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Halogen-Bonded Liquid Crystals

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It is a great pleasure to write this article to mark the retirement of Professor *Robert Deschenaux*. An excellent scientist, a very good colleague, and a long-standing and dear friend.

While the halogen bond has been recognised and studied for over a hundred years, it is only in more recent times that chemists have begun to apply it and see its possibilities as another supramolecular interaction that can be deployed in the preparation of materials. This review takes one of those areas, liquid crystals, and considers examples of motifs that have been deployed successfully to generate new mesogens. In particular, rather than attempting to be comprehensive, the article reviews critically data from well-characterised systems and seeks to first make some comparisons with analogous hydrogen-bonded materials, before considering how the lability and flexibility of the halogen bond expresses itself in liquid crystal behaviour.

Keywords: halogen bonds, hydrogen bonds, liquid crystals, supramolecular chemistry.

Introduction

Liquid Crystals

Phase Types and Classification

Before contemplating the deployment of halogen bonding, it is helpful to provide a short, contextual introduction to liquid crystals. The liquid crystal state represents a fourth (true) state of matter and can be thought of as intermediate in its properties between the solid and liquid states that it borders. There are two major classes of liquid crystal, namely *lyotropic* liquid crystals, where the order of the solid state is disrupted by the action of a solvent – often but not always water – and *thermotropic* liquid crystals where solid-state order is disrupted (primarily) by temperature. It is these latter materials that will be discussed in this article.

Liquid-crystalline materials tend to be characterised by their structural anisotropy, which leads to anisotropic dispersion forces between molecules that are strong enough to stabilise the intermediate states of order that are liquid crystal mesophases. As such, the self-organisation of the molecules originates from non-covalent, intermolecular forces and so, *de facto*, *all* liquid crystals are supramolecular materials. It is not the intention here to give a long introduction to the subject, but the following brief overview is appropriate. Thermotropic liquid crystals may be classified in many ways, some of which are now given.

Low molar mass liquid crystals are non-polymeric materials and so it follows that *high molar mass* liquid crystals are polymeric in nature. There are three principle molecular shapes that lead to thermotropic behaviour (*Figure 1*) – elongated rods, discs and molecules that have a bend (often *ca.* 120°) at the molecular core (bent-core liquid crystals). Disc-like molecules have a strong tendency to aggregate into columns which then organise on some 2D lattice, but these do not figure in the following discussions and so are not considered further, although an example is given in *Figure 1*.

Rod-like (calamitic) liquid crystals form two main types of liquid crystal phase – the *nematic phase* (N), which is characterised by the presence of orientational order in one dimension and the absence of

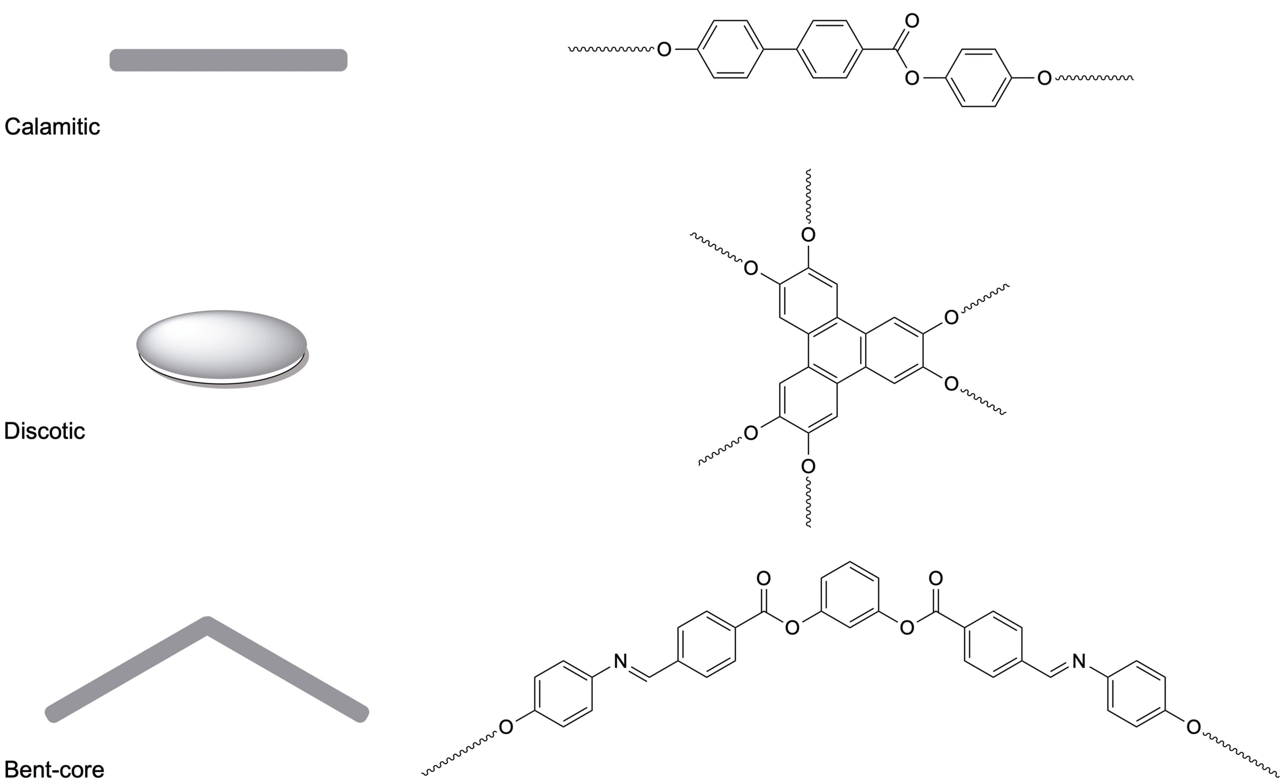

Figure 1. Examples of the three major shape of low molar mass liquid crystal mesogen.

In 2002, Carsten Präsang completed his dissertation at the Philipps-University Marburg with Armin Berndt in the field of boron chemistry. Thereafter, he joined the group of Guy Bertrand as a Humboldt fellow in Riverside, CA, USA where he stayed until 2005. In 2006, he became member of the Materials Chemistry group of Duncan Bruce at the University of York, UK. During the next two years they were able to obtain research findings that were reported in a number of scientific publications on halogen bonding and halogen-bonded liquid crystals, some of the latter in cooperation with the group of Giuseppe Resnati and Pierangelo Metrangolo in Milan, Italy. Following a stay at the Berlin Institute of Technology, in 2012 he moved to Universität des Saarlandes, Germany where he is currently working as a Senior Researcher. His research interests are primarily the molecular chemistry of the main group elements and their interface with materials chemistry.

Following a PhD at the University of Liverpool with David Cole-Hamilton in 1984, Duncan Bruce spent eleven years at Sheffield as a Royal Society Research Fellow, Lecturer and then Senior Lecturer before being appointed to the Chair of Inorganic Chemistry at the University of Exeter in 1995. In 2005, he moved to the University of York as Professor of Materials Chemistry, where he was Head of Department from 2015–2021. His research interests are in many aspects of molecular materials chemistry, mainly involving liquid crystals and transition metals. He is a former Chair of the British Liquid Crystal Society (BLCS) and President of the Materials Chemistry Division of the Royal Society of Chemistry (RSC). The work of his group has been recognised through the Peter Day Award (2014), Tilden Prize (2010) and Corday-Morgan Medal (1996) of the RSC and the Young Scientist Prize (1990) of the BLCS. He is the 2022 recipient of the Gold Medal Award of the Chirantan Rasayan Sanstha of India.

positional order, and a large family of *smectic phases* which, in addition to orientational order, possess partial translational ordering, too (*Figure 2*). The nematic phase and some of the smectic phases also have chiral variants.

The behaviour of bent-core liquid crystals can be quite involved, but briefly it is dominated by the formation of smectic-like phases (*i.e.*, organisation into layers). However, the fact that the molecules found within those layers have a bent geometry (C_{2v} or even simply C_h symmetry) has an effect on both organisation and symmetry, and can lead to some interesting observations, such as macroscopic chirality and ferroelectricity (*i.e.*, symmetry-breaking) in the absence of molecular chirality.[1–4]

Thermal Behaviour and Characterisation

In general, on heating a liquid crystal material it is observed to melt from the solid state into a liquid crystal mesophase (the *melting point*) and a given compound might show one or more mesophases as the temperature is increased. In particular, for rod-like liquid crystals (see below) there is a generally accepted thermodynamic ordering of phases, which can help to characterise observed phases sequences. In decreasing order, this is: N→SmA→SmC→SmI→SmF→SmB, but note that this includes only what might be termed the 'classical' mesophases and ignores some of the many variants that are known. Further, it is also possible, on occasion, for a phase to appear 'out of order', for example with re-entrant behaviour.[5,6]

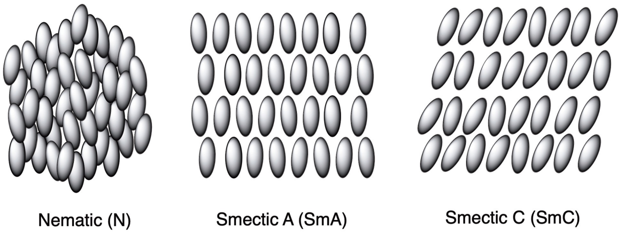

Figure 2. Simplistic, schematic representation of principle classes of mesophase of rod-like mesogens.

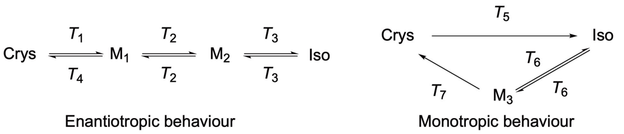

Figure 3. Diagram to exemplify the differences between enantiotropic and monotropic phase behaviour. Crys = crystalline solid, M_x = some mesophase and Iso = isotropic liquid. In the enantiotropic example, $T_4 \leq T_1$ to account for the possibility of supercooling. In the monotropic example, both T_6 and T_7 will be lower than T_5.

Continued heating then leads the compound to leave the liquid-crystalline regime and form a 'normal', isotropic liquid (Iso), which happens at the *clearing point*. Where the phase behaviour is said to be *enantiotropic*, then the same sequence is seen in reverse on cooling (*Figure 3*). However, in some cases the crystalline phase is more stable than the liquid crystal mesophase, so that the compound melts directly from a solid into the isotropic liquid and the mesophase is seen only on cooling. Such materials are said to exhibit *monotropic* behaviour (*Figure 3*).

Liquid crystal phases are typically characterised primarily by polarised optical microscopy (to give characteristic optical textures),[7] differential scanning calorimetry[8] (phase transitions are characterised by changes in enthalpy (1st order) or heat capacity (2nd order)) and small-angle X-ray scattering (SAXS) as all but the nematic phases have some periodicity.

In experienced hands, the most powerful of these techniques is polarised optical microscopy, which relies on the fact that on passing through a liquid crystal sample, linearly polarised light become polarised elliptically and the two refracted rays interfere to give a characteristic optical texture when viewed through crossed polarisers. The nature of the texture reflects, *inter alia*, the symmetry of the phase that gives rise to it and so textures can be typical of a particular mesophase, although the same mesophase can give rise to more than one textural type depending on how the sample is prepared and treated (*Figure 4*). It should be noted, however, that optical textures are also found for crystalline materials, which are also birefringent and so it is not simply the case that observation of an interference pattern shows the existence of a liquid crystal phase.

Microscopy should be carried out in conjunction with calorimetry in order to check that each thermal event in the DSC is matched by a change in optical texture and *vice versa*, understanding that some transitions (SmA to SmB on cooling being an excellent example) can sometimes be very difficult to see optically. By-and-large, melting points (happening between the crystalline state and a mesophase) tend to be thermodynamically first-order transitions with appreciable enthalpies that can exhibit supercooling. However, most clearing transitions (happening between a mesophase and the isotropic liquid) tend to be weakly first order with very much smaller

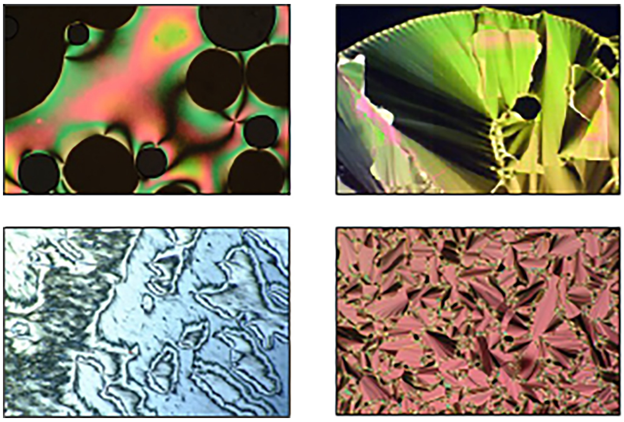

Figure 4. Top row: schlieren texture of the nematic phase (left); focal-conic fan texture of the SmA phase (right). Bottom row: silvery, schlieren texture (left) and broken fan (right) texture of the SmC phase.

enthalpy changes and no supercooling. Transitions between liquid crystal mesophases can be first order, weakly first order or even second order in nature, but DSC alone is not able to confirm the existence of a liquid crystal mesophase (*Figure 5,a*). Finally, SAXS is also very powerful and, in some circumstances (particularly, but not exclusively, where mesophases have 2D symmetry, such as the smectic phases with hexagonal order or with columnar phases), can help materially in the identification of a phase. Generally, the information density is low, and it is often the case that SAXS does not lead to unequivocal phase identification (*Figure 5,b*). As such, it is a combination of all three techniques complemented by knowledge and experience that gives the best results.

