ChemComm

RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 3946

Received 15th February 2013,
Accepted 20th March 2013

DOI: 10.1039/c3cc41227j

www.rsc.org/chemcomm

Halogen-bonded liquid crystals of 4-alkoxystilbazoles with molecular iodine: a very short halogen bond and unusual mesophase stability†

Linda J. McAllister,[a] Carsten Präsang,[a] Joanna P.-W. Wong,[a] Robert J. Thatcher,[a] Adrian C. Whitwood,[a] Bertrand Donnio,[b] Peter O'Brien,[a] Peter B. Karadakov[a] and Duncan W. Bruce*[a]

Complexes of molecular iodine with alkoxystilbazoles are liquid crystals with unusually high mesophase stability, predicated on an intermolecular I···I contact. Attempts to prepare analogous complexes with bromine led to an unexpected electrophilic substitution product.

Halogen bonding is an established tool in supramolecular chemistry.[1] Some time ago, we reported the first examples of liquid crystals formed using halogen bonding, namely complexes between an alkoxystilbazole and pentafluoroiodobenzene.[2] Since then, we have obtained 2 : 1 complexes of stilbazoles with α, ω-diiodoperfluoroalkanes,[3] with 1,4-[4] and 1,3-diiodotetrafluoro-benzenes[5] (the latter showing chiral mesophases in the absence of molecular chirality) and 2,3,5,6-tetrafluoro-1-iodophenol,[6] as well as performing an extensive study of more than ninety 1 : 1 complexes.[7] Keen to extend the range of materials containing halogen bonds, we set out to prepare complexes of stilbazoles with molecular iodine (I_2) and bromine (Br_2).

Iodine is known to form strong halogen bonds,[8] and indeed, while incorrectly formulated, Guthrie's paper of 1863 described the iodine adduct of ammonia. The classic work of Hassel then demonstrated an example in a co-crystal with 4-picoline[9] in which the I···N separation was 2.31 Å – 65% of the sum of the van der Waals' radii. As our halogen bonding work described above demonstrates, extending 4-alkoxystilbazoles *via* functionalisation of the pyridine nitrogen is a good way to induce mesomorphism,[10] which we have demonstrated also using metal complexation[11] and hydrogen bonding.[12] Thus, crystallising solutions containing I_2 and alkoxystilbazole led to the yellow/orange complexes **1**-*n* (Fig. 1) which, from elemental analysis, showed a 1 : 1 stilbazole : I_2 stoichiometry.

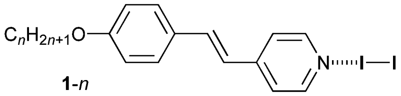

1-*n*

Fig. 1 Molecular iodine complexes of alkoxystilbazoles.

In the case of octyloxystilbazole, single crystals were obtained and the molecular structure is shown in Fig. 2. Thus, there is a N···I halogen bond at 2.353(5) Å, which at 67% of the sum of the van der Waals radii of iodine and nitrogen, is almost the shortest N···I separation recorded in complexes of I_2. The I–I bond in the complex is at 2.8298(7) Å, compared to 2.715(4) Å in I_2, while the N···I–I angle at nitrogen (measured using the bound iodine, the nitrogen and the *ipso* carbon of the pyridine ring) is close to linear at 176.4(2)°. In complexes with strongly basic donors, iodine can be polarised strongly giving rise to so-called amphoteric adducts,[8a] characterised by a right-angled 'Type 2' interaction. The structure here features an intermolecular interaction that is topologically Type I, with an iodine–iodine separation of 3.8891(7) Å which, given a van der Waals' radius for iodine of 1.98 Å, is at 98% of twice this radius. This would not normally be held to be significant (intermolecular I···I distances in molecular iodine are 3.496(4) Å).

The liquid crystal properties of **1**-*n* (Table 1) were determined using polarised optical microscopy, which showed that the longest-chain homologues, **1**-10 and **1**-12, gave straightforward behaviour. Thus, **1**-10 melted directly to a SmC phase at 108.5 °C giving way to a SmA at 117 °C. Both phases showed characteristic textures and DSC showed the transition to be

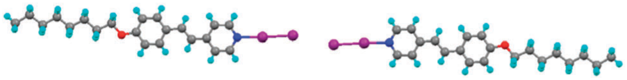


Fig. 2 Molecular structure of the 1 : 1 complex between octyloxystilbazole and I_2.

