On the structure of the Nx phase of symmetric dimers: inferences from NMR

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Abstract

NMR measurements on a selectively deuterated liquid crystal dimer CB-C9-CB, exhibiting two nematic phases, show that the molecules in the lower temperature nematic phase, N_X, experience a chiral environment and are ordered about a uniformly oriented director throughout the macroscopic sample. The results are contrasted with previous interpretations that suggested a twist-bend spatial variation of the director. A structural picture is proposed wherein the molecules are packed into highly correlated chiral assemblies.

The classical nematic phase (N) with only orientational ordering of the molecules is theoretically and experimentally the LC phase which, due to its structural simplicity and technological importance, is by far the most investigated and best understood of all LC phases[1]. Thus the detection of LCs forming two nematic phases is of very high interest, as such observations pose the challenge to test and recalibrate fundamental concepts of LC phase behaviour. Direct transitions between two uniaxial thermotropic nematic phases are typically associated with the formation of more complex molecular aggregates in the low temperature nematic phase, such as column formation in the transition to the columnar nematic phase[2] of discotic or bent core materials[3]. For main chain LCPs, examples have been reported where a first order phase transition can occur between two nematic phases[4].

The recent observation of an additional, low temperature, nematic phase, initially termed N_X,[5,6] and more recently N_{tb}, in cyanobiphenyl based dimers with positive dielectric anisotropy, where the mesogens are separated by odd-numbered hydrocarbon spacers[5–12], and in specifically prepared difluoroterphenyl mesogens[11] with negative dielectric anisotropy, as well as in non-symmetric dimers[13], has sparked a rapidly increasing interest in this class of LCs, and particularly in the structure of this new nematic phase in thin films and in the bulk. These LCs exhibit characteristic periodic stripe patterns and rope textures in thin films and an electro-optical response typically found in chiral systems, though the molecules are non-chiral[6,10,11,14]. XRD investigations show clearly the absence of layer reflections, confirmed by extensive miscibility calorimetric studies[5]. The presence of stripes and Bouligand arches with periodicities in the 8-10nm regime in freeze fracture TEM[12] was interpreted as formation of chiral structures on surfaces, however recent

evidence based on AFM studies might suggest these features could be artefacts due to the onset of surface crystallisation[15]. Lastly, in a series of papers[8,9,16] focused on an extensive NMR characterization of CB-C7-CB it is argued that the interpretation of the NMR measurements is consistent with a helicoidal conical ("heliconical") nematic phase wherein the spatial distribution of the nematic director is $\mathbf{n}(Z) = (\sin\theta_0 \cos kZ, \sin\theta_0 \sin kZ, \cos\theta_0)$, defining a conical helix of constant pitch $q = 2\pi/k$ and constant "tilt" angle θ_0 between $\mathbf{n}$ and the helix axis Z. Whilst this is in line with a spontaneous twist-bend elastic deformation predicted[17] for the nematic phases of achiral banana-shaped molecules, it should be stressed that the structural periodicity of 8-10 nm observed in the N_X phase of dimers[11,12] cannot be readily identified with the periodicity implied by the theoretical proposals of the "twist-bend" nematic phase[17]. Such proposals are based on the continuum theory of elasticity for the nematic phase, involving the elementary (twist, bend, splay) deformations according to the Frank-Oseen formulation of the elastic free energy. However, the validity of the fundamental assumptions of the continuum theory concerning the slow variations of the director field[1] is problematic when the macroscopic director supposedly undergoes a reorientation of $2\theta_0$ over the distance of a half-pitch, which might be as short as one or two molecular lengths. In an attempt to by-pass this inconsistency, the notion of the "half-molecular director", representing the local average orientation of the long axis of a biphenyl half-molecular core, is introduced[12] in place of the macroscopic nematic director $\mathbf{n}(Z)$. Computer simulations, on the other hand, are not subject to the small length-scale restrictions of continuum models and there it is found that bent core molecules with flexible arms[18], a model bearing structural analogies with the odd-spacer dimers, can form nematic phases consisting of chiral domains which spontaneously self-

assemble into larger helical structures. Notably, chiral domains in the nematic phase of achiral compounds exhibiting dimerisation through hydrogen bonding were reported more than 15 years ago[19]; however, such domains were found to exhibit macroscopic twist deformation of the director in the optical regime. Lastly, although the twist-bend model has been proposed[8,9,11,12,16,20] for the consistent interpretation of various experimental observations on the dimer N_X phase, there is, to our knowledge, no direct identification of the heliconical structure and, furthermore, there are indications[21,22] that the dominant molecular arrangement in the N_X phase could differ from that of the twist-bend model.