The vast majority of liquid-crystalline materials are composed of purely covalent materials but is it true that the use of specific non-covalent interactions can also lead to the modification of liquid-crystalline properties or even their induction from non-liquid crystal components. This topic has been reviewed and four interaction types were identified: quadrupolar interactions, charge-transfer interactions, hydrogen bonding and halogen bonding.[11] It is halogen bonding that is of interest here, but it is perhaps helpful to begin by a brief introduction to the better-known, related and more widely deployed hydrogen bonding.

Hydrogen-Bonded Liquid Crystals

Hydrogen bonding is ubiquitous, and all chemists know what a hydrogen bond is – don't they? The answer is perhaps 'yes' and 'no'. 'Yes' because in probably the vast majority of instances they are readily identifiable as existing between a *Lewis* base (hydrogen acceptor) and an electropositive hydrogen atom (hydrogen donor) bound to an electronegative, second-row elements such as N, O or F. Yet unless somehow exposed to relevant examples, some may be surprised that they can also be formed between *Lewis* bases and hydrogen atoms bound to elements

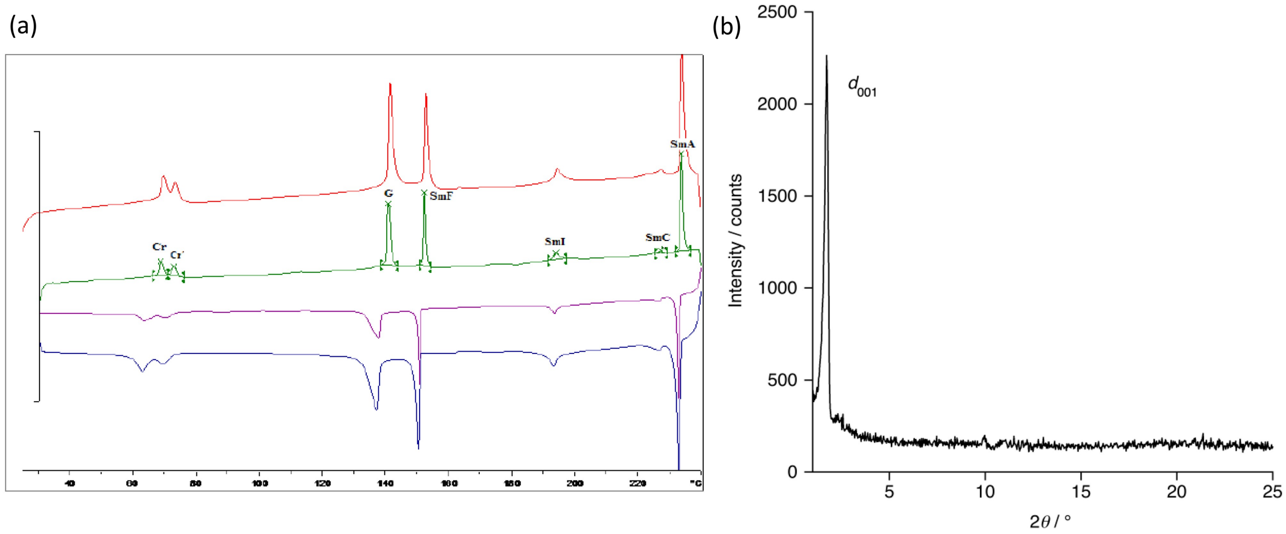

Figure 5. (a) Example DSC trace for a compound (2,5-di(4-hexyloxyphenyl)pyridine) showing multiple liquid crystal phases;[9] (b) small-angle X-ray scattering (SAXS) pattern of the halogen-bonded complex of dodecyloxystilbazole with I_2 showing the layer spacing at low angle (d_{001}) – replotted from the original data.[10]

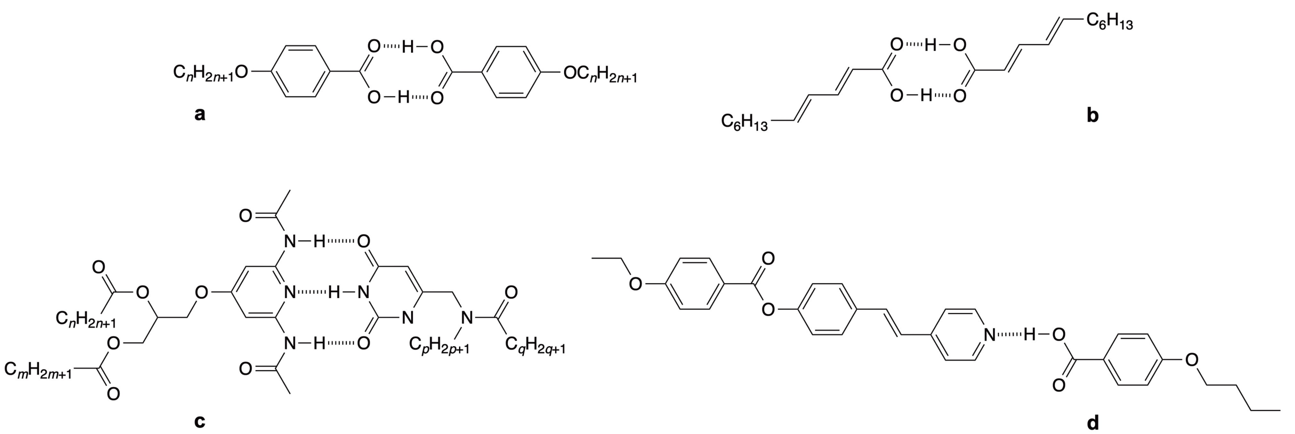

Figure 6. Examples of liquid crystals formed (a and b) by dimerisation of carboxylic acids, (c) through multi-site, complementary hydrogen bonding and (d) from a pyridine and a carboxylic acid.

such as S, P and even C, even if these are now much better recognised than they were years ago.[1]

Examples of hydrogen bonding in liquid crystals go back to the early part of the twentieth century in carbohydrate systems and of course there are many early examples of dimeric liquid-crystalline carboxylic acids from the original work of *Jones* with 4-alkoxybenzoic acids (*Figure 6,a*)[13–15] to some elegantly imagined dienyl carboxylic acids where the central rigidity is provided by the diene unit (*Figure 6,b*).[16] However, more systematic work started in the late 1980s from the work of *Lehn* and his co-workers (*e.g. Figure 6,c*)[17] and, in particular, from the work of *Kato* and *Fréchet* (*Figure 6,d*).[18]

In general, two broad approaches can be identified. The first is where one or both components of the hydrogen-bonded moiety is liquid crystalline in its own right and so the liquid crystal properties are modified when the hydrogen bond forms. The second is when neither component has liquid-crystalline properties, rather they are induced when the hydrogen bond forms. There are plentiful examples of both cases.[19]

However, considering the combination of hydrogen bonding (and indeed, as will be seen below, halogen bonding) with liquid crystal properties raises the question of the nature and lability of the interaction. This arises quite naturally because in order to access liquid crystal mesophases (and all of this discussion is restricted to thermotropic materials), the sample has to be heated above its melting point. As such, the ability of the hydrogen bond to remain intact under thermal stress matters and, related to this is the possibility that the effect of temperature, combined with the nature of the hydrogen bond, manifests itself in other ways. This is relevant to a discussion both of the behaviour at the clearing point and the temperature at which clearing occurs. Thus, is it the case that when the liquid crystal mesophase clears it does so with the intermolecular hydrogen bonding intact, or is it the case that the rupture of the hydrogen bond under thermal stress breaks the hydrogen-bonded complex apart into components, so destroying the mesophase? Further, what is the degree of flexibility about the hydrogen bond and to what extent does it impinge on the effective anisotropy of the mesogen?

Behaviour at the Clearing Point

While it is rarely a good idea to make universal claims, it is likely that perhaps in the majority of hydrogen-bonded liquid-crystalline systems, there is not appreciable rupture of the hydrogen bond prior to clearing from the mesophase. This implies that it is the intact hydrogen-bonded complex that undergoes the transition into the isotropic liquid, rather than this transition being driven by the rupture of the hydrogen bond (*Figure 7*). This is claim is supported by empirical and experimental observations, examples of which are below.

Thus, in a rather beautiful piece of work, *Fukumasa et al.*[20] showed that liquid crystal phases may be formed in simple complexes between 4-alkylpyridines

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[1] For a thought-provoking discussion of hydrogen bonding, see reference [12].

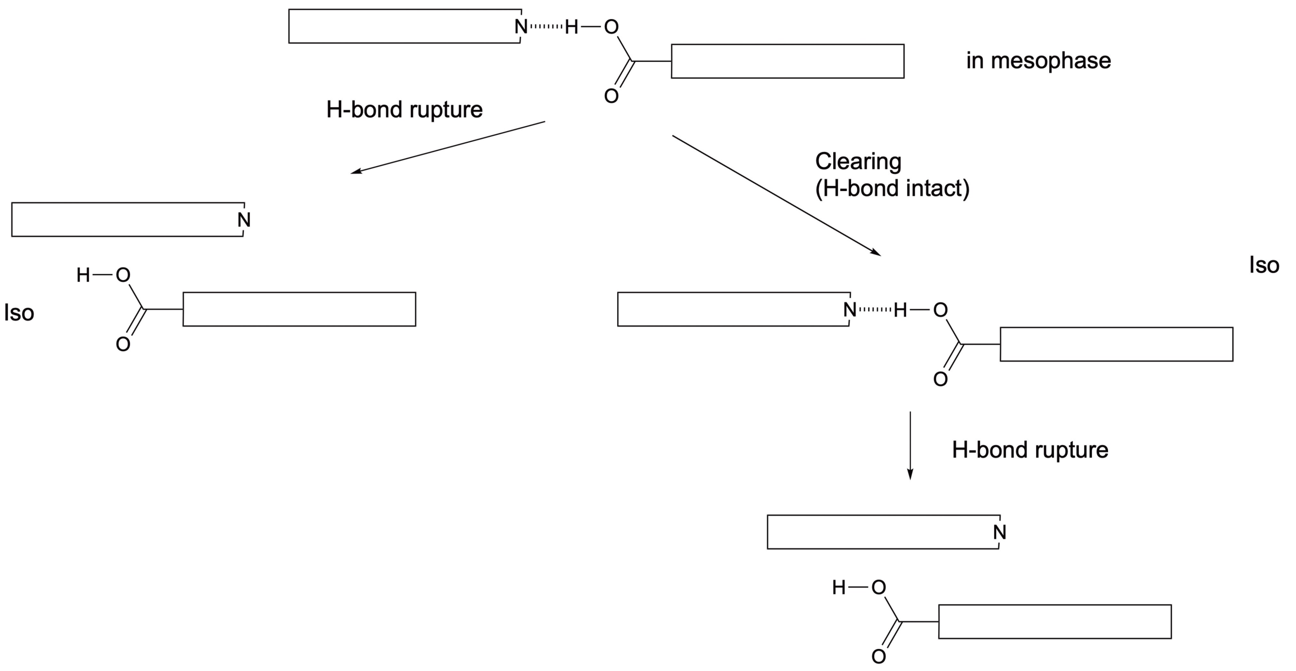

Figure 7. Schematic diagram to show the two possible clearing events for a hydrogen-bonded liquid crystal.

and 4-alkoxybenzoic acids (*Figure 8*). Thus, the complex between 4-hexyloxybenzoic acid and 4-octylpyridine forms a nematic phase that clears to the isotropic liquid at 48 °C, at which temperature 4-hexyloxybenzoic acid is a solid. As such, decomplexation might be expected to show evidence of precipitation, which was not recorded.

