Twist-bend heliconical chiral nematic liquid crystal phase of an achiral rigid bent-core mesogen

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The chiral, heliconical (twist-bend) nematic ground state is reported in an achiral, rigid, bent-core mesogen (UD68). Similar to the nematic twist-bend (N_{TB}) phase observed in bent molecular dimers, the N_{TB} phase of UD68 forms macroscopic, smecticlike focal-conic textures and exhibits nanoscale, periodic modulation with no associated modulation of the electron density, i.e., without a detectable lamellar x-ray reflection peak. The N_{TB} helical pitch is $p_{TB} \sim 14$ nm. When an electric field is applied normal to the helix axis, a weak electroclinic effect is observed, revealing 50-μm-scale left- and right-handed domains in a chiral conglomerate.

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I. INTRODUCTION

In the entire history of liquid crystals, only four distinct nematic ground states have been found: the uniaxial, the biaxial, and, for chiral molecules, the helical nematic and blue phases. Recently, the twist-bend (TB) nematic (N_{TB}) phase, a unique type of nematic ground state of achiral molecules, exhibiting layer-free, helical liquid crystal ordering of nanoscale pitch, has been structurally identified and characterized [1,2]. The twist-bend nematic phase was initially suggested as a theoretical possibility by Meyer over 40 years ago [3] and discussed in 2000 by Dozov [4] and Memmer [5], who suggested that the tendency for local bend curvature in the director field of bent-core molecules [for example, see Fig. 1(a)] could stabilize a twisted and bent director distribution with the molecules precessing on a cone [Fig. 1(c)]. Observations of an unusual phase of bent molecular dimers, such as CB7CB [Fig. 1(b)], in which a pair of rigid monomers are linked together by means of a flexible odd-carbon number aliphatic spacer [6,7] having nematic characteristics, spontaneous chirality [8,9], and smectic textural features [10–12] but no smecticlike lamellar x-ray diffraction peaks [13], have been interpreted in terms of the N_{TB} structure [4]. The N_{TB} phase is, in general, polar and structurally chiral despite being formed from achiral molecules. The helix periodicity has recently been directly observed in CB7CB and other dimers using freeze-fracture transmission electron microscopy (FFTEM) [1,2] which revealed that the TB helix of CB7CB, for example, has an amazingly short pitch ($p_{TB} \sim 8$ nm), making it the liquid crystal coherent ordering that is closest in scale to the molecular size (about 3 nm in the CB7CB case). This structure also agrees with the predictions of atomistic computer simulation [1].

The Dozov theory [4] and Memmer simulations [5] suggest that the twist-bend nematic could also be found in rigid bent-core systems. Unusual filament textures and evidence for chiral conglomerate domains have been found by Gortz *et al.*, in rigid bent-core bis-(phenyl)oxadiazole derivatives, which the authors discuss in terms of the twist-bend, bend grain boundary, and twist grain boundary phases [14]. Also, low values of bend elastic constant in the nematic phase, characteristic of the bent molecular dimers and predicted by Dozov in the vicinity of the twist-bend nematic, have also been found in a rigid-bent-core system [15,16]. Here we report the observation of a twist-bend nematic phase in the rigid-bent-core liquid crystal UD68 [Fig. 1(a)], an extraordinary addition to the family of liquid crystals showing the N_{TB} phase, and just the sort of system treated theoretically by Dozov [4] and in simulation by Memmer [5]. We provide direct evidence of the chiral, periodic, heliconical structure of UD68, using freeze-fracture transmission electron microscopy (FFTEM), x-ray diffraction (XRD), depolarized transmission light microscopy (DTLM), and electro-optical measurements. UD68 was synthesized by Schröder *et al.* [17], who proposed in the bent-core series in Fig. 1(a) for $n < 7$ an unusual nematic-to-nematic phase transition, with the molecules in the lower-temperature phase stacked in the bend direction, forming bundles of nondefined length as the precursor of the columnar phase. We show that the structural characteristics of this low-temperature nematic phase are nearly identical to those found in the N_{TB} phases of the bent molecular dimers, opening up the vast array of rigid bent mesogens to exploration for twist-bend phases.

