# Trimeric liquid crystals assembled using both hydrogen and halogen bonding†

**Carsten Präsang,[a] H. Loc Nguyen,‡[a] Peter N. Horton,[b] Adrian C. Whitwood[a] and Duncan W. Bruce*[a]**

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**New liquid crystals are reported that are formed from non-mesomorphic components assembled using both halogen and hydrogen bonding.**

The use of non-covalent interactions to realise new liquid-crystalline species has become an area of increasing interest in recent times.[1] Thus, use of quadrupolar[2] and charge-transfer[3] interactions has been shown to lead to new mesomorphic materials, while hydrogen-bonded liquid crystals have been the subject of a resurgence in interest following the elegant studies by Kato and Fréchet and co-workers in the 1990s.[4]

We have worked extensively with alkoxystilbazoles as components of various types of molecular materials[5] and, as part of these studies, have investigated hydrogen-bonded systems, primarily employing phenols as the hydrogen donor.[6] More recently, we became aware of the work pioneered mainly by the Milan group that uses halogen bonding[7,8] to construct a number of supramolecular motifs. Taking note of the analogy between hydrogen bonding and halogen bonding, we reported the first examples of liquid crystals formed employing the latter interaction.[9] Thus, we reported that a complex could be formed between a 4-alkoxystilbazole and iodopentafluorobenzene (Fig. 1) and that while neither component was liquid crystalline, the resulting complexes showed nematic and smectic A mesophases. Subsequently, with Metrangolo, Resnati and others we reported on the formation of trimeric systems from stilbazoles in combination with α,ω-diiodoperfluoroalkanes[10] and with 1,4-diiodotetrafluorobenzene.[11] Other trimeric and polymeric examples have also been reported.[12] More recently, we have reported on spontaneous symmetry breaking in the mesophases of alkoxystilbazole complexes of 1,3-diiodotetrafluorobenzene.[13]

The levels of control that can be exerted in assembling molecular units into useful materials potentially increase if more than one interaction is used and so we were intrigued to see what might result from using both hydrogen- and halogen-bonding to assemble new liquid-crystalline species. Indeed, Aakeröy *et al.* recently reported the creation of infinite, one-dimensional chains using isonicotinamide in conjunction with iodine and with 1,4-diiodotetrafluorobenzene.[14]

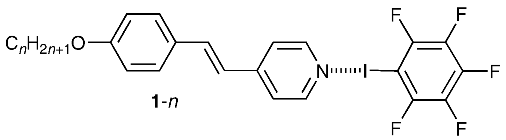

**Fig. 1** Structure of the first halogen-bonded liquid crystals.

We therefore prepared some complexes of 4-alkoxystilbazoles with 4-iodotetrafluorophenol[15] (Fig. 2) and were curious to see whether the mesomorphism would reflect the angular geometry suggested by the combination of linear halogen and hydrogen bonds (Fig. 2). Thus, complexes with a 2 : 1 (stilbazole : iodophenol) stoichiometry (**2**-4 to **2**-10) were prepared by crystallisation from thf solutions and, in the case of **2**-6, detailed structural information in the solid state was obtained by solving the single crystal X-ray structure.† Complex **2**-12 was prepared as described below for **4**-*n*.

Two views of the structure are shown in Fig. 3 and they reveal both that the three components of the complex are close to being co-planar and that, despite what might have been predicted, the overall shape of the complex is rather rod-like. This is due to the non-linear nature of both the halogen and hydrogen bonds, so that the *ipso*-C–$N_{pyr}\cdots$I angle is 164.88°, while the *ipso*-C–$N_{pyr}$–$O_{phenol}$ angle is 161.07°, the combination of which means that the two *ipso*-C–$N_{pyr}$ vectors are within 4.06° of being parallel. The halogen bond in the complex is 2.872 Å long and it is often the case that longer bonds tend to lead to greater

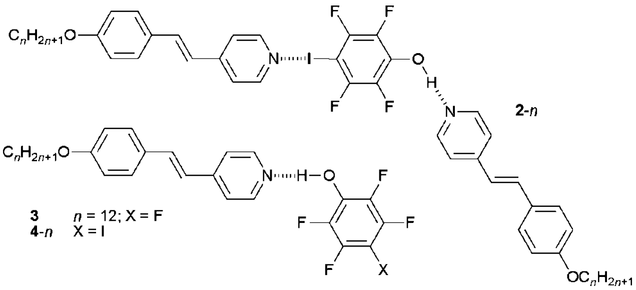

**Fig. 2** The 2 : 1 complex of stilbazole and 4-iodotetrafluorophenol (**2**-*n*); the 1 : 1 complex between 4-dodecyloxystilbazole and pentafluorophenol (**3**) and between stilbazole and 4-iodotetrafluorophenol (**4**-*n*).