We prepared a series of complexes between different benzoic acids and either 4,4′-bipyridine or 4-substituted stilbazoles in which neither component had a flexible chain appended and neither component had a liquid crystal mesophase (*Figure 9* and see also *Figure 31* below).[21] In liquid crystals, flexible chains enhance the anisotropy of the material, but on account of their flexibility they also tend to destabilise the crystal phase so giving rise to mesophases at accessible temperatures. As such, potential mesogens without flexible chains either do not show liquid crystal phases or do so only at high temperatures. Thus, for example, the 1:1 complex between biphenylcarboxylic acid and 4-cyanostilbazole melts to form a nematic phase at 160 °C, which clears to an isotropic liquid at 222 °C. Of the components, 4-cyanostilbazole melts at 130 °C,[22] while biphenylcarboxylic acid melts at 220 °C, showing a monotropic nematic phase at 211 °C. The fact that the melting and clearing points are sharp and that the nematic

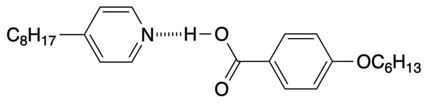

Figure 8. The very simple hydrogen-bonded complex reported by *Fukumasa et al.*[20]

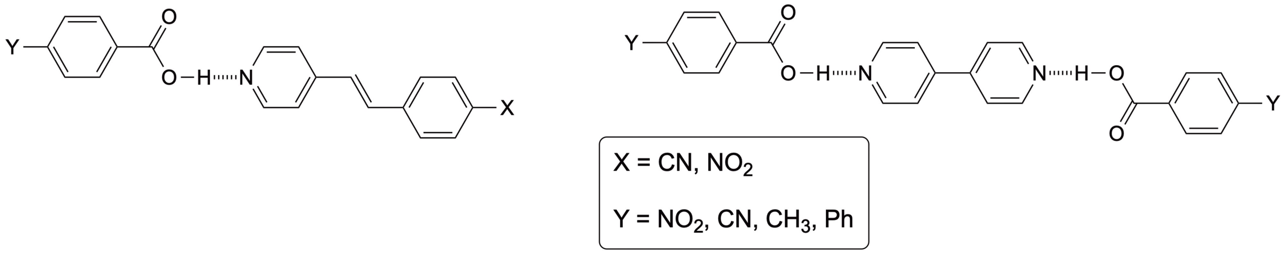

Figure 9. Structures of hydrogen-bonded mesogens without terminal chains.

phase observed was homogeneous point to the existence of the hydrogen-bonded complex as giving rise to the mesophase without any appreciable decomplexation. In fact, the existence of the hydrogen bond at these temperatures is quite remarkable.

From an experimental point of view, we then studied the evolution of the electronic spectrum of the complex formed between 4-decyloxystilbazole and 2,4-dinitrophenol as it is heated from the crystalline state through its SmA phase into the isotropic liquid.[23,24] What is observed clearly is that on entering and moving through the SmA phase, the absorption associated with each component moves to longer wavelength and, moreover, the conversion shows two isosbestic points (*Figure 10*). As the absorption wavelength of the stilbazole red shifts on protonation while that of the dinitrophenol also red shifts in forming the corresponding phenate anion, then evidently what is being observed is proton transfer to form a stilbazolium cation and a 2,4-dinitrophenate anion. Thus, the hydrogen bond transitions from being neutral in the solid state to ionic in the liquid crystal mesophase and in making this observation it is noted that ionic hydrogen bonds are in general significantly stronger than their neutral equivalents. Also important was the realisation that as the isotropic phase was entered, the proportion of the ionic species decreased. Precisely what happens in the isotropic phase could not be elucidated in the experiments carried out, but what was evident was that the integrity of the (now ionic) hydrogen-bonded species was maintained throughout the mesophase right up to the clearing point. As such, it can be stated unequivocally that here, clearing is not driven by dissociation.

On the basis of all of the above evidence, we would suggest that the default position is that hydrogen bond dissociation does not drive clearing.

Halogen Bonding

Much has been written about the halogen bond,[25,26] its history and the nature of the interaction, but there appears still not to be consensus as to the precise nature of the interaction. In this overview it is not intended to wade into this debate as it is not necessary in order to conduct the discussion that follows – the description that will be used ought to suffice. Thus, the halogen bond forms between a *Lewis* base and an electrophilic halogen, and at its

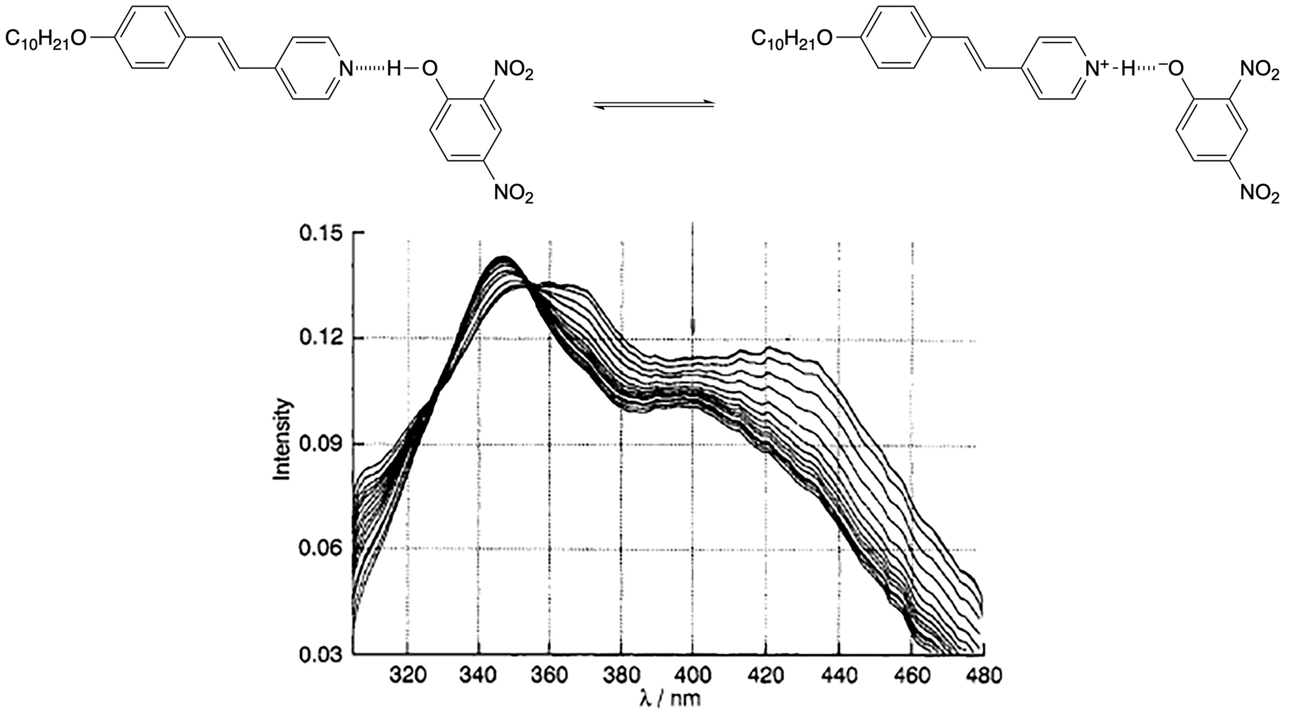

Figure 10. Illustration of the temperature-dependent proton transfer from 2,4-dinitrophenol to 4-decyloxystilbazole through the decrease in the absorptions associated with the neutral species (345 and 400 nm) and the increase in the absorptions associated with the charged species (370 and 425 nm). Reproduced from ref. [23] by permission of the *Royal Society of Chemistry*.

most fundamental level has a strong electrostatic component. A major contribution to understanding of the interactions arises from the work of *Murray*, *Politzer* and co-workers,[27] who coined the term 'σ-hole' to describe the positive electrostatic potential on the halogen, created owing to the effect of an electron-withdrawing group, normally some type of fluorocarbon, in polarising a valence-level p-orbital on that halogen (*Figure 11*).

Thus, the more polarisable (and hence less electronegative) the halogen, the greater the potential effect of the electron-withdrawing group, which leads to a great σ-hole for iodo species compared with its direct congeners bromine and chlorine. As such, the strongest halogen bonds will be formed with electrophilic iodine atoms and it remains the case that no liquid crystals have been reported that involve chlorine in the halogen bond with one limited series involving bromine. Furthermore, almost without exception and as noted below, the halogen bond found in liquid crystals is to a pyridine nitrogen, which will simplify the discussion (*Figure 12*).

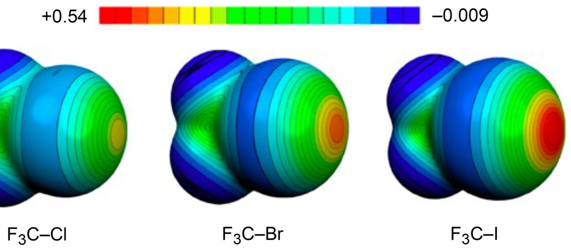

Figure 11. Representation of the molecular electrostatic potential in Hartrees, at the 0.001 electrons Bohr^{-3} isodensity surface for CF_3Cl, CF_3Br and CF_3I, showing the developing σ-hole (area of positive electrostatic potential) in moving from Cl to Br to I. Modified from ref. [27] with kind permission of *Springer*, noting that the original copyright restrictions apply to the figure (reproduced with the permission of the publisher, noting that rights in this material are owned by *Springer Nature*).

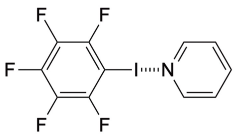

Figure 12. Archetypal halogen bonding motif and by far the most common found in halogen-bonded liquid crystals.

Thus, structurally, halogen bonds between pyridines and an electrophilic iodine attached to fluorocarbon fragments are typically around 2.8 Å in length, which represents *ca.* 80 % of the sum of the *van der Waals* radii of the two elements. There are examples that are shorter, for example in the 2:1 complex between 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and 1,4-diodotetrafluorobenzene (*Figure 13*).[28] This distance here is 2.6672(17) Å and it is postulated that very good crystallographic packing (evidenced by the high density of the complex in the crystals) leads the bond to be shorter, but examples of such short interactions are not very common. The distance is known to vary with the basicity of the halogen acceptor[29] and the degree of polarisation on the halogen donor.[30]

Purpose of the Review and First Examples

The motivation in writing this review, apart from honouring the person to whom it is dedicated, is to try to bring a critical approach. As such, while there will be a brief overview of some of the major structural types of halogen-bonded liquid crystals known, this is not meant to be comprehensive and those interested in learning about the wider spectrum of halogen-bonded liquid crystals are directed to other reviews.[31–35]

The first examples of halogen-bonded liquid crystals came from our own work.[36] Being aware of the gas-phase studies of halogen bonding by my colleague *Legon* at Exeter,[37–39] we then learnt of the work of the Milan group headed at that time by *Resnati* and *Metrangolo*. We had experience of using hydrogen-bonding to induce liquid crystal behaviour and so inspired by work from Milan we attempted to

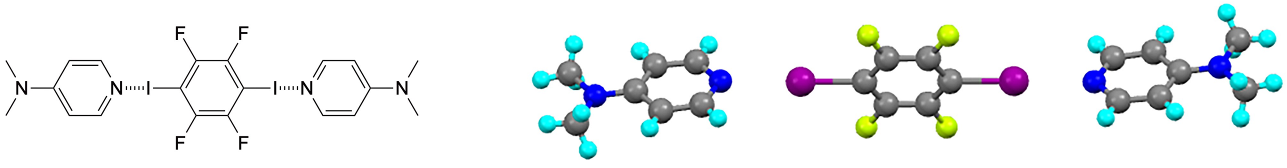

Figure 13. Drawing and molecular structure of the 2:1 complex between DMAP and 1,4-diiodotetrafluorobenzene (structure redrawn from the cif file).

co-crystallise an alkoxystilbazole (known to form liquid crystal materials when hydrogen-bonded to benzoic acid derivatives)[40] with iodopentafluorobenzene. This proved possible and to our delight we got X-ray crystal structures of halogen-bonded materials that turned out to have liquid crystal properties. We were then successful in having a grant funded to extend these initial findings and *Metrangolo* came to visit and worked alongside the new postdoctoral fellow to realise some of the ideas in the proposal. This led to a super and productive collaboration with the Milan team, which generated six papers, including one containing >90 new halogen-bonded liquid crystals.

