ELECTRIC FIELD MEDIATED GROWTH HABITS IN B7

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The ground state of the novel liquid crystal phase formed by achiral
banana-shaped nitro-molecules and known as B7 is not understood.
While spirals and myelins spontaneously appear on cooling from the
isotropic liquid, neither mature to form B7 monocrytals. We tried
suppressing the flow associated with these growth transients by
applying large electric fields to thin samples (1-4μm thick). While a
field untwists some spirals and coarsens the less mobile myelin
textures, it stimulates even more flow and a B7 texture with variable
but exceedingly small length scales.

Keywords: Achiral banana liquid crystals; spontaneous flow patterns;
achiral tetrahedratics.
INTRODUCTION
Neither the symmetry nor the ground state of the novel liquid crystal phase formed by achiral banana-shaped nitro-molecules and known as B7 is understood. Indeed, B7 may not have a simple ground state but rather many states with comparable energy. To improve our understanding of the fundamental structural properties of the mysterious B7 phase exhibited by nitro-substituted banana (NB) compounds [1], we studied the growth habits of NB8 (Figure 1) in an electric field.

![Chemical Structure of NB8](image)

Figure 1. NB8 synthesized by W. Weissflog. The B7-Isotropic transition was $T_{B7-I} \sim 180^\circ C$ (heat of transition $\sim 7.5$cal/gm). After 3 cycles at 3K/minute in a DSC (total scanning time $\sim 5$ hours), the B7 Isotropic Liquid (I) transition temperature decreased from $180.6^\circ C$ to $180.2^\circ C$.

A “single crystal” of B7 has not yet been made. X-ray data shows a liquid like outer ring and many diffraction peaks suggesting that B7 phase is not simply layered [1,2]. More evidence against a simple layered structure are the observations that freely suspended films break-up into thread-like structures [1-3]

The growth patterns of B7 in NB8 are particularly interesting. They are always time dependent and show a richer variety of patterns in samples thicker than about 10$\mu m$ [4]. When the temperature is
decreased, they grow. But, at fixed temperature, they become unstable. In an effort to suppress the flow associated with the growing B7 phase, we studied NB8 in thin samples and with strong electric fields. We were surprised to find that the effect of an electric field was to induce a turbulent flow in the isotropic liquid surrounding emerging growth objects leading to a disordered granular pattern with even smaller length scales than grown without an applied electric field.

GROWTH HABITS OF B7
No electric field, sample thickness greater than 10μm

Without a field, NB8 exhibits predominantly 2 growth habits in the vicinity of $T_{\text{B7-I}}$ [1]: spirals and myelins. Neither grow to a monodomain B7 phase.

Figure 2 shows the evolution at constant temperature ($T=178.4^\circ\text{C}$) of a spiral pattern when cooling from the isotropic liquid into the B7 phase in a sample about 15μm thick. The spiral appeared when a scroll-shaped object rolled up from its edges. The smallest picture is a plot of one video line centered on the axis of the spiral (st-plot). It shows the pitch increasing from about 1.75μm to about 3.9 μm during one of its many transitions. With the passage of the transition zone, the spiral jumped off the st-line. Shortly after the last picture in Figure 2, the spiral disappeared leaving behind only isotropic liquid. Decreasing the temperature again resulted in new spirals appearing which also eventually died leaving behind isotropic liquid or granular small scale textures.

In thicker samples, the spiral exhibited bending and bifurcating instabilities not observed in an electric field nor in thinner samples [4].
This we attribute to a larger number of degrees of freedom available to flow structures in 3D.

![Image](image.png)

Figure 2. The spiral formed from the scroll pattern (sketched on left), goes through various changes in pitch and structure, then dies shortly after the picture labeled $t=635.8s$; $T=178.4^\circ C$. From [4].

Thin samples in an electric field

Samples, ranging in thickness from 1 to 4\(\mu\)m, were prepared by vacuum filling NB8 between conducting indium tin oxide (ITO) electrodes passivated with \(\sim 1000\AA\) SiO. Silica beads controlled sample thickness to a precision of \(\pm 5\%\) checked by dielectric measurements. While NB8 (Figure 1) tended to de-wet from SiO, this passivated layer enabled the application of much larger fields without dielectric breakdown than bare ITO. Another reason for using passivated electrodes was to suppress electroconvective flows [5] arising from charge injection into B7. With this sample preparation, dielectric breakdown occurred at fields $E_{db}\sim 80V/\mu$m. The large value for $E_{db}$ suggests the absence of extraneous ionic impurities. This and
the fact that frequencies of 30Hz and higher were used suggest that the new dynamics reported here are fundamental features of the B7 phase rather than sample preparation.

Figure 3. The many textures after cycling B7 in an electric field. T=168.4°C. The picture size is 168x140µm.

Figure 3 shows the rich variety of shapes exhibited by the former spiral and myelin patterns after having been cycled in an electric field (typically 25V/µm at frequency, v=30Hz).

When the field is turned on, spirals and myelins surrounded by isotropic liquid “dance” in the field of view (Figure 4). Those not surrounded by isotropic liquid remain nearly static. The spirals appear to unwind in shear to form nearly
transparent strings. Myelins in contact with the isotropic liquid exhibit fast splay dynamics becoming unstable when they have maximum splay. However, once the splay is optimized so that they now form ring-like objects, they too vanish leaving behind more isotropic liquid. The temperature range of stability of an isotropic liquid co-existing with these growth forms increased considerably for patterns grown in an electric field.

While the spirals eventually disappeared, some myelins could grow to be surrounded by other myelins. Some of these eventually developed a 2D pattern. In an electric field, such myelins remained immobile in the field but fields of $E=\pm25\text{V}/\mu\text{m}$ destroyed the 2D patterns that returned when the field was turned off (Figure 5).

![Figure 5. Disappearance of the 2D pattern when $E=25.4\text{V}/\mu\text{m}$ and its reappearance when $E=0$.](image-url)
CONCLUSION
We studied the electric field mediated growth habits shown by the B7 phase of NB8 which does not have a simple layer structure \[1,6\]. In contrast to another compound exhibiting the B7 phase and found to be ferroelectric \[7\], in NB8, the electric field creates flow in the isotropic liquid surrounding the growth forms \[8\] even when passivated electrodes are used and the compound is very pure. The only known achiral order parameter predicted to have this property is the isotropic tetrahedral phase \[9\].

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REFERENCES


[6] We exclude from comparison here those compounds that have been identified as B7 because they also show spiral growth forms similar to NB8 but for which x-ray diffraction shows a simple layer structure: W. Weissflog, H. Nadas, U. Dunemann, G. Pelzl, S. Diele, A. Eremin, H. Kresse, *Influence of lateral substituents on the mesophase behaviour of banana-shaped mesogens*, J. Mater. Chem. 11, 2748 (2001)).