II. EXPERIMENTS AND RESULTS

The chemical structure and phase sequence of UD68 (compound 6 in [17]) are shown in Fig. 1(a). When UD68 is filled in a nylon-coated cell weakly rubbed for planar alignment, the nematic phase comes in from the isotropic liquid on cooling with a typical Schlieren texture with $s = 1$ and $s = 1/2$ defects, and visible fluctuations of the director field [Fig. 2(a)]. On further cooling, the director fluctuations disappear and the twist-bend nematic phase grows in, forming typical focal-conic domains with dark brushes parallel to the

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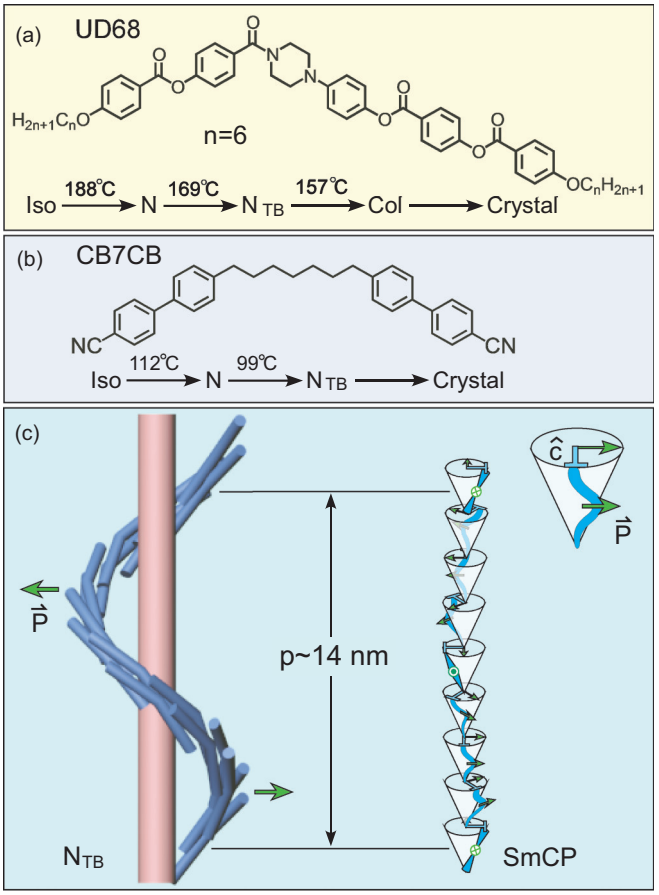

FIG. 1. (Color online) Chemical structures and phase sequences of the bent-core molecule UD68 (a) and the bent molecular dimer CB7CB (b). (c) Molecular organization of the N_{TB} and Sm*CP* phases of bent-core molecules. Both the N_{TB} and Sm*CP* phases are chiral and polar with the molecules forming a heliconical structure. In the N_{TB} phase, the molecules are intercalated, while in the Sm*CP* phase the bent-core molecules form well-defined smectic layers, the combination of macroscopic polarization and molecular tilt making the layers chiral.

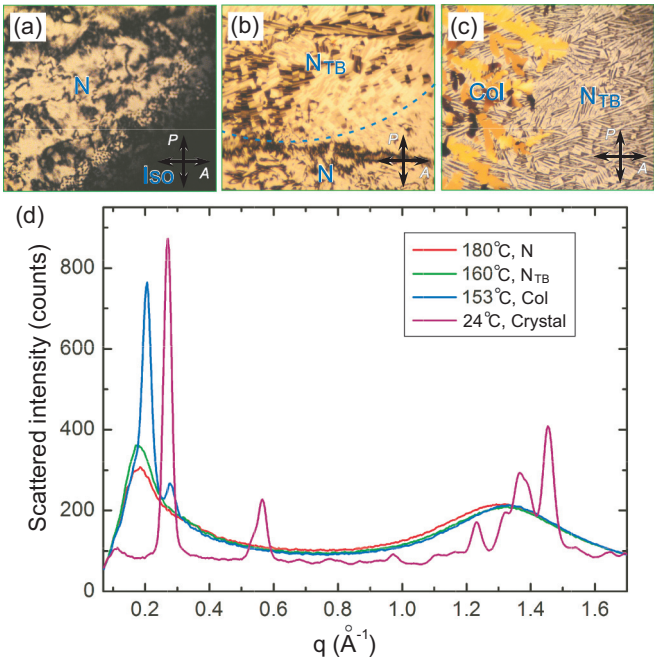

FIG. 2. (Color online) DTLM textures in a weakly rubbed cell and XRD of the mesophases of UD68. (a) Nematic phase (top left) with characteristic Schlieren texture indicating nematic with random planar alignment grows in from the isotropic phase (bottom right), which is dark under crossed polarizers ($T = 186$ °C). (b) In the N_{TB} mesophase ($T = 167$ °C), focal-conic domains (top half) form from the nematic phase (bottom half), with the dark brushes parallel to the polarizers. (c) At lower temperature ($T = 155$ °C), yellow dendritic aggregates of the Col phase (left) grow into the N_{TB} texture (right). Images (a)–(c) were obtained in a 2-μm nylon-coated planar cell with weak rubbing. (d) XRD of the N, N_{TB}, Col, and Cry phases. The measurements were taken on cooling from the nematic phase at 180 °C, except for the measurement at 24 °C, which was taken after the samples were kept at room temperature for 5 days.