Thus, the first examples[36] of halogen-bonded liquid crystals were five chain lengths of alkoxystilbazole (*Figure 14*; $n=4$, 6, 8, 10, 12) with iodopentafluorobenzene, which showed nematic and/or smectic A (SmA) phases as a function of the chain length. Two derivatives were characterised by X-ray crystallography: $n=8$[36] having $d(\mathrm{N}\cdots\mathrm{I})=2.811(4)$ Å and an N···I–C angle of 168.4(1)° and $n=10$[41] having $d(\mathrm{N}\cdots\mathrm{I})=2.789(2)$ Å and an N···I–C angle of 177.86(7)°. The latter is shown in *Figure 14*. While it might be tempting to correlate that shorter N···I separation with the more linear N···I–C angle, an early survey collated by *Rissanen*[42] showed that routine correlations of this type could not be made.

From this work, we felt it important to make certain observations and to draw certain conclusions. First was that none of the parent stilbazoles has a liquid crystal phase. They do form crystal smectic E phases as identified by small-angle X-ray scattering, but these are too ordered to be regarded as liquid-crystalline in nature.[43] Thus, it must be the new, halogen-bonded entity that gives rise to the observed N and SmA phases and we ruled out the possibility of a quadrupolar interaction between the two components by showing no complexation with C_6F_6. In addition, we did observe a slight colour change from colourless (stilbazole) to very pale yellow (halogen-bonded complex) and, while this is a very much weaker effect than seen when hydrogen bonding to stilbazoles (see the example above with dinitrophenol complexes), it does point to the interaction with nitrogen (noting that a simple quadrupolar interaction would not involve induction of colour). Second, we were unable to demonstrate the formation of an analogous complex between a stilbazole and C_6F_5Br. We could not obtain single crystals and heating the material formed from co-crystallisation led to thermal behaviour that mimicked the native stilbazole. However, while the halogen bond with the bromo analogue was not thermally stable, the fact that the complex of iodopentafluorobenzene with dodecyloxystilbazole showed a SmA phase that persisted to 84 °C gives a minimum upper temperature to which the halogen bond is stable in that melt.

Interestingly, replacement of only one fluorine by hydrogen in these complexes (in one of the 2-, 3- or 4-positions with respect to the iodine) suppresses mesomorphism completely and with little effect on the N···I separation (*ca.* 2.83 ± 0.2 Å).[44]

And then There Were Trimers

The next publications to appear on the subject were all formally trimeric materials, whose structures are shown in *Figure 15*.[45–48] All four series employed a stilbazole as the halogen acceptor and a dihalogenated, bridging compound as the halogen donor. All of the pure materials showed monotropic mesophases, which were exclusively nematic for **a**, **c** and **d** (albeit with a bit of a twist in these last complexes), and (almost) exclusively SmA for **b**. It is also noteworthy that the trimer using a 1,4-dibromotetrafluorobenzene linker (**c**, X = Br) did show evidence of forming in as much as single crystals were obtained and the complex melted at a temperature higher than that of either component, but there was no evidence of a mesophase on cooling.[47]

Perhaps the most important point about these pieces of work, however, is that the discussions in the papers began to consider or show evidence for the necessity of considering the kinetic and thermody-

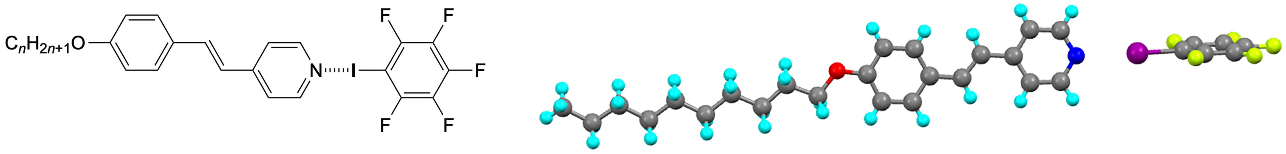

Figure 14. Drawing and molecular structure (from X-ray) of the halogen-bonded complex between 4-decyloxystilbazole and iodopentafluorobenzene.

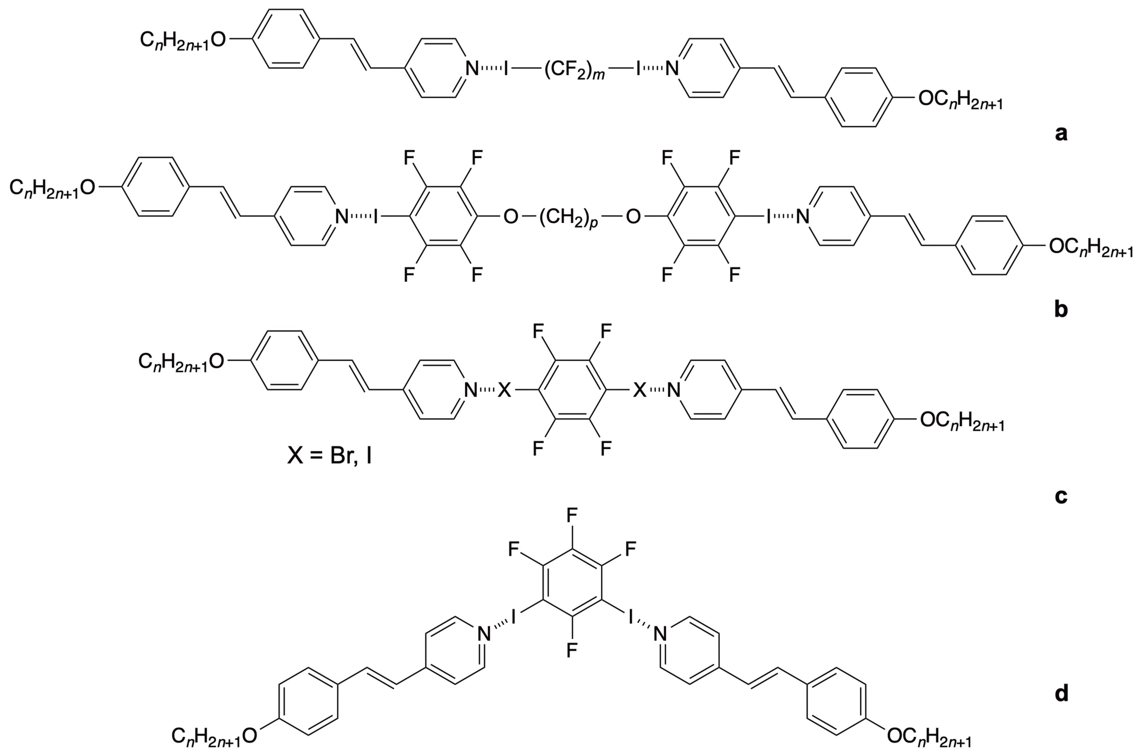

Figure 15. Four series of trimeric, halogen-bonded liquid crystals.

namic stability of the halogen bond. This point will be revisited.

Other Motifs Used to Form Halogen-Bonded Liquid Crystals

As stated earlier, this article does not seek to be another catalogue of all of the known halogen-bonded materials known. Other reviews achieve this end[31–35] and contain many examples of variations on the theme of a pyridine as the halogen acceptor in conjunction with an electrophilic iodine. For example, there are polymeric examples[49] that have been prepared from two bifunctional components (*Figure 16,a*), examples of polycatenar systems (*Figure 16,b*),[50] low-molar-mass systems (*Figure 16,c*) in which a diazo unit has been incorporated in order to add additional functionality through the *trans-cis* isomerisation of the chromophoric unit[51] and an example of complexes prepared with both halogen and hydrogen bonding (*Figure 16,d*).[52] All of these have produced interesting chemistry and liquid crystal behaviour, courtesy of the functionalisation of the basic donor-acceptor motif.

Arguably, there are then three other motifs that are a little different, which are now considered. Thus, although only one paper was published using the following approach, it is worth noting iodoalkynes as halogen donors as reported by *González et al.* (*Figure 17*).[53] They reported both 1,3- and 1,4-di(iodoethynyl)benzene as the halogen donor and here it is interesting that the remaining carbons on the central ring are not functionalised with fluorine. Iodoalkynes are rather powerful halogen donors on account of the polarisability of the alkynyl unit,[54] although the two crystal structures reported in the paper show N···I distances of 2.757 and 2.946 Å, which are rather typical. The paper reports ordered lamellar phases (SmB and crystal G for the 1,4-linker) and phases of bent-core mesogens (1,3-linker) up to quite elevated temperatures (*ca.* 150 °C) and with little reported evidence of dissociation.

Halogens and interhalogens tend to form rather strong halogen bonds[55] and there are reports of liquid-crystalline complexes formed with iodine, bromine and some interhalogens (*Figure 18*).[10,56,57] Some of the complexes were characterised crystallographically and, for example, in a complex between an alkoxyphenylpyridine and ICl, a N···I distance of 2.276(2) Å was found, which represents only 64 % of the sum of the *van der Waals'* radii. In general, these complexes showed mesophases to quite elevated

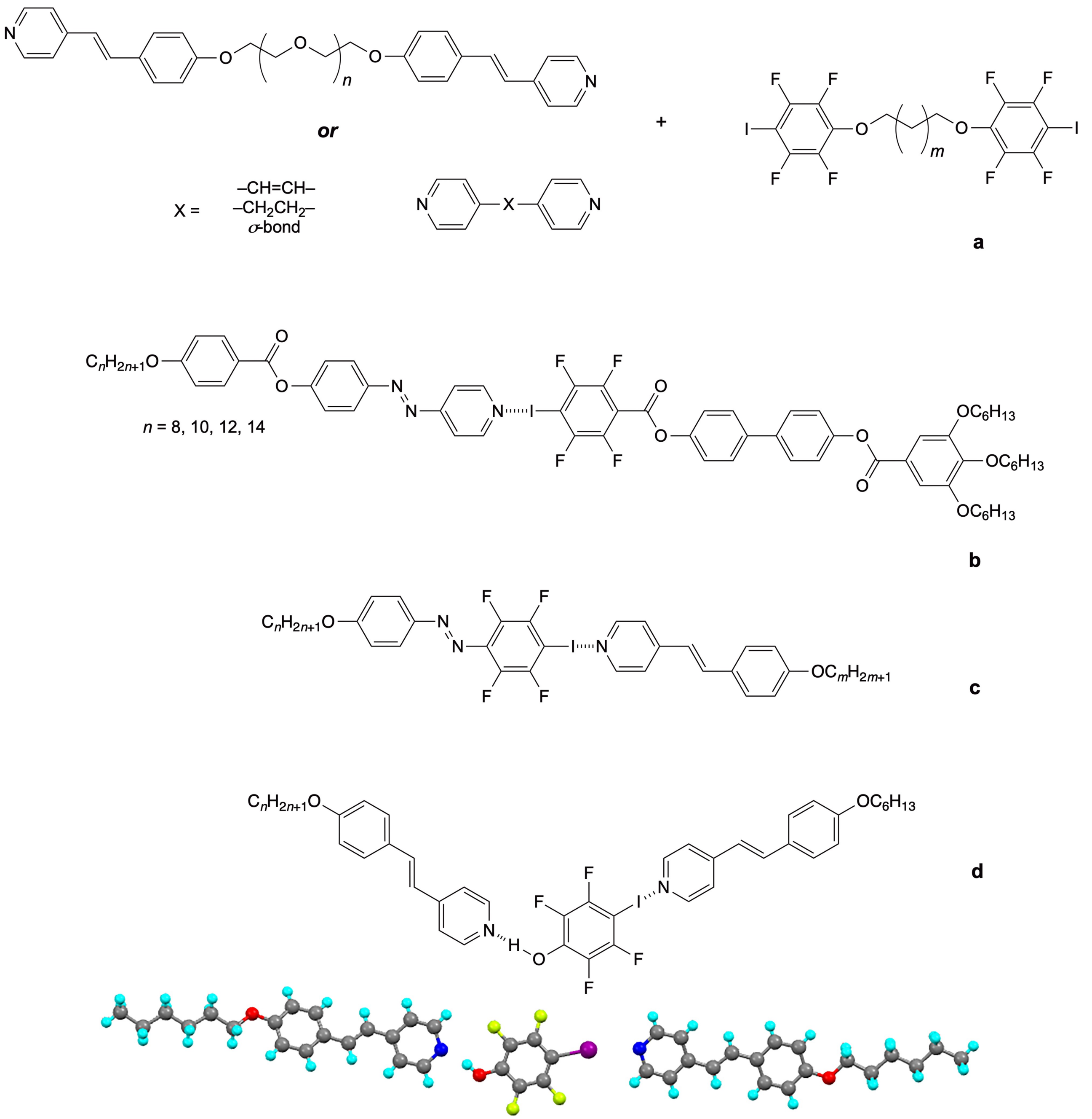

Figure 16. Other examples of halogen-bonded liquid crystals. The molecular structure is given for d to show how flexing at the two non-covalent interactions leads to an overall almost linear arrangement.

temperatures, maybe *ca.* 140 °C for the azo derivatives and >200 °C for the stilbazoles. Iodine and interhalogen complexes of the 4-alkoxyphenylpyridines tended to show melting points between *ca.* 100–170 °C depending on the pyridine and the halogen, and all showed signs of decomposition in the melt.

