

Nematic biaxiality in a bent-core material

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The results of a recent investigation of the nematic biaxiality in a bent-core mesogen (A131) are in apparent disagreement with earlier claims. Samples of mesogen *A131* used in the two studies were investigated with polarized optical microscopy, conoscopy, carbon-13 NMR, and crossover frequency measurements. The results demonstrate that textural changes associated with the growth of biaxial nematic order appear at ~ 149 °C. The Maltese cross observed in the conoscopic figure gradually splits into two isogyres at lower temperatures indicating phase biaxiality. Presence of the uniaxial to biaxial nematic phase transition is further confirmed by temperature trends of local order parameters based on ¹³C chemical shifts in NMR experiments. Frequency switching measurements also clearly reveal a transition at 149 °C. Differences between the two reports appear to be related to the presence of solvent, impurities, and/or adsorbed gases in samples of A131 used in the study of Van Le *et al.* [Phys. Rev. E **79**, 030701 (2009)].

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I. INTRODUCTION

Ever since the theoretical prediction of the biaxial nematic (N_b) phase by Freiser [1] in 1970, a number of groups around the world have pursued experiments to demonstrate the existence of this elusive phase. In 2003, based on x-ray diffraction and NMR measurements, clear evidence of the existence of the N_b phase in thermotropic rigid bent-core mesogens was presented by Kumar *et al.* [2] and Samulski *et al.* [3]. Since then a number of compounds [4–8] have been reported to form the N_b phase. Infrared [4] and Raman spectra in the polarization mode have been used [9] to obtain uniaxial (P2 and P4) as well as biaxial (P220, P420, and P440) order parameters. Dynamic light scattering [10], electro-optical [11], and electroconvection [12] investigations of oxadiazole-based bent-core compounds [2,3] not only confirmed the biaxial phase but also revealed the uniaxial (N_u) to N_b transition previously not detected by optical [3] and calorimetric [13] methods.

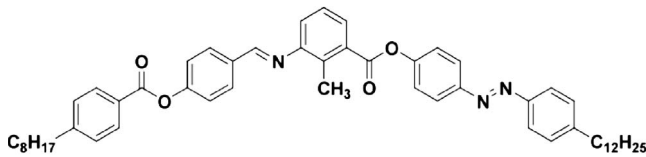
Following the reports [2–8] of the thermotropic N_b phase, the experimental and theoretical research activities have rapidly grown. However, given the fact that a number of claims of its discovery prior to 2003 [14] were eventually shown to be incorrect [15], there exists healthy skepticism in scientific community. An example of such skepticism is a recent paper by Van Le *et al.* [16]. They resynthesized and conducted conoscopy and electro-optical experiments on bent-core mesogen, *A131* shown in Fig. 1, previously reported [5,6,17] to exhibit the N_u , N_b , and Smectic-C (SmC) phases.

The inferences drawn in [16] are (a) *A131* has only one nematic phase, i.e., no transition at ~ 149 °C, (b) an anchoring transition occurs at ~ 138 °C, and (c) there is no evi-

dence of biaxiality from ~ 149 to 118.5 °C. These conclusions are in contrast to quantitative x-ray [5] and NMR [6] evidences that have previously established the presence of the N_u - N_b phase transition in *A131*. We have repeated measurements with the same experimental techniques as employed in [16] on the samples used in [5,6] as well as in [16] that were synthesized in two different laboratories. In this report (A) we show that all inferences in [16] are not supported by their own results; in fact, the results therein lead one to conclusions that are contrary to theirs; (B) we present results of comparative experimental investigations of two samples, the sample (*sample A*) previously used by us in [5,6,17], and the sample (*sample B*) used in [16]. The presence of the N_u - N_b phase transition is observed in both samples. The results of these experiments also provide a possible explanation for the discrepancy.

