Liquid Crystals Hot Paper

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A Twist-Bend Nematic Phase Driven by Hydrogen Bonding**

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Abstract: *The liquid crystalline phase behavior of 4-[6-(4′-cyanobiphenyl-4-yl)hexyloxy]benzoic acid (CB6OBA) and 4-[5-(4′-cyanobiphenyl-4-yloxy)pentyloxy]benzoic acid (CBO5OBA) is described. Both acids show an enantiotropic nematic phase attributed to the formation of supramolecular complexes by hydrogen bonding between the benzoic acid units. In addition, CB6OBA provides the first example of hydrogen bonding driving the formation of the twist-bend nematic phase. The observation of the twist-bend nematic phase for CB6OBA, but not CBO5OBA, is attributed to the more bent molecular shape of the complexes formed by the former, reinforcing the view that shape is a key factor in stabilizing this new phase. Temperature-dependent FTIR spectroscopy reveals differences in hydrogen bonding between the two nematic phases shown by CB6OBA which suggest that the open hydrogen-bonded complexes may play an important role in stabilizing the helical arrangement found in the twist-bend nematic phase.*

Liquid crystal dimers consist of molecules containing two mesogenic units linked by a flexible spacer and have been a rich source for the discovery of new types of mesophases.[1,2] Most recently, a nematic–nematic transition has been reported for members of the α,ω-bis-4-(4′-cyanobiphenyl)-alkanes with an odd number of carbon atoms in the alkane spacer.[3,4] Cestari et al. assigned the lower-temperature nematic as a twist-bend nematic phase, N_{tb}.[4] This was later confirmed in studies based on freeze-fracture transmission electron microscopy.[5,6] In the N_{tb} phase, the achiral molecules form a helix and the director is tilted with respect to the helical axis (see Figure 1). The induced twist may be either left- or right-handed and equal amounts of both types of helix are expected. The N_{tb} phase had previously been predicted to exist for bent molecules by Dozov, who suggested that in a nematic phase the director may bend around bent molecules.[7] To stabilize such a bend, either splay or twist must be introduced, resulting in two new nematics with nonuniform director distributions, splay-bend or twist-bend.

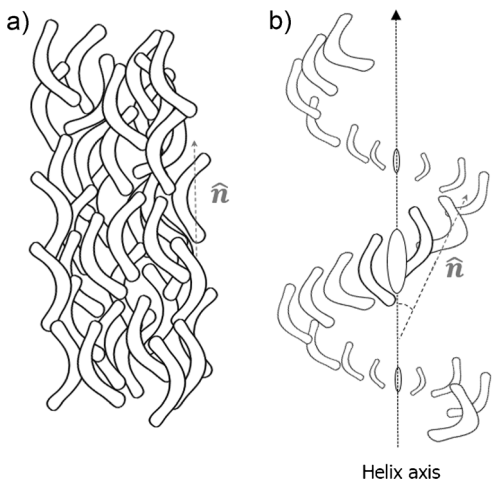

Figure 1. Sketches of a) the nematic and b) the twist-bend nematic phase composed of bent molecules. $\hat{n}$ denotes the director.

To date, the twist-bend nematic phase has been reported for just a dozen liquid crystal dimers[3,4,8–13] and a rigid bent-core mesogen.[14,15] In consequence, the development of the empirical relationships linking molecular structure to the observation of this exciting new phase is very much at an embryonic stage.[16] However, all the liquid crystal dimers reported are odd-membered, i.e., contain an odd number of carbon atoms in the alkane spacer, and thus, possess a bent molecular shape. The majority of these examples contain methylene-linked spacers, which accentuate the molecular bend, and it was believed that this was an essential structural feature. Recently, however, an ether-linked liquid crystal dimer has been shown to exhibit the N_{tb} phase.[9]

The 12 liquid crystal dimers known to exhibit the N_{tb} phase may be considered conventional liquid crystals in that they each consist of discrete molecules. In recent years, however, assembling promesogenic noncovalently bonded molecular complexes has become an increasingly important design approach by which to obtain new materials. Here we describe for the first time how hydrogen bonding can be used to drive the formation of the N_{tb} phase and report the phase behavior of 4-[6-(4′-cyanobiphenyl-4-yl)hexyloxy]benzoic acid (see Scheme 1). The acronym we use to refer to this acid is CB6OBA in which CB denotes the cyanobiphenyl group, 6 indicates the six methylene units, O the ether link, and BA the benzoic acid fragment. For comparative purposes, we also report the phase behavior of the corresponding compound containing the same number of atoms linking the two anisometric units but in which the spacer contains two

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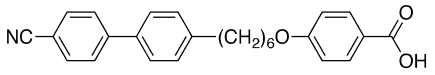
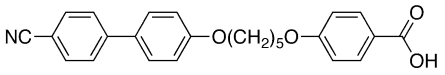


4-[6-(4′-Cyanobiphenyl-4-yl)hexyloxy]benzoic acid, CB6OBA



4-[5-(4′-Cyanobiphenyl-4-yloxy)pentyloxy]benzoic acid, CBO5OBA

Scheme 1. Structures of the acids CB6OBA and CBO5OBA.

