Spontaneous symmetry-breaking in halogen-bonded, bent-core liquid crystals: observation of a chemically driven Iso–N–N* phase sequence†‡

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A chiral nematic phase is observed in a halogen-bonded, bent-core mesogen, which is itself achiral; the phase sequence arises from the lability of the halogen-bonded complex.

In the last ten years or so, bent-core liquid crystals have become a major area of interest, initiated by the observation of the formation of, and switching behaviour in, chiral mesophases formed from achiral molecules.[1] In these systems, symmetry-breaking arises from the reduced symmetry (C_{2v}) of the molecules coupled with tilting in the layered phases.[2]

As part of our work using stilbazoles as components of liquid-crystalline and other functional molecular materials,[3] we demonstrated that halogen bonding[4] could be employed as a new interaction leading to the formation of liquid-crystalline complexes from non-mesomorphic components. Our initial paper[5] described stilbazole:pentafluoroiodobenzene complexes, which showed nematic and/or smectic A phases as a function of chain length, and subsequently we reported on the formation of trimeric systems from stilbazoles and α,ω-diiodoperfluoroalkanes,[6] and from 1,4-diiodotetrafluorobenzene with Metrangolo et al. (Fig. 1).[7] Other trimeric and polymeric examples have also been reported.[8]

To expand halogen-bonded mesogens into the arena of bent-core systems, we undertook a study of 2 : 1 complexes (Fig. 2) formed between stilbazoles and 1,3-diiodotetrafluorobenzene.[9]

Complexation was achieved by co-crystallisation of the two components from THF by slow evaporation of the solvent at 2 °C. Single crystals suitable for X-ray analysis could only be obtained of the hexyloxy derivative 1-6; crystals of other complexes always exhibited significant disorder along one crystallographic axis.

The molecular structure of 1-6 is shown in Fig. 3, confirming the bent nature of the complex.[10] The unit cell‡ contains the two independent 1-6 complexes and 1.5 molecules of THF (see ESI†)—bend angles for the two different complexes (measured from the oxygen of each stilbazole to the centroid of the central benzene ring) are 113.2 and 106.2°. In one complex, the two stilbazoles and the diiodotetrafluorobenzene core are almost co-planar, and the N⋯I distances are 2.830(15) and 2.905(10) Å, with the associated C4$_{pyr}$–N–I angles being 171.2 and 173.4°,

respectively. The other complex (Fig. 3) has a more twisted structure, but while the N⋯I distances are identical with those of the first complex, the C4$_{pyr}$–N–I angles this time are 166.5 and 161.5°, respectively. The N⋯I distances are, on average, somewhat longer when compared to a complex of iodopentafluorobenzene and stilbazole (2.81 Å),[5] but are still about 18–22% shorter than the sum of the van der Waals radii for I and N. As far as the C4$_{pyr}$–N–I angles are concerned, the more acute examples were found to be associated with longer N⋯I distances, indicating a weakening of the halogen bond as this angle deviates from its ideal value of 180°. These magnitudes are in the typical range of halogen-bonded pyridine–iodine complexes.[4]

The liquid crystal phase behaviour of the new materials was studied by polarising optical microscopy (POM) and differential scanning calorimetry (DSC). On heating, all complexes melted directly to the isotropic phase, but on cooling exhibited a monotropic nematic phase about 25 °C below the melting point (for data, see ESI†). In complexes 1-6 and 1-10, this phase is observed only transiently before rapid crystallisation takes place, but with complex 1-8, it was possible to observe monotropic mesomorphism consistently and over several degrees.

Thus, during the isotropic-to-nematic phase transition, a wavefront of nematic phase with a typical schlieren texture (Fig. 4A) passed through part of the visible area. A second transition then followed in close succession to generate a very fluid texture consisting of large, birefringent planar domains with well-defined boundaries (Fig. 4B). The chiral nature of the phase was shown clearly upon rotating the analyser, when dark domains turned light and *vice versa* (Fig. 4C and D), indicating that the different domains are chiral and exhibit opposite handedness. The preceding nematic phase was clearly not chiral. Both events were clearly detected by DSC during the cooling cycle (Fig. 5) as overlapping transitions. On reheating, microscopy clearly showed the sequence reverse.

Transitions from nematic to chiral nematic phases are forbidden on symmetry grounds unless the N* phase contains both right- and left-handed helical structures. This is clearly the case here, but one aspect of the Iso–N–N* transition that we found puzzling was in the DSC data. Transitions from nematic to isotropic phases have small enthalpies (typically 1–2 kJ mol^{-1}),
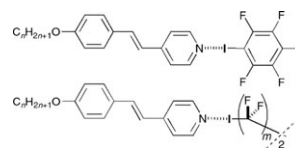
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‡ CCDC 671520 and 671521. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719555a
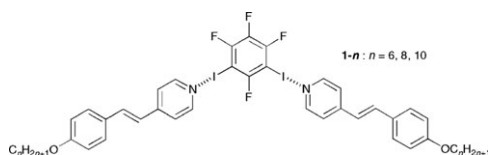

Fig. 1 Examples of known halogen-bonded liquid crystals.