Two particular observations are perhaps noteworthy. First, when attempting to prepare bromine complexes of the stilbazoles, we found that bromine added across the double bond and then eliminated HBr to give a compound with bromine substituted on the linking double bond but without formation of an adduct, whereas with the phenylpyridines, a complex formed but no mesophase was seen on melting,

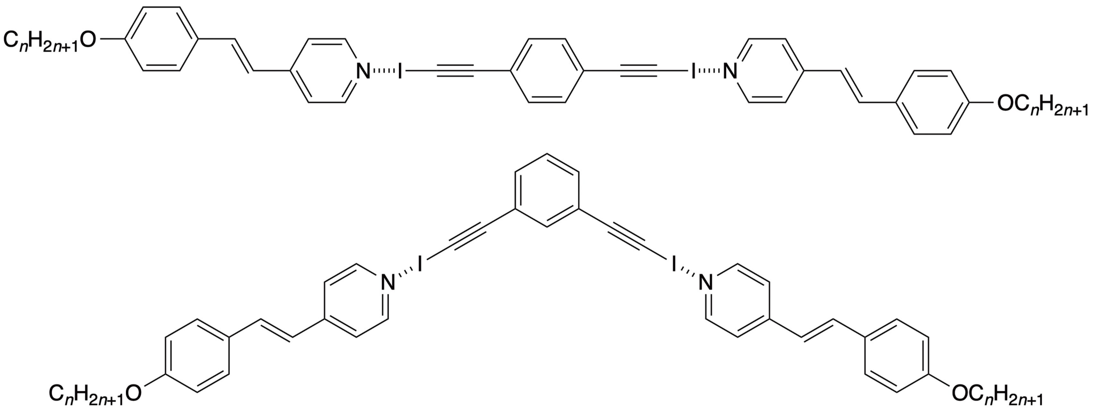

Figure 17. Two isomers of liquid-crystalline bis(alkoxystilbazole) complexes of di(iodoalkynyl)benzene.

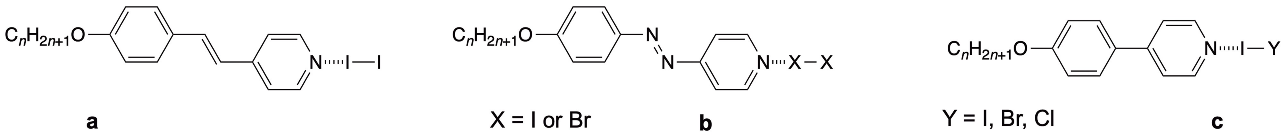

Figure 18. Liquid-crystalline, halogen-bonded complexes employing halogens or interhalogens.

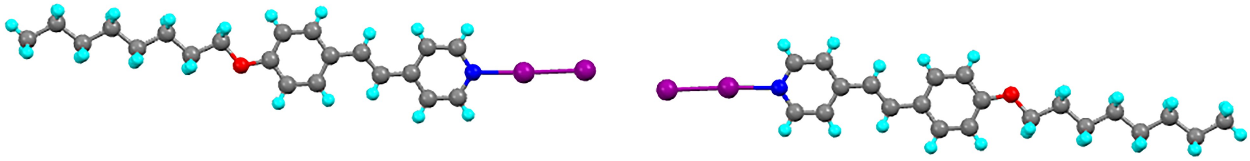

Figure 19. Molecular structure of the octyloxystilbazole complex with I_2 showing the head-to-head arrangement (re-drawn from the cif file).

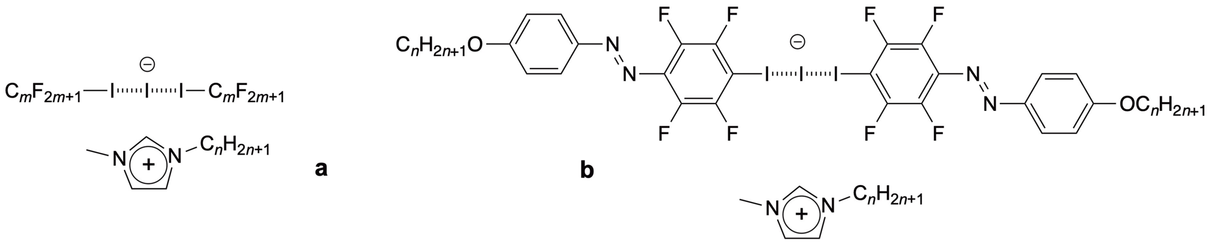

Figure 20. Materials with anisotropic anions formed by halogen bonding to iodide by electrophilic iodines. The mesophases of salts a are characterised unequivocally.

rather bromine was eliminated.[10] In contrast, in reporting the behaviour of the azopyridines, *Chen et al.* not only prepared complexes of bromine but showed them to have liquid crystal properties, with textures given in the manuscript.[57] There are some aspects of the thermal behaviour that are not explained and the characterisation of the complexes is perhaps incomplete, but nonetheless, it is believed that these latter complexes are the only examples of liquid crystals with a halogen bond to bromine. Second was the observation that the longer-chain homologues of the stilbazole···I_2 complexes showed a

SmC phase. This was unexpected as simple, dipolar mesogens would normally show a N or SmA phase.[58] However, data from SAXS experiments showed the lamellar spacing to be *ca.* 50 Å, which was much longer than the length of *ca.* 30 Å evaluated for an individual complex. The single crystal structure (*Figure 19*) showed an interesting head-to-head arrangement in the solid state and evidently this must be somehow retained in the mesophase in order to account for the observed spacing. The I⋅⋅⋅I separation cannot really be considered to represent an interaction (it is 98 % of twice the *van der Waals* radius of iodine) and in any case, such an interaction would be Type I in nature and so repulsive,[2] and so why any such dimeric arrangement might persist remains to be explained.

However, perhaps the most different materials are those where the liquid crystallinity is driven by an anion formed by halogen bonding between an iodide anion and two iodoperfluoroalkanes, with a 1-methyl-3-alkylimidazolium cation.[60] While it is well known that long-chain 1-methyl-3-alkylimidazolium salts can form liquid crystal phases,[61,62] in the present materials mesophases are observed when the cation chains are short, unequivocally identifying the complex anion as the driving force for liquid crystal formation. Such an observation is exceedingly rare. The halogen bonding in these salts was certainly reasonably strong in as much as phases were observed in excess of 80 °C and cycling of the materials showed the behaviour to be reproducible over three cycles. Analogous complexes were reported where the iodide anion of an alkylimidazolium cation was bound by a diazo-functionalised iodotetrafluorobenzene, with two salts characterised crystallographically (*Figure 20*). Formation of SmA phases was reported, although the textures are unclear and there are aspects of the thermal data that appear incomplete.[63]

Discussion

In a relatively short space above, the article has covered over two hundred compounds and many tens of papers without doing proper justice to the work and efforts of those involved, and without discussing some of the interesting behaviour reported. However, as noted already, there are recent reviews and, in addition, many of the observations related to what are liquid crystal properties rather than the role and effects of the halogen bond. It is this latter area which is intended to be the focus of this article.

Size of the Halogen

When considering calamitic liquid crystals (the subject of the vast majority of this review), it is important to recall that what can seem relatively small structural changes can have a very real effect on the liquid crystal behaviour, be it in terms of the phase observed or its transition temperatures. Perhaps the most developed aspect of this is in the use of lateral fluorination to influence both of these parameters.[64,65] As such, the size of the iodine present in (the majority) of systems ought to be considered as in principle it has the potential to affect the structural anisotropy of the complexes formed. *Figure 21* shows the molecular structure of hexyloxystilbazole complexed to 4-hexyloxy-2,3,5,6-tetrafluoroiodobenzene in a space-filling representation.[66] It can be seen that while the iodine does extend slightly above and below the extent of the aromatic rings, the overall effect on the structural anisotropy is negligible, particular when the terminal chains are also accounted. Further, the dipolar contribution is in-line with the principle molecular axis and so is likely to have a reasonably small effect (although where present in bent-core molecules, this would obviously not be true). As such, it is proposed that in making the comparisons below, any steric effect of the halogen's size may safely be ignored.

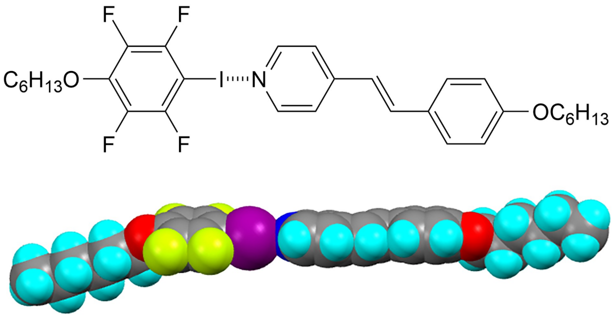

Figure 21. Molecular structure of the complex between hexyloxystilbazole and 4-hexyloxy-2,3,5,6-tetrafluoroiodobenzene. Structure re-drawn from the cif file.

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[2] For a recent perspective on intermolecular halogen⋅⋅⋅halogen interactions, see ref. [59].

Complex Preparation

One of the issues to be considered is how complexes are made, their integrity and how this might reflect on their behaviour. Halogen bonds have the advantage that they are complementary in nature (between an electrophilic halogen donor and a nucleophilic halogen acceptor) and in some cases (*e.g.* complexes with (inter)halogens or with iodoalkynes) they can be quite strong. Nonetheless, care must be taken in the preparation as it is not necessarily given that a donor and acceptor will meet with 100% efficiency and stay together. For example, in the large systematic paper published with the Milan group, in most cases we were able to study the liquid crystal properties of crystalline complexes obtained by co-crystallisation of the components.[66] In these cases, we observed sharp melting points and in the majority of cases sharp clearing points. However, inevitably in some cases co-crystallisation was unsuccessful and so complexes were prepared by melting together precisely weighed mixtures. To determine the efficacy of this approach, the thermal behaviour was compared for complexes where crystallisation was possible. It was found that independent of the method of preparation, the phase behaviour was reproducible in as much as the phase obtained did not change. However, it was typically also found that the melting and/or clearing points may be 1–3 °C lower, which would suggest that complex formation was not absolutely complete and that a small amount of the components remained uncomplexed (*i.e.*, were present as an 'impurity'). As such, in reporting the phase behaviour of halogen-bonded mesogens, it is important to factor in these considerations and to report on the precise methods of preparation, with co-crystallisation as the preferred strategy whenever possible.

Lability and Flexibility

Although potentially addressing slightly different aspects of halogen-bonded liquid crystals, there is likely also a relationship between lability and flexibility, which will be highlighted. Lability is simply that – the propensity of the halogen bond to break regenerating the components that led to its formation. Understanding this is important as part of arguments that seek to understand the reasons behind aspects of the thermal behaviour. Flexibility considers the movement possible about the halogen bond, which will be possible when the complex is molten and which will be reflected in certain aspects of the thermal behaviour. Folded into this comparison will be consideration of analogous hydrogen-bonded systems. Some aspects of these arguments were articulated earlier, but the comparisons have been more carefully assembled, more data have been used and the conclusions made are broader and include comparison with hydrogen bonding.

Covalent Mesogens – Chains, Linkers and Flexibility

To begin to explore these effects, it is perhaps first helpful to know something of how covalently bonded liquid crystals behave and the first variable to consider is terminal chain length. The vast majority of rod-like liquid crystalline materials have an extended, anisotropic and fairly rigid core, which gives them the ability to pack efficiently in the solid state. As such, they tend to have high melting points and few show liquid crystal phases, although *p*-quinquephenyl melts a little below 400 °C and shows a nematic phase that exists to around 425 °C.[67] In general, the more anisotropic the molecule, the more stable its liquid crystal phase[3] as greater anisotropy leads to greater intermolecular anisotropic dispersion forces, which stabilise the phase. When in their fully extended, all *trans* conformation, alkyl chains are anisotropic and so appending them to one or both ends of a molecule with a rigid core will enhance its anisotropy and so promote liquid crystallinity. However, such chains are also flexible and as such they act to destabilise the crystal phase and bring down melting points. This is very well exemplified by the phase behaviour of the 4-alkyl-4′-cyanobiphenyl liquid crystals,[68] which is shown in *Figure 22*. Thus, the melting point decreases from 109 °C for the methyl homologue down to 13.5 °C at the hexyl homologue. Each homologue, however, does show a nematic phase which is monotropic for methyl to butyl, becoming enantiotropic only at pentyl and, while the clearing point shows the well-known odd-even effect, the chain length has less effect on the nematic phase stability. Both effects are understood owing to the rather short rigid core of these compounds.

