

Synopsis

Physical studies on some liquid crystals

by

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In this thesis we report our studies on several physical properties of nematic and twist grain boundary (TGB) liquid crystals. We describe the first experiment on the effect of strong electric fields on the paranematic-nematic transition on a system with negative dielectric anisotropy. We find that the quenching of director fluctuations under the action of a strong electric field not only enhances the orientational order parameter but also significantly affects the thermodynamics of the phase transition. Our experiments show that the orientational order parameter of nematic liquid crystals with aromatic cores in thin cells (1-2 μm) is enhanced considerably (~10%) compared to that in thick cells (7-15 μm). We have used the usual Landau theory to partly account for this effect. We also show that the experimental value of the effective dielectric constant in a thin cell (1-2 μm) and its variation with temperature are dramatically different from those in thick cells. Using a simplified model we show that impurity ions which are present in the system contribute to the dielectric properties in thin cells at low frequencies (10-1.1KHz). We describe some new experimental results in mixtures of a nonchiral and a chiral compound exhibiting TGB phases. We find that the type-II character is enhanced in the mixtures with increasing concentration of the *nonchiral* component, which in turn enlarges the temperature range of twist grain boundary-A (TGB_A) phase. We also theoretically estimate the structural parameters of the TGB_A phase namely the distance between two dislocations (l_d) within a grain boundary and that between two neighbouring grain boundaries (l_b). The calculated values of l_d and l_b as well as their temperature dependences reflect experimentally observed trends.

In **chapter-I** we give a general introduction to the topics which are relevant to the work reported in the remaining chapters.

There have been several reports on the effect of strong electric and magnetic fields on the isotropic to nematic phase transition [1-4]. The earlier electric field experiments were performed on systems exhibiting positive dielectric anisotropy ($\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp}) > 0$), where the subscripts refer to directions in relation to \hat{n} . The dielectric anisotropy is proportional to the order parameter ($S \approx \frac{\Delta\epsilon}{\Delta\epsilon_0}$, where $\Delta\epsilon_0$ is the dielectric anisotropy in the fully aligned state) and couples with E^2 to lower the free energy density ($F_e = -\frac{\Delta\epsilon_0 S E^2}{12\pi}$) where E is the applied electric field. The field induces a weak orientational order even above the nematic-isotropic transition temperature, as a result of which all the physical properties in the medium become weakly anisotropic (*paranematic phase*). The field-induced birefringence in the paranematic phase due to the electric field is called the Kerr effect. When there is a phase transition under field the paranematic to nematic transition temperature is shifted towards higher values and the order parameter is increased in the nematic phase at any temperature. At low fields the transition occurs with a finite jump in the order parameter in a first order phase transition. With increasing field the jump decreases and above a critical field there is a continuous evolution of the order parameter from paranematic to nematic phase. When $\Delta\epsilon > 0$, the director is aligned along the direction of the applied electric field and the enhancement in the order parameter is due to the Kerr effect as well as quenching of director fluctuations but the system remains uniaxial [2].

Studies on the effect of strong electric fields on liquid crystals with negative dielectric anisotropy ($\Delta\epsilon < 0$) are considerably interesting because the phase diagram is very different in nature compared to that in a system with $\Delta\epsilon > 0$ [5,6]. In the former system a strong dipolar group makes a large angle with the long axis of the molecule. To study the electric field effect, a nematic liquid crystal with a large negative $\Delta\epsilon$ is sandwiched between two ITO (indium-tin oxide) coated glass plates, which are treated for planar alignment. The field is applied between them (i.e. along the z -axis) as shown in Fig.(1). In the paranematic phase, the dipoles of the molecules tend to align along the field direction. As a result the long molecular axes tend to be perpendicular to the field direction. It should be pointed out that in the paranematic phase the distribution of

azimuthal angles of the molecules in the plane (XY) perpendicular to the field is random. The projections of the long axes of the molecules in the XY plane are shown in Fig.(1). In the paranematic phase the distribution function of the long axes around the field direction shows a small peak at polar angle $\theta = \pi/2$. With increasing field the peak height increases in the paranematic phase as schematically shown in Fig.(2).