Fig. 2 The bent-core, halogen-bonded complex.

and this will be the same for an N–N* transition too. Fig. 5 shows that the Iso–N transition does indeed have a small change in enthalpy (0.9 kJ mol^{-1}), but the transition to N* has a rather large enthalpy (7.3 kJ mol^{-1}), which is unexpected.

Recently, we reported on the mesomorphism of 2 : 1 complexes formed between stilbazoles and 1,4-diiodotetra-fluorobenzene.[7] In this paper, we speculated that at the N–Iso transition, there was some dissociation of the N···I halogen bond. The main reason behind this was the fact that, for both single compounds and mixtures, the clearing point was effectively independent of the chain length of the stilbazole. Support for this proposal came from DSC data recorded for a mixture with an enantiotropic nematic range, which showed an enthalpy change at the N–Iso transition of some 8 kJ mol^{-1}. This large enthalpy change was attributed to halogen bond breaking/formation (for the full trace, see the ESI†).

The materials described in that paper are simple isomers of the materials described here, and so we began to wonder whether analogous behaviour may be responsible, and if so, how this might help account for both the observed meso-morphism *and* the large observed enthalpy change.

As a first step, it was found possible to crystallise a 1 : 1 complex between methoxystilbazole and 1,3-diiodotetrafluoro-benzene, and a representation of the structure is given in Fig. 6. The structure shows the expected N···I halogen bond, with an N···I separation of 2.801(4) Å. However, devoid of a second nitrogen to bind to, the second iodine now forms a halogen bond to the methoxy oxygen to give a pseudo linear polymer, in which the O···I distance is 3.080(3) Å. Halogen bonds to oxygen are equally well known, and have structural parameters comparable with those of halogen–nitrogen analogues.[4]

While this complex is not mesomorphic, analogous preparations using 4-octyloxystilbazole were. Growing single crystals has not yet proved possible, and so the complex was obtained by melting the components together with a small excess of stilbazole (*ca.* 10%), required to observe the mesophase. The material so-obtained melted at 89.5 °C to the isotropic state, and then formed a nematic phase at 64 °C, extremely close to the temperature observed in the 2 : 1 system (68 °C). However,
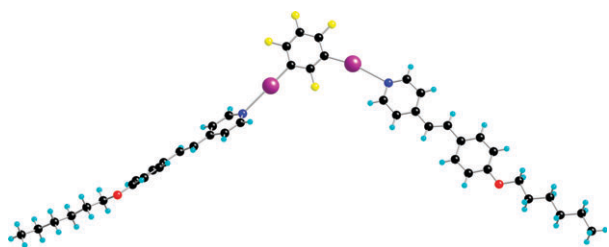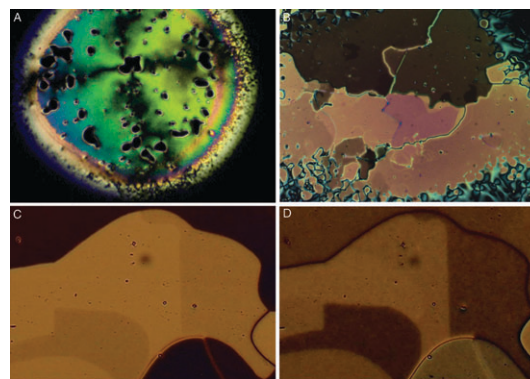

Fig. 4 Optical textures of **1**-8: (a) Iso–N transition, (b) the planar texture of the N* phase; (c) and (d) the N* phase with the polarisers uncrossed in one direction (c) and then the other (d).

no other phase transitions were seen on further cooling, and the nematic phase eventually crystallised homogeneously.

Returning to the 2 : 1 complexes, we propose the following explanation for their behaviour. In common with the proposal advanced for the complexes of 1,4-diiodotetrafluorobenzene, we believe that there is some rupturing of the N···I halogen bonds on melting to the isotropic fluid, leaving a mixture composed predominantly of the 1 : 1 complex plus free stilbazole. On cooling, the 1 : 1 complex, which is approximately linear, forms a nematic phase (small ΔH from DSC), and almost immediately after, the 2 : 1 complex reforms (large enthalpic change in the DSC). By virtue of the 1,3-relationship between the two iodines, the 2 : 1 complex is bent, and so the chiral nematic phase can form. Thus, the N–N* transition is in fact driven *chemically*.

So what of the observation of a chiral nematic phase in these achiral complexes? The observation of phases with sponta-neously broken symmetry in bent-core mesogens is well known when they exist in *layered* phases, and they arise in one of two ways. In the first, the low-symmetry molecules (C_{2v} symmetry) pack into layers and then tilt, and there are four possible ways in which this can happen. Of these, the synclinic ferroelectric and anticlinic antiferroelectric arrangements (so-called SmC$_S$P$_F$ and SmC$_A$P$_A$, respectively) lead to two enantiomeric possibilities (see ESI†). In this case, symmetry-breaking is simply the result of low-symmetry packing of low-symmetry molecules. The other case relates to so-called 'conglomerate' phases, most examples of which are low bi-refringence variants of the family of B$_2$ phases. The origin of symmetry-breaking is unclear in these cases, but is manifest due to the co-existence of domains of opposite chirality. An important additional observation relates to the B$_7$ phases of
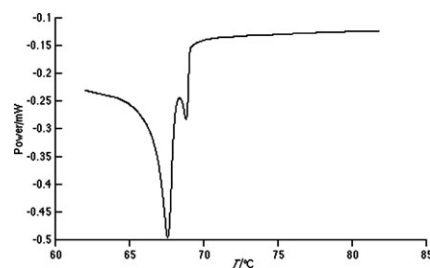

Fig. 3 Molecular structure of one of the independent **1**-6 complexes.

