Chemically induced twist-bend nematic liquid crystals, liquid crystal dimers, and negative elastic constants

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Here we report the chemical induction of the twist-bend nematic phase in a nematic mixture of ether-linked liquid crystal dimers by the addition of a dimer with methylene links; all dimers have an odd number of groups in the spacer connecting the two mesogenic groups. The twist-bend phase has been identified from its optical texture and x-ray scattering pattern as well as NMR spectroscopy, which demonstrates the phase chirality. Theory predicts that the key macroscopic property required for the stability of this chiral phase formed from achiral molecules is for the bend elastic constant to tend to be negative; in addition the twist elastic constant should be smaller than half the splay elastic constant. To test these important aspects of the prediction we have measured the bend and splay elastic constants in the nematic phase preceding the twist-bend nematic using the classic Frederiks methodology and all three elastic constants employing the dynamic light scattering approach. Our results show that, unlike the splay, the bend elastic constant is small and decreases significantly as the transition to the induced twist-bend nematic phase is approached, but then exhibits unexpected behavior prior to the phase transition.

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I. INTRODUCTION

Dozov predicted the existence of two nematic phases differing in their director distributions [1]. He had realized that if the bend elastic constant becomes negative [2], although more strictly goes to zero, then in the ground state the director would no longer be uniformly aligned as in a standard nematic but would be bent [1]. He also appreciated that the bend deformation could not exist in isolation but would require an accompanying and stabilizing splay or twist deformation. It is the twist-bend nematic that is of particular interest here. This phase is a generalized version of the conventional chiral nematic phase but differs from it in that the director is tilted with respect to the helix axis and not simply orthogonal to it. The phase is of particular interest in that its chirality appears spontaneously even though the molecules are achiral. As a consequence of this molecular achirality it seems reasonable to require that the phase be composed of two chiral degenerate domains having opposite handedness. He also appreciated that a molecular requirement for a negative bend elastic constant [2] is a bent molecule such as that of a bent-core or banana mesogen.

Subsequently Niori *et al.* reported that a nonsymmetric bent-core system composed of achiral molecules exhibited a nematic phase having optical characteristics suggesting its chirality, consistent with those predicted for the twist-bend nematic. An account of this appeared in Ref. [3]. Subsequently the nematic phase of other bent-core mesogens was found to show chiral domains of opposite handedness [4]; again this surprising result is consistent with that expected for the twist-bend nematic phase predicted by Dozov [1]. Earlier [5] it had been recognized that liquid crystal dimers with odd spacers should have, on average, a bent structure [6], the extent of which would depend on the nature of the link between the mesogenic groups and the flexible spacer connecting them. To enhance the bent shape of the dimer it had been suggested that a methylene group should be the preferable link rather than the more common ether link [7]. One consequence of this structural difference for symmetric dimers with cyanobiphenyl groups was the significantly reduced orientational order of the odd dimers with methylene links in comparison with those having ether links. Another puzzling difference was that although the ether-linked dimers with odd spacers only form a single nematic phase [8] for those with methylene links, there is a second liquid crystal phase [5,9,10]. More recently a very detailed investigation [11] of the cyanobiphenyl dimer having a heptane spacer 1″,7″-bis(4-cyanobiphenyl-4′-yl)heptane (CB7CB) has suggested that the phase following the nematic is the twist-bend nematic phase predicted by Dozov [1]. Here we report the chemical induction of the twist-bend nematic phase in a mixture of ether-linked liquid crystal dimers by the addition of an odd methylene-linked dimer and its detailed characterization.

The layout of this paper is as follows. We begin with the construction of the phase diagram using the optical textures to locate the transitions, especially that to the twist-bend nematic phase. We then describe the results from an extensive range of techniques used to confirm our identification of the twist-bend nematic phase. These include optical microscopy, x-ray scattering, and NMR spectroscopy. Of particular importance in the predicted formation of the twist-bend nematic phase are the elastic constants and especially the sign of the bend constant [1]. In the previous study of CB7CB they were obtained theoretically [11]. However, for the mixtures described here they have been determined experimentally using both the classic Frederiks transition and dynamic light scattering methods necessarily for the nematic phase.

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II. EXPERIMENTAL STUDIES AND DISCUSSION