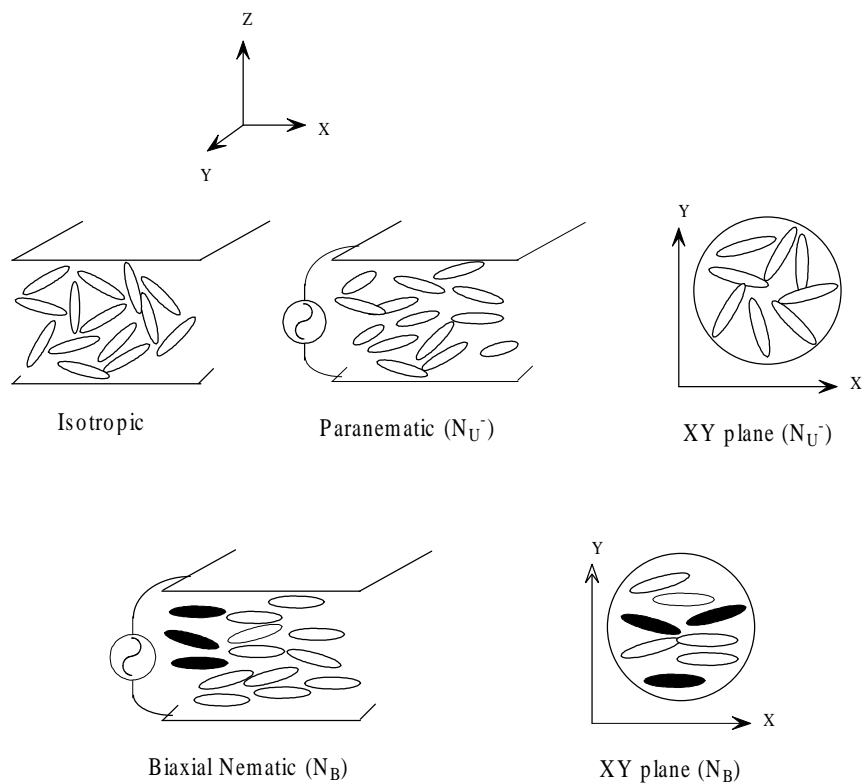


Figure 1: Schematic diagrams of the field induced paranematic (N_U^-) and biaxial nematic (N_B) liquid crystals. The molecules are shown in an exaggerated scale for clarity.

Therefore the order parameter (S) in the paranematic phase is negative giving rise to a negative uniaxial (N_U^-) phase as depicted schematically in Fig.(1). When the system is cooled under the field, below the paranematic–nematic transition temperature the long axes of the molecules tend to align in a preferred direction (x-axis) because of the surface interaction with the treated plates. In the nematic phase there is a partial quenching of the director fluctuations due to electric fields in the ZX plane. Thus the fluctuations in the ZX plane are different from those in the (XY) plane perpendicular to the field as shown in

Fig.(1). The differential quenching of fluctuations leads to induced biaxiality under field [7-8]. Under field the paranematic to nematic transition corresponds to uniaxial nematic (N_U) to biaxial nematic (N_B) transition. The theoretical calculation have shown that [7,8] with increasing field the N_U to N_B transition temperature is shifted to higher values and the order parameter is increased in the N_B phase. The jump in the order parameter reduces and finally the transition becomes *continuous* above the tricritical field, at which a first order transition goes on to second order phase transition.

There are several difficulties in conducting high electric field experiments in liquid crystals, mainly because of heating due to ionic conductivity of the sample as well as dielectric relaxation. There can also be hydrodynamic instability [9] for the systems

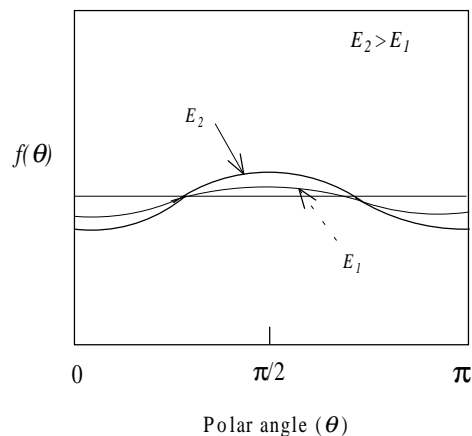


Figure 2: Schematic representation of the distribution function in the presence of electric field ($\Delta\epsilon < 0$) above T_{PN} . Dotted line represents the distribution function without the field in the isotropic phase and the continuous line represents the same with field in the paranematic phase. The peak around $\pi/2$ is exaggerated for clarity.

with $\Delta\epsilon < 0$. In our experiments reported in **Chapter-II**, we have adapted a technique developed by Geetha et al [3]. The local temperature of the sample under the field is measured and the data points are collected continuously. This technique enables us to perform optical as well as electrical measurements simultaneously.