Fig. 5 DSC trace of **1**-8 on cooling showing I–N and N–N* transition.
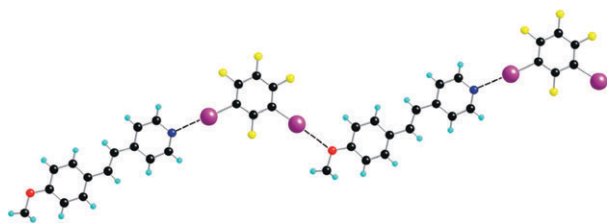
Fig. 6 The polymeric structure of a 1 : 1 complex between an alkoxystilbazole and 1,3-diiodotetrafluorobenzene showing the I···O halogen bonding.

bent-core mesogens, where the observed textural helicity is a consequence of the nucleation event, and so there is no superstructural chirality in the phase. Nevertheless, there is helicity of molecular orientation within the individual layers (domains within the layers that change sign as a sensitive function of temperature on a length scale of *ca.* 10^1 to 10^3 Å), which arises as the phase escapes from an arrangement that would otherwise be ferroelectric.

The observation of chirality in the nematic phase of bent-core materials does have a limited precedent. Pelzl *et al.* reported the first example in a chlororesorcinol (**2**),[11] Niori *et al.* described a material based on an unsymmetric 3-hydroxybenzaldehyde core (**4**),[12] while Görtz and Goodby[13] identified its existence in some 2,5-disubstituted oxadiazoles (**3**)—structures that have been reported to show the biaxial nematic phase[14] (Fig. 7). Considering these structures and comparing them with the present materials reveals little by way of common structural features. Compounds **1** and **2** are flexible at the centre, whereas **4** is not, although **4** does have a strong, lateral dipole moment. The bend angle for **4** (at least in the static structures) is rather shallow, yet it is more acute in **1**. Both **2** and **3** will be required to twist due to the presence of sterically demanding chlorine atoms.

Studies of the chiral nematic phase of **2** by X-ray diffraction[15] implied the presence of chiral, tilted, cybotactic domains (tilt angle close to $50°$), with an equivalent population of the opposite chirality. It is interesting that this material goes on to form a conglomerate phase on further cooling, meaning that this nematic phase is, in some regards, a pre-transitional state. The transient nature of the phases has meant that, so far, similar measurements have not been made here. In their review of bent-core systems, Reddy and Tschierske[1] suggest that in layered conglomerate phases, conformational chirality could exist and, as the layers are rather well correlated, be stabilised. Conformational chirality is also at the heart of the proposal by Görtz and Goodby,[13] but in the nematic phase, there are no layers that exist to stabilise such an arrangement.
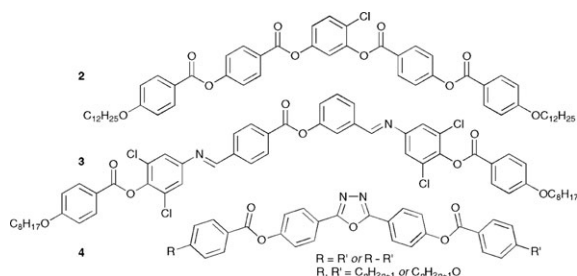
However, it is worth considering that reduced phase symmetry may contribute to the origin of the chiral structure. Theoretical studies[16] have predicted the existence of nematic phases with symmetry lower than $D_{\infty h}$ in bent-core mesogens, and one of these phases is the biaxial nematic phase N_B, with D_{2h} symmetry.[17] Furthermore, Dozov has predicted that bent-core mesogens might exhibit a negative bend elastic constant (k_{33}),[18] causing a local bend of the director and inducing a conical twist–bend deformation, resulting in a transition to a helical superstructure. This exact phenomenon was later found in a Monte Carlo simulation.[19]

Given that there is evidence that compounds **4** have a biaxial nematic phase, it could be that the chirality is an expression of the N_B phase. However, having D_{2h} symmetry—*i.e.*, the presence of three mirror planes—it is not clear why the system would wish to twist-up, as the net polarisation is already zero. However, if the phase symmetry were lowered further to C_{2v}, then the system would be polar, and so an escape from this polarity would be more understandable. Of course, C_{2v} symmetry is a characteristic of the ferroelectric nematic phase, and so such a thought is advanced with due caution and will, of course, require rigorous examination.

Fig. 7 Structures of other compounds showing spontaneous symmetry-breaking in the nematic phase.

Notes and references

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