A. Phase diagram

The base mixture is composed of five odd-membered liquid crystal dimers with ether linkages having substituted biphenyl mesogenic groups [see Fig. 1(a)] and is denoted as KA. The nematic-isotropic transition occurs at 75 °C and the nematic freezes at 44 °C. To induce the twist-bend nematic phase we have added the methylene-linked odd dimer 1″,9″-bis(4-cyano-2′-fluorobiphenyl-4′-yl)nonane (CBF9CBF), which melts at 98 °C. Below this there are monotropic nematic and twist-bend nematic phases with the transition temperatures T_{NI} of 86 °C and $T_{N_{\mathrm{TB}}N}$ of 80 °C. The occurrence of the twist-bend nematic is in keeping with the average bent molecular structure produced by the methylene links [11,12]. The phase diagram for the mixture of KA with CBF9CBF is shown in Fig. 2. The nematic-isotropic transition temperature exhibits a slight concave dependence on composition as often found for conventional nematics. More interestingly the twist-bend nematic-nematic transition has a modest convex curvature. The small deviation from linearity allows $T_{N_{\mathrm{TB}}N}$ for the base mixture KA to be estimated by extrapolation; this virtual transition temperature is found to be about 22 °C, which is below the melting point of 44 °C. This result shows that the bend in the average structure of the odd ether-linked dimers, while not sufficient to produce a zero value of K_3, approached from the positive side, at high temperatures, can achieve this at relatively low temperatures. Here the orientational order is high and, in keeping with theory, the Landau-like bend coefficient becomes negative [2,13]. The addition of a methylene-linked dimer to the mixture of five ether-linked dimers clearly enhances the stability of the twist-bend nematic phase, as is to be expected. The nematic-isotropic transition is found to be first order as is the twist-bend nematic-nematic transition when the concentration of CBF9CBF is very high. However, as the nematic range increases the N_{TB}-N transition tends to be second order, presumably passing through a tricritical point; such behavior is analogous to that when the nematic is followed by a smectic-A phase where the Sm-A–N transitional entropy is reduced as the nematic range is increased [14]. This variation is clearly explained by the McMillan molecular field theory, which is an extension of the Maier-Saupe theory of the nematic phase to the smectic-A phase [15]. This theory is based on two order parameters, an orientational one for the nematic phase and another involving the translational order of the smectic-A phase. There is in effect a coupling between the orientational and translational order and as the strength of this grows the nematic range decreases and the transitional

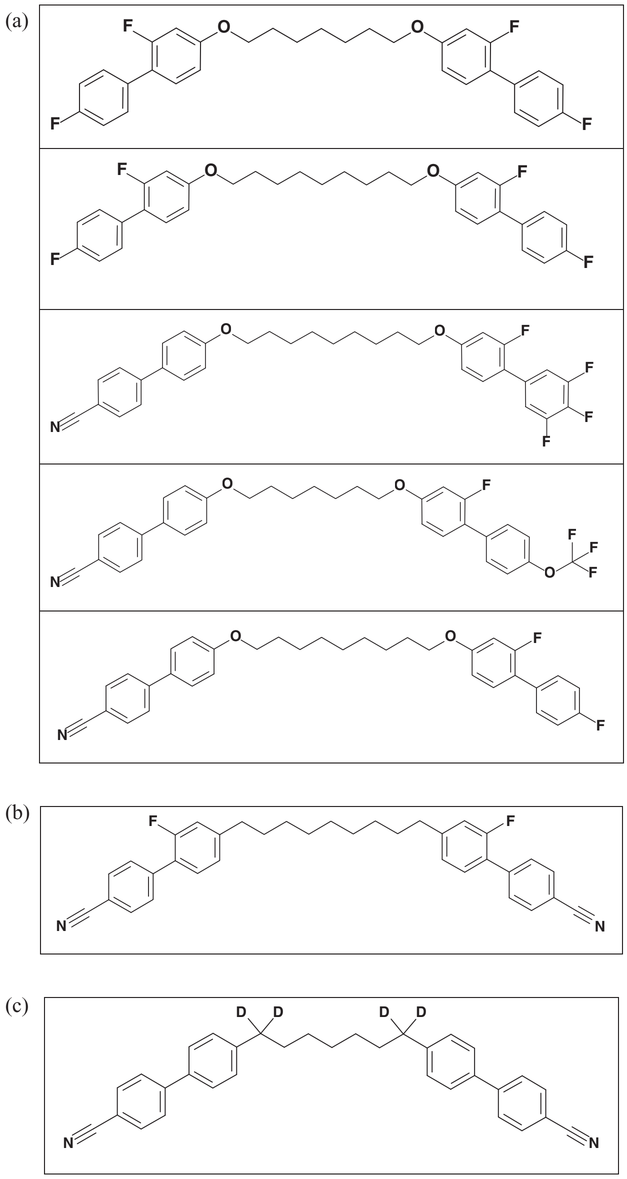

FIG. 1. Chemical structures of (a) the odd ether-linked liquid crystal dimers composing the base mixture KA, (b) the methylene linked dimer 1″,9″-bis(4-cyano-2′-fluorobiphenyl-4′-yl)nonane (CBF9CBF), and (c) the NMR spin probe 1″,7″-bis(4-cyanobiphenyl-4′-yl)heptane-1″,7″-d_4 (CB7CB-d_4).

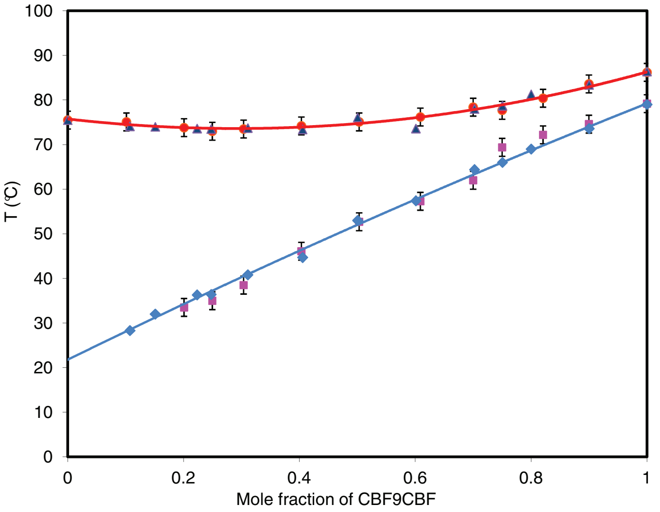

FIG. 2. (Color online) Phase diagram for a mixture of KA and the liquid crystal dimer CBF9CBF; the amount of this is given as the mole fraction. The nematic-isotropic transition is denoted by ▲,● and the twist-bend nematic-nematic transition by ■,♦; the separate symbols refer to different experiments. The solid lines denote the best empirical fit to the experimental data.

