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Spontaneous chirality through mixing achiral components: A twist-bend nematic phase driven by hydrogen-bonding between unlike components

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The spontaneous formation of a chiral phase *via* molecular recognition in a system consisting of achiral components is reported. Specifically, the liquid crystalline behaviour of two molecular complexes assembled by hydrogen bonding between a stilbazole-based template and alkoxybenzoic acids has been characterised. The complexes exhibit the heliconical twist-bend nematic phase (N_{TB}) over a broad temperature range despite the hydrogen-bond acceptor not being liquid crystalline and the donor exhbiting the conventional achiral nematic phase.

The recent discovery of the twist-bend nematic phase, N_{TB},[1] nearly 30 years after its prediction, first by Meyer[2] and later independently by Dozov[3] has generated considerable research interest. In the N_{TB} phase a conical helix is formed, in which the director is tilted with respect to the helical axis. The helices may be either left- or right-handed and equal amounts of both are expected to form. The helical pitch length in the N_{TB} phase is strikingly small, typically around just 10 nm,[4] which corresponds to 3-4 molecular distances. A particularly fascinating feature of the N_{TB} phase is the observation of spontaneous chirality in a fluid system composed of effectively achiral molecules. This breaking of mirror symmetry in a fluid is of fundamental importance in chemistry, physics and biology and believed to play a central role in the origin of biological homochirality.

The primary structural requirement for the observation of the N_{TB} phase is widely believed to be molecular curvature. This is in accord with Maier-Saupe theory for V-shaped particles, for which the N_{TB}-nematic (N) transition temperature is found to be particularly sensitive to the bend angle, and shows that the N_{TB} phase is formed only for a narrow range of molecular curvatures [5]. This molecular curvature is most often realised using dimers which consist of two mesogenic groups linked through a flexible spacer having an odd number of atoms[6]. Such molecules have, on average, a bent molecular shape in which the two mesogenic groups are inclined at some angle with respect to each other (see, for recent examples,[7]). If the N_{TB} phase is preceded by a conventional nematic phase with uniform director structure, this has an anomalously low bend elastic constant which may be exploited in new applications[8]. It should be noted, however, that the N_{TB} phase need not be preceded by a conventional nematic phase, and direct N_{TB}-isotropic phase transitions have been observed[9].

Hydrogen bonding has recently emerged as an alterative approach in the design of new twist-bend nematogens. Specifically, the N_{TB} phase exhibited by 4-[6-(4'-cyanobiphenyl-4-yl)hexyloxy]benzoic acid (***CB6OBA***) has been attributed to the formation of hydrogen-bonded complexes between pairs of acids yielding bent supramolecular complexes[10]. However, there is no element of molecular recognition in the ***CB6OBA*** system because the complexes consist of two identical molecules. Here for the first time we show that the N_{TB} phase can be induced in mixtures containing unlike hydrogen bond donors and acceptors and report the thermal behaviour of equimolar complexes between the hydrogen bond acceptor,4-[(E)-2-(4-{[6-(4'-methoxy[1,1'-biphenyl]-4-yl)hexyl]oxy}phenyl)ethenyl]pyridine (***1OB6OS***) and the hydrogen bond donor, alkoxybenzoic acid (***nOBA***) with different lengths of terminal alkoxy chain, *n* (Fig. 1).

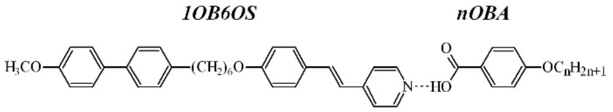

Fig. 1. Molecular structure of the hydrogen-bonded complex ***1OB6OS:nOBA***.

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These particular complexes were chosen for study because the overall odd-membered hexyloxy spacer has been shown to impart a sufficiently bent molecular shape to promote the N_{TB} phase in conventional liquid crystal dimers[11], and the hydrogen bond between pyridyl-based fragments and benzoic acids is strong enough to promote liquid crystalline complexes[12]. The synthesis of ***1OB6OS*** and characterisation methods are described in detail in the ESI. The equimolar binary mixtures of ***1OB6OS*** and ***4OBA*** or ***5OBA*** were prepared by co-dissolving pre-weighed amounts of each compound in dichloromethane and allowing the solvent to evaporate slowly at room temperature. The mixtures were further dried in a vacuum oven at 50 °C for 16 h. The phase properties of the ***1OB6OS:nOBA*** complexes and their components are listed in Table 1, and their DSC traces obtained on cooling from the isotropic phase and subsequent reheating are shown in Fig. S1 and S2.