We report the following results on a material with $\Delta\epsilon \approx -8$ (at 20°C).

- Electric field induced enhancement of order parameter. Fig.(3) shows Δn as a function of temperature at different applied fields. We have calculated the order parameter from Δn data and discuss the enhancement of the order parameter in terms of microscopic Kerr effect as well as the quenching of macroscopic thermal fluctuations.
- Shift in the paranematic to nematic transition temperature (T_{PN}) with field. The variation of T_{PN} is linear with field as shown in Fig.(4).
- Observation of surface induced order at zero field just above T_{NI} .
- Divergence of order parameter susceptibility under strong fields near second order paranematic to nematic transition temperature as measured by 3rd harmonic electrical signal.
- Detection of a small 2nd harmonic electrical signal near paranematic to nematic transition temperature under a strong field, which implies the presence of polarized domains that do not reorient with the field.

We argue that the linear dependence of T_{PN} on $|E|$ can be understood by including the entropic energy cost of quenching of director fluctuations by the field in the Landau de Gennes theory.

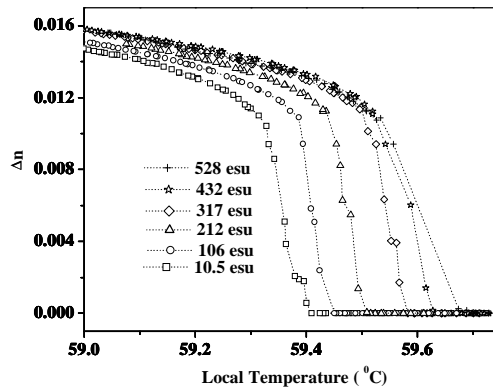


Figure 3: Variation of birefringence across the paranematic-nematic transition region as a function of local temperature at different fields. Cell thickness: 16.8 μ m. Frequency of the applied field: 4111 Hz. Points are the experimental data and the dotted lines are drawn as guides to the eye.

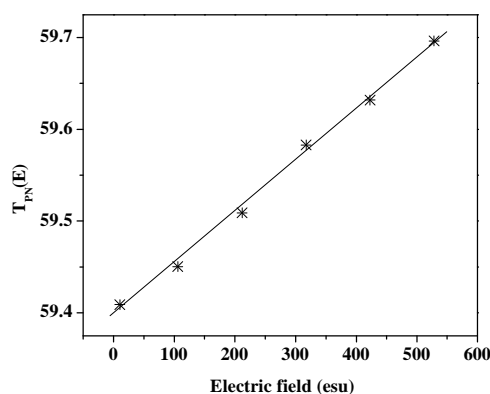


Figure 4: Paranematic to nematic transition temperature as a function of applied field. T_{PN} is the temperature at which the birefringence starts to rise from zero value in Fig.(3).

There have been a couple of reports that the orientational order parameters of nematic liquid crystals in thin cells are higher than those in thick cells [10-11]. These experiments were conducted on compounds having the longitudinal cyano (-CN) end group. In order to check if it is a general feature of nematic liquid crystals we performed such experiments on several systems having transverse as well as longitudinal cyano groups as reported in **chapter-III**. The following compounds were studied: (1) trans-4-pentyl-(4-cyanophenyl)-cyclohexane (Cr. 30 N 55 I) (2) 2-cyano 4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate [7(CN)5 for short] (Cr. 45 N 102 I) (3) 4-cyanophenyl 3'-methyl 4'-(4''-n-decylbenzoyloxy) benzoate (Cr. 100.5 N 154 I) and (4) a mixture of the last compound with another one having banana shaped molecules. We have measured the birefringence (Δn) of the compounds at two different thicknesses, in the ranges 1-2 μm and 8-15 μm respectively. We found significant enhancement (by 10 to 18%) of birefringence in thin cells in compounds with aromatic cores (Fig.(5)). However in a compound which does not have any aromatic core, no significant difference is observed. In this case the surface potential appears to be extremely small on the polyimide coated surfaces and hence the enhancement of order parameter at the surface is not significant.