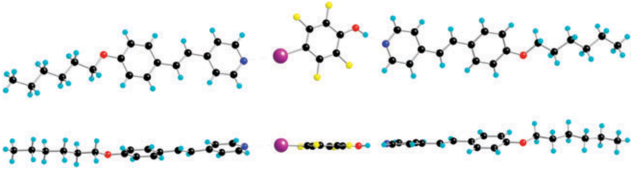

**Fig. 3** Two views of the molecular structure of complex **2**-6.

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[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: db519@york.ac.uk; Tel: +44 1904 434085*
[b] *EPSRC Crystallographic Service, Department of Chemistry, University of Southamton, Southampton, UK SO17 1BJ*

† Electronic supplementary information (ESI) available: Crystal data for **2**-6, **3** and **4**-1; representation of disorder and helical arrangement in **4**-1. CCDC 694375–694377. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811716k

‡ Present address: High Force Research Limited, Bowburn North Industrial Estate, Bowburn, Durham, UK DH6 5PF.

deviations from linear halogen bonds. However, at 164.88°, the deviation is greater than that typically observed for such an N···I separation, suggesting that the more efficient crystal packing offered by the more anisotropic motif is likely responsible for this greater bending of the angle. However, space-filling models indicate that interaction between the nitrogen non-bonded electron pair and the σ-hole[16] on the iodine is still readily possible. Interestingly, this results in the two I–C–$C_{ring}$ angles being 123.1° and 120.2°, although it is noted that a similar effect is seen in the structure of **1**-8.[9] The hydrogen bond is also distorted from an ideal alignment, contributing to the linearity. The hydrogen was positioned in riding mode and was placed at 0.91 Å from oxygen and 1.69 Å from nitrogen with an O–H···N angle of 169°. The angle at oxygen (C–O–N) is 130°, deviating appreciably from the ideal value of close to 105°.

As 4-iodotetrafluorophenol presents two possible sites with which the stilbazole nitrogen can interact and because we have already given examples of the lability of halogen bonds at elevated temperatures,[11,13] we then elected to prepare some examples of a 1 : 1 complex. Grown from thf solution, single crystals of **4**-4 showed the stilbazole *hydrogen* bonded to the phenol with a molecule of thf *halogen* bonded to the iodine; this structure will be reported separately. However, grown from diethyl ether, a solvent-free, 1 : 1 complex of **4**-1 was obtained in which the stilbazole is hydrogen bonded to the phenolic hydrogen (see Fig. 4). Thus, the stilbazole nitrogen is hydrogen bonded to the phenolic oxygen and there is an N···O separation of 2.596 Å. The hydrogen is attached to oxygen ($d_{O–H}$ = 0.80 Å and $d_{H\cdots N}$ = 1.82 Å) and the hydrogen bond is not linear so that the $C_{ipso}$–N–$O_{phenol}$ angle is 159.8°, with an O–H···N angle of 165° (hydrogen located by difference map). The stilbazole itself is almost planar but makes an angle of nearly 120° to the plane of the phenolic ring. Then, in common with the structure of a 1 : 1 complex of methoxystilbazole with 1,3-diiodotetrafluorobenzene,[13] the iodine forms a halogen bond to the ether oxygen of the methoxy group, leading to a polymeric arrangement, this time *via* both hydrogen and halogen bonding. The I···O distance is 3.05 Å and the C–I···O angle is 175.16°; these data compare with 3.08 Å and 171.06°, respectively, as reported previously.[13] The stilbazole is disordered by virtue of occupying two positions, related by a 180° rotation about the N–O axis. The two sites for each of the ethylenic carbons were resolved readily and are included in the model. Separate positions for the carbons of the aromatic rings could not, however, be resolved, and the disorder manifested itself by an elongation of the ADP ellipsoids for these atoms, which increased with proximity to the double bond. The relative proportions of each stilbazole was refined in the ratio 70 : 30. Representations of the disordered structure are found in the ESI.† Curiously, the complex crystallised in the chiral space group $P2_12_12_1$, the origin of the chirality being a right-handed, helical precession of the polymer as shown in the ESI.† We assume that the handedness in this structure is random and that other crystals will have the enantiomeric arrangement.