Table 1: Transitional properties of CB6OBA and CBO5OBA.

Acid	T (Cr–N) [°C]	T (N_{tb}–N) [°C]	T $(N–I)_{NI}$ [°C]	ΔH(Cr–N) [kJ mol^{-1}]	ΔH(N_{tb}–)N [kJ mol^{-1}]	ΔH(N–I) [kJ mol^{-1}]
CB6OBA	160	(159)	197	28.3	0.44	4.11
CBO5OBA	196	–	209	34.6	–	4.04

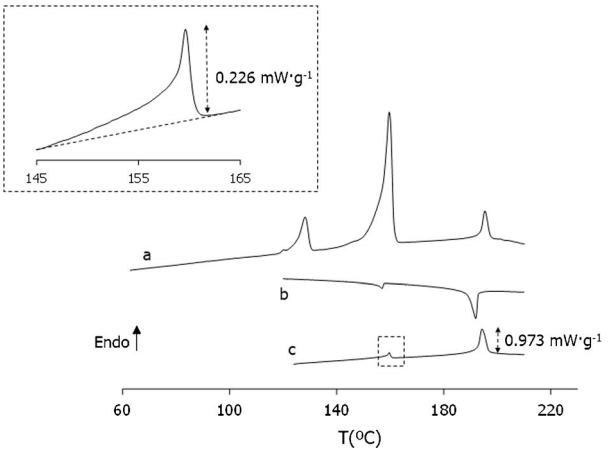


Figure 2. DSC traces obtained for CB6OCB obtained on the a) first heating, b) cooling and c) reheating scans. The inset magnifies the N_{tb}–N endotherm seen in the reheating scan.

ether links, 4-[5-(4′-cyanobiphenyl-4-yloxy)pentyloxy]-benzoic acid, and by analogy refer to this as CBO5OBA (Scheme 1).

The transitional properties of CB6OBA and CBO5OBA are listed in Table 1. Figure 2 shows the differential scanning calorimetry (DSC) traces obtained for CB6OBA on heating and cooling. On initial heating, three endotherms are observed (Figure 2a). The lower-temperature endotherm is associated with a crystal–crystal transition, the strongest endotherm with a crystal–nematic transition, and the highest-temperature endotherm with a nematic–isotropic transition. The nematic phase was identified on the basis of the observation of characteristic Schlieren optical textures containing both two and four brush point singularities when viewed through the polarized light microscope, and which flashed when subjected to mechanical stress. A representative nematic texture observed for CB6OBA is shown in Figure 3a. On cooling, two weak exotherms are observed (see Figure 2b). The lower-temperature exotherm is associated with the twist-bend nematic–nematic phase transition. The twist-bend nematic phase was identified on the basis of the observation of an optical texture containing regions of focal conic and parabolic defects, both indicative of periodic ordering, and rope-like texture (see Figure 3b). In addition, at the N–N_{tb} transition Brownian motion associated with director fluctuations seen in the conventional nematic phase ceased. These observations are characteristic of the twist-bend nematic phase and the magnitude of the N_{tb}–N entropy change is also consistent with this assignment.[4] On reheating the sample, and prior to crystallization, the DSC trace contains two endotherms associated with the N_{tb}–N and N–I transitions, respectively, (see Figure 2c). Crystallization of the twist-bend nematic phase occurred on cooling at about 70 °C in the calorimeter but the phase could be cooled to room temperature under the microscope. By comparison, for CBO5OBA only a conventional, enantiotropic nematic phase was seen, which could be supercooled to 128 °C prior to crystallization.

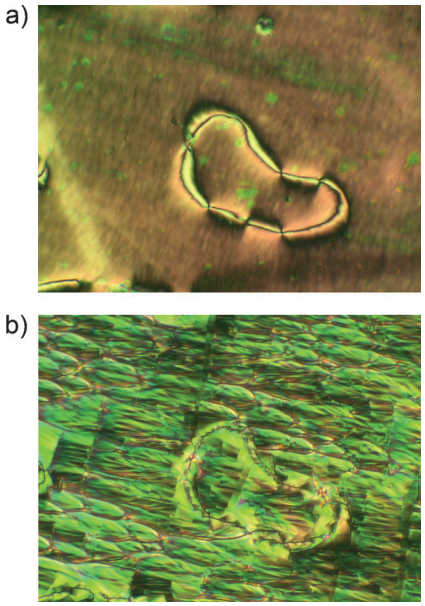


Figure 3. Optical textures of the same area of the sample of a) the nematic phase (165 °C) and b) the twist-bend nematic phase (158 °C) observed for CB6OBA.