Table 1. Phase transition temperatures (°C) and associated enthalpy changes (in parentheses, kJ mol^{-1}) extracted from the second heating trace unless noted otherwise.

	Phase sequence
4OBA	Cr 146.8 (17.9) N 158.9 (2.4) I
5OBA	Cr 126.1 (20.3) N 152.3 (1.9) I
1OB6OS	Cr 142.8 (93.0) I
1OB6OS:4OBA	Cr 121.9 (46.7) [SmX 86.2 (7.2) N_{TB} 109.4(≈0)]^b N166.4 (2.4) I
1OB6OS:5OBA	Cr 112.0 (39.3) [SmX 85.5 (4.1) SmA 93.5 (0.2) N_{TB} 98.0^a]^b N 157.7 (2.1) I

^{a} from microscopy; ^{b} extracted from cooling DSC scan.

The complexes show several LC phases and over a broad temperature range even though ***1OB6OS*** is not liquid crystalline and ***nOBA****,* with *n*=4 or 5, exhibits only a short temperature range nematic phase[13]. On cooling from the isotropic phase, the ***1OB6OS:4OBA*** complex exhibits two nematic phases distinguished by their optical textures: in cells with planar anchoring the upper temperature nematic phase shows a perfectly uniform texture, and at the transition to the lower temperature phase, a stripe texture develops characteristic of the twist-bend nematic phase (Fig. 2). The formation of the N_{TB} phase was accompanied by the cessation of the optical flickering due to director fluctuations observed in the nematic phase. The N–N_{TB} transition was detected using DSC as a small jump in the heat capacity (Fig. S2). This is in accord with the general observation that, as the temperature range of the preceding nematic phase increases, the N–N_{TB} transition tends towards becoming second order in nature, *i.e.* $\Delta H \approx 0$[7h]. In thin cells, in which sample crystallisation is suppressed, a reversible N_{TB}–smectic X (SmX) transition is detected (Fig. 2). Unfortunately, the monotropic nature of this phase precluded its study using X-ray diffraction, but given the large enthalpy change associated with the transition (Fig. S1), it is assumed to be a highly ordered smectic phase. For the ***1OB6OS:5OBA*** complex the temperature range of the N_{TB} phase narrows to ~5 K, insufficient for the stripe texture to develop. Below the N_{TB} phase, SmA and SmX phases are observed.

The N and N_{TB} phases have similar X-ray diffraction patterns with broad signals indicative of a liquid-like arrangement of the molecules. For ***1OB6OS:5OBA*** weak, broad signals in the low angle region correspond to spacings of about 39 Å and 13 Å while the estimated all-*trans* molecular length of the hydrogen-bonded complex is 39.4 Å. In the wide angle region both nematic phases show a broad signal corresponding to about 4.5 Å that is related to the molecular distance along the direction perpendicular to the director. The X-ray patterns indicate that the signals in the low angle region for both nematic phases correspond to the first and third harmonics in the crystal pattern (Fig. 3). The absence of the second harmonic in the nematic phases' patterns implies an unusual electron density profile along the director in the local aggregates (cybotactic groups). The reverse Fourier transform of the X-ray pattern gives an electron density profile with three maxima per repeating period. Assuming a head-to-tail molecular arrangement, the electron density maxima can be ascribed to the regions in which the aromatic fragments of neighbouring complexes overlap (Fig. 3). On decreasing the temperature for the ***1OB6OS:5OBA*** complex, the signal corresponding to the full molecular length sharpens showing that the smectic A phase locks to a monolayer structure with layer spacing ~ 40 Å, close to the molecular length of the complex.

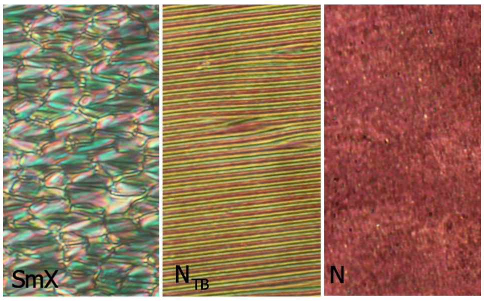

Fig. 2. Optical textures obtained for the equimolar **1OB6OS:4OBA** mixture in nematic (N), twist-bend nematic (N_{TB}) and SmX phases.

