC_{alt}}$), respectively. To find the amplitudes, frequencies and activation energies of both modes, the experimental data were fitted to:

$$\varepsilon(\omega) = \sum_k \Delta\varepsilon_k(\omega) + \varepsilon_\infty - \mathrm{i}\sigma_{\mathrm{d.c.}}/\omega\varepsilon_0 \qquad (1)$$

where $\sigma_{\mathrm{d.c.}}$ accounts for the d.c. conductivity and ε_∞ for the high frequency permittivity. Each dielectric mode, $\Delta\varepsilon_k(\omega)$, has been fitted to the Havriliak–Negami function:

$$\Delta\varepsilon_k(\omega) = \frac{\Delta\varepsilon_k}{[1 + (\mathrm{i}\omega\tau)^\alpha]^\beta} \qquad (2)$$

Although the spectra for all temperatures only show two maxima, we always need a third relaxation (approx 10^9 Hz) to fit the data. We do not represent the results for this mode because it is at the limit of our set-up and is not properly characterized. We will call mode l the one on the low frequency side and mode h the one on the high frequency side. The continuous, thick line in figures 4 and 5 is the fitting of the experimental data and the thinner lines are plots of equation (2) for each mode. Mode l is almost Debye $\alpha = \beta = 1$ and mode h is almost Cole–Davidson $\alpha = 0.8$, $\beta = 1$. Figure 6 shows the temperature dependence of the dielectric amplitude of the two modes. At the SmC–$\mathrm{SmC_{alt}}$ phase transition the amplitude of both modes shows a jump, but for the l mode this is a decrease and for the h mode an increase. Figure 7 is an Arrhenius plot of the temperature dependence of the frequencies. Mode h does not show any change at the SmC–$\mathrm{SmC_{alt}}$ phase transition. Its behaviour is Arrhenius–like being the activation energy 29 kJ mol^{-1}

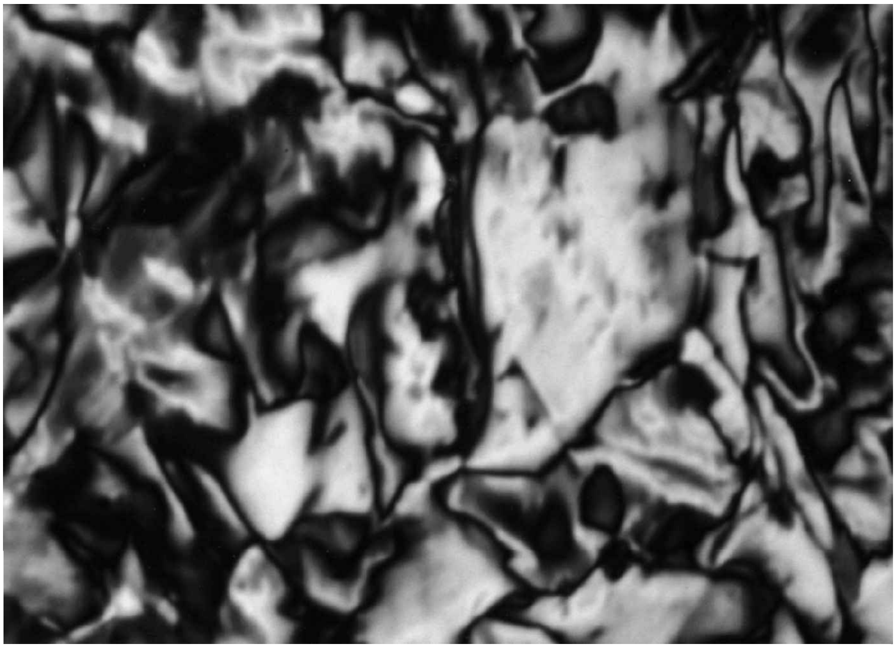
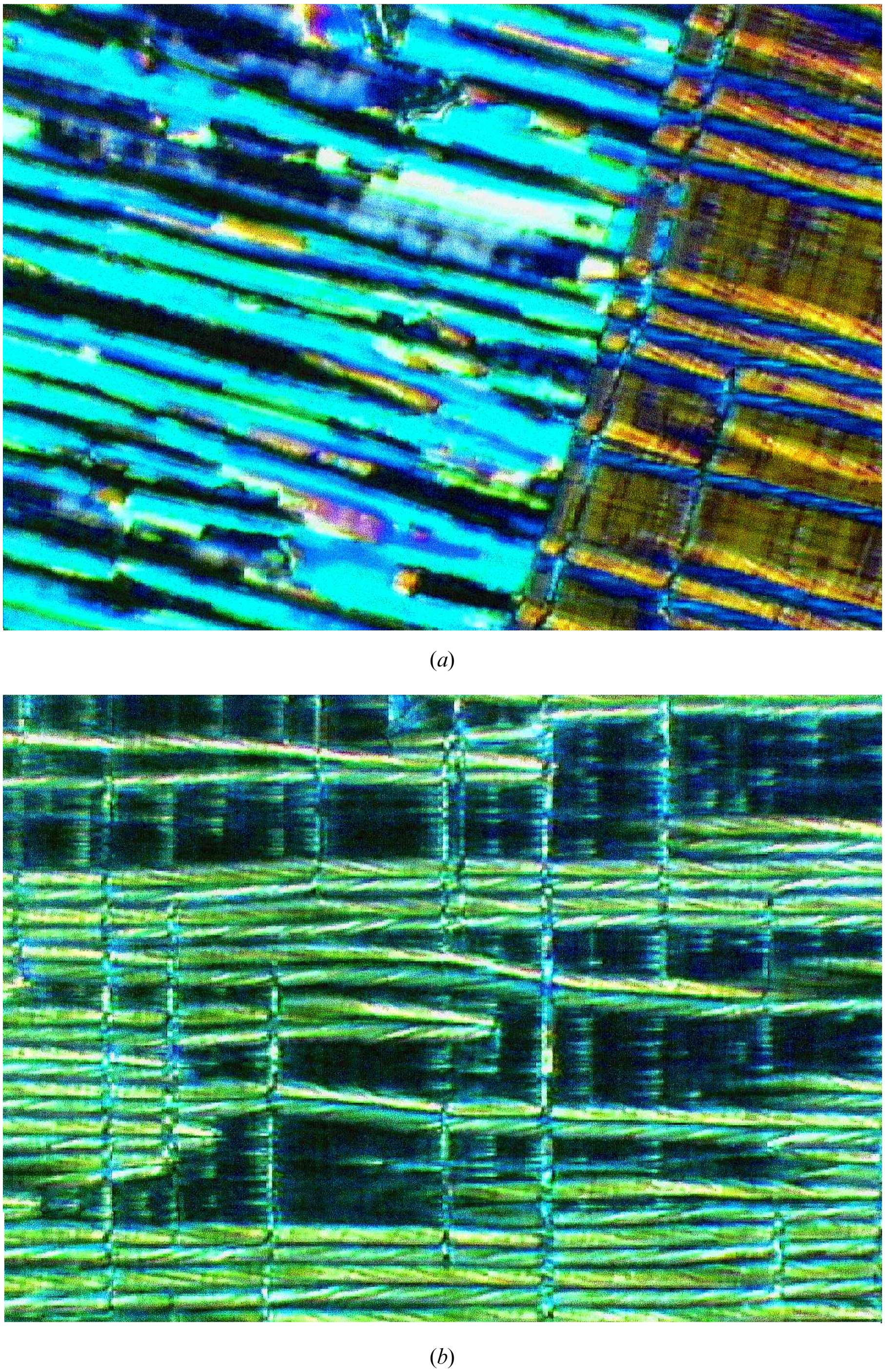