In this communication we show, based on NMR studies of a selectively deuterated material of the structure CB-C9-CB presented in Figure 1a, that the helicoidal conical structure is not identified as the organisation of the N_X phase in the bulk.

The phase sequence of this statistically achiral compound is as follows. Heating: Cr 83.9 N_X 106.5 N 122.7 Iso (˚C); cooling: Iso122.1 N 106.4 N_X 48.5 Cr (˚C). The sequence is determined by DSC at 10ºC min^{-1} (see ESI-4[23]and is close to that of non-deuterated CB-C9-CB for which the N_X phase was observed first[5] and to CB-C7-CB[8]. The materials in the N phase are typical, relatively viscous, uniaxial nematics. The onset, through a first order phase transition, of the low temperature N_X phase is accompanied by a significant increase of the viscosity (see also ESI-2 [23]).
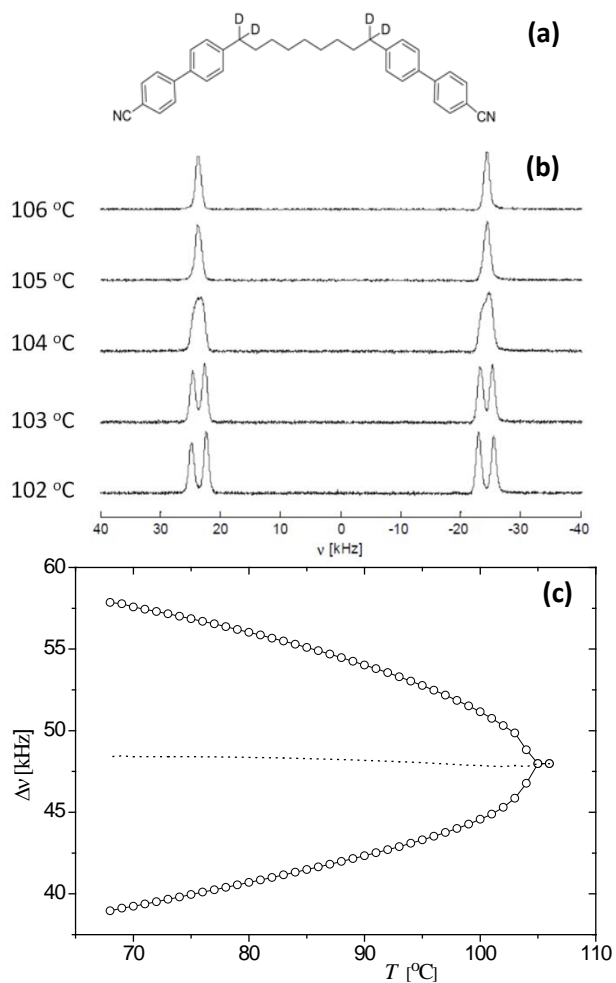
Figure 1: (a) Structure of the deuterated molecule CB-C9-CB, (α,ω-bis(4,4′-cyanobiphenyl) nonane-(1,1,9,9-d$_4$)). (b) Measured ^{2}H NMR spectra recorded close to the N-Nx phase transitions (cooling run). (c) The dependence of the measured quadrupolar splittings, $\Delta\nu$, on the temperature T for the 1,9 deuterons. The dotted line represents the mean value of the two splitting.

Figures 1(b, c) show the quadrupolar spectrum of aligned CB-C9-CB in the temperature range from 110-80°C. The line shape and the width of the peaks suggest that the sample is uniformly oriented along the magnetic field of the spectrometer. (For experimental details see ESI-1 in [23]).