Figure 4 shows X-ray diffraction patterns for CB6OBA obtained in the crystal, and in twist-bend and conventional nematic phases. The X-ray patterns observed in the conventional and twist-bend nematic phases are essentially identical, and contain a broad wide-angle scattering peak indicative of a liquid-like arrangement of the molecules. The absence of layer reflections in the lower-temperature phase supports the assignment of a twist-bend nematic phase. The crystal phase appears to be lamellar with a periodicity of 27.3 Å.

The liquid crystalline behavior of benzoic acid based materials is most often attributed to the formation of

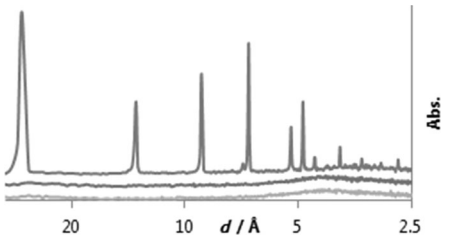


Figure 4. X-ray diffraction patterns obtained for CB6OBA in the crystal (25 °C, top), twist-bend nematic (140 °C, middle) and nematic (180 °C, bottom) phases. Curves displaced arbitrarily along the *y* axis.

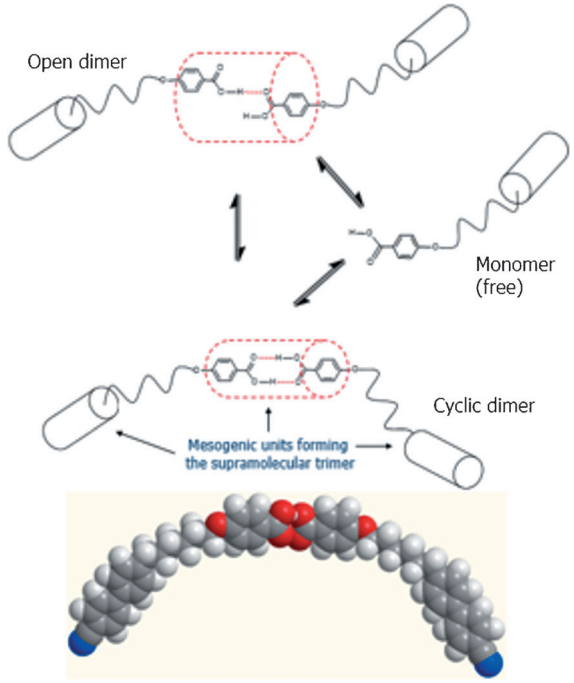


Figure 5. Schematic representation of hydrogen bonding in benzoic acid based systems.

complexes arising from the dimerization of the benzoic acid groups resulting in so-called cyclic dimers. These exist in equilibrium with open hydrogen-bonded complexes and monomeric (free) species (see Figure 5). This dynamic equilibrium is most readily studied using FTIR spectroscopy (see, for example, reference [17]). Figure 6 shows the temperature dependence of the 2400–3500 cm^{-1} region of the FTIR spectrum for CB6OBA. The Fermi resonance vibration bands (B-type, 2654 and 2539 cm^{-1}; C-type, 1918 cm^{-1} (see Figure SI1 in the Supporting Information)) and the O–H stretching contribution at less than 3500 cm^{-1} are indicative of strong hydrogen bonding within the system. In addition, the carbonyl stretching region is dominated by a band centered around 1685 cm^{-1}, which contains contributions associated with cyclic (at lower frequency) and open (at higher frequency) hydrogen-bonded dimers (Figure 6b). These features are also evident in the spectra obtained for CBO5OBA.

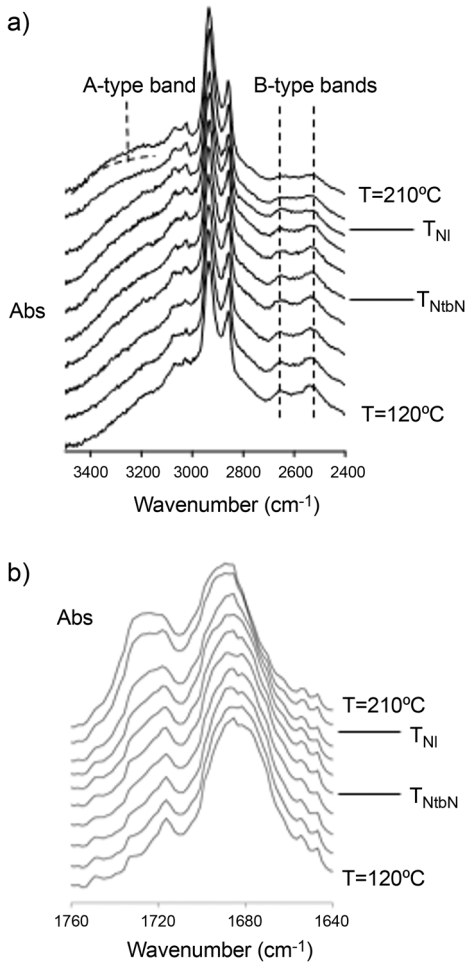


Figure 6. Temperature-dependent FTIR spectra of CB6OCB obtained on cooling showing the a) O–H (and C–H) and b) carbonyl stretching regions. Curves displaced arbitrarily along the *y* axis in steps of 10 °C.