Figure 2. Texture of the $\mathrm{SmC_{alt}}$ at 85°C (untreated cell).


(*a*)

(*b*)

Figure 3. Polyimide coated cell; cell thickness 5 μm: (*a*) transition from SmC (left) to $\mathrm{SmC_{alt}}$ (right), (*b*) $\mathrm{SmC_{alt}}$ phase in the extinction position.

in both mesophases. Mode l is also Arrhenius–like in all mesophases (in this case we also include the SmA phase), but shows small jumps and changes in the activation energy: 102 kJ mol^{-1} in the SmA phase, 104 kJ mol^{-1} in the SmC phase and 93 kJ mol^{-1} in the $\mathrm{SmC_{alt}}$ phase.

We think that mode l should be related to the overall orientation of the molecules around the short axes and mode h to the rotation around the molecular long axes. The mode around GHz could be related to intramolecular motions, for example of the dipoles in the terminal chains. It is also important to remark that even after including this mode in equation (1), the high frequency permittivity is around 3, much higher than the square of the refractive index, showing that there are still some unrelaxed 'orientational' contributions.

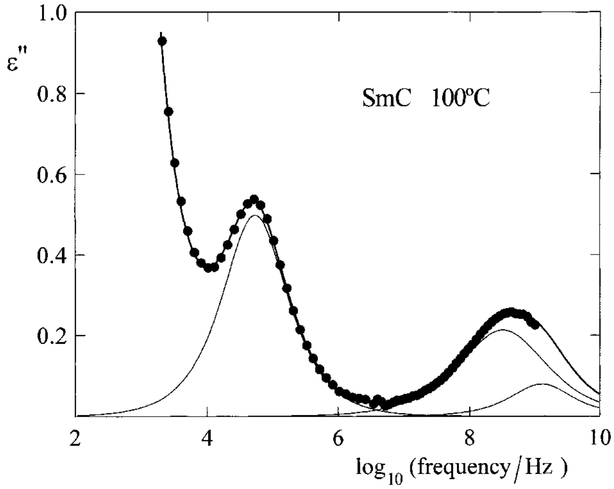


Figure 4. (●) Imaginary component of the complex dielectric permittivity versus the logarithm of the frequency at 100°C in the SmC phase. Continuous lines: fitting to equations (1) and (2).