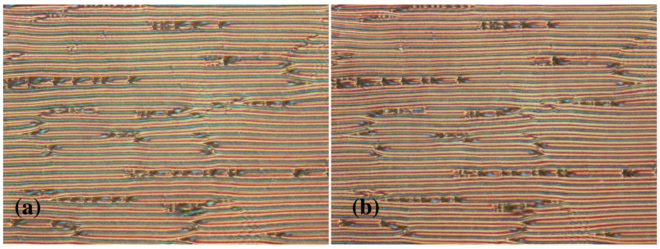

FIG. 3. (Color online) Optical textures for the twist-bend nematic phase of the dimer mixture KA(0.2) in a rubbed polyimide cell, 5.6 μm thick, in the range 30 °C − 35 °C; with the polarizers at (a) − 20° and (b) 20°.

entropy increases [15]. The potential similarity in the behavior of the N_{TB}-N to the Sm-A–N system hints at a similarity in the theory for the N_{TB} phase to that for the smectic-A phase involving a coupling between the nematic order parameter and those for the twist-bend phase [1]. However, in the original theory proposed by Dozov [1] the nematic order is taken to be constant and so a possible coupling between the order parameters for the N and N_{TB} phases does not appear. The extension of the theory to include the orientational order in this way is a nontrivial task and outside the scope of this paper.

It is also of interest that the phase behavior of a simpler binary mixture composed of an odd, ether-linked dimer with an odd, methylene-linked dimer showed a marked deviation from linearity not only for T_{NI}, but especially for $T_{N_{\mathrm{TB}}N}$ [12].

B. Optical textures

The optical textures used to locate the phase transitions were also used to provide an indication of the identity of the low-temperature liquid crystal phase. Some typical textures observed for the KA mixture containing 0.2 mole fraction of CBF9CBF are shown in Fig. 3; since most of our measurements were made for this mixture we shall denote it by KA(0.2). These textures were obtained for the sample contained in a parallel-plate cell, 5.6 μm thick, coated with rubbed polyimide within the temperature range 30 °C–35 °C. The two textures, obtained with the polarizer and analyzer uncrossed by ± 20°, clearly show the ropelike texture with the ropes parallel to the direction of rubbing. This striking texture has been observed for the twist-bend nematic phase of the odd dimer CB7CB [11] and other odd liquid crystal dimers with methylene links [10,16], although not necessarily identified as forming the twist-bend nematic phase. The two textures in Figs. 3(a) and 3(b) are joined in the center so that the change in their appearance (colors) on uncrossing the polarizers can be clearly seen. Thus the light (red) rope becomes dark (blue) and the dark (blue) becomes light (red); the exchange of these complementary colors between regions of the textures is consistent with the chiral domains having opposite handedness. Analogous changes in the optical texture are also observed when the polarizer and analyzer remain crossed and the sample is rotated. We should also note that a second series of chiral domains, apparently unrelated to the stripes, has been observed for an odd liquid crystal dimer having methylene links, although in the presence of a high dc electric field of 100 MV m^{-1} [17].

C. X-ray scattering

To confirm that the phase induced by the addition of CBF9CBF to the five-component KA mixture is indeed a nematic and not a smectic phase we have used x-ray scattering. In these experiments the sample was aligned with a magnetic field of about 1 T with the x-ray beam orthogonal to the field. The scattering patterns were recorded as a function of temperature from slightly above the nematic-isotropic transition until about 10 °C into the second phase. Two of the scattering patterns are shown in Fig. 4 at temperatures on either side of the N_{TB}-N transition. In the nematic phase the director is aligned parallel to the magnetic field and the scattering pattern [see Fig. 4(a)] contains the expected diffuse outer and inner arcs associated with short-range positional correlations between molecules side by side and end to end, respectively. The distances obtained from the locations of these arcs are approximately 4.4 Å and 14.9 Å. This latter separation corresponds to about half the molecular length estimated from molecular models and is consistent with an intercalated organization in the nematic phase [18]; this has been found for CB7CB [11] and other

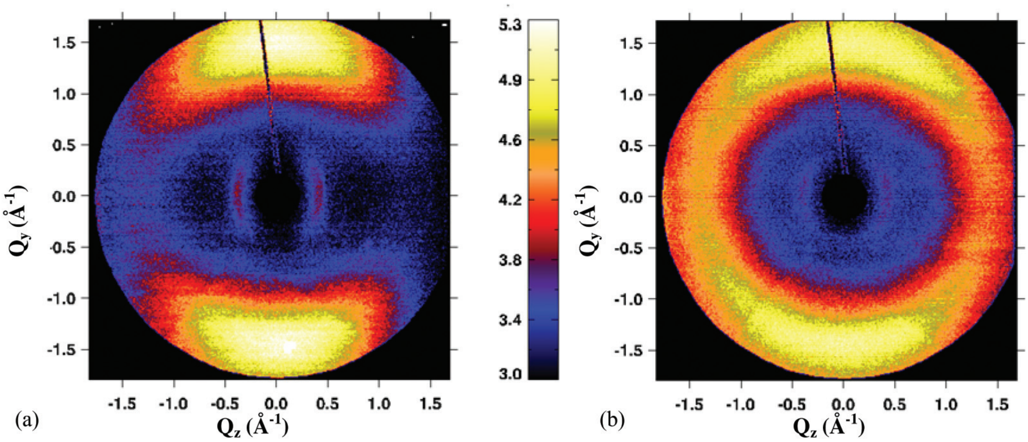

FIG. 4. (Color online) The two-dimensional x-ray scattering patterns for the mixture KA(0.2) aligned with a 1 T magnetic field orthogonal to the x-ray beam (Cu $K\alpha$ radiation with a Ni filter and a graphite monochromator). In the figure the field is along the horizontal direction. The results are for temperatures (a) 45 °C and (b) 30 °C on either side of the twist-bend nematic-nematic transition at 37 °C.