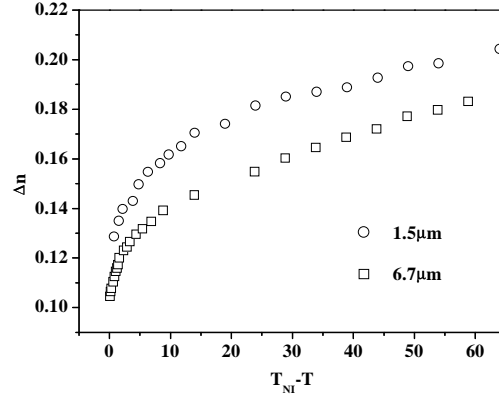


Figure 5: Variation of birefringence as a function of temperature at two different cell thicknesses measured in 7(CN)5.

In order to understand the observed phenomena we used the usual Landau-de Gennes theory for uniaxial nematic. Within this framework and assuming that the uniaxial surface order is unity ($S_0=1$) for the compounds with the aromatic cores, our calculation leads to an enhancement of order parameter of $\sim 5\%$ at $T_{NI} - 0.2^\circ$, which reduces to $\sim 2\%$ at $T_{NI} - 5^\circ$. The suppression of out of plane thermal fluctuations due to confinement can lead to a weak biaxiality in thin cells. We extended our calculation taking into account the weak biaxiality, but this does not improve upon the uniaxial result.

There have been several studies both experimentally and theoretically on the effect of ions on the dielectric properties of nematic liquid crystals in the isotropic phase [12]. The studies were made in cells of thicknesses of $\sim 5\mu m$ or more. In view of the emerging interest in using much thinner cells in LCDs, as well as an intrinsic interest in the problem we carried out experiments in thinner cells, with thickness $< 2\mu m$ as reported in **chapter-IV**. We carried out measurements on the dielectric properties of a nematic liquid crystal viz. 7(CN)5 in planar aligned cells with two different thicknesses (1.2 and $6.7\mu m$). We have conducted detailed dielectric measurements in the frequency range of 10 Hz-1.1 KHz on both the cells. We have found that the temperature variation of the

effective dielectric constant (ϵ_{\perp}) of the thick cell reflects that of the orientational order parameter as shown in Fig.(6). On the other hand, the thin cell exhibits a higher value of ϵ_{\perp} which is essentially temperature independent. This behavior is explained on the basis of the effect of space charge polarisation arising from the impurity ions under the action of an applied low frequency ($\sim 10 - 1000$ Hz) field. We have described a simplified model which takes into account the ionic contribution and enables us to estimate the temperature dependences of the number density and diffusion constant of the impurity ions. Our experiment shows that in very thin cells the ionic contribution to the dielectric response of liquid crystals can be significant. In order to make thin display devices the sample should be highly purified to avoid the ionic contribution to the dielectric response and hence to the electrooptic response.

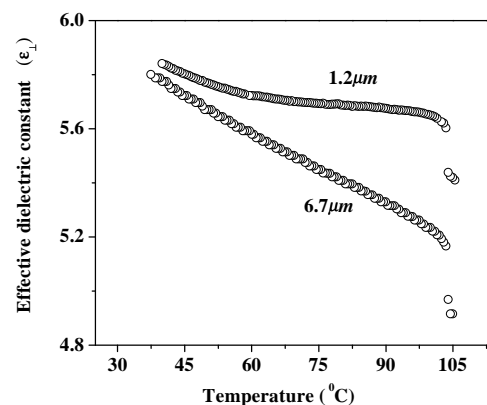


Figure 6: Temperature dependence of the effective dielectric constant of the liquid crystal 7(CN)5 taken in cells with two different thicknesses, at a frequency of 1.1 KHz. Note the higher value for the thinner cell, which hardly varies with temperature in the nematic phase above 60 °C.