polarizers [Fig. 2(b), top]. The initially smooth, fanlike texture subsequently breaks into a cross-hatched texture [Fig. 2(c), right]. At even lower temperature, dendritic aggregates typical of the columnar phase grow in [Fig. 2(c), left]. In homeotropic cells, the N_{TB} phase is essentially dark under crossed polarizers, suggesting that the phase is uniaxial. The nematic phase shows no x-ray layer reflection peak, but only diffuse wide and small angle scattering with maxima at $q = 1.32$ and 0.18 Å^{-1} resulting from the lateral distances and those along the molecular long axes, respectively, of positionally short-range ordered molecules [Fig. 2(d)]. When cooled to the N_{TB} phase, the x-ray diffraction pattern is essentially the same as that in the nematic phase, with no layer reflection peak. Although the N_{TB} phase shows focal-conic textures characteristic of soft systems with one-dimensional periodic ordering, the absence of lamellar x-ray reflections indicates that there is no modulation of the electron density associated with this periodic structure. When cooled to the columnar phase at $T = 153$ °C, the XRD pattern shows two peaks, one at $q \sim 0.205$ Å^{-1} and one at $q \sim 0.281$ Å^{-1} [18], corresponding to a rectangular columnar lattice with parameters $a \sim 30.7$ Å and $b \sim 22.4$ Å [17].

In a strongly rubbed, planar cell, the nematic phase is well aligned [Fig. 3(a)], with uniform birefringence. The texture of the N_{TB} phase, in contrast, is not optically uniform, growing in with stripes [Fig. 3(b)] similar to those observed in [19]. It has been shown that the periodicity of the pattern is about twice that of the cell thickness [19]. Under an applied electric field, domains with two different molecular tilts are apparent, with distinct boundaries [Fig. 3(c)], that are visible even at zero field [Fig. 3(e)], similar to the domain boundaries seen in bent molecular dimers [Fig. 3(f)], as first reported by Panov *et al.* [9]. When the E field is reversed, the molecular tilts in the two sets of domains are reversed and their colors interchange [Fig. 3(d)]. This chiral response is direct evidence that the N_{TB} phase is a conglomerate of left- and right-handed domains. In the twist-bend configuration, the molecular dipoles of the bent-core mesogens are along the molecular bows, perpendicular to the helix axis. In an applied electric field, the uniform heliconical structure becomes distorted and electroclinic tilts of opposite sign are induced in the left- and