methylene-linked dimers [12]. The scattering pattern for the twist-bend nematic phase shown in Fig. 4(b) has a structure similar to that for the nematic phase. There are both outer and inner diffuse arcs at comparable positions and having similar widths to those in the nematic phase. These widths were obtained by fitting a Lorentzian to the scattering intensity. Of particular significance the width of the inner arc suggests that the correlation length for the end-to-end positions is about 15 Å, which is consistent with the intercalated structure of a nematic phase and certainly not with a standard smectic phase. We have made further x-ray scattering measurements at smaller scattering angles and these reveal that there are no smectic reflections with a period of less than 300 Å.

Before leaving the x-ray results we note an interesting difference in the extent of the arcs; thus in the twist-bend nematic the wide-angle arcs are spread further around the azimuth than in the nematic phase. A similar but more extensive change has been observed for a methylene-linked dimer where the spacer has 11 methylene groups and the mesogenic group is a substituted terphenyl [10]. This dimer also exhibits a nematic-nematic transition and the properties of the low-temperature nematic have strong similarities to those of CB7CB; we would therefore tentatively identify this as a twist-bend nematic. For this dimer the two-dimensional x-ray scattering pattern for the nematic phase shows diffuse inner and outer arcs. However, on lowering the temperature into the twist-bend nematic the arcs evolve into circles, which suggest that the director is now uniformly distributed in a plane orthogonal to the x-ray beam. Curiously, in the twist-bend nematic for the analogous dimer CB11CB, the extents of the inner and outer arcs do not change significantly, which indicates that the director remains more or less parallel to the magnetic field. It is not clear what causes the difference in behavior, although the major spread in the arcs seems to occur when the N_{TB}-N transition is weak.

D. NMR spectroscopy

NMR spectroscopy is proving to be a powerful technique with which to demonstrate the chirality in the bulk phase of a liquid crystal free from the influence of surface effects [11,19]. This technique can be applied by studying both the mesogen, suitably deuterated, or a specifically deuterated probe molecule, although other magnetic nuclei can also be used [19]. In both cases the deuterons must be located in prochiral groups such as the methylene groups in the heptane spacer of CB7CB-d_4 at positions 1″ and 7″ [see Fig. 1(c)]. In an achiral nematic phase the deuterons in such methylene groups are equivalent and so only a single quadrupolar doublet is observed. This equivalence results from the mirror plane of symmetry, which bisects the $D\hat{C}D$ bond angle and is orthogonal to the DCD plane. In a chiral liquid crystal phase with its D_∞ point group symmetry the plane of symmetry for the methylene group is effectively lost [20]; the deuterons are no longer equivalent and so now two quadrupolar doublets are observed. This approach has been employed to demonstrate, unambiguously, the chirality for the twist-bend nematic phase of CB7CB-d_4 in the bulk [11,19]. Here we have employed this NMR technique to explore the formation and structure of the N_{TB} phase in the mixture KA(0.2) using CB7CB-d_4 as a spin probe. This choice was made because of the similarity of its structure to that of the dimer CBF9CBF responsible for the induction of the twist-bend nematic phase and because of the detailed study of this in the nematic phases formed by CB7CB [11]. However, this similarity also means that the probe will contribute to the stabilization of the twist-bend nematic phase, although this contribution should be small because the concentration of the probe is also small, being approximately 3 wt. %.

However, for comparison we start with the base mixture KA composed of ether-linked dimers. The NMR spectrum of the spin probe in the nematic phase of this mixture contains a single quadrupolar doublet and the quadrupolar splitting $\Delta\nu$ associated with this is plotted as a function of the shifted temperature T_{NI}-T in Fig. 5. The quadrupolar splitting is seen to grow continuously as the shifted temperature increases, as might be expected. However, at about 48 °C below T_{NI} there is a hint that the splitting passes through a maximum and as we shall see this seems to be consistent with the observation that the mixture should form a twist-bend nematic phase at a shifted temperature of about 55 °C. The quadrupolar splitting for the methylene deuterons is proportional to the order parameter $S_{zz,}$ of the para axis for the cyanobiphenyl groups; in fact, $S_{zz} \approx \Delta\nu/84$ (both in kHz) [11]. The orientational order of CB7CB-d_4 in the base mixture is significantly larger than in CB7CB itself [11]. This is entirely consistent with the presence of ether links in the odd liquid crystal dimers in the mixture since the larger bond angles will make the mesogens less biaxial and so more highly ordered than the CB7CB dimer with its methylene links [5].