II. FREQUENCY MEASUREMENTS

One of the strongest evidence that the inferences in [16] are not on sound footing comes from measurements of the crossover frequency (f_c) at which the dielectric anisotropy changes sign. The data in Fig. 1(b) of [16] are from $1/T \sim 2.37 \times 10^{-3}$ to 2.54×10^{-3} K⁻¹ corresponding to approximately 149 and 121 °C, respectively. This is essentially the temperature range of the N_b phase reported in [5]. The *inexplicable* absence of data between 149 and 176.5 °C in the paper which claims that the N_u phase spans the entire nematic range (i.e., from 118.5 to 176.5 °C), leaves one wondering about the reason behind this omission. It led us to measure f_c over the entire nematic temperature range on, both, *sample A* and *sample B* in a manner similar to that used in



Isotropic (I) – [176.5 °C] – N_u – [149.0 °C] – N_b – [118.5 °C] – SmC

FIG. 1. Molecular structure and phase sequence of A131.

[16]. For these measurements, *sample B* was degassed as discussed later in this report.

We used an indium-tin-oxide-coated glass cell of 3.4 μm gap. Substrate surfaces were coated with polymer RN1286 and rubbed to create homogeneous anchoring condition for the N_u phase. Square wave electric field of 1.5 V/ μm was used over a frequency range 1 kHz to 3 MHz. Measured values of f_c as a function of temperature are shown in Fig. 2.

The results clearly show that the data do not fit a single linear fit as would be the case if the same nematic phase existed over the entire temperature range. The activation energy E_c , given by the slope in Fig. 2, changes by a factor of 2.3 at the N_u to N_b transition at approx. 150 °C. Also, it is *important to note* that neither our data nor the data in [16] show any indication of the purported anchoring transition at 138 °C.

III. SAMPLE PURITY AND OPTICAL TEXTURAL CHANGES

We prepared optical cells using a polyimide (*S659*) from Samsung Electronics Co. (SEC) as homeotropic alignment layer. One of the cells was filled with *sample A* and the second cell with fresh (not degassed) *sample B*. We were able to reproduce the results of [5] on *sample A*. Optical textures of *sample B*, Fig. 3, were observed with low levels (and only when needed) of illumination. These textures exhibited interesting time and temperature dependence. During the first cooling cycle, a faint (not a perfect homeotropic) texture was observed below the clearing point. Texture did not change significantly until after the temperature dropped

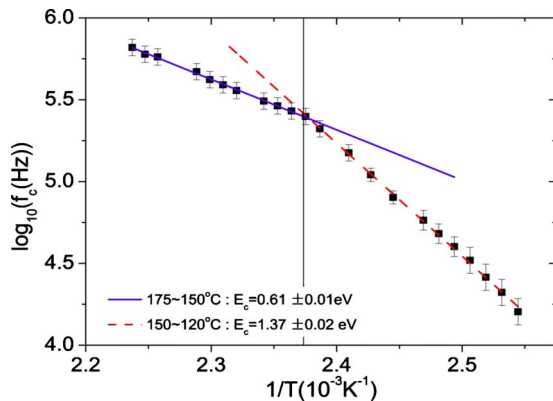


FIG. 2. (Color online) Temperature dependence of crossover frequency f_c for *sample B*. The straight lines represent linear fits in the two regions with slopes differing by a factor of greater than 2.

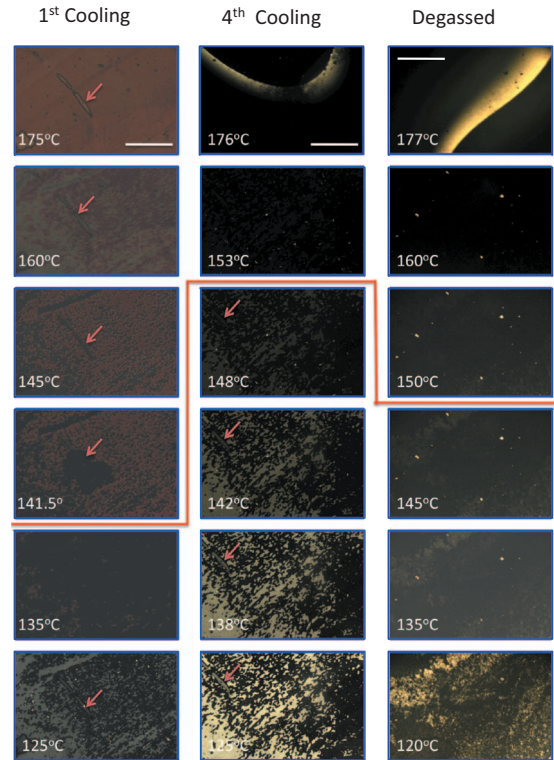


FIG. 3. (Color) Optical textures of *sample B*, used in Ref. [16], during (left) the first cooling, (middle) the fourth cooling cycle, and (right) after degassing the sample. Arrows point to the same physical location marked by an oblique streak. Gradual textural changes at the N_u to N_b transition occur between 141.5 and 135 °C during first cooling, between 153 and 148 °C for the fourth cooling, and between 150 and 145 °C for the degassed sample. The red line marks the boundary between the two nematic phases. Scale bars in top panels represent 500 μm .