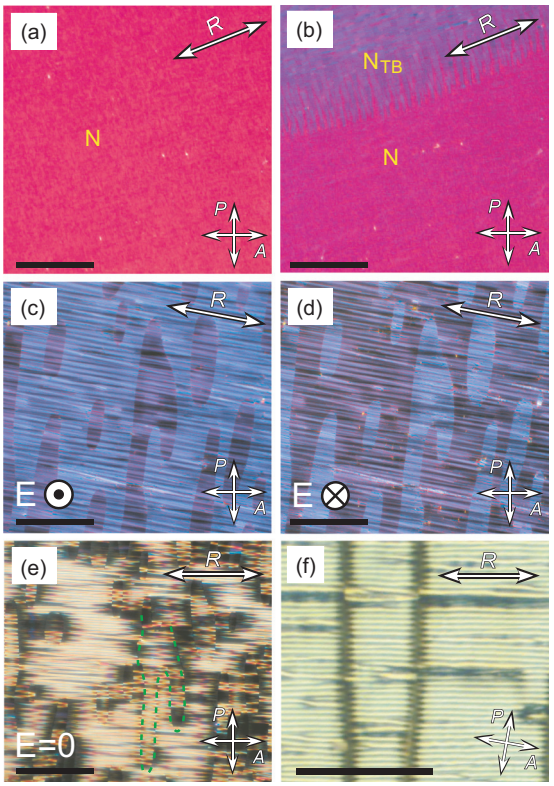

FIG. 3. (Color online) Microscopic textures and electro-optic response of the N_{TB} phase in a strongly rubbed cell. (a) Uniformly aligned nematic phase at $T = 170\,^{\circ}C$ with the director along the rubbing direction R. (b) Stripes are a characteristic feature of the N_{TB} phase as it grows in at $T = 167\,^{\circ}C$. (c) In an applied E field of $20\,V/\mu m$, two regions of different molecular tilt can be distinguished, with the dark and bright regions interchanging when the E field is reversed (d). (e) In the absence of external electric field, the boundaries of domains of opposite chirality are characterized by discontinuities in the stripe pattern, for example, along the dashed green line. (f) The texture of the N_{TB} phase in a 2-μm planar cell of a bent molecular dimer diluted with its monomer (35 wt %) reported in [9] shows chiral domain boundaries similar to those in (e). Reproduced with permission from Applied Physics Letters **101**, 234106 (2012). Copyright 2012 AIP Publishing LLC. Images (a)–(e) were taken in an Instec 4-μm planar cell. The scale bars are 100 μm.

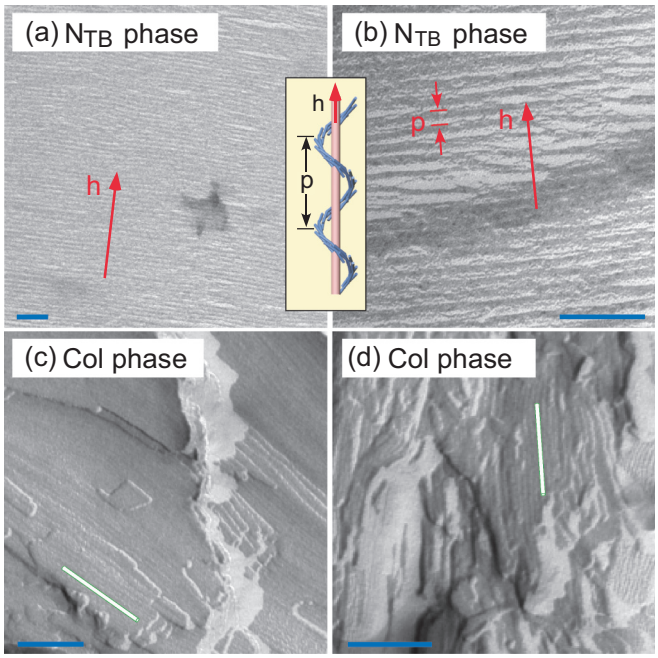

FIG. 4. (Color online) : Freeze-fracture images of the N_{TB} and Col mesophases. (a) and (b) FFTEM images of the N_{TB} phase, showing the conical helical structure of period $p_{TB} \sim 14$ nm. In both images, the helix axis h is approximately parallel to the fracture plane as modeled in the inset and indicated by the red arrows. No layer surfaces are observed in the N_{TB} phase. The sample was sandwiched between two clean glass planchettes and quenched at $T = 167\,^{\circ}C$. (c) and (d) FFTEM images of the Col phase, quenched at $T = 155\,^{\circ}C$. The Col phase shows a two-dimensional periodic structure, with layers parallel to the fracture plane and layer modulations along the layer surface. The column orientation is sketched in the inset. Distinct layer steps can be observed in the Col phase. The scale bars are all 100 μm.

right-handed domains. The electroclinic effect in nematics has been observed previously in cholesteric liquid crystals [20]. Recently, Dozov *et al*. further clarified the electroclinic effect in the twist-bend nematic phase of the bent molecular dimer CB7CB [21] which is similar to that observed in the bent-core molecules UD68.

Freeze-fracture transmission electron microscopy, a technique which enables direct visualization of the microstructure of liquid crystals on the nanometer scale [22], was used to explore further the internal structure of the N_{TB} and Col phases. The one-dimensional, periodic structure corresponding to the conical helix of the N_{TB} phase is clearly visible in the FFTEM images in Figs. 4(a) and 4(b). In contrast to typical smectic samples, it is hard to find layer surfaces in the N_{TB} phase, as the molecules are intercalated in the conical helical structure and there are no distinct layer interfaces as in smectics. This observation is consistent with the fact that we are unable to draw a freely suspended film of UD68 in the N_{TB} phase. The periodicity of the bent-core N_{TB} phase is about $p \sim 14$ nm, a little longer than the pitch measured in the bent molecular dimers CB7CB ($p \sim 8$ nm) [1]. Taking the molecular length as $L = 44.5$ Å [estimated by CPK model (space-filling model, a type of three-dimensional molecular model where the atoms are represented by spheres whose radii are proportional to the radii of the atoms and whose center-to-center distances are proportional to the distances between the atomic nuclei, assuming a core bend angle of 120° and an all-*trans* conformation of the alkyl chains], there are only several molecules in each helical turn [Fig. 1(c)]. At lower temperature, the N_{TB} phase transforms to the Col phase. The two-dimensional periodic structure of the rectangular columnar phase is shown in Figs. 4(c) and 4(d), with the layer and in-plane layer modulation parallel to the fractured surface.