The addition of the CBF9CBF dimer has, as we have seen, induced a nematic-nematic transition with the second nematic phase expected to have a twist-bend structure. This is entirely consistent with the NMR results for CB7CB-d_4 acting as a

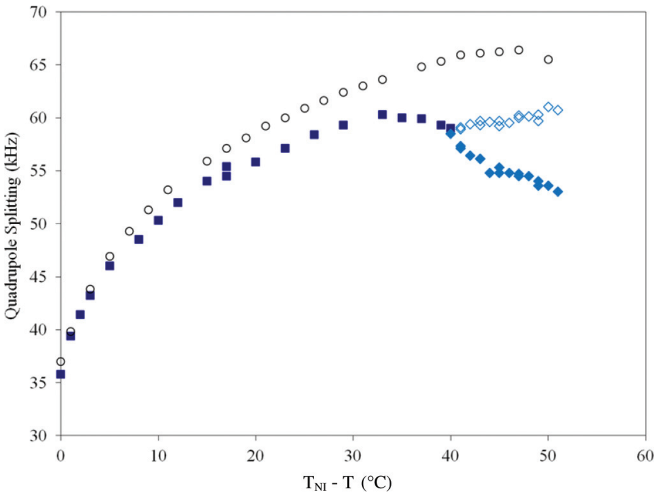

FIG. 5. (Color online) Temperature dependence of the deuterium NMR quadrupolar splittings for the spin probe CB7CB-d_4 as a function of the shifted temperature (T_{NI}–T) in the mixture KA (○) and this mixture with a 0.2 mole fraction of CBF9CBF, KA(0.2) (■). The two quadrupolar splittings in the twist-bend nematic phase are shown as ◊ and ♦. The deuterium NMR spectra were measured using a Varian Infinity Plus 300 spectrometer with a quadrupolar echo sequence [19].

probe in the mixture KA(0.2). Thus in the nematic phase there is a single quadrupolar doublet, as expected, and its splitting increases as the shifted temperature T_{NI}-T increases, until this is 33 °C when the splitting passes through a maximum. The splitting then continues to decrease until 40 °C, at which point the lines of the quadrupolar doublet start to split into two, in keeping with the second-order nature of this transition. As we have seen this additional splitting is a signature of phase chirality and suggests that the twist-bend nematic has been formed. This value for the shifted temperature of 40 °C is close to that measured optically of about 38 °C for the twist-bend nematic-nematic transition shifted temperature (see Fig. 2). As the results in Fig. 5 show, the difference in the quadrupolar splittings, which originates from the phase chirality [19], grows with increasing shifted temperature. The predictions of the Dozov model [1] suggest that this phase is composed of degenerate chiral domains having the same pitch but opposite handedness. The NMR spectra of the probe CB7CB-d_4 in the domains will be the same, that is, two quadrupolar doublets but with the difference in the splittings having opposite signs. If the rate of diffusion of the probe molecules between the domains is fast on the NMR time scale then we would observe just a single quadrupolar doublet. The fact that two doublets are observed tells us that if there are chiral domains of opposite handedness the rate of translational diffusion between them must be slow. The largest difference is about 7 kHz at approximately 11 °C below $T_{N_{TB}N}$, which is not significantly different from the result for CB7CB where the difference is about 11 kHz at the same shifted temperature from $T_{N_{TB}N}$ [11]. We should also note that the mean of the two quadrupolar splittings should be comparable to the splitting in the associated achiral nematic phase [11,19]. For the probe CB7CB-d_4 in the mixture KA(0.2) the average is observed to decrease as the shifted temperature grows in the twist-bend nematic phase; this contrasts with the behavior in CB7CB where the mean quadrupolar splitting is essentially independent of temperature over a wide range [11]. Such a reduction would be unusual for a nematic, but would be consistent with the tilted structure of the twist-bend nematic. That is, the director is tilted with respect to the magnetic field of the NMR spectrometer.

E. Elastic constants

The key element in Dozov's prediction of the twist-bend nematic phase is that the bend coefficient should be negative [2] and that this should be related to the bend elastic constant [1]. However, a methodology has yet to be developed that could be used to measure the bend coefficient in the twist-bend phase itself. We have therefore determined the temperature dependence of K_3 in the nematic phase preceding the N_{TB} phase. Extrapolation of these results should then give an indication of the value of the bend coefficient in the twist-bend nematic especially as the N_{TB}-N transition is second order and, as we have seen, both phases are devoid of long-range translational order.