---

[a] *Department of Chemistry, University of York, Heslington, York YO10 5DD, UK. E-mail: duncan.bruce@york.ac.uk*

[b] *CNRS-Université de Strasbourg (UMR 7504), Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess BP 43, 67034 STRASBOURG Cedex 2, France*

† Electronic supplementary information (ESI) available: X-ray data; cif files; NMR spectra; experimental details. CCDC 905968–905970. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc41227j

Table 1 Thermal data for iodine complexes **1**-*n*

Complex	Transition	*T*/°C
1-4	Cr–Cr + Iso	145
	Cr + Iso–Iso	217
	(Iso–SmA)	(214)
1-6	Cr–Cr + Iso	155
	Cr + Iso–Iso	213
	(Iso–SmA)	(204.5)
1-8	Cr–SmA	146.7
	SmA–Iso	207
1-10	Cr–SmC	108.5
	SmC–SmA	117.0
	SmA–Iso	230
1-12	Cr–SmC	112.0
	SmC–SmA	139.5
	SmA–Iso	208

second order. Clearing was found at 230 °C and was evidently accompanied by some decomposition as cooling the sample did not reproduce the phase sequence. The behaviour of **1**-12 was the same at the temperatures included in Table 1. It is testament to the stability of the stilbazole···iodine halogen bond that the only real evidence of decomposition is found at elevated temperatures or on prolonged heating, as previously we provided evidence of the lability of halogen bonds between stilbazoles and iodobenzenes.[4,5,7]

Complex **1**-8 was a little different as on heating to 146.7 °C, the crystalline solid melted to form a SmA phase. If slow heating continued, the mesophase crystallised at 157 °C before re-melting to a SmA at 177.5 °C and then clearing at 207 °C with decomposition. However, if the sample was heated rapidly above 146.5 °C, crystallisation and re-melting were not observed and heating led straight to the isotropic state. Thus, the crystalline phase obtained on solution crystallisation appears to be metastable. No liquid crystal behaviour was obtained, however, for **1**-4 and **1**-6. In each case, the complex melted to give a mixture of an isotropic liquid and a crystalline solid, which persisted until the new solid also melted. The first melting was accompanied by a darkening attributed to extrusion of molecular iodine (molten above 114 °C), which was confirmed gravimetrically. Stoichiometry would suggest the formation of a 2 : 1 complex, although such structures have previously been felt unlikely where strong donors are concerned.[8a]

However, it is surprising that a SmC phase is observed for these complexes, as the weak intermolecular $I_2 \cdots I_2$ interaction would suggest that in the mesophase the complex exists as shown in Fig. 1, *i.e.* a 1 : 1 complex. There is little or no precedent for such simple, dipolar mesogens forming a SmC phase. Therefore, complexes **1**-10 and **1**-12 were investigated by X-ray diffraction in the SmC phase just above the Cr–SmC transition, as the complexes were unstable over time at elevated temperature and in the X-ray beam in the mesophase. In each case, a single, small-angle reflection – *d*(001) – was observed, consistent with a lamellar phase (Fig. S1, ESI†); the measured *d*-spacings were 49.9 Å (**1**-12 at 120 °C) and 50.1 Å (**1**-10 at 110 °C). These distances are clearly much greater than the length (26.8 Å) of the monomeric stilbazole$\cdots I_2$ unit and show conclusively (and surprisingly) that the species giving rise to the mesophase is in fact the 2 : 2 dimer found in the crystal structure, consistent with the observation of a SmC phase. Determination of the molecular areas[13] reveals a tilt angle of *ca.* 30° in the mesophase for each complex. Despite having the tilt angle and being able to compute the molecular length of the 1 : 1 adduct, it is not then straightforward to determine the parameter of real interest, namely the intermolecular iodine separation as there is too much geometric flexibility that cannot be pinned down. Nonetheless, the X-ray data show unequivocally that the SmC phase arises from a 2 : 2 arrangement, which must be stabilised by the development of the intermolecular I···I contact. The implied strength of this contact in the mesophase is then remarkable given the temperatures at which it is found.

Having found iodine complexes, attempts were then made to prepare a bromine analogue by allowing an alkoxystilbazole and molecular bromine to crystallise together from THF. However, rather than forming a halogen-bonded adduct, the crystals that were obtained were of the stilbazolium bromide (Fig. 3) in which one of the ethylenic hydrogens had been replaced by bromine (vinyl bromide *trans*-**2** – Scheme 1).[14]