In terms of ^{2}H-NMR analysis, the characteristic feature of the N-N$_X$ phase transition is the onset of the doubling of the quadrupolar peaks of the CD$_2$ sites (Figure 1(b, c)). Specifically, on entering the N$_X$ range, each of the spectral lines of the α-CD$_2$ groups splits into two lines with splittings $\Delta\nu_1$ and $\Delta\nu_2$, of essentially equal integrated intensity (see ESI-1.2 [23]) and with continuously increasing separation with decreasing temperature. The quantity $\overline{\Delta\nu} = (\Delta\nu_1 + \Delta\nu_2)/2$ is insensitive to temperature, with only a slight increment on cooling; see Figure 2c. While this peak-doubling alone does not allow to directly single out a particular underlying mechanism among several possibilities, the mechanism of loss of equivalence of the two deuterated sites[24] as a result of the onset of local chiral asymmetry in the N$_X$ phase is strongly supported by the detailed NMR studies in[8,9] on CB-C7-CB together with other results[25] which suggest the presence of chiral asymmetry. Accordingly, our analysis and interpretation of the present data is based on adopting the hypothesis of the onset of local chiral asymmetry in the N$_X$ phase on a longer time scale than the time-averaging inherently involved in the NMR measurement. Within this interpretation, the intensities of the two sub-peaks should be strictly equal as they correspond to equal numbers of (orientationally inequivalent) deuterated sites. Also, since the individual dimer molecules are statistically achiral, it is expected that a chirally unbiased bulk sample should consist of domains exhibiting both senses of chirality and with equal molecular populations for either sense. It should be noted that in the present work, contrary to the assumptions in refs[8,9,16,20], the origin of the chirality is not necessarily attributed to the twist-bend deformation of the director. In fact it is shown here that such deformation is not implied by the NMR measurements and, moreover, that a number of additional assumptions, of

questionable validity, would need to be invoked in order to make the assumed presence of the twist-bend deformation compatible with these measurements.

The measured splitting in the quadrupolar spectrum of the α-CD$_2$ group in the nematic phase is related to the respective orientational order parameter $S_{\alpha-CD}^{(H)} = \left\langle P_2(\hat{\mathbf{e}}_{\alpha-CD} \cdot \hat{\mathbf{H}}) \right\rangle$ according to $\Delta\nu = -\frac{3}{2}q_{CD}S_{\alpha-CD}$, with $\hat{\mathbf{e}}_{\alpha-CD}$ denoting the orientation of the CD bond, $\hat{\mathbf{H}}$ the direction of the spectrometer magnetic field, the superscript (H) indicating that the order parameter is evaluated relative to that direction, q_{CD} the quadrupolar coupling constant (here set at the value of $168\,kHz$), P_2 the second Legendre polynomial and the angular brackets indicate ensemble time-averaging[26]. From the quadrupolar spectrum of the α-CD$_2$ group in the high temperature N phase (Figure 1b) at 106ºC, with a splitting of $\Delta\nu \square 48\,kHz$, we obtain the value -0.19 for $S_{\alpha-CD}^{(H)}$. The order parameter of the mesogenic core unit $S_{core}^{(H)} = \left\langle P_2(\hat{\mathbf{e}}_p \cdot \hat{\mathbf{H}}) \right\rangle$, with $\hat{\mathbf{e}}_p$ denoting the unit vector along the para-axis of the cyanobiphenylunit, is related to $S_{\alpha-CD}^{(H)}$ according to $S_{\alpha-CD}^{(H)} = S_{core}^{(H)} P_2(\hat{\mathbf{e}}_p \cdot \hat{\mathbf{e}}_{\alpha-CD})$. Assuming a fixed tetrahedral angle of the a-CD bonds relative to the para-axis of the cyanobiphenyl mesogenic core, we obtain for $S_{core}^{(H)}$ the value 0.57; this falls within the typical range for nematics. In the low temperature N$_X$ phase, $S_{core}^{(H)}$, obtained analogously from $\overline{\Delta\nu}$, shows only a slight further increase on cooling and appears to saturate at the value of 0.6. It is noted here that the order parameter $S_{core}^{(H)}$ quantifies the orientational ordering of the mesogenic cores relative to the magnetic field. In a locally uniaxial nematic phase, the direction of maximal orientational ordering defines the local director $\mathbf{n}$ and the respective

order parameter, here denoted by $S_{core}^{(n)}$, is related to the experimentally accessible $S_{core}^{(H)}$ according to $S_{core}^{(H)} = S_{core}^{(n)} P_2(\mathbf{n} \cdot \mathbf{H})$.