1. *Frederiks transition*

First, we measured the bend and splay elastic constants using the standard Frederiks methodology in which the director distribution is controlled by surface and elastic torques in competition with an electric torque [21]. The field is then varied and the change in the director distribution monitored via the capacitance of the sample placed in a 5 μm-thick guard-ring cell. An electric field of 1 kHz was employed in these experiments and at this frequency the influence of the flexoelectric effect on the results is expected to be negligible [22]. In view of the relatively high viscosity of the nematic phase of odd liquid crystal dimers, care was taken to ensure that the equilibrium director distribution was achieved. To this end the electric field was started at its highest value of 4 MV m^{-1} so that the director was parallel to the field and then the voltage was slowly reduced to zero. The entire voltage dependence of the capacitance, determined in this way, was then fitted to theory [23] to obtain the elastic constants and the dielectric anisotropy. These properties were measured for a range of temperatures for the mixtures KA and KA(0.2); the lowest temperature at which both were studied was 38 °C. The elastic constants K_1 and K_3 for these two mixtures are shown in Fig. 6 as a function of temperature. For comparison we start with the results for the mixture KA. The splay elastic constant is relatively large and increases somewhat with decreasing temperature. In fact, the values are comparable, at the same reduced temperatures, with those found for the odd ether-linked liquid crystal dimer 1″-(2′,4-difluorobiphenyl-4′-yloxy)-9″-(4-cyanobiphenyl-4′-yloxy)nonane (FFBO9OCB) [24], which is one of the components of KA [see Fig. 1(a)]. For conventional nematics K_3 is larger than K_1 [21], but for odd dimers this situation is reversed and, as we see in Fig. 6, K_3 is significantly smaller than K_1 and, in addition, the bend elastic constant decreases with decreasing temperature. Again, analogous behavior has been observed for FFBO9OCB [24], although the values are somewhat larger than for KA and the rate at which K_3 decreases with decreasing temperature is slightly slower than for KA. In marked contrast, results for K_3/K_1 reported much earlier for the odd ether-linked dimer 1″,9″-bis(4-pentyloxyphenylbenzoate-4′-yloxy)

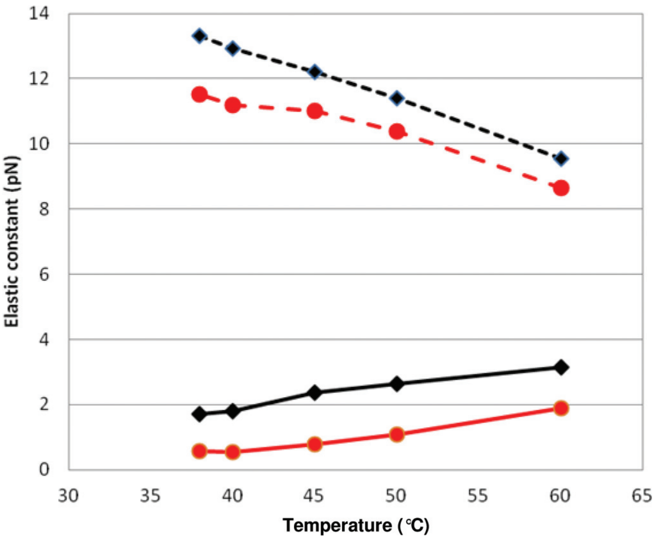

FIG. 6. (Color online) Temperature dependence of the elastic constants K_1 (– – –) and K_3 (━) in the nematic phase of (a) mixture KA (♦) and (b) mixture KA(0.2) (●) with 0.2 mole fraction of CBF9CBF.

nonane (PPBO9OPPB) showed quite different behavior [25]: Here the elastic constant ratio is larger. Thus K_3/K_1 close to T_{NI} is about 0.5, comparable to the value found for KA, but then the ratio increases rather than decreases with decreasing temperature, reaching a value of about 1.7, significantly greater than that of just 0.23 for the mixture. Such a dramatic difference in behavior may result from the difference in the structure of the pentyloxyphenylbenzoate mesogenic group. We now return to our primary task, which is to explore the elastic behavior of the mixture KA. Extrapolation of the results for the bend elastic constant is difficult, but it would appear to vanish just below 20 °C and according to the phase diagram, shown in Fig. 2, this is close to the virtual N_{TB}-N transition, in accord with Dozov's prediction [1].

We turn now to the elastic behavior of mixture KA(0.2), which forms an enantiotropic twist-bend nematic phase. The results for K_1 and K_3 are also shown for comparison with those of the mixture KA in Fig. 6. The addition of the methylene-linked dimer CBF9CBF is seen to reduce the average of the splay elastic constant by about 1.2 pN. A similar absolute reduction is found for the bend elastic constant, but now, because K_3 is already so small, the effect is far more dramatic. It is of interest that the change in the value of both K_1 and K_3 caused by the addition of CBF9CBF results from the depression of both elastic constants rather than a change in their temperature dependence. A linear extrapolation of the results suggests that K_3 should vanish at about 33 °C, which is within experimental error of the N_{TB}-N transition temperature shown in Fig. 2. These experimental results for the bend elastic constant of KA and KA(0.2) seem to suggest that the twist-bend nematic phase does indeed appear when K_3 vanishes and presumably the bend coefficient [2] would become negative in the new phase, as predicted by Dozov [1]. In addition, for this to be the twist-bend nematic it is necessary for $K_1 > 2K_2$ and, as we shall see, this seems likely to be the case, again in keeping with theory [11,13].

2. *Light scattering*

To confirm our results for the elastic constants it would be valuable, however, to be able to measure them closer to the N_{TB}-N transition. Since this is not possible with the Frederiks methodology for the splay and bend elastic constants we have employed the dynamic light scattering approach [26] to determine these elastic constants. This has the advantage that the twist elastic constant can also be measured. A monodomain sample of KA(0.2) was prepared using surface alignment with polyimide-coated glass plates with a 20 μm spacing. The intensity of the dynamically scattered light, that is, the autocorrelation function of the amplitude of scattered light resulting from director fluctuations around its equilibrium orientation, was measured as a function of the scattering vector. This yields, in the appropriate scattering geometry, among other things, three quantities $p_i K_i/\Delta\varepsilon^2$, where i takes values 1–3, the p_i are proportionality constants that are independent of temperature, K_i are the elastic constants, and $\Delta\varepsilon$ is the anisotropy of the optical dielectric tensor. This anisotropy has been measured for KA(0.2) as a function of temperature in a separate experiment. This gives us the quantities $p_i K_i$; the proportionality constants p_1 and p_3 were determined from the K_1 and K_3 available from the Frederiks experiment at 60 °C. This temperature was chosen because K_3 is largest here and it is also furthest from the N_{TB}-N transition so that any pretransitional influence of the N_{TB} structure is minimal. This leaves the twist elastic constant and to determine p_2 for this we have measured the ratio K_2/K_3 from the dependence of the relaxation rate on the orientation of the scattering vector, at 73 °C and 40 °C. The value of K_3, found from the Frederiks experiment then allows us to calculate K_2, which can be used to give the proportionality constant p_2. The temperature dependence of the three elastic constants determined in this way is shown in Fig. 7.