This observation was at first sight surprising and a search of the literature found only one example of such a stilbazole derivative (Katritzky archive,[15] no experimental data). Efforts to isolate appreciable quantities of vinyl bromide, **2**, gave a solid that was shown by ^{1}H NMR spectroscopy (Fig. S2, ESI†) to be a 10 : 1 mixture of *trans*-**2** and *cis*-**2** (Scheme 1). The minor component was confirmed as *cis*-**2** by NOE experiments: *trans*-**2** showed a NOE between the vinyl proton and both aromatic rings whereas *cis*-**2** showed a NOE only to the alkoxyphenyl ring (no NOE to the pyridyl ring was observed). A mechanistic rationale for the reaction is depicted in Scheme 1. Thus, cleavage of the C–Br bond adjacent to the alkoxyphenyl ring could occur either from a bromonium ion or dibromo intermediate, generating a carbocation stabilised by conjugation from the lone pair on the alkoxy oxygen. Two conformations for

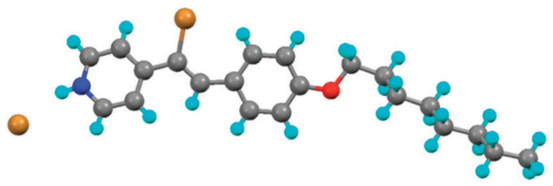
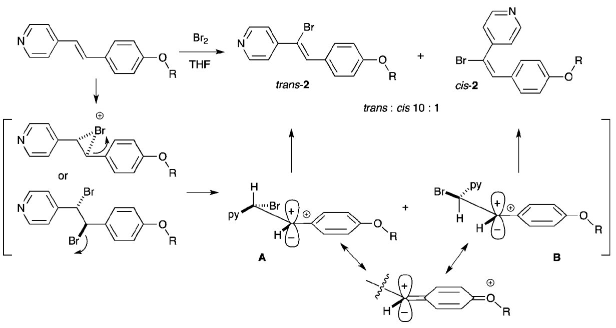


Fig. 3 Molecular structure of **2**.



Scheme 1 Proposed mechanism for the formation of compound **2**.

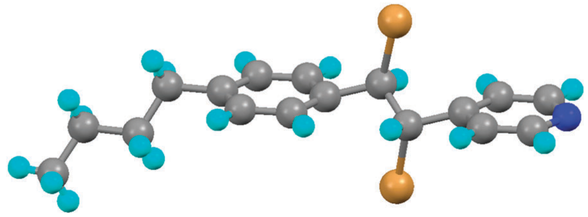
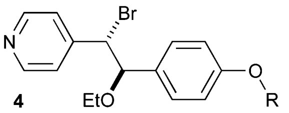


Fig. 4 Single crystal X-ray structure of compound **3**. Further details are found in the ESI.†

HBr elimination (with the C–H bond approximately parallel to the carbon p-orbital) of the carbocation **A** and **B** are shown. Elimination from **A** (to give *trans*-**2**, the major product) is presumably favoured as it minimises steric interactions between the two aryl groups.

If this mechanistic conjecture is correct, then using a 4-alkylstilbazole should inhibit elimination of bromide and disfavour formation of vinyl bromide **2**. Therefore, 4-butylstilbazole and Br_2 were mixed in THF solution under a range of conditions. Evidence from ^1H NMR spectroscopy and from single crystals obtained showed (see also ESI†) only the formation of the 1,2-dibromo adduct (**3**, Fig. 4). Thus, the ^1H NMR spectrum showed an AB spin system centered on $\delta = 5.37$ with $J_{AB} = 11$ Hz, as expected for anti stereochemistry about the carbon–carbon bond. That this was the 1,2-dibromo adduct was verified by its independent preparation by reacting alkyl- or alkoxy-stilbazole with a mixture of Bu_4NBr and Bu_4NBr_3 according to Bellucci *et al.*[16]

In the case of the alkyloxystilbazoles, all attempts to obtain solid samples of the 1,2-dibromo adduct using the conditions employed for the alkylstilbazole were unsuccessful and indeed in contact with EtOH, the dibromo adduct was solvolyzed, with the bromine attached to the ethylenic carbon next to the alkoxyphenyl ring being replaced by EtO (**4**).



4

Interestingly, this NMR spectrum (Fig. S3, ESI†) showed that a single diastereoisomer is produced on addition of bromine, consistent with the predicted lability of C–Br bonds expressed in Scheme 1. The stereochemistry is presumed to be anti and the value for $^3J_{AB}$ of 5.3 Hz is consistent with related methanol adducts of anti-stereochemistry obtained from methanolysis of 1,2-dibromo adducts of stilbenes.[17]

The complexes between the alkoxystilbazole and I_2 show a very short halogen bond and are also found to be liquid crystalline; the mesophases are unusually stable compared to other systems we have investigated. More remarkably, the weak-to-non-existent, intermolecular I···I interaction found in the crystal structure clearly changes its nature and strength in the mesophase and appears crucial in promoting the formation of the SmC phase, which proposal is supported by the results on X-ray diffraction in the mesophase. Attempts to prepare analogous complexes of bromine lead to electrophilic substitution in the ethylenic fragment of the alkoxystilbazole.