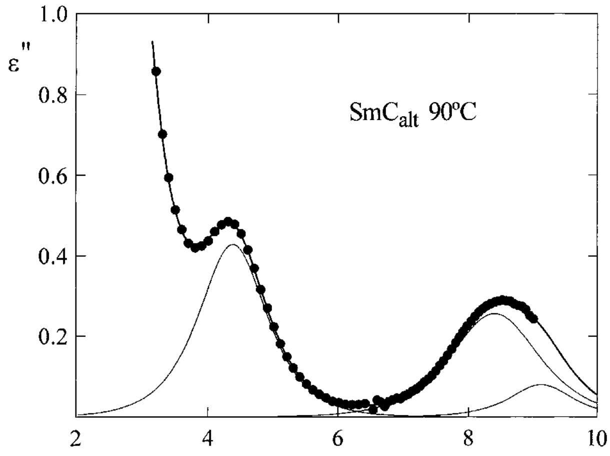


Figure 5. (●) Imaginary component of the complex dielectric permittivity versus the logarithm of the frequency at 90°C in the $\mathrm{SmC_{alt}}$ phase. Continuous lines: fitting to equations (1) and (2).

The behaviour of the frequencies is more or less the usual one when there are transitions between different (non-ordered) smectic mesophases. However the behaviour of the amplitudes is a little strange: at the SmC–$\mathrm{SmC_{alt}}$ phase transition the amplitude of mode l decreases and that of mode h increases. The cell is not treated; it has to be misaligned. If the alignment were planar, mode l (related to the longitudinal dipole moment) could not be present in the spectrum, neither for the orthogonal smectic nor for the tilted smectics. The only plausible explanation we have found is that we have a part of the sample in homeotropic alignment in the SmC phase, but with the molecules perpendicular (and the smectic layers tilted) with respect to the electrodes. In the $\mathrm{SmC_{alt}}$ phase a half of these molecules would make an angle 2θ with respect to the normal to the electrodes; then the amplitude of mode h should increase and the amplitude of mode l should decrease. It should be stressed that it is very difficult to handle this material because of its tendency to polymerize.

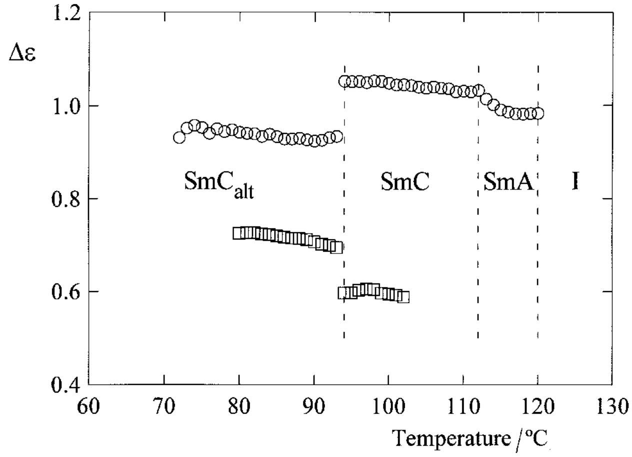


Figure 6. Dielectric amplitudes versus temperature: (○) mode l, (□) mode h.

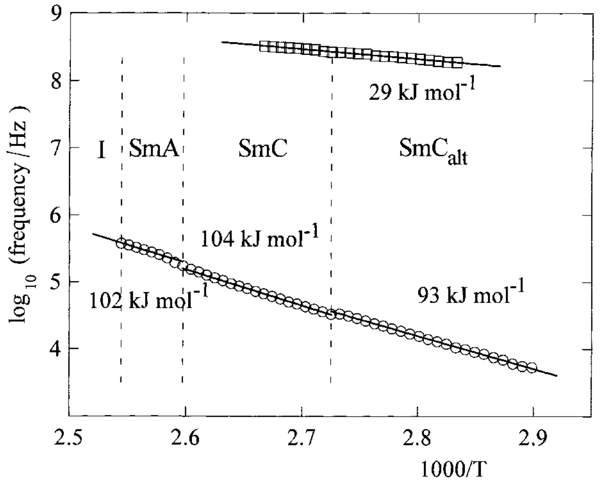


Figure 7. Frequencies versus temperature (Arrhenius plot): (○) mode l, (□) mode h.

To conclude, we think that we have enough evidence to suggest that this compound has a $\mathrm{SmC_{alt}}$ phase. This fact would open a synthetic pathway different from that for the swallow-tailed structures to obtain this mesophase. The core is the same as in an important number of antiferroelectric compounds (MHPOBC and analogues) [6]. The associated dipoles tend to favour the paired situation to form the alternated tilt structure. In our case this material has been mixed with antiferroelectric materials to obtain antiferroelectric gels giving resulting properties that are very interesting [5].

This research was supported by the Spanish Government through project C.I.C.Y.T. MAT 97-0986-C01-C02, and by the Universidad del País Vasco through project UPV060.310-G16/98.

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