The temperature dependent Fourier transform infrared (FT-IR) spectra for the ***1OB6OS:4OBA*** complex show in the high frequency region (Fig. 4) the intense C-H stretching signals are superimposed on a broad band at ν ~ 2900 cm^{-1}, associated with the fundamental vibration of hydrogen-bonded hydroxyl groups, referred to as the Fermi A-type band[14]. The observation of the A-type band and the absence of contributions arising from free hydroxyl groups at ν >3500 cm^{-1} indicates strong hydrogen bonding. This view is further supported by the presence of Fermi B-type (~2700-2400 cm^{-1}) and C-type (~1900 cm^{-1}) bands[14]. The inset in Fig. 4 compares the high frequency region of the FT-IR spectrum for the

1OB6OS:4OBA complex to that of pure ***4OBA***. The absence of two well-defined maxima in the B-type region characteristic of benzoic acids[14], together with the shift of the band to lower frequencies, and the marked increase in the intensity in the C-type band also supports the formation of a hydrogen-bonded complex between the unlike components. The shift in the carbonyl stretching band from 1690 to 1700 cm^{-1} on cooling (Fig. 4) further confirms the formation of the ***1OB6OS:4OBA*** complex[10b].

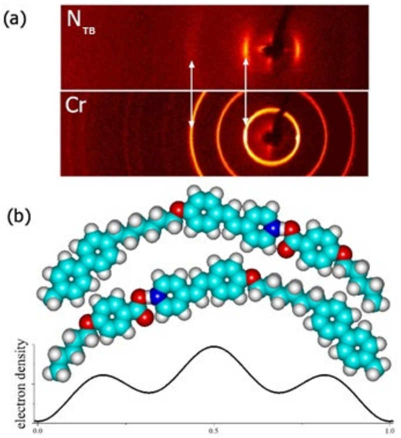

Fig. 3. (a) X-ray patterns obtained in the N$_{TB}$ phase near the transition to the SmA phase, and in the crystal (Cr) for **1OB6OS:5OBA**, clearly the second harmonic in the N$_{TB}$ phase is missing. (b) Sketch of a head-to-tail molecular arrangement and corresponding electron density profile with three nearly equally spaced maxima per complex length, obtained by reverse Fourier transform of the X-ray signals (all Fourier components are taken as positive, their magnitude is the square root of the signal intensities after Lorentz correction).

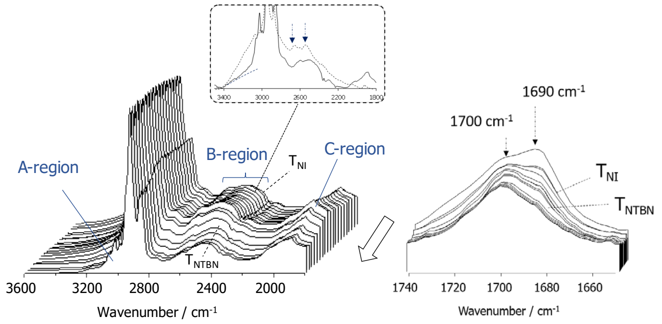

Fig. 4. Temperature dependence of the FT-IR spectra of the **1OB6OS:4OBA** complex; broad arrow indicates the direction of cooling from 179°C to 77°C. (left) High-frequency range showing the Fermi vibration bands. Inset shows a comparison of the spectra of **4OBA** (dotted curve) and the **1OB6OS:4OBA** complex (solid curve) in the isotropic phase, the dotted arrows highlight the B-type bands seen for **4OBA**. (right) Carbonyl stretching region.

The geometric parameters, electronic properties, and hydrogen bond dissociation energies of the ***1OB6OS:4OBA*** complex were determined using quantum mechanical density functional theory (DFT) calculations (see the ESI for details). Geometric optimisation was performed with the spacer in the all-*trans* conformation. It is known, however, that for dimers containing the hexyloxy spacer the gauche state of the O-C-C-C dihedral is more stable than the *trans* state[11] due to favourable interactions between the oxygen atom and the CH$_2$ group. Thus geometric optimisation was also performed with the spacer containing this gauche state. The space filling models and electrostatic potential isosurfaces for the ground state and all-*trans* conformations of the ***1OB6OS:4OBA*** complex are shown in Fig. 5. The ground state of the complex was found to contain the gauche linkage although the difference in energy between the two states is small, 0.8 kJ mol^{-1}, and this is likely to be substantially different in an ordered liquid crystal phase in which the more linear all-*trans* conformation will be favoured[15]. Both conformations show a bent geometry consistent with the observation of the N$_{TB}$ phase, and also possess a lateral dipole moment which may assist in the packing of these bent structures.