The crucial NMR experiment for testing the formation of the helicoidal conical structure in the bulk makes use of the high viscosity of the N_X phase. This allows collection of NMR spectra with the sample oriented perpendicular to the magnetic field. Specifically, when rotating the initially aligned sample to $90°$ with respect to the magnetic field, there is sufficient time to measure the NMR spectrum in this configuration before the magnetic field reorients the sample. Figure 2a shows the quadrupolar spectrum at $90\,°C$ before (red) and after (blue) a rotation of the sample by $90°$ with respect to the magnetic field. The spectrum of the flipped sample, when measured 10s after the flip (blue in Figure 2b), shows essentially identical splittings with the initial spectrum (red) but is still not fully relaxed back along the direction of $\mathbf{H}$ in this time interval. From the spectra in Figure 2a we observe that the $90°$ flipped sample (i) does not exhibit any line broadening, the line shape being the same as the initially aligned sample, in fact with some slight narrowing and (ii) the quadrupolar peaks are essentially at half the initial splitting. Moreover, the spinning sample patterns of Figure 2c are typical of a cylindrical distribution of the director about the axis of spinning.
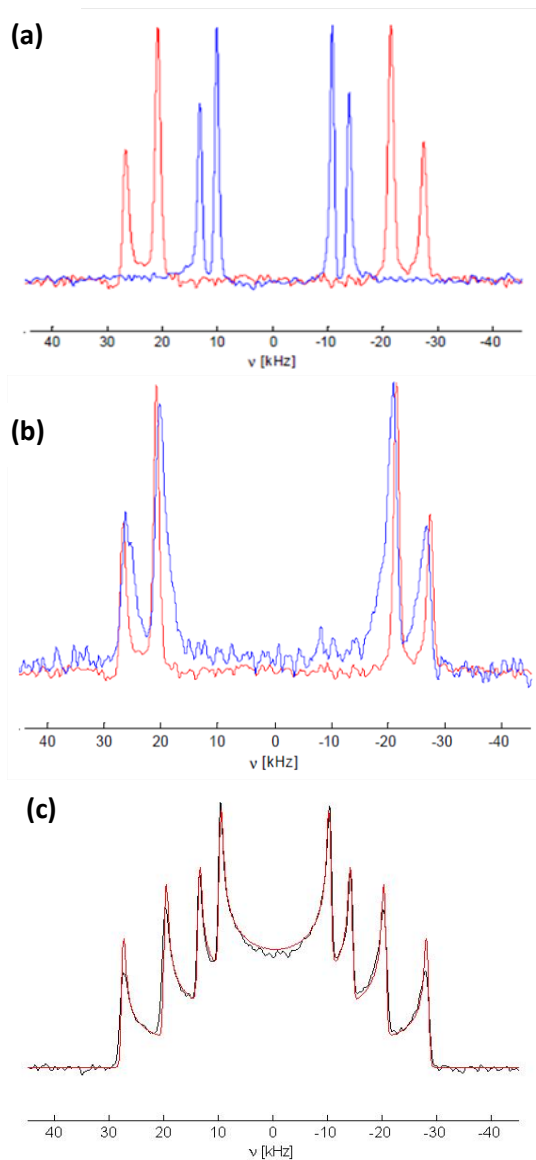
Figure 2. (a) ^{2}H NMR spectra of the aligned sample (red) and after a flip by $90°$ with respect to the magnetic field (Blue) in the N_X phase at $90\,°C$. (b) ^{2}H NMR spectrum 10s after the $90°$ flip (blue); the red line corresponds to the initial spectrum (in the N_X phase at $90\,°C$).(c) Spinning sample (100rpm) ^{2}H NMR spectrum in the N_X phase at $80\,°C$.