The formal similarity between smectic liquid crystals and superconductors was pointed out by de Gennes [9]. The twist grain boundary (TGB) phase is the analog of vortex state in a type-II superconductor under strong magnetic fields. The detailed structure of the TGB phase was theoretically predicted by Lubensky [13]. The TGB_A phase consists of a regular twisted arrangement of smectic-A blocks separated by grain

boundaries made of arrays of screw dislocations. Goodby et al [14] reported the first observation of TGB phase in some highly *chiral* liquid crystals. Later observations of TGB phases in mixtures of *chiral* and *nonchiral* compounds were also reported by several authors. The discovery of a new phase called the undulated twist grain boundary smectic-C* (UTGB_C^{*}) was reported on binary mixtures of a *chiral* compound 4-(2-methyl butyl) phenyl 4' -n -octylbiphenyl-4-carboxylate (CE8) and a *nonchiral* compound 2-cyano 4 - heptylphenyl 4' -pentyl 4- biphenyl carboxylate (7(CN)5) from our laboratory by Pramod et al [15]. It is noticed from the phase diagram (Fig.(7)) of this mixture that the temperature range of TGB_A phase increases with the concentration of the *nonchiral* compound and above 34wt% of the latter the UTGB_C^{*} phase is also induced. As described in **chapter-V**, we have measured the optical reflection band in the cholesteric phase of a few mixtures to show that the chiral strength ($1/P$, where P is the pitch in the cholesteric phase) indeed decreases as the concentration of 7(CN)5 is increased (Fig.(8)).

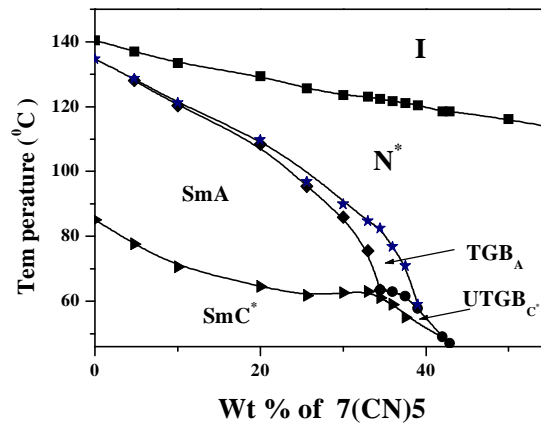


Figure 7: Part of the phase diagram containing the TGB phases in binary mixtures of CE8 and 7(CN)5 (adapted from ref.[15]).

With decreasing chiral strength the increase in the temperature range of TGB_A phase and also the induction of UTGB_C^{*} phase is unexpected. It is known that apart from having a sufficiently large chiral strength the material must have type-II character to exhibit the TGB_A phase [13,14,16]. The Ginzburg parameter $\kappa_2 = \lambda_2/\xi$ must be greater than $1/\sqrt{2}$, where λ_2 is the twist penetration length defined by $\sqrt{(K_2/D)}$ [9], K_2 and D being

the elastic constants for the director twist and molecular tilt in the layer respectively and ξ the smectic order parameter coherence length. We performed an electroclinic measurement of D in the smectic-A phase which is proportional to the relevant Landau coefficient ' a ' shown in Fig.(9). The decrease of ' a ' with the concentration of the *nonchiral* compound (7(CN)5) demonstrates that κ_2 correspondingly increases. Thus the type-II character is enhanced in the mixture studied by us by increasing the concentration of the nonchiral component, which in turn enlarges the temperature range of TGB phases.

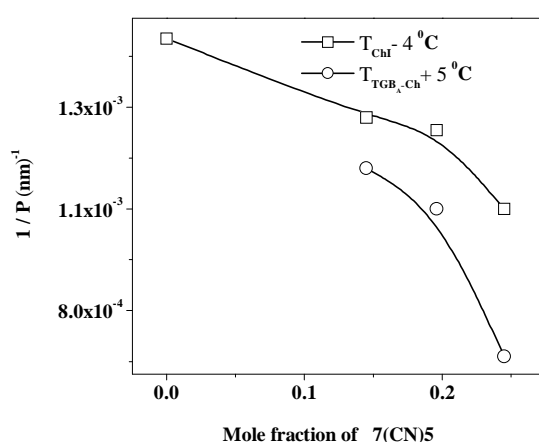


Figure 8: Variation of $1/P$ with mole fraction of 7(CN)5. The continuous lines are drawn as guides to the eye.