below 140 °C, where it first became darker and then gradually brighter. Apparently, this change was attributed in [16] to an anchoring transition. However, repeated thermal cycling of the sample raised the temperature at which this change was observed. On fourth cooling, the texture became homeotropic in the N_u phase below the clearing point (T_{NI}) and changed to schlieren in the proximity of 150 °C, gradually becoming brighter in a manner similar to that of *sample A* in [5]. T_{NI} was found to rise by $\sim 1^\circ$ between the first and fourth cooling cycles clearly showing loss of solvent and/or adsorbed gases at elevated temperatures. To verify this, we degassed *sample B* in a vacuum oven at 190 °C for 2 h. The textural changes in the degassed sample occurred at ~ 150 °C and were very similar to those of *sample A* and during fourth cooling of fresh *sample B*. T_{NI} was found to be 2° higher than in the first cycle, further suggesting the presence of volatile impurities in otherwise pure *sample B*. Thin layer chromatography of a fresh *sample B* revealed the presence of three components, two of which were in very small quantities. However, the degassed sample had only one component. These results ruled out any sample decomposition during degassing and confirmed the presence of volatile impurities in fresh *sample B*. This inference was supported by thermogravimetric analysis of fresh *sample B* which revealed

a weight loss of $\sim 0.4 \pm 0.1$ wt % at the same temperature as used in degassing.

It is critical to have the sample free from impurities, solvents, or adsorbed gases because their presence depresses [18] a second-order transition more strongly than a first-order transition. The “anchoring” transition reported in [16] at 138 °C was likely the (second-order) N_u - N_b transition, albeit significantly suppressed. This transition may have been further depressed [19] due to conformational changes in this photosensitive molecule under moderate illumination. The second-order (or, continuous) nature of the N_u - N_b transition makes it difficult to pinpoint the exact transition temperature from textural changes. Furthermore, the surface memory effect [20,21] causes the (faint) texture to persist above the transition temperature, masking the actual transition.

IV. IS THERE AN ANCHORING TRANSITION?

The polyimide, SE-5300, which provides homeotropic boundary condition for calamitic nematic fluids, was used in [16]. However, a highly birefringent schlieren texture was obtained for the bent-core mesogen *A131* from ~ 176.5 to 120 °C. Evidently, the anchoring of this bent-core mesogen is not homeotropic and SE-5300 appears to provide tilted anchoring for *A131*, as previously found [7] for another bent-core system. The transmitted intensity was found [16] to change abruptly near 138 °C, which was attributed to an anchoring transition. It is surprising and difficult to comprehend how an abrupt anchoring transition can occur with *their* anchoring conditions. The authors of Ref. [16], however, have failed to specify the initial and final anchoring conditions. Our observations discussed above lead us to believe that it is the N_u to N_b transition that appeared at a much lower temperature.

It is further claimed in [16] that “an anchoring transition may appear to be an N_u - N_b phase transition.” It should be pointed out that the homeotropic to planar anchoring transition has been observed in a number of systems [22], and it has never been mistaken for or attributed to biaxiality. It is very difficult, if not impossible, to mistake an anchoring transition for the N_u - N_b transition.

The schematic illustration [Figs. 4(b) and 4(c) in [16]] of the molecular anchoring at the surface leading to pretilt is a very naïve description. There exists no credible model for any nematic liquid crystal that attempts to explain anchoring at a detailed molecular level such as claimed here. It is difficult to imagine, as stated in Ref. [16], that “the alignment layers align only one of the arms of bent-core molecules in the vicinity of substrate surfaces, and thus a schlieren texture results due to the free orientation of the other arm.” As both arms of the molecule have long aliphatic chains at the ends, how can one arm preferentially anchor normal to the surface leading to adjacent domains with different orientation, which then propagates deep into the bulk to give rise to the four brush schlieren texture? A perfect registration of the other arm in each domain in the bulk is very difficult to imagine in a realistic situation.

V. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

No signatures of the N_u to N_b transition were detected in DSC scans as reported in [5] and confirmed in [16]. It is

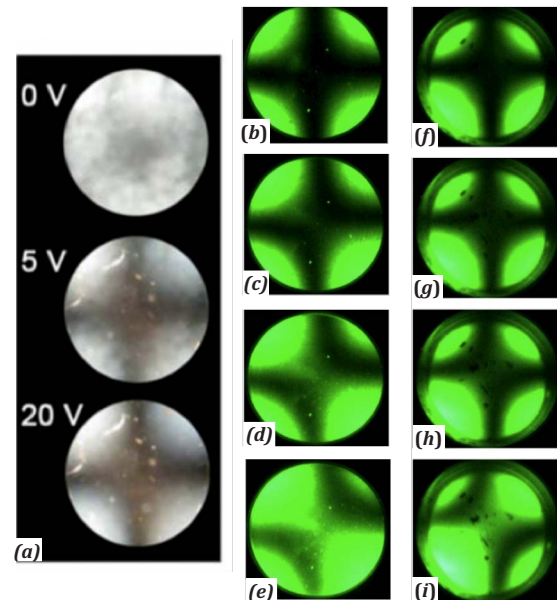


FIG. 4. (Color online) Conoscopic patterns of *A131* (a) reproduced from Ref. [16] were taken with sample under a high frequency (10 kHz) and high-strength (4×10^6 V/m) electric field. In the middle column are conoscopic patterns of *sample A* with no applied field and using green filter in (b) the N_u phase at 155 °C and in the N_b phase at (c) 138, (d) 128, and (e) 120 °C. Right column shows conoscopic patterns of *sample A* aligned with polyimide *S659* under a 1 kHz square wave, 2.3×10^6 V/m electric field (f) 150, (g) 145, (h) 130, and (i) 120 °C.

common knowledge that DSC is not an optimum technique to detect and/or study second-order transitions. The absence of latent heat at such transitions makes them difficult to detect by DSC. The N_u - N_b transition of C7 and C12 homologs of mesogens based on oxadiazole core also remained initially undetected [13] by DSC. It was eventually observed several years later by careful DSC and optical [10], and Raman [12] techniques. The situation is not unique to bent-core mesogens. Cordoyiannis, *et al.* [23], recently used high-resolution adiabatic calorimetry but did not find a signature of the N_u - N_b transition in an organosiloxane tetrapod system in which the N_u to N_b transition has been unequivocally established with Deuterium NMR [24], dynamic light scattering [10], and conoscopy and IR absorption spectroscopy [4].

VI. CONOSCOPY

Reference [16] also reports the results of a conoscopic study while the sample is subjected to a strong (20 V across 5 μ m, or 4×10^6 V/m) high-frequency electric field. The authors conclude that *A131* does not possess a biaxial phase based on the assertion that they observe a “Maltese cross” over the entire nematic range (176.5–120 °C) as a homeotropic sample would exhibit. However, a Maltese cross observed in a uniaxial phase with optic axis parallel to the microscope axis must always have a dark center due to perfect extinction condition. Their results, shown here in Fig. 4(a) on an expanded scale, have a relatively bright center. This is quite puzzling. One possible explanation appears to