These results have immediate implications on the structures possible for the N_X phase. First, there is no indication of the heliconical structure. Secondly, the presence of such structure appears to be directly contradicted by the 90-flip and the spinning sample spectra:

The configuration of the nematic director for this hypothetical structure is given in Figure 3a for the magnetically aligned sample. With the helix axis aligning parallel to the external magnetic field, the director makes a fixed angle $\theta_{n,H} = \theta_0$ with the field. In such a distribution of the director, rotating the sample by $90°$ about an axis perpendicular to the magnetic field generates a distribution of angles, $\theta_{n,H}$, in the range $\pi/2 - \theta_0 < \theta_{n,H} < \pi/2 + \theta_0$, whose breadth increases with increasing θ_0. Accordingly, a direct indication of the presence of a heliconical configuration of the director would be a spectrum consisting of the superposition of peaks corresponding to the continuous distribution of the $\theta_{n,H}$ angle over the above range. No sign of such distribution is detected in the measured spectra of Figure 2a. Instead, a spectrum typical of the rotation of a uniformly distributed director, from parallel to perpendicular orientation relative to the magnetic field, is seen. The combined resolution of the experimental measurement and spectral fitting procedure for the detection of fluctuations of the $\theta_{n,H}$ angle is $5°$ (see ESI-3.1[23]). At this level of resolution, the $90°$-rotated and the spinning sample spectra clearly indicate that the twist-bend helical configuration of the director, either throughout the sample or in domains of opposite handedness, is not observed in the N_X phase.
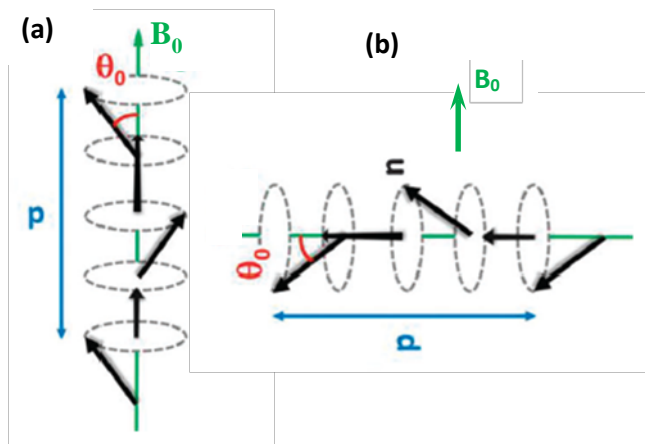
Figure 3. Schematic representation of the hypothetical (not supported by the present findings) heliconical configuration of the nematic director for (a) the magnetically aligned sample[16] and (b) the sample rotated by $90°$ relative to the magnetic field.

Could the twist-bend configuration of the director be present but escape detection by the present experiments? Two possibilities could be readily considered:

(i) A possible option would be if the hypothetical twist-bend has a very small value of the "tilt" angle θ_0, i.e. below the resolution threshold of $5°$. However, this would be well below the reported estimates for θ_0 from various experimental and theoretical considerations[8,9,12,16] which place it in the range $10° < \theta_0 < 38°$. Moreover, according to the twist-bend model[17], the free energy contributions of the twist and bend deformations are proportional to $k^2\theta_0^2$ and $k^2\theta_0^4$ respectively; therefore a marginal value of θ_0 would correspond to marginal twist (as well as bend) which is not in accord with the measured effects of chirality on the NMR spectra.

(ii) Assuming that the translational diffusion of entire dimer molecules along the hypothetical helix axis over distances of one pitch length are rapid on the NMR time scale

(in this case 10^{-4} s), the time-averaged molecular motions, by sampling different orientations of the heliconically distributed director, would produce an effectively uniaxial spectrum about the helix axis. The assumed rapid diffusion should extend only within domains of a given chirality and be slow across domains of opposite chirality in order to preserve the observed doubling of the splittings. To our knowledge there is no quantitative evidence to directly prove or disprove such assumptions. Furthermore, it is not clear how the assumed combination of rapid/slow diffusion would come about in a positionally disordered phase and how it would be in accord with the observed dramatic increase of the rotational viscosity in the N_X phase. However, if such assumption is proven valid it would simply mean that the NMR techniques used here and in refs[8,9,16], are "blind" to the possible presence of a heliconical twist-bend structure of the director in the N_X phase.