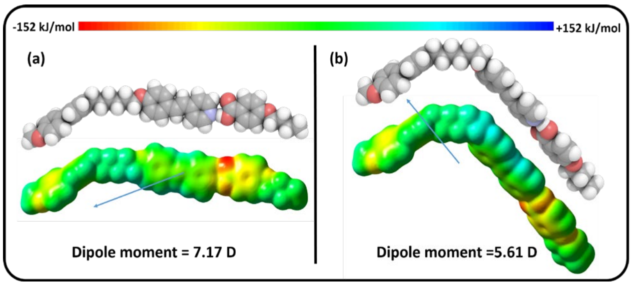

Fig. 5. The space filling model (top) and electrostatic isosurface (lower) for (a) the all-*trans* conformation of the **1OB6OS:4OBA** complex and (b) the ground state of the complex in which the spacer in the **1OB60S** fragment contains a gauche conformation.

The hydrogen bond dissociation energy of the complex was estimated by comparing the energy of the all-*trans* conformation of the ***1OB6OS:4OBA*** complex with that of the system in which the hydrogen bond length had been increased to 5 Å. Similar calculations were performed for the acid dimer, see Table S1 in the ESI, which lists the calculated hydrogen bond lengths and dissociation energies of the two systems. The hydrogen bond length is shorter in the ***4OBA*** dimer (1.672 Å) than in the ***1OB6OS:4OBA*** complex (1.759 Å) and the dissociation energy higher (86.50 and 61.41 kJ mol^{-1}, respectively). However, it should be remembered that the **4OBA** dimer contains two hydrogen bonds such that the bond dissociation energy per hydrogen bond is 43.25 kJ mol^{-1}, and considerably smaller than that seen for the hydrogen bond in the ***1OB6OS:4OBA*** complex. This is consistent with the interpretation of the FT-IR spectra. Although the single ***4OBA*** dimer is enthalpically favourable over a single ***1OB6OS:4OBA*** complex, in the equimolar mixture of ***1OB6OS*** and ***4OBA***, the ***1OB6OS:4OBA*** complex is both enthalpically and entropically favoured. The hydrogen bond in the ***1OB6OS:4OBA*** complex is relatively weak but sufficient to stabilize the molecular complex.

In summary, hydrogen-bonded complexes of achiral ***1OB6OS*** and ***nOBA*** show twist-bend nematic behaviour providing an example of how molecular recognition can induce spontaneous chirality in a condensed phase. Molecular curvature is widely thought to be the critical structural parameter in promoting the N_{TB} phase. This is normally described in terms of the angle subtended by the long axes of the two mesogenic units and their relative lengths, although we note that the relative length of the spacer also contributes to the curvature of molecule. In the ***1OB6OS:nOBA*** complexes, the curvature is determined by the shape of the hydrogen bond acceptor, ***1OB6OS***, which by itself does not show liquid crystalline behaviour even on supercooling the isotropic phase to temperatures around 105˚C. Thus, hydrogen bonding is not driving the formation of the N_{TB} phase simply as a result of the creation of a bent complex, as was the case for ***CB6OBA***[10a]. Instead, in the ***1OB6OS:nOBA*** complexes hydrogen bonding extends the length of one of the mesogenic units creating a hockey-stick-shaped unit, and raises the question as to how to define the molecular curvature for such a unit. Presumably, the induction of the twist-bend nematic phase in the ***1OB6OS:nOBA*** complexes is associated with changes in properties such as the elastic constants arising from the hydrogen bonding but how this is related to shape is unclear. Increases in the N_{TB}-N transition temperatures have been observed for similarly shaped conventional covalent molecules[16]. We also note that for **CB6OBA** an additional driving force was considered to be the formation of laterally hydrogen-bonded chains which may stabilize the helical arrangement found within the twist-bend nematic phase[10b] and the dynamic nature of the hydrogen bond. These intriguing possibilities are now the subject of further study.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

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