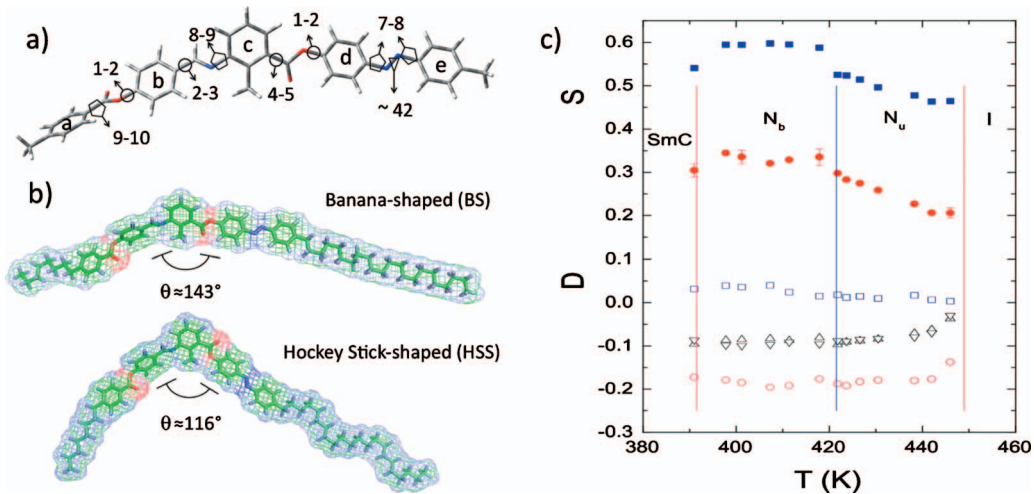


FIG. 5. (Color) (a) Molecular structure of the five-rings model “abcde” of A131 and the most relevant torsional barriers with range values (kcal/mol) found in the conformational analyses of the three-rings models (“abc,” “bcd,” “cde”) [26]. Circles and pentagons refer to low (<5 kcal/mol) and high (>5 kcal/mol) rotational barriers, respectively, while the down triangle refers to —N=N— *cis-trans* interconversion barrier. (b) Two prevalent conformations available to A131 as predicted by DFT from the five-rings model. (c) Plot of typical local S (solid symbols) and molecular biaxial D (open symbols) order parameters versus the temperature. Squares, and circles are for rings “d” and “b,” respectively; up and down triangles are for rings “c” and “e,” respectively.

be that increasing applied field is forcing the primary nematic director \mathbf{n} to become homeotropic while the secondary director \mathbf{m} of the biaxial nematic phase is randomly aligned (in small domains) permitting some leakage of light to make the center of the pattern bright. It clearly establishes that this phase is not uniaxial. The authors of [16] attributed the red tint in the middle of these conoscopic patterns [Fig. 4(a)] to red focusing LED of the camera. Clearly, intense white light was used for conoscopic measurements [16], which is known to suppress the ratio of *trans* to *cis* isomers and lower the measured transitions [19] by as much as 4 °C.

We performed conoscopy using high quality green filter (Andover Co., 550FS40–50, with 1% bandwidth of ~ 87 nm) and polyimide S659 from SEC to help obtain homeotropic orientation in the N_u phase. Green light ($\lambda \sim 550$ nm) offers a number of advantages: (i) the effective retardation ($\sim 1/\lambda$) is nearly double over, say, red light rendering the results more definitive, (ii) green filter eliminates all other wavelength thereby reducing possible sample decomposition, and (iii) the wavelengths transmitted by the green filter overlap with the absorption band at 440 nm responsible for *cis* to *trans* isomerization. In one case, the darkest (or, homeotropically well-aligned) area of the cell was selected for measurements. This area exhibited the Maltese cross with a *dark center* in the N_u phase, Fig. 4(b), at 155 °C. One begins to see a slight splitting of the cross into two hyperbolic isogyres at 148 °C. The separation between them increases, Figs. 4(c)–4(e), at lower temperatures. These superior quality conoscopic images clearly demonstrate the growth of the biaxial order, in excellent agreement with x-ray [5] and NMR [6] results.

In the second case, conoscopic measurements were performed on an area that was not homeotropically aligned. An electric field [1 kHz square wave of 15 V across 6.3- μm -thick cell (or 2.3×10^6 V/m)] was used to ensure homeotropic alignment of director \mathbf{n} . The Maltese’s cross

with dark center was obtained in the N_u phase at 150 °C [Fig. 4(f)]. Splitting of the Maltese cross into a pair of arcs gradually becomes discernible at the N_u - N_b transition below 150 °C. The splitting continues to increase as the temperature is lowered into the N_b phase [Figs. 4(g)–4(i)]. These results show that the phase below ~ 149 °C is the N_b phase. It should be pointed out that very similar conoscopic results were obtained on (degassed) *sample B* of Van Le *et al.* Again, the biaxial nature of the nematic phase is evident below ~ 150 °C for both samples.