Upon cooling from the isotropic to the nematic phase, the changes observed in the FTIR spectra of the two acids are essentially identical, and reveal a decrease in the concentration of monomeric (free) species and an increase in the concentration of cyclic dimers. This can be seen in Figure 6b from the simultaneous reduction of the 1720 cm^{-1} band and the increase of intensity in the low-frequency component of the 1690 cm^{-1} band, and is also consistent with the increase in intensity of the B-type Fermi bands seen in Figure 6a. In the case of CB6OBA, however, the FTIR spectra reveal differences between the conventional and twist-bend nematic phases in terms of the equilibrium between the different acid species. Specifically the relative concentration of cyclic and open dimers remains essentially constant in the twist-bend nematic range, although the concentration of monomeric species (free) continues to decrease.

We have seen that the liquid crystalline behavior of both CB6OBA and CBO5OBA may be attributed to the formation of cyclic hydrogen-bonded dimeric complexes between pairs of acid moieties yielding supramolecular liquid crystal trimers (see Figure 5). A conventional liquid crystal trimer consists of molecules containing three mesogenic units linked in a linear sense by two flexible spacers.[2] Here the central mesogenic

unit constitutes a cyclic dimer formed by hydrogen bonding between the benzoic acid moieties.

The nematic–isotropic transition temperature of CBO5OBA is 12 °C higher than that of CB6OBA while the associated entropy changes are essentially identical (see Table 1). In odd-membered liquid crystal dimers, replacing an ether by a methylene link reduces both the nematic–isotropic transition temperature and the associated entropy change,[18] and these reductions may be accounted for solely in geometric terms.[19] Specifically, the bond angle between the *para* axis of the mesogen and the first bond in the spacer is 113.5° for a methylene link and 126.4° for an ether link. This difference results in the all-*trans* conformation of an odd-membered methylene-linked liquid crystal dimer being more bent than its ether-linked counterpart. Even though a similar study on covalently bound liquid crystal trimers has not been performed, it is reasonable to assume similar relationships should be found, but, given the larger molecules and greater number of conformations available, that the differences between ether and methylene-linked liquid crystal trimers will be smaller than seen in liquid crystal dimers. This appears to be true in the case of the nematic–isotropic transition. By comparison, CB6OBA exhibits a N_{tb}–N transition temperature which is at least 31 °C higher than seen for CBO5OBA. This strongly suggests that the stability of the N_{tb} phase is more sensitive to changes in the average molecular shape than the nematic phase, and this may be accounted for in terms of the dependence of the bend elastic constant on molecular shape.[20] In Figure 5, the hydrogen-bonded complex formed by CB6OBA is shown as having a bent molecular shape. An alternative possibility is that the complex adopts an S-shape as seen for liquid crystal trimers[21] but in this case the N_{tb} environment preferentially selects the bent conformations.

A common feature amongst the small number of liquid crystal dimers known to exhibit the N_{tb} phase is a locally intercalated arrangement of the molecules within both the nematic phases. In the case of CB6OBA it was not possible to measure the effective molecular length in the nematic phases, but it is noteworthy that the lamellar spacing in the crystal phase of 27.3 Å is considerably shorter than the estimated molecular length of the all-*trans* supramolecular liquid crystal trimer of 38.8 Å. This implies an intercalated arrangement of the molecules in the crystal phase, and therefore, suggests an intercalated arrangement may also be present in the nematic phases. This strongly suggests that the intercalation of the molecules stabilizes the helical arrangement.

CB6OBA is the first example for which hydrogen bonding drives the formation of the twist-bend nematic phase and also provides the first example of a supramolecular liquid crystal trimer to show the N_{tb} phase. The transitional properties of CB6OBA are broadly similar to those observed for the small group of liquid crystal dimers known to show the N_{tb} phase, and this reinforces the view that molecular shape is a key factor in promoting the formation of the N_{tb} phase. It is important to note, however, that the temperature dependence of the concentrations of the hydrogen-bonded species differs in the two nematic phases. These differences suggest that the open hydrogen-bonded units play a significant role in stabilizing the helical arrangement found in the twist-bend nematic phase. A more detailed temperature-dependent FTIR spectroscopic study of these materials is now required to investigate this intriguing possibility.

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