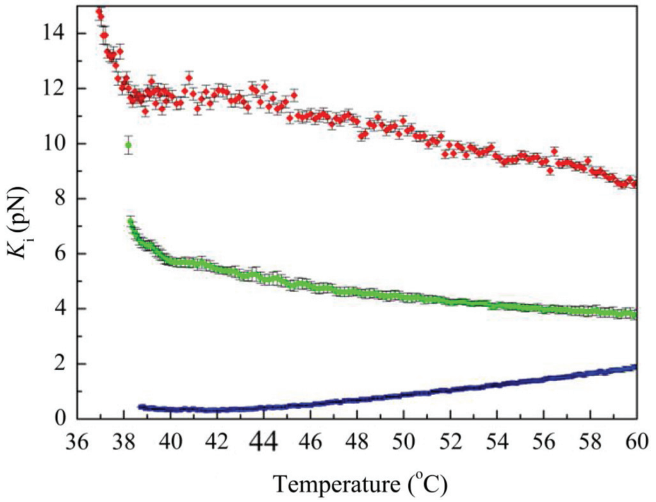

FIG. 7. (Color online) Temperature dependence of the elastic constants K_1 (♦), K_2 (●), and K_3 (■) for the mixture KA(0.2). The experimental errors in the K_i, estimated from the fits to the scattered light correlation function, are shown as the vertical bars.

We start with the splay elastic constant. This is the largest of the three and increases with decreasing temperature in keeping with that of the odd ether-linked dimer FFBO9OCB [24]. However, for KA(0.2) the splay elastic constant increases more rapidly within the first few degrees of the twist-bend phase, although the methodology used to determine the elastic constant here is based on the assumption of a standard nematic phase and not the twist-bend form, so the relevance of the values is uncertain. The twist elastic constant also increases with decreasing temperature, but now values are not available within the twist-bend phase because at the transition to this, the twist-bend director fluctuations are necessarily quenched. There is, however, a clearly enhanced increase in the twist elastic constant over the 2 °C just before the N_{TB}-N transition, which may indicate a pretransitional effect. The rate at which K_2 increases is about the same as that for K_1, so the ratio K_1/K_2 is more or less constant with a value of a little more than 2. There are a few experimental results for the odd dimer PPBO9OPPB [25] with which this result can be compared. Here K_1/K_2 is 2.5 at 10 °C below T_{NI}, which is comparable to our result for the mixture KA(0.2), but the absolute values are about a factor of 2 smaller that those we have obtained. Again this difference may be associated with the different mesogenic groups in the dimer. The elastic constants have also been calculated for the odd dimer CB7CB [11] based on a molecular field approach and our results for the mixture are

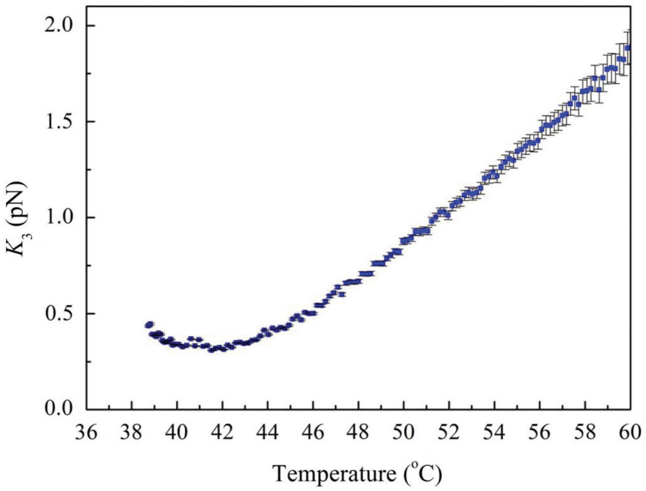

FIG. 8. (Color online) Temperature dependence of the bend elastic constant shown on an expanded scale.

consistent with these predictions. The fact that K_1 is slightly larger than $2K_2$ in the nematic phase indicates that it might also be the case in the twist-bend nematic phase for the splay and twist coefficients [2]. This is in keeping with the prediction by Dozov [1] that for the twist-bend phase to be stable with respect to the splay-bend phase $K_1 > 2K_2$.