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[3] It is important here to be clear that in talking about the stability of a mesophase, this refers explicitly to the maximum temperature to which the phase exists and is not related to the temperature range over which the phase may be observed.

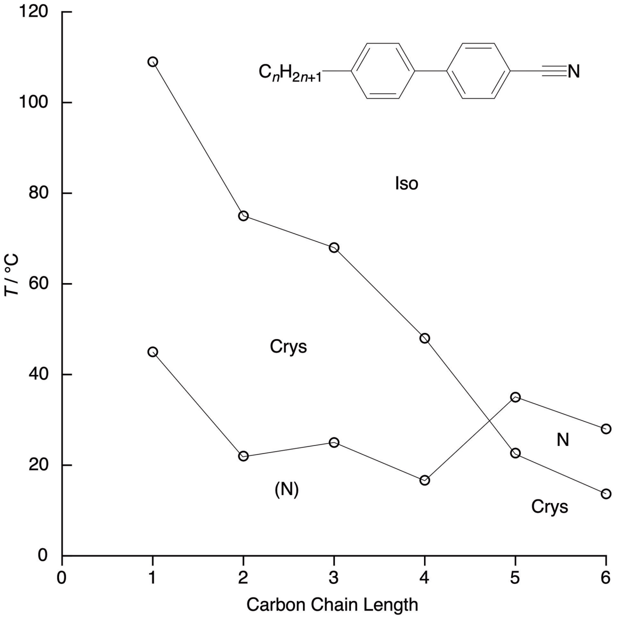


Figure 22. Phase diagram for the first six homologues of the 4-alkyl-4′-cyanobiphenyl liquid crystals. Use of (N) indicates where the nematic phase is seen monotropically.

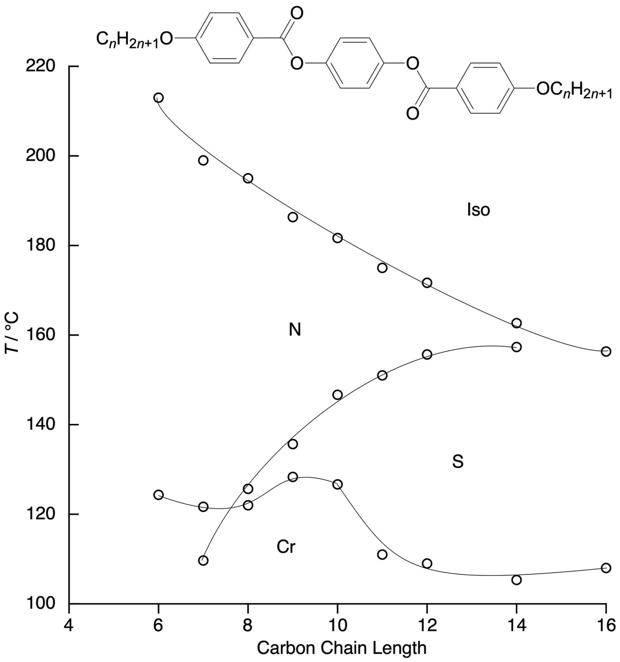
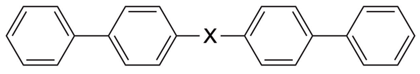


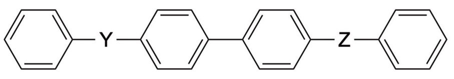
Figure 23. Phase behaviour of 1,4-di(4-alkoxybenzoato)benzene – diagram re-drawn with data from ref. [68].

Where the liquid crystal has two terminal chains, the behaviour is slightly nuanced in that the flexibility associated with two chains brings about phase diagrams of a different general form where increasing the chain length destabilises the uppermost liquid crystal phase. Furthermore, whereas nematic phases are often favoured at shorter chain lengths, smectic phases will tend to appear as the chains get longer. The type of phase diagram is exemplified by the bis(4-alkoxybenzoyl) esters of hydroquinone, shown in *Figure 23*. Thus, all but the very longest-chain homologue shows a nematic phase, with a smectic phase (unidentified in the original publication) growing in from the heptyloxy derivative.[69] The main point of both diagrams is, however, to show that for the clearing point, there is a marked dependence on the terminal chain length, which must be borne in mind in the discussion that follows.

One other thing to be taken into account is that the introduction of linking groups between phenyl rings will have an effect as shown by the comparisons given in *Figure 24* where the linking groups are σ-bond (parent for comparison), ester, imine and diazo groups.[70] It is not intended to give an exhaustive discussion, rather to point out three main factors in play. First, while the introduction of any of these



X	M.Pt. / °C	*T*(N-Iso)
σ-bond	320	(250)
–COO–	222	(213)
–CH=N–	250	251
–N=N–	256	(255)



Y	Z	M.Pt. / °C	*T*(N-Iso)
σ-bond	σ-bond	320	(250)
–COO–	–OOC–	251	(232)
–OOC–	–COO–	213	245
–CH=N–	–N=CH–	234	260

Figure 24. Comparison of the melting and nematic clearing points for two series of related *p*-quaterphenyl compounds. Clearing points shown in parentheses indicate monotropic transitions.

groups maintains the overall linearity of the compound, the structural anisotropy will reduce compared to the parent. Second, different groups will introduce different degree of flexibility so that, for example, in the series where there is a single linking group, the melting points with –N=N– and –CH=N– are very similar, whereas using –COO– the melting point is lower. Third, where the linking groups have a dipolar nature, then this will also have an effect as shown by the two different orientations of the ester functions where two of them are present. All of these compounds also show a nematic phase whose stability reflects the same influences.

Lability

The first materials to be considered are perhaps the simplest, namely the original complexes between alkoxystilbazoles and iodopentafluorobenzene.[36] A plot of clearing point against terminal carbon chain length (*Figure 25*) shows a simple monotonic increase, suggesting that the rupture of the halogen bond (whose strength would not be expected to vary with chain length) is not driving clearing. There are related 1:1 complexes formed from the diazastilbazole analogues and where the halogen donor is 1,2-diiodotetrafluorobenzene. These have clearing points at around 35–40 °C but a similar trend is less evident.[71] Lower mesophase stability appears to be a general feature of stilbazole derivatives where the internal 'connecting' –CH=CH– unit is changed in any way[40] and further, the steric influence of the second, non-complexed iodine, which is likely to be found out of the main molecular plane, makes the two series much less easy to compare.

The behaviour of an extensive series complexes formed between alkoxystilbazoles and the iodostyrene derivatives is considered in *Figure 26*.[66] Five chain lengths for each component were prepared giving a matrix of 25 complexes, all of which showed an enantiotropic nematic phase with nine also showing a (mostly monotropic) SmA phase. *Figure 26* shows the way in which the clearing point depends on the total chain length in the complexes and reveals an effectively linear relationship. Such an observation is important as it shows that for these materials the clearing point is determined by, and varies with, the terminal chain lengths and so again is not driven by rupture of the halogen bond. Thus, in these materials at least the halogen bond can persist to temperatures in excess of 120 °C.

However, if the comparison now expands to include trimeric complexes, then a different story emerges and *Figure 27* shows the clearing points plotted against total terminal carbon chain length for three series of trimeric complexes:[45–47] the best-fit lines are calculated. Given the range of values of the total number of terminal carbon atoms considered,

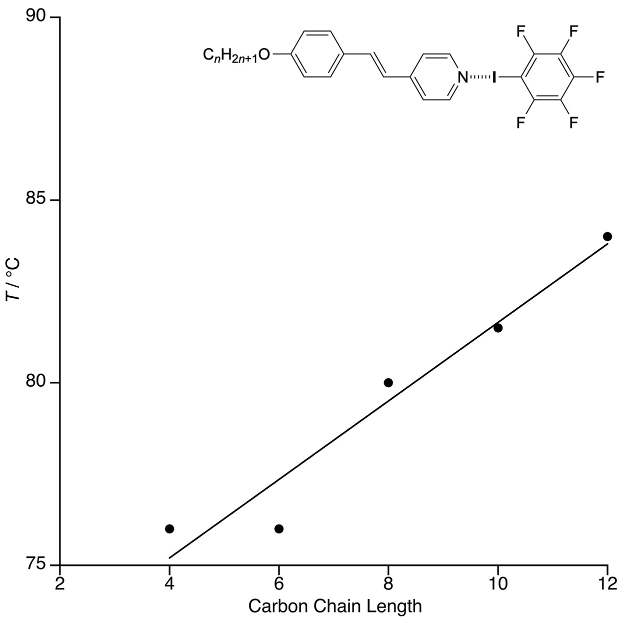


Figure 25. Plot of clearing point against carbon chain length for the complexes shown.

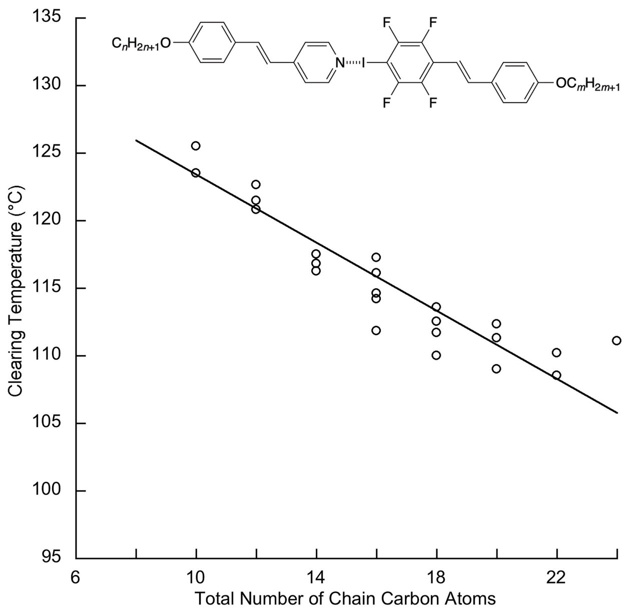


Figure 26. Plot from ref. [65] showing the dependence of the clearing point on the total alkyl chain length ($n+m$) for the halogen-bonded complexes shown.

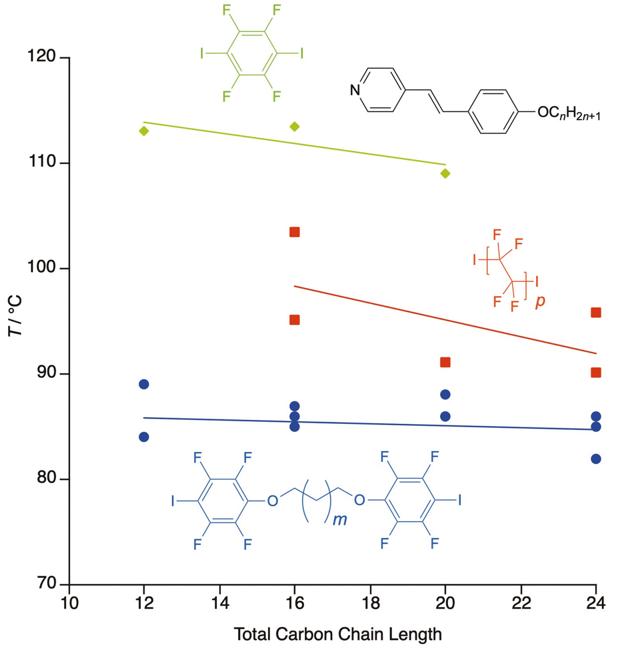


Figure 27. Plot showing the variation in clearing point with total number of terminal carbon atoms for three series of symmetric, trimeric, 2:1 halogen-bonded complexes. In each case the halogen acceptor is an alkoxystilbazole. The three halogen donors are shown in the figure and *m* takes the values 4, 6, 8, 10, while *p* takes the values 2 or 3.

the dependence is at best weak, more remarkably so when it is realised that the data for the trimers with the flexibly linked central unit do not factor in the length of that carbon spacer. Here it is much more difficult to argue that rupture of the halogen bond does not play a role in driving the transition to the isotropic liquid and it is perhaps significant that the complexes contain two halogen bonds as discussed later.