Aside from the absence of any indication of a twist-bend structure, the following can be inferred from the spectra in figures 1 and 2:

a. The chiral domains in the N_X sample exhibit molecular orientational ordering along a unique direction (the local director of the domain) which aligns parallel to the magnetic field, as shown schematically in Figure 4, middle.

b. Rotating the N_X sample about the magnetic field preserves the collective mutual alignment of the domains sufficiently long (~ 10 s) on the NMR time scale (~10^{-4} s) before relaxing back along the magnetic field (Figure 4, right).

c. The complete separation of each peak into two sub-peaks (i.e. with marginal intensity between the two sub-peaks), exhibited by the measured spectra toward the low temperature end of the N_X phase (see Figure 1b), indicates that the sample consists

entirely of chiral domains, with practically no achiral regions which could be detected within the experimental resolution of the measurements. This would imply that the "volume over surface-area" of the domains is large, rendering the number of molecules in the domain interface negligible in comparison with the molecules in the domain interior.

d. At higher temperatures in the N_X phase, the sub-peaks are overlapping and it cannot be excluded that part of the intensity might correspond to a substantial achiral contribution whose extent, however, cannot be directly estimated from the spectra.

As the NMR technique used is not sensitive to the distribution of molecular positions and the data presented here are from just the dueteriated termini of the dimer spacer, no firm inferences can be drawn on the detailed molecular organization within the chiral domains of the N_X phase. An extensive consideration of the possible structures is undertaken in a forthcoming communication[27] based on a wide set of available observations. On the other hand, combining the present results with existing knowledge of the conformational statistics of the CB-C9-CB dimers[26,28,29] and their packing in the solid phase[30], a general picture could be proposed where the dimer molecules within these domains assume predominantly twisted, chiral, conformations[26] and the enantio-selective local molecular packing confers to the domain its chirality. This picture is in accord with a periodicity of 9 nm of the twist found in crystalline samples[30] and in similar systems, where TEM data indicate periodicities of 8 nm[12], as well as with structures identified in recent AFM and FFTEM observations[22] in thin films. It is also consistent with the dramatic increase of the viscosity on going from the N to the N_X phase, as the reorientation processes in the latter

would involve the rotation of domains of strongly correlated molecules. Lastly, it readily accounts for the experimental observation that the ordering of the mesogenic units along the magnetic field remains relatively low (0.5 to 0.6) throughout the N_X range. Specifically, the mesogenic units of the dimers, due to the statistical dominance of nonlinear conformations, cannot attain a simultaneous alignment along any given direction ("orientational frustration", see Figure 4, left). Accordingly, though a direction of maximal alignment (i.e. the local director) can be uniquely defined, within each domain, and for the entire aligned sample, the respective value of the order parameter is low. This is also the case for the crystal phase of the CB-C9-CB dimers where[30] the molecules are packed in twisted conformations and the order parameter of the mesogenic units is significantly lower than 1.
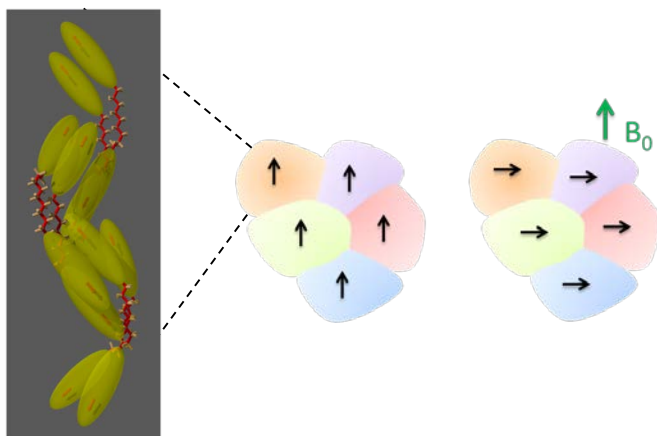

Figure 4. Proposed chiral domain structure of the Nx phase. The inset (left) shows a possible disposition of the mesogenic units within each domain, stressing the lack of full alignment of all the units parallel to a unique direction. The internal orientational order of each domain is represented by a domain director. The magnetic field aligns the domain directors (middle). On rotating the sample (right), the mutual alignment of the domain directors persists sufficiently long on the NMR measurement time-scale.

To summarise, in agreement with the findings of a number of previous studies, the results presented here confirm the chirality of the N_X phase but they call into question the attribution of this chirality to the heliconical distribution of the nematic director according to the twist-bend model. A structural picture is proposed for the consistent interpretation of these results based on the packing of the chiral molecular conformations of the dimers. This picture does not preclude the possibility that, in the absence of the aligning magnetic field, the chiral domains could produce, via soft self-assembly, helical structures on a larger length scale under particular surface anchoring.

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