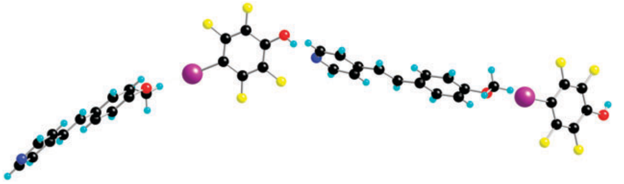
**Fig. 4** The crystal structure of **4**-1, showing the two halogen bonds.

Interestingly, we note that both here and previously,[13] solvent-free, 1 : 1 complexes were obtained only when the terminal chain was methoxy. This suggests that there is a substantial driving force for the second iodine to find something with which to interact (in this case forming a halogen bond with the oxygen of the methoxy group) and that the stepped, polymeric arrangement found in each case is sterically incompatible with longer chains.

It is interesting that in this example, the stilbazole coordinated preferentially *via* a hydrogen bond, which is intuitively what might have been expected due to the generally lower strength and higher lability of halogen bonds in such simple, neutral systems. However, there is a report from Corradi *et al.*[17] where, in competitive experiments, the halogen-bonded polymer between 1,2-bis(4-pyridyl)ethane and 1,4-diiodotetrafluorobenzene was found to crystallise in preference to the analogous polymer where 1,4-hydroquinone acted as the Lewis acid.

For the purposes of comparison, the single crystal structure of the complex between dodecyloxystilbazole and pentafluorophenol was obtained; the molecular structure is shown in Fig. 5. The structure shows some broad similarities to that of **2**-6 in respect of the hydrogen bond, so that the *ipso*-C–$N_{pyr}$–$O_{phenol}$ angle in **3** is 166.67(12)°, somewhat straighter than that found in **2**-6 yet still some 13° from linear; the N–O–C angle is 128°. The hydrogen (again located by difference map is once more attached to oxygen ($d_{O–H}$ = 0.95 Å and $d_{H\cdots N}$ = 1.69 Å) and $d_{N\cdots O}$ = 2.612(3) Å.

In order to study the thermal properties of the bulk materials, the complexes were prepared by crystallisation from thf to give crystalline solids, which were characterised by elemental analysis. Thus, the thermal properties of the materials were investigated by polarised optical microscopy and the transition temperatures are collected in Table 1. The shortest-chain homologue investigated, **2**-4, showed a high melting point (*ca.* 117 °C) below which a monotropic nematic phase was identified from its characteristic schlieren texture with two- and four-brush disclinations. The remainder of the complexes studied showed enantiotropic mesophases. Thus, while the clearing points did not vary very much with chain length, the melting point dropped sharply for **2**-6 by almost 30 °C to 88.4 °C (compared to **2**-4), while the clearing point of the nematic phase was identical to that of **2**-4. As the chain length increased through $C_8$ to $C_{10}$ and $C_{12}$, the stability of the nematic phases dropped slightly reaching a minimum at **2**-10 (100 °C), recovering slightly at **2**-12 (102 °C), for which homologue a SmA phase is observed for two degrees above the melting point.

Consistent with their structural similarity, the stability of the nematic phases of these 2 : 1 complexes is comparable with that of the 2 : 1 complexes of alkoxystilbazoles with 1,4-diiodotetrafluorobenzene[11] where, for example, the $C_8$ and $C_{10}$ homologues clear ($T_{NI}$) at 113.5 and 109 °C, respectively. The slightly lower phase stability in the present case is most likely due to the complexes adopting a more angular shape in the fluid phase consistent with

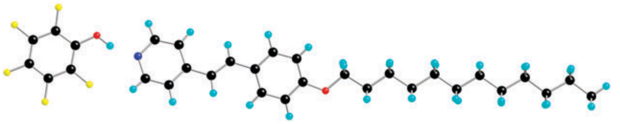
**Fig. 5** The molecular structure of **3**.