More concrete evidence relating to the possible rupture of the halogen bond at clearing comes from a study of related 2:1 complex between 4-octyloxystilbazole and 1,3-diiodotetrafluorobenzene (*Figure 28*).[48] The complexes are examples of bent-core liquid crystals, one feature of which is the possibly to show chiral mesophases in the absence of molecular chirality, even if the chirality is not resolved into optically pure mesophases. Remarkably, on cooling these materials from the isotropic state, a conventional nematic phase was first observed followed by a fluid chiral phase, considered as a nematic variant (details of aspects of the chirality will not be rehearsed here but can be found in the original publication). The clue to the behaviour came from the DSC traces, which showed an inordinately large enthalpy of transition from the nematic to the chiral nematic phase, which would normally be expected to be small.

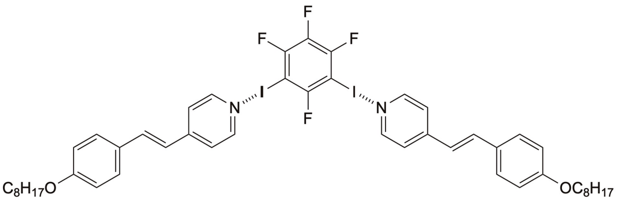


Figure 28. Structure of the 2:1 complex between 4-octyloxystilbazole and 1,3-diiodotetrafluorobenzene.

The following was proposed that accounts for the observations. The complex melts at 88 °C directly into the isotropic phase and then on cooling, a 'conventional' nematic phase is first observed at 68.1 °C, which almost immediately gives way to a chiral phase. In the absence of molecular chirality, the chiral phase must arise from a bent 2:1 complex.[4] To account for the rather large enthalpy for the N-to-chiral phase transition ($7.3\ \mathrm{kJ\,mol^{-1}}$ compared to $0.9\ \mathrm{kJ\,mol^{-1}}$ for Iso-N), it was proposed that the nematic phase observed is of a 1:1 complex and that the large transitional enthalpy represents a transition dominated by re-complexation of a second stilbazole to give the bent entity that shows the chiral phase. Support for such an assertion is provided in two ways. First, it proved possible to prepare the 1:1 complex which, in this pure state, formed a nematic phase at a temperature very similar (64 °C) to that observed with the trimer. Second, a series of mixtures was prepared in which the ratio between the stilbazole and the 1,3-diiodotetrafluorobenzene was varied from 0.8:1 all the way to 2.4:1. The resulting phase diagram (*Figure 29*) shows that as the ratio of stilbazole to diiodo compounds drops away from 2:1, eventually the chiral phase disappears entirely (by 1.4:1), whereas above a 2:1 ratio where dissociation would be suppressed, the nematic phase is absent and only the chiral phase is seen. (These are new data reported here for the first time.)

Thus, in considering lability and on the basis of the evidence presented above where there are arguably sufficient data points to begin a meaningful comparison, in complexes where there is a single halogen bond, lability appears not to be an issue, but

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[4] Chirality in nematic phases of bent-core mesogens has been well established, see *e.g.* ref. [72].

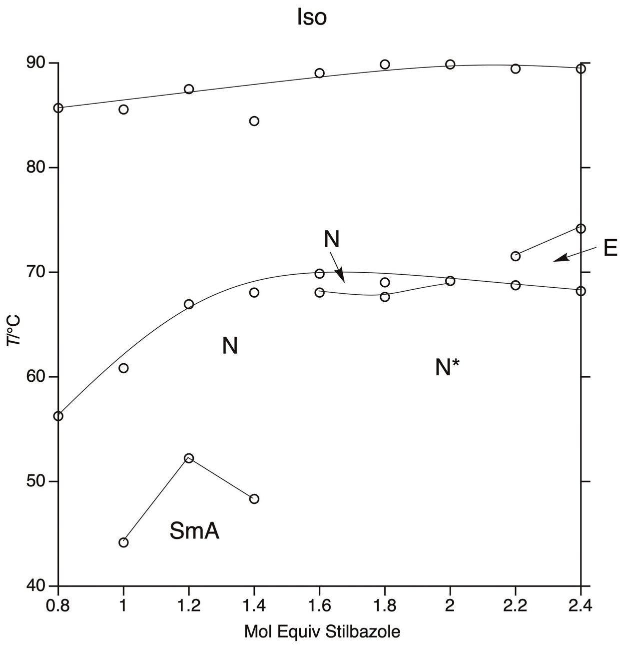

Figure 29. Binary phase diagram between 4-octyloxystilbazole and 1,3-diiodotetrafluorobenzene.

this changes significantly where there are two such bonds. And, in fact, seeing evidence for halogen bond rupture and re-formation through the magnitude of the enthalpy change gives cause to revisit previous papers where in some cases substantial clearing enthalpies are found, consistent with bond formation/disruption.

Flexibility

Inevitably, the flexibility and lability of the halogen-bonded species will be related, but they have the potential to express themselves in different ways as is now presented.

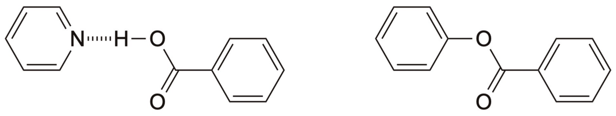

Figure 30. A pyridine⋯benzoic acid hydrogen bond and the covalent ester link used for comparison.

The starting point here is work carried out with hydrogen-bonded mesogens and as part of these studies it has been of some interest to attempt to delineate the effect on the mesophases and transition temperatures of replacing a covalent link with one that is non-covalent. For these purposes, the comparison is made between an ester and a hydrogen-bond formed between a carboxylic acid and a pyridine as shown in *Figure 30*.

It is understood that the comparison is not, and in fact cannot, be perfect, but four major differences are observed. First, the unit is longer by perhaps at least 1.5 Å on account of the hydrogen bond and second the hydrogen bond is easier to break. It is not believed that either of these is likely to change the phase that is seen and neither is the third factor, which is a slightly greater degree of polarity where there is a hydrogen bond. However, the factor that is likely to have a significant influence is flexibility, for the hydrogen bond is formed in effect by the overlap of a σ-type orbital on nitrogen with the 1s orbital of hydrogen giving significant motional freedom at hydrogen, compared with the much lower motional freedom in the covalent ester link (see above for the effect of introducing an ester linking group). Two examples are considered as shown in *Figure 31*.[21]

In the first example, the covalent material is the *p*-toluic ester of a cyanostilbene while the hydrogen-bonded material has components of *p*-toluic acid and cyanostilbazole. Both show a nematic phase, which

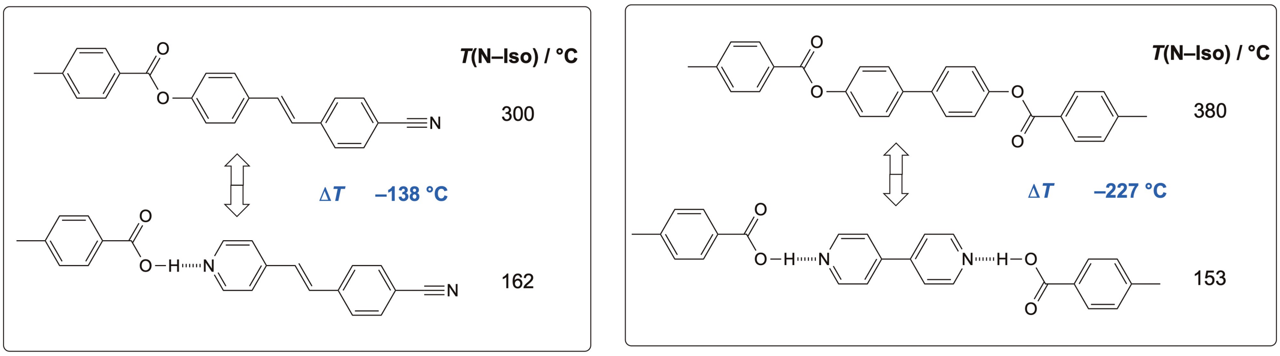

Figure 31. Two comparisons between structurally related covalent and hydrogen-bonded systems.

clears at 300 °C for the covalent material and 162 °C for the hydrogen-bonded analogue. As such, the nematic phase stability is reduced by around 140 °C.

In the second example, the two materials are first the *p*-toluic diester of 4,4′-biphenol and the hydrogen-bonded complexes between *p*-toluic acid and 4,4′-bipyridine. Again, both materials show a nematic phase which clears at 380 °C for the covalent material and *ca.* 153 °C for the hydrogen-bonded complex. Here, nematic phase stability is reduced by around 230 °C.

The ready availability of esters made the above comparisons fairly straightforward, but for the halogen-bonded materials this is a little more involved as is set out below. Thus, the working hypothesis is that the halogen bond can be replaced by a simple σ-bond, so that the family of complexes between stilbazoles and iodostilbenes might be compared with distyryltetrafluorobiphenyl compounds (*Figure 32*). However, such a direct comparison is not possible simply because the only examples of distyrylbiphenyl compounds are non-fluorinated and they are contained mainly in the patent literature for their applications in luminescence and liquid crystal properties were not reported.[73] As such, it is necessary to adopt a stepwise approach and to use comparisons that can be obtained from literature materials. These are summarised diagrammatically in *Figure 32*.

Thus, as mentioned already, a precise covalent model of a distyryl-2,3,5,6-tetrafluorobiphenyl is not known and so 4,4′-di(4-octyloxybenzoyloxy)biphenyl[74] is chosen as a starting reference, with a measured clearing point of 290 °C. Then, to compare the effect of a vinyl *versus* an ester link, the clearing points of 4,4′-di(4-decyloxybenzoyloxy)benzene[69] and 4,4′-di(4-decyloxystyryl)benzene[75] are compared, with the latter compound have a clearing point (270 °C) some 90 °C higher than the former (182 °C). Finally, the effect of the presence of a 2,3,5,6-tetrafluorophenyl is taken into account by comparing 4,4′-di(4-decyloxybenzoyloxy)benzene (N·Iso at 182 °C) with 4,4′-di(4-decyloxybenzoyloxy)-2,3,5,6-tetrafluorobenzene (N·Iso at 139 °C).[76,77] This corresponds to a reduction of *ca.* 40 °C. Thus, taken together, a clearing point of *ca.* 340 °C could be predicted for the covalent analogue, representing an overall destabilisation of *ca.* 220 °C.

The next question is ‘How reliable is this number?’ First of all, note that in making the comparisons, there has been a small rounding of numbers, which reflects the view that any prediction is not intended to be precise to a small few °C. In that sense it is no different to the comparisons made above for the

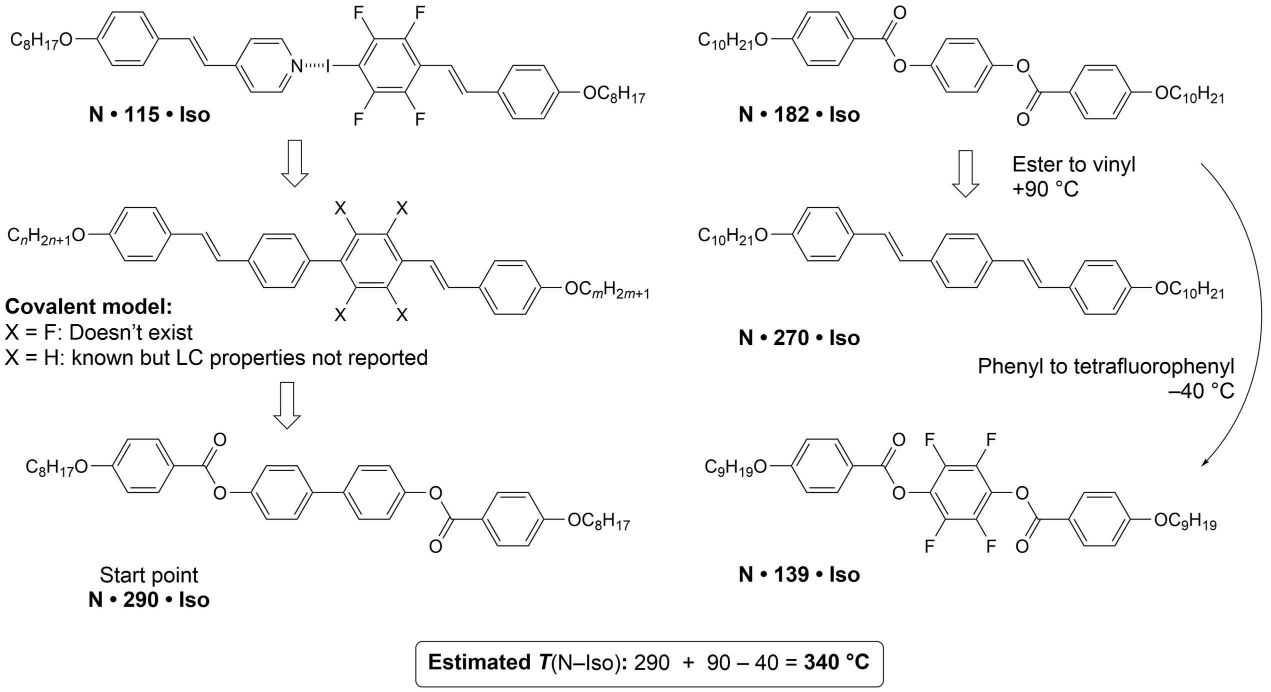

Figure 32. Structures and phase transition temperatures used to derive an approximate clearing point for a covalent analogue of the halogen-bonded complex shown.

hydrogen bonding systems, which are also not meant to be accurate to that degree. On the other hand, if 220 °C as a change is seen as 'approximately 200 °C', then it is postulated that the comparison is realistic.