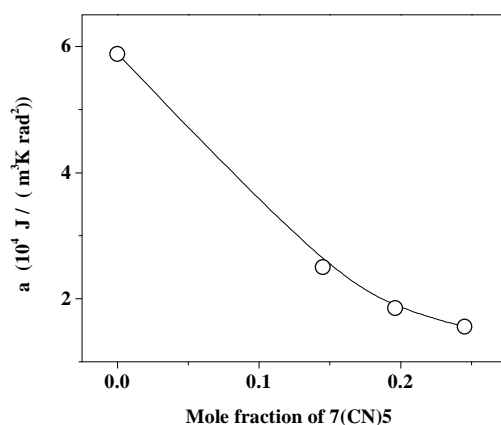


Figure 9: The tilt elastic constant ' a ' plotted as a function of mole fraction of 7(CN)5.

We also describe the effect of low frequency electric fields on the stability of the TGB_A and $UTGB_C^*$ phases. We have also observed a new type of periodic radial structure in the meniscus region of free -standing films of the mixtures in the smectic and TGB_A phases. It is suggested that the occurrence of this structure depends on the type-II character of the materials.

Navailles et al [17] measured by x-ray diffraction the variation of structural parameters, *viz*, l_b (distance between two grain boundaries) and l_d (distance between two dislocations) as functions of temperature in a pure compound that exhibits the commensurate TGB_A phase. In **chapter -VI** we have calculated the Gibbs free energy of the TGB_A phase using linear elasticity theory. The calculation includes the interaction between nearest-neighbor grain boundaries. We have carried out a two dimensional minimisation of the Gibbs free energy to find a well- defined minimum as functions of l_b and l_d . The structural parameters decrease as the chiral strength (h) is increased (Fig.(10)) for a fixed value of κ_2 (Ginzburg parameter).

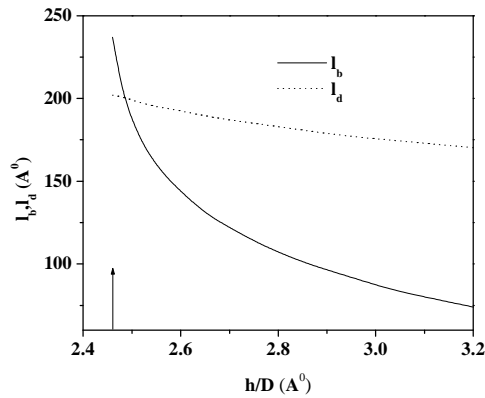


Figure 10: Variations of l_b and l_d as functions of h/D for $\kappa_2 = 1$ ($\lambda_2 = 38 \text{\AA}$, $\xi = 38 \text{\AA}$ and $d = 38 \text{\AA}$). Vertical arrow denotes the lower critical value of $h_{c1} / D = 2.46$.

We have used the mean field dependences of ξ (smectic correlation length), λ_2 (twist penetration depth) and D (tilt elastic constant) to show that l_b and l_d both decrease as the TGB_A to cholesteric transition point is approached. The ratio l_b/l_d also reflects the experimentally observed trend with temperature. We also comment on some other experimental results on the TGB_A phase, on the basis of our calculations.

Some of the results in this thesis have been published in the following references:

1. Surajit Dhara and N. V. Madhusudana, “Ionic Contribution to the Dielectric Properties of a Nematic Liquid Crystal in Thin Cells.,” *Journal of Applied Physics*, **90**, (7) 3483 (2001).
2. Surajit Dhara, Pratibha R. and N. V. Madhusudana. “Some Experimental Investigations on Type-II Chiral Liquid Crystals.,” *Ferroelectrics*, **277**, 13 (2002).

The following papers are in preparation.

1. Surajit Dhara and N.V. Madhusudana, “Influence of Director Fluctuations on the Electric Field Phase Diagrams of Nematic Liquid Crystals” Surajit Dhara and N. V. Madhusudana, “Enhancement of Orientational Order Parameter of Nematic Liquid Crystals in Thin Cells.”
2. Yashodhan Hatwalne, Surajit Dhara and N. V. Madhusudana, “Theoretical Estimation of Structural Parameters of the Twist Grain Boundary -A Liquid Crystals.”

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