**Table 1** Thermal behaviour of the new complexes

| Complex | Transition | $T$/°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|
| **2**-4 | Cr–I | 116.5 | 60.4 |
| | (N–I)[a] | (107.4) | (2.8) |
| **2**-6 | Cr–N | 88.4 | 57.6 |
| | N–I | 107.4 | 2.1 |
| **2**-8 | Cr–N | 85.6 | 88.8 |
| | N–I | 101.7 | 2.5 |
| **2**-10 | Cr–N | 89.8 | 62.0 |
| | N–I | 100.0 | 1.9 |
| **2**-12[b] | Cr–SmA | 97.8 | — |
| | SmA–N | 100.2 | 86.9[c] |
| | N–I | 102.0 | 5.4 |
| **3**[d] | Cr–I | 96.0 | 49 |
| | (SmA–I) | (94.0) | (2.0) |
| **4**-4[b] | Cr–I | 105.8 | 29.9 |
| **4**-6[b] | Cr–I | 103.6 | 34.0 |
| **4**-8 | Cr–I | 107.0 | 56.5 |
| | (N–I) | (92.4) | (1.8) |
| **4**-10[b] | Cr–SmA | 85.2 | 28.1 |
| | SmA–I | 98.1 | 1.5 |
| **4**-12[b] | Cr–SmA | 87.1 | 39.9 |
| | SmA–I | 102.1 | 3.9 |

[a] Monotropic transitions in parentheses. [b] Prepared by evaporation of 1 : 1 solution in thf. [c] Combined enthalpy for Cr–SmA–N; not resolved by DSC. [d] Data from ref. 5.

slightly more linear halogen and hydrogen bonds, able to form when the constraints of crystal packing are lifted.

In previous studies of trimeric, halogen-bonded liquid crystals containing two stilbazole molecules,[11,13] we had postulated the dissociation of one of these at the clearing point, evidenced by the rather large enthalpy changes observed (typically 8 to 9 kJ mol$^{-1}$). The clearing enthalpies for **2**-*n* are much smaller at between 2 and 3 kJ mol$^{-1}$, which we take as evidence that clearing is not accompanied by dissociation. Certainly studies carried out on purely hydrogen-bonded liquid crystals showed conclusively that clearing was neither driven nor accompanied by rupture of the hydrogen bond[18] and so in the present materials where there is only one halogen bond, the clearing transition appears to be that of the intact complex.

1 : 1 Complexes (**4**-*n*) between the stilbazoles and 4-iodotetrafluorophenol were also obtained for comparison. Preparation of these complexes was not so straightforward and only for **4**-8 was a crystalline complex obtained from thf. We believe that this complex had thf halogen bonded to the free iodine, but this thf is readily removed *in vacuo* and does not influence the mesomorphism. Indeed, **4**-8 was the first homologue to show any mesomorphism and, following melting to the isotropic phase at 107.0 °C, a monotropic nematic phase was found at 92.4 °C. Because of the difficulty associated with preparing crystalline derivatives, other homologues were obtained by dissolving the components together in thf, evaporating the solvent slowly and then finally pumping to ensure complete removal. While we have found this method to be very good where hydrogen-bonded materials are concerned, in general it has proved less satisfactory where halogen-bonded materials are concerned. Nonetheless, we re-prepared **4**-8 by this method and found Cr–I at 105.8 °C and (I–N) at 90.2 °C. The lower temperatures and slightly broader transitions are indicative of a material that is not perfectly pure, which in this case means that it is not single phase. Nonetheless, the temperatures are rather close and so for the purposes of comparison, it was felt that the data were acceptable and fit for purpose. Thus, the higher homologues, namely **4**-10 and **4**-12, showed enantiotropic SmA phases. Complex **4**-10 melted at 85.2 and cleared at 98.1 °C, while **4**-10 melted at 87.1 and cleared at 102.1 °C.

It is interesting to compare these temperatures with those of complex **3** and also complexes **1**-*n*.[9] Thus, **3** also shows a SmA phase but in this case, the crystal phase is more stable and so it appears monotropically with $T_{\mathrm{SmA-I}}$ at 94 °C. Similarly, **1**-12 also showed a SmA phase, this time enantiotropic melting at 81 and clearing at 84 °C. Thus, the transition temperatures are lower where stilbazole is bound to $C_6F_5I$ when compared to $C_6F_5OH$, and lower where the stilbazole is bound to $C_6F_5OH$ rather than $p$-$IC_6F_4OH$. On one hand, this would suggest that the more electrostatic nature of the hydrogen bond contributes favourably to phase stabilisation, and on the other it suggests that $p$-$C_6F_4$–I is a more effective terminal group than $p$-$C_6F_4$–F for phase stabilisation, presumably due to the great polarisability anisotropy.

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