On the same basis, what comparisons might then be possible for a material with two halogen bonds? An analogous mode of comparison is shown in *Figure 33*, which is explained as follows. Thus, as the figure shows, the direct comparison would be a dialkoxystyrylterphenyl, which is not known with or without a tetrafluorophenyl and so it was necessary to take a slightly different approach. Thus, it is shown in the figure (and consistent with data in *Figure 24*) that the inclusion of an imino link in place of a σ-bond has a small effect on the clearing point and so it is possible to extrapolate from the five-ring phenylenediamine compound shown[78] to the terphenyl diester and then factor in the replacement of ester by vinyl and of phenyl by tetrafluorophenyl (the latter two changes were introduced above in *Figure 32*). However, in this comparison there is a slightly greater degree of uncertainty as the actual clearing point of the five-ring phenylenediamine derivative is not known and 422 °C represents the temperature where decomposition sets in rapidly. Bringing all of this together leads to an estimate for the T_{N-Iso} of 450 °C, which represents a destabilisation of *ca.* 320 °C, some 100 °C greater than for the example with a single halogen bond. Seen against the comparisons made with the hydrogen-bonded systems, the destabilisation is, in each case, *ca.* 100 °C greater for the halogen-bonded systems. The question is whether any of this should be surprising and also what else it tells us.

What Does It All Mean?

Thus, it is certainly the case that in considering the notional covalent analogues for both the hydrogen- and the halogen-bonded complexes considered, the clearing point in the complexes are appreciably lower than might have been expected. As a starting point, higher clearing temperatures result from greater structural anisotropy and so it is evident that the flexibility of each non-covalent interaction contributes to increased motion so destabilising the mesophase. Further, in both cases the presence of two hydrogen or halogen bonds results in greater destabilisation compared to the situation when there is only one, which is then self-consistent.

However, there is evidently a much greater destabilisation in the case of halogen bonds com-

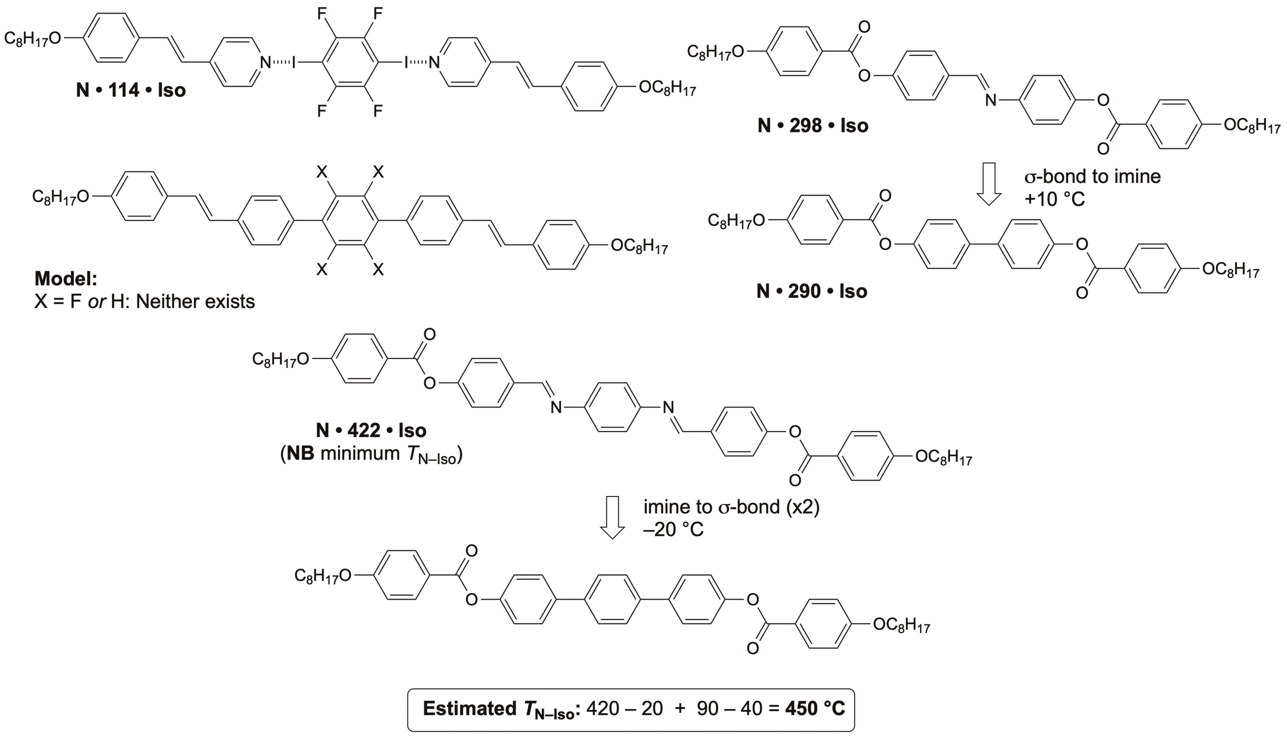

Figure 33. Structures and phase transition temperatures used to derive an approximate clearing point for a covalent analogue of the halogen-bonded complex shown. Clearing point for the diester imine from ref. [79].

pared to hydrogen bonds, which can be understood on the basis of the nature of the interaction. In developing this argument, it is important from the outset to understand that this is not a comparison of the strength of the two interactions, which is a ground state, thermodynamic feature and which at least in the case of halogen bonding can be fairly well approximated by the extend of the contraction away from the sum of the *van der Waals* radii of the two components in the link. Rather this is a dynamic, kinetic phenomenon that in the present examples considers the flexibility in the link in the molten state and, as such, in the presence of thermal energy above room temperature.

In considering the differences, the following extracts from the IUPAC definitions are perhaps helpful:

- 'The forces involved in the formation of a **hydrogen bond** include those of an electrostatic origin, those arising from charge transfer between the donor and acceptor leading to partial covalent bond formation between H and Y, and those originating from dispersion.' It also notes that, 'If an interaction is primarily due to dispersion forces, then it would not be characterized as a hydrogen bond.'[80]
- 'The forces involved in the formation of the **halogen bond** are primarily electrostatic, but polarization, charge transfer, and dispersion contributions all play an important role. The relative roles of the different forces may vary from one case to the other.'[81]

Much is shared in common between the two definitions, but the one major difference is that for the hydrogen bond the definition talks of 'partial covalent bond formation' which, in the case for the example of a benzoic acid with a pyridine, can be envisaged as some degree of overlap between the non-bonded pair of electrons on the nitrogen and the hydrogen 1s orbital of the acid hydrogen. Furthermore, the possible position of that hydrogen is almost a continuum between it sitting closest to the oxygen for a conventional hydrogen bond to it actually sitting closest to the nitrogen in an ionic hydrogen bond as described above in the complexes between an alkoxystilbazole and 2,4-dinitrophenol.[23,24]

In the case of the halogen bond, the interaction is considered to be primarily electrostatic and so the interaction is between the positive electrostatic potential of the σ-hole on the iodine (which is the halogen considered almost exclusively in this article) and the non-bonded pair of electrons on nitrogen.

When any compound melts, the thermal energy available will start to populate a range of conformers as bonds stretch and bend, and in liquid crystals this will be seen to the greatest extent in the terminal alkyl chains which will flex their conformation and, as shown in *Figure 22*, can help drive the transition to the isotropic liquid as they lengthen. Flexing will also be possible in the non-covalent links (comparisons in *Figure 24*) and, whereas there is some small covalency in the hydrogen bond, in the halogen bond this is not the case and as the interaction moves away from linearity then the non-bonded electron pair on nitrogen will begin to see reduced positive electrostatic potential. Indeed, simple visual comparison between the electrostatic potential of the σ-hole on bromine and that on iodine (*Figure 11*) shows that it does not take a huge deviation from linearity for the potential to drop to that of bromine and in making the comparison, recall that there is evidence that almost all complexes with bromine do not form liquid crystal phases, rather the halogen bond ruptures on heating.

From the evidence presented above, it seems to be the case that where there is a single halogen bond, whatever rupture occurs on heating is either non-existent or small enough that clearing is driven by terminal chain length albeit at temperatures that reflect the inherent flexibility that the halogen bond brings. However, where there are two halogen bonds then the evidence points to very significant flexibility and the clearing being driven to some appreciable degree by halogen bond rupture as the dependence on the terminal chain length diminishes or even disappears. Indeed, in some of the systems studies in our lab where there are two halogen bonds, repeated temperature cycling leads to complete degradation of the complex and the disappearance of liquid-crystalline properties.

Conclusions

Halogen bonding is now a very well-established component in various aspects of supramolecular chemistry and bears significant comparison with hydrogen bonding with which it shares a number of analogous features. As this article and the reviews that precede it have shown, it can also be used to fabricate liquid crystals and it is now some twenty years since we reported the first examples. Interest in the field continues and so the purpose of this article is to set out some guiding thoughts with the benefit of hindsight. While halogen bonds formed between pyridines and either (inter)halogens appear rather strong, those formed with fluorinated iodobenzenes or perfluorinated iodoalkanes are less so. As such and in our experience, while it is possible to mix two components in the melt to generate the complex, this does not appear to lead to 100% complex formation as evidence by small temperature ranges for melting and clearing indicative of 'impurities' (*i.e.*, small amounts of the individual components). As such and wherever possible, determining the phase behaviour using crystalline materials should be the method of choice and melting ranges (where appropriate) should be reported.

As a non-covalent interaction, a halogen bond introduces both lability and flexibility. While inexorably related, the former is really about halogen bond dissociation and relates to the ability of the halogen bond to retain its integrity under the thermal stress of being heated into, and cooled from, the (liquid crystal) melt. Where there are sufficient good-quality data to enable comparison, it seems that the 'conventional' liquid crystal behaviour whereby transition temperatures depend on terminal chain length can be well reproduced where the complex possesses a single halogen bond. However, where there are two halogen bonds (and specifically this refers to complexes with 1,3- or 1,4-disubstituted benzene rings), then this dependence appears to be suppressed suggesting that there is more ready dissociation, a conclusion supported by a more detailed consideration of the behaviour of the 2:1 complex between octyloxystilbazole and 1,3-diodotetrafluorobenzene.

Ultimately, the lability is driven by the flexibility and the ability of the halogen bond to 'flex its orientation' in the melt. This effect is seen in hydrogen-bonded mesogens, but is evidently more pronounced in halogen-bonded systems, where quite substantial mesophase destabilisation is observed when compared with reasonable covalent analogues. As such, the transition temperatures for halogen-bonded complexes are very significantly lower than might otherwise be expected for such an anisotropic structures. It is then quite likely that the observed lability in liquid crystals with two halogen bonds arises owing to the 'stresses' of the simultaneous movement at two non-covalent linkages.

Commercial applications of liquid crystals in displays require them to be stable indefinitely over temperature ranges of perhaps −60 to +60 °C. While the desired temperature ranges can be (as at present) achieved using mixtures, the stability is perhaps more of a challenge, at least at the present time. However, in hydrogen bonding there are many examples of motifs formed through multiple hydrogen bonds and, no doubt inspired by DNA base pairing, the uracil-based complex in *Figure 6,c* represents an example. Could a similar approach be designed for halogen-bonded materials and would the links be more thermally inert?

In the title of his book, *Collings* famously describes liquid crystals as 'Nature's Delicate Phase of Matter'.[82] Among the synonyms for 'delicate', one can find refined, skilled, accurate and even graceful, but also tricky and even awkward. These terms (among others) sum up for me a good deal the chemical experience of combining the study of liquid crystals with the study of halogen bonds, but overcoming things that are awkward leads to an appreciation of things that then become refined. There is a great deal more refinement to be had here for those who would seek it.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Contribution Statement

D. W. B. wrote the article. C. P. carried out the new mixture studies reported, and C. P. and D. W. B. analysed and interpreted these data.

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