EPSRC (LJM and CP), the University of York (RJT) and the University of York Wild Fund (JPKW) are thanked for support.

Notes and references

1 P. Metrangolo, H. Neukirch, T. Pilati and G. Resnati, *Acc. Chem. Res.*, 2005, **38**, 386–395; A. C. Legon, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7736–7747.
2 H. L. Nguyen, P. N. Horton, M. B. Hursthouse, A. C. Legon and D. W. Bruce, *J. Am. Chem. Soc.*, 2004, **126**, 16–17.
3 P. Metrangolo, C. Präsang, G. Resnati, R. Liantonio, A. C. Whitwood and D. W. Bruce, *Chem. Commun.*, 2006, 3290–3292.
4 D. W. Bruce, P. Metrangolo, F. Meyer, C. Präsang, G. Resnati and A. C. Whitwood, *New J. Chem.*, 2008, **32**, 477–482.
5 C. Präsang, A. C. Whitwood and D. W. Bruce, *Chem. Commun.*, 2008, 2137–2139.
6 C. Präsang, H. L. Nguyen, P. N. Horton, A. C. Whitwood and D. W. Bruce, *Chem. Commun.*, 2008, 6164–6166.
7 D. W. Bruce, P. Metrangolo, F. Meyer, T. Pilati, C. Präsang, G. Resnati, G. Terraneo, S. G. Wainwright and A. C. Whitwood, *Chem.–Eur. J.*, 2010, **16**, 9511–9524.
8 (*a*) W. T. Pennington, T. W. Hanks and H. D. Arman, in *Halogen Bonding Fundamentals and Applications*, ed. P. Metrangolo and G. Resnati, Springer, Berlin, 2008, vol. 126, pp. 65–104; (*b*) R. B. Walsh, C. W. Padgett, P. Metrangolo, G. Resnati, T. W. Hanks and W. T. Pennington, *Cryst. Growth Des.*, 2001, **1**, 165–175; (*c*) E. L. Rimmer, R. D. Bailey, T. W. Hanks and W. T. Pennington, *Chem.–Eur. J.*, 2000, **6**, 4071–4081.
9 O. Hassel, C. H. R. Romming and T. Tufte, *Acta Chem. Scand.*, 1961, **15**, 967–974.
10 D. W. Bruce, *Adv. Inorg. Chem.*, 2001, **52**, 151–204; D. W. Bruce, D. A. Dunmur, M. A. Esteruelas, S. E. Hunt, R. Le Lagadec, P. M. Maitlis, J. R. Marsden, E. Sola and J. M. Stacey, *J. Mater. Chem.*, 1991, **1**, 251–254; J. P. Rourke, F. P. Fanizzi, N. J. S. Salt, D. W. Bruce, D. A. Dunmur and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1990, 229–231; J. P. Rourke, F. P. Fanizzi, D. W. Bruce, D. A. Dunmur and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1992, 3009–3014; D. J. Price, K. Willis, T. Richardson, G. Ungar and D. W. Bruce, *J. Mater. Chem.*, 1997, **7**, 883–891.
11 See *e.g.*: D. Fazio, C. Mongin, B. Donnio, Y. Galerne, D. Guillon and D. W. Bruce, *J. Mater. Chem.*, 2001, **11**, 2852–2863; D. W. Bruce, *Acc. Chem. Res.*, 2000, **33**, 831–840.
12 See *e.g.*: J. P.-W. Wong, A. C. Whitwood and D. W. Bruce, *Chem.–Eur. J.*, 2012, **18**, 16073–16089; D. J. Price, K. Willis, T. Richardson, G. Ungar and D. W. Bruce, *J. Mater. Chem.*, 1997, **7**, 883–891.
13 Method in: Z. T. Nagy, B. Heinrich, D. Guillon, J. Tomczyk, J. Stumpe and B. Donnio, *J. Mater. Chem.*, 2012, **22**, 18614–18622.
14 When applied to the stilbazole derivatives, *trans* and *cis* refer to the mutual disposition of the two six-membered rings.
15 http://www.ark.chem.ufl.edu/ (CAS 300396-11-6) and A. R. Katritzky, private communication 2011.
16 G. Bellucci, R. Bianchini, C. Chiappe, R. S. Brown and H. Slebocka-Tilk, *J. Am. Chem. Soc.*, 1991, **113**, 8012–8016.
17 M. F. Ruasse, G. Lo Moro, B. Galland, R. Bianchini, C. Chiappe and G. Bullucci, *J. Am. Chem. Soc.*, 1997, **119**, 12492–12502.