III. DISCUSSION

Although dimers with odd-numbered spacers such as CB7CB superficially resemble bent-core molecules like UD68, their conformational energy landscape is very different. In the dimers, the energy difference between *trans* (180°) and

TABLE I. Comparison of the N^*, SmC^*, N_{TB}, and SmCP phases, all of which form the helical structure.

	N^*	SmC^*	N_{TB}	SmCP
Molecular shape	Rodlike	Rodlike	Bent-core	Bent-core
Molecular chirality	Chiral	Chiral	Achiral	Achiral
Layers?	No	Yes	No	Yes
Polarization?	No	Yes	Yes	Yes
Twist deformation?	Yes	Yes	Yes	Yes
Bend deformation?	No	Yes	Yes	Yes

gauche (±60°) dihedral orientations is of the order of only 0.5 kcal/mol, which at 97 °C is less than 1 k_BT of energy per molecule, so that the alkyl spacer is quite flexible and plenty of gauche conformations are expected as a result of thermal fluctuations [1]. The CB7CB N_{TB} phase therefore can easily be supercooled to room temperature and a glass transition occurs at around 7 °C [23]. The UD68 N_{TB} phase with a rigid bent core, on the other hand, transforms to the Col phase on cooling.

So far, the helical structure has been observed in the N^*, SmC^*, N_{TB}, and SmCP phases, which are compared in detail in Table I. In the N^* and SmC^* phases, the molecules are rodlike and chiral, while the N_{TB} and SmCP phases can be formed by bent, achiral molecules. Due to their rigid, bent molecular shape, the flexoelectric response resulting from linear coupling between the polar order normal to the director and bend director deformations is much larger for bent-core liquid crystals than for rodlike liquid crystals [24], and this flexoelectricity enhances the heliconical structure with twist and bend molecular deformation in the N_{TB} phase [25,26]. However, in order to form the N_{TB} phase instead of the SmCP [Fig. 1(c)], the tendency for layering must be weak or absent. One way to tune this is by altering the alkyl tail, with molecules with longer alkyl tails being more likely to form smectic layers. The homologs of the unsymmetrical bent-core molecule UD68 that have long alkyl tails ($n > 7$) form the SmCP phase, while molecules with short alkyl tails ($n < 7$) show the N_{TB} phase. Analogous behavior is seen in dimers. For example, in modification of CB7CB with terminal alkoxy chains, only dimers with short terminals ($n = 4$) are able to form the N_{TB} phase [27]. If the bent shape is lost altogether, for example in odd-numbered trimers, no N_{TB} phase is observed [28].

The observations reported here show that at least one rigid bent-core system exhibits the twist-bend nematic with optical textural features markedly similar to those of the bent molecular dimers. The only other suggested finding of the twist-bend phase in rigid bent cores, by Gortz *et al.* [14], was based on quite different textures, indicating that their phase is likely a different type of spontaneously chiral nematic.

IV. SUMMARY

The mesophases of the bent-core liquid crystal UD68 have been characterized using DTLM, XRD, FFTEM, and electro-optical measurements. Due to the natural tendency of banana-shaped molecules to induce a local bend of the molecular director, this material forms the N_{TB} phase with a conical twist-bend helix, a phase observed previously only in bent molecular dimers linked by flexible, odd-numbered alkyl chains. Although the liquid crystal molecules are achiral, the N_{TB} phase is polar and chiral. Due to the electroclinic effect, left- and right-handed domains are observed under the influence of an electric field showing opposite molecular tilt. Unlike in the dimers where the N_{TB} phase is easily supercooled, UD68 has an N_{TB}-Col phase sequence where the molecules are locked into a structure with two-dimensional order at lower temperature. Study of molecular architecture and ordering reveals that only homologues with short alkyl tails (i.e., weak layering) favor the twist-bend director field and nematic order, while longer homologues form conventional SmCP phases.

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