VII. MOLECULAR CONFORMATION

^{13}C NMR experiments [6] were carried out at 100.6 MHz using a standard cross-polarization pulse sequence and the ^{13}C signals acquired using a proton-decoupling field of 29 kHz. Details of two-dimensional (2D) “SUPER” experiment have appeared elsewhere [25]. The measured ^{13}C chemical shifts [6] show, Fig. 5, a plateau region with its onset at 149 °C coinciding with the onset of the N_b phase as observed in optical and x-ray measurements [5]. The NMR data have revealed that the ring (“d”) located next to the central ring on the side with the longer arm is most orientationally ordered, while the two rings (“a” and “b”) placed in the shorter arm of the bent core have more orientational freedom, thereby participating in modifying the shape of the bent core. At least two dominant conformers were found by searching the potential energy surface (PES) of the five rings (“abcde”) model [Fig. 5(a)] based on density functional theory (DFT) calculations at B3LYP/6–31G(d) level of theory [26].

The conformers found in the PES of the five-rings model of A131 have been indirectly verified by the good agreement between the experimental (2D SUPER) and calculated (gauge-invariant atomic orbital DFT) chemical shift tensor components and their isotropic shifts [27]. Our newly de-

rived local nematic order S (P_2) and molecular biaxial order parameters D are found to be consistent with the theoretical torsional barriers [shown in Fig. 5(a)] found in the $A131$ mesogen, which give an indication of the degree of rotational freedom of one ring with respect to the closest ones. Some typical local S and D order parameters are plotted versus the temperature in Fig. 5(c). Among the five rings, ring “d” has the highest S but lowest $|D|$ while ring “b” has the lowest S and the largest $|D|$ parameter. Moreover, the plateau seen in the ^{13}C chemical shifts also appears for most rings in the D (and S) values except ring “a” whose D has small (and much scattered) values (not shown). In particular, the S of rings “b” and “d,” which reflect the least and the most ordered parts of the $A131$ aromatic core, respectively, seem to show discontinuous jumps at the N_u - N_b transition (149 °C). Note also in Fig. 5(c), ring “d” has vanishingly small D values at temperature above 149 °C but has positive D values below this temperature in contrast to those of other rings. Hence the aromatic bent core must have notably changed its average configuration below 149 °C. In fact, all the conformers obtained from the PES are found to belong to two distinct structural groups as shown in Fig. 5(b), which is either a banana-shaped (with a bend angle $\theta \sim 143^\circ$), or a hockey-stick-shaped ($\theta \sim 116^\circ$) conformation, depending on the relative orientation of the ring “d” with respect to the central ring “c,” through the connecting carboxylic (COO) group. The average bend angle below 150 °C was estimated [27] to be close to 120° based on the NMR data. Van Le *et al.* used MOPAC/AM1 quantum chemical calculations to optimize $A131$'s molecular structure and obtained a bend angle of 134° . However, this corresponds to the bend angle of neither of the conformers. Any inferences based on single-conformer nature of the AM1 approach at a semiempirical level are inaccurate and should be discarded.

VIII. ELECTRO-OPTICAL EFFECTS AND ELECTRO-CONVECTION

The authors of Ref. [16] claimed that for materials having positive dielectric anisotropy, nematic biaxiality can be tested by measuring the transmitted light intensity as a function of electric field. This technique has been applied to a material in which the dielectric anisotropy changes sign at a temperature dependent f_c and where molecular conformation changes with temperature from *banana* core to *hockey stick* (see Sec. VI above). The $A131$ molecule has several chemical groups with nonzero dipole moment that further complicate the interpretation of their observation. Interpretation of results is further complicated by the observed electroconvection dependent on the waveform, frequency, and field strength. Clearly, the electro-optical technique solicits a very complex sample response which must not be grossly oversimplified. There are several other issues that should be noted:

(A) It is stated on page 1 of [16] that “if the material is biaxial, the schlieren texture should not disappear (transmitted intensity is not zero) even at very high fields, since the field does not affect the distribution of the second director \mathbf{m} normal to the main director \mathbf{n} .” This statement is, in fact,

validated by their results. From the results in the N_u phase at 170 °C, Fig. 3(c) of [16], it is evident upon extrapolation that the transmittance (T) reaches zero at $1/V^2 \sim 0.002$, or $V \sim 22.5$ V. When the same measurement is repeated at 130 °C (in the N_b phase) in the same sample and at the same site in *the same cell*, extrapolation of the linear fit in Fig. 3(d) clearly shows that even for $1/V^2 \rightarrow 0$ (or $V \rightarrow \infty$), T remains finite! Their estimation of δn from the intercept of T vs $1/V^2$ is based on the faulty assumption that the transmission will continue to decrease linearly even in the biaxial phase. In fact, it should reach a minimum and then stop changing. Indeed, their data stop at a value of $T=0.01$. In fact, the last three data points show no change. If we take this to be the minimum transmission achievable at 130 °C, then the value of δn will be five times larger even in their less than ideal sample. It seems somewhat disingenuous to invoke [16] “very tiny defects or dust” as being responsible for nonzero value of T in the N_b phase. If tiny defects or dust are present at 130 °C, they will not disappear at 170 °C. In fact, rapidly decreasing effective elastic constant at higher temperature should make this effect more prominent in the N_u phase. These results of theirs clearly establish the phase biaxiality at 130 °C albeit under complex electric-field conditions, which likely reduced the effective biaxiality.

A number of other factors related to sample impurity and experimental artifacts may also have influenced their results, as discussed below:

(i) It is known that in materials with positive dielectric anisotropy and a nonzero component of electric dipole along molecular long axis, an additional relaxation process occurs at low frequencies. This has been interpreted in terms of spatially uncorrelated large rotations of the molecule around its short axis [28], which can lead to a drastic reduction in measurable bulk biaxiality. Hence, this technique is prone to yielding false results.

(ii) Another factor to be concerned about is the dielectric heating induced in samples when driven at high fields and high frequencies. An increase in temperature of ~ 10 °C can be estimated from the data reported by Wen and Wu [29].

(B) Historically, the initial experiments claiming biaxiality in thermotropic nematics employed optical techniques [14]. Those claims of biaxiality based on optical observations were not accepted since biaxiality can arise due to surface effects. Hence, to conclusively demonstrate the existence of biaxiality, it was necessary to go to techniques that probe bulk samples, e.g., x-ray [2,5,9] and NMR methods [3]. Surface anchoring and the electro-optic technique employed by authors of Ref. [16] are prone to detecting surface-induced biaxiality or destruction of the bulk biaxiality due to multiple effects discussed above, which must not be ignored.

(C) The electro-optic technique used in [16] was originally used [11] and published in 2007 to prove that the nematic phase of two oxadizole-based bent-core liquid crystals [2,3] has two (uniaxial and biaxial) nematic regions. They relied on the nonextinction of transmitted light and attempted to confirm the biaxiality of the lower temperature nematic phase. It should also be noted that the phenomena of dielectric sign inversion in bent-core mesogens was previously reported by other researchers [30,31].

IX. SUMMARY

In conclusion, we have shown that the existence of two nematic phases in A131 is based on very clear changes, at ~ 149 °C, in: (i) the temperature dependence of dielectric anisotropy crossover frequency, (ii) the length scale and positional order correlations measured by x-ray diffraction [5], (iii) the temperature trends of ^{13}C chemical shifts, from a continuous increase (N_a) to a plateau region (N_b), marked by small jumps for some ^{13}C resonances [6], (iv) the local uniaxial (S) and biaxial (D) order parameters for different aromatic cores as determined by NMR measurements, (v) molecular conformation from *banana core to hockey stick* found by means of a combined DFT and solid-state NMR computational approach, (vi) optical textures of samples used in our previous study [5] and in [16], and (vii) the splitting of the Maltese cross into two hyperbolic isogyres which increases with decreasing temperature in the N_b phase. In addition, recently measured values of the uniaxial and biaxial order parameters by micro-Raman measurements [17] clearly establish the existence of the N_b phase in this

system. As discussed above, results of transmitted intensity measurements by Van Le *et al.* in [16] also support the presence of a biaxial nematic phase. The results presented here on *sample B*, reveal sample contamination as one of the possible causes of the erroneous conclusions drawn in [16].

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