Our main interest, however, is in the bend coefficient [2] for, according to the Dozov theory, the driving force for the formation of the twist-bend phase is likely to be associated with the negative value of this. What we have found and is clearly apparent from the expanded plot of K_3 against temperature shown in Fig. 8 is that this elastic constant decreases rapidly with decreasing temperature, faster in fact than that found from the Frederiks experiment, and is small. This behavior contrasts with that found for the odd ether-linked dimer FFBO9OCB [24], where the bend elastic constant is about 3.3 pN and essentially independent of temperature, whereas for the mixture KA(0.2) we see a change by a factor of 2 over a comparable temperature range. However, what is quite unexpected is that K_3 passes through a shallow minimum of approximately 0.3 pN at about 2 °C prior to the N_{TB}-N transition; it then increases slightly by about 0.2 pN before the twist-bend phase appears. This observation is not unique and analogous minima have been observed for other odd methylene-linked liquid crystal dimers [27]. The origin of the minimum and its implications for the bend coefficient in the twist-bend nematic are not understood. We now return to the significant observation that the bend and twist but not the splay elastic constants exhibit a pretransitional increase in the nematic phase as the twist-bend phase is approached. Such behavior is reminiscent of that for a nematic just above a smectic-A phase [28]. This might suggest that there is a smectic-A phase below the twist-bend nematic phase, which results in local smectic-A correlations in the N_{TB} phase. This idea finds some support from the fact that in the nematic phase formed by bent-core molecules, which to some extent resemble odd dimers, the bend elastic constant can also be rather small, but here the transition is always to a smectic phase. It is conceivable, therefore, that the upturn in the elastic constants might result from short-range smectic fluctuations.

An alternative explanation could be associated with the periodic structure of the director within the twist-bend nematic. The periodicity of this is the pitch of the helix, which is expected to be small [1,29,30]. There is a similarity between this structure and that of a smectic-A phase as well as an equivalence with a short pitch chiral nematic. This results in optical textures for these three phases that are comparable [29]. It might therefore be expected that the periodic structure of the N_{TB} phase could result in the pretransitional increase in the bend and twist elastic constants for the nematic phase.

Nonetheless, it would seem that there is no extrapolation of our results for K_3 that would allow it to pass through zero and so lead to the negative value required by the Dozov continuum-based theory for N_{TB}. However, what is clear is that the second nematic phase that is formed by the KA(0.2) mixture has some of the key characteristics of the twist-bend nematic phase, in particular its intrinsic chirality. It would seem, therefore, that the negative value of K_3 is not essential for the formation of the N_{TB} phase, but that the small value of this elastic constant is an essential part of the conditions.

III. CONCLUSION

The induction of the twist-bend nematic phase by the addition of a methylene-linked odd liquid crystal dimer to a mixture of ether-linked odd dimers is consistent with the prediction by Dozov [1]. That is, the key molecular requirement for the existence of this phase is a highly bent molecular structure and for the odd dimers this results because the methylene link creates a greater average bend than for ether links [5]. At a more fundamental level the particular director distribution adopted by the phase is related to the negative value of a Landau-like bend coefficient [1,2]. This behavior is consistent with experimental values of the bend elastic constant measured in the preceding nematic phase using the Frederiks transition and dynamic light scattering techniques. Certainly K_3 is unusually small and becomes smaller with decreasing temperature. Extrapolation from high temperature shows that the bend elastic constant would vanish at approximately the transition temperature $T_{N_{\mathrm{TB}}N}$, which is to be expected. What is not expected is the small increase in K_3 just prior to the transition to the twist-bend phase. This pretransitional increase remains to be explained and, more importantly, its implications for the theory explored. Another feature of the N_{TB} phase is its spontaneous chirality, shown optically for thin films and with NMR spectroscopy for bulk samples; this is remarkable given its constituent achiral molecules. The NMR experiment also shows that the orientational order of the cyanobiphenyl mesogenic groups of the probe CB7CB-d_4 passes through a maximum just prior to the transition to the N_{TB} phase. Such pretransitional behavior is unexpected [11], although it would be consistent with the observed reduction in the mean order within the twist-bend phase. This reduction would be in accord with the anticipated growth in the tilt angle between the helix axis and the director with decreasing temperature in the N_{TB} phase [1]. It is clear that we are continuing to learn about the peculiarities of the twist-bend nematic phase, but that there are certainly aspects of its novel behavior remaining to be explored.

Note added in proof. Recently we were made aware of the work by Chen *et al.* [30] reporting an impressive direct study, using freeze fracture transmission electron microscopy, of the structure of the twist-bend nematic phase of the liquid crystal dimer CB7CB, confirming earlier speculations about this phase [11].

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[2] The notion of a negative bend elastic constant may appear strange. Partly this is because, for a conventional or uniform nematic, the three elastic constants K_1, K_2, and K_3 are necessarily positive. Consequently, the elastic energy must increase when the director distribution deviates from its uniform equilibrium state. However, as Dozov [1] has predicted, when K_3 tends to a negative value the ground state tends to one having a nonuniform director distribution. In the resulting conical twist-bend nematic phase, of prime interest here, the equilibrium director distribution is characterized by two order parameters, the pitch of the helix and the cone angle between the helix axis and the director. Dozov has also shown that the deformation energy can be cast in terms of products of these order parameters rather like a Landau expansion but with the coefficients related to the elastic constants of the nematic phase. Such Landau-like coefficients then determine the equilibrium values of the two order parameters for the twist-bend nematic phase and it is the bend coefficient, proportional to K_3, that must become negative to stabilize the new phase. This occurs because the free energy expansion is about its maximum and not its minimum. The coefficients should not be confused with the elastic constants for the twist-bend nematic phase that control the elastic energy determining the deviation of the director distribution away from the ground state and so must be positive.

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