

## Halogen Bonding: A New Interaction for Liquid Crystal Formation

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A hydrogen bond  $B\cdots HX$  results when an electrophilic hydrogen atom  $H^{\delta+}$  of an acid  $HX$  interacts with a nucleophilic center on the Lewis base  $B$ , namely a nonbonding or a  $\pi$ -bonding electron pair. This noncovalent interaction is associated with characteristic angular geometries, which have been interpreted<sup>1</sup> in terms of a simple electrostatic interaction of  $B$  and  $HX$ , and with binding energies in the range ca.  $10\text{--}50\text{ kJ mol}^{-1}$ .

The hydrogen bond is often referred to as unique, a property attributed to the absence of an inner electron core in the H atom and the consequent ability of this atom to approach closely the nucleophilic center of  $B$ . Recently, however, a systematic investigation<sup>2</sup> of a wide range of  $B\cdots XY$ , formed by Lewis bases with homo- or heterodihalogen molecules  $XY$ , has established precisely the intrinsic properties of this type of complex when in isolation in the gas phase. A striking parallelism was demonstrated between the properties of the  $B\cdots XY$  and their  $B\cdots HX$  analogues, especially for angular geometries, and the term *halogen bond* was suggested to describe the  $B\cdots XY$  interaction. The only significant difference, apart from larger intermolecular distances in  $B\cdots XY$ , was a noted propensity for the hydrogen bond, but not the  $B\cdots XY$  system, to be nonlinear when symmetry allowed. Hassel<sup>3</sup> used the equivalent term *halogen molecule bridge* to describe conclusions of his pioneering work in the solid state.

Recently, Resnati<sup>4</sup> has demonstrated the use of halogen bonding as a directing force in the realization of three-dimensional, solid-state structures and has employed interactions between, for example, basic amine and imine nitrogens, and iodine atoms found in species such as pentafluoroiodobenzene or in 2,3,5,6-tetrafluoro-1,4-diiodobenzene.

Alkoxystilbazoles have been shown by some of us to be versatile materials for the construction of molecular materials including optically nonlinear systems, pyroelectric Langmuir–Blodgett fabrications, and metallomesogens.<sup>5</sup> As part of these studies, hydrogen-bonded mesogens<sup>6</sup> also interested us, and, we were able to show, for example, that a liquid-crystalline material resulted on forming a hydrogen-bonded complex between an alkoxystilbazole and various substituted phenols where neither component was liquid crystalline.<sup>7</sup> Thus, hydrogen bonding, along with quadrupolar interactions,<sup>8</sup> represents an example of a noncovalent, intermolecular interaction capable of inducing mesomorphism from nonmesomorphic species. This communication reports the first example of the use of another noncovalent interaction, halogen bonding, also able to induce liquid-crystallinity from nonmesomorphic components.

Resnati's work<sup>4</sup> has shown that the strongest complexes formed with Lewis-basic nitrogen atoms are with iodine atoms whose Lewis acidity is enhanced through attachment to an electron-poor fluorocarbon unit. Hence, we first undertook to form complexes of

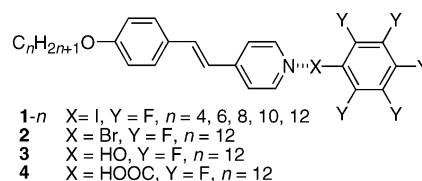


Figure 1. General structure of the complexes studied.

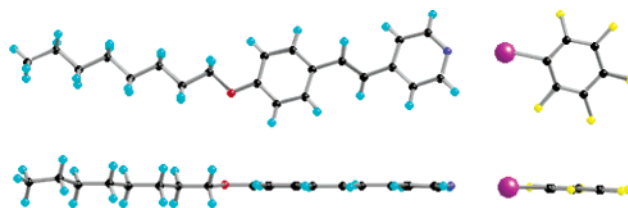


Figure 2. Two views of the molecular structure of complex 1-8.

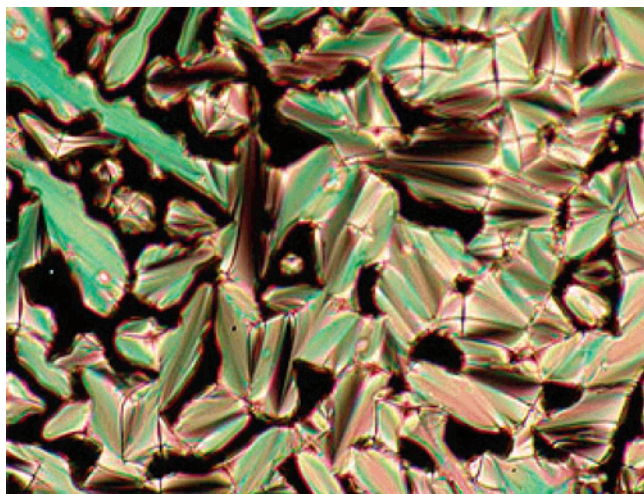
iodopentafluorobenzene with a range of nonmesomorphic 4-alkoxystilbazoles.<sup>9</sup> We also made some related complexes to allow comparison with hydrogen-bonded analogues. The materials studied are collected in Figure 1.

The “synthesis” of the desired materials is normally trivial and requires mixing of the two components in a common solvent in precise, equimolar proportions followed by the removal of that solvent. This is essentially what was done in these cases, so that the two components were mixed in THF in equimolar proportions and stirred for 3 h before the solvent was allowed to evaporate under ambient conditions. That complex formation was successful was indicated by the color of the product. Thus, the parent stilbazoles are colorless, whereas when protonated, the absorption red-shifts, and the compounds are bright yellow. The products obtained after evaporation of the THF were pale yellow, implying that the pyridine nitrogen was interacting with a group which reduced its electron density, in this case the  $\delta^+$  iodine atom. That the complexes are colored is also significant as it shows that the dominant interaction is the halogen bond and not a quadrupolar interaction, as in the latter case there is no charge transfer and thus no color change.

However, to demonstrate complex formation more directly, single crystals of 1-8 were obtained from THF and then analyzed by X-ray diffraction (Figure 2). The molecular structure shows the halogen bond clearly with an observed N–I distance of  $2.811(4)\text{ \AA}$  and a N–I–C angle of  $168.4(1)^\circ$ . The angle deviates significantly from the predicted linearity, and the contact is shorter than the majority of comparable Resnati structures (range  $2.762\text{--}3.127\text{ \AA}$ ). As the second view in Figure 2 shows, the ring systems of the two components were effectively coplanar (angle between the planes of the two rings is  $2.38(14)^\circ$ ). Analysis of the packing of the complexes also showed the absence of quadrupolar phenyl/perfluorophenyl interactions.

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**Figure 3.** Optical texture of the SmA phase of 1-6 at 69 °C on cooling from the nematic phase.

Despite the nonmesomorphic nature of the parent stilbazoles, complexes **1** were all liquid-crystalline (Table 1), and the mesophases were readily identified using polarizing optical microscopy. Thus, the three longer-chain complexes, 1-8, 1-10, and 1-12 showed enantiotropic SmA phases, and importantly, it was seen that the solids melted cleanly with no appearance of the biphasic regions which would characterize a nonstoichiometric complex. It was sometimes possible to observe a focal conic fan texture for the SmA phase of these materials (e.g. Figure 3), but on cooling in particular, strongly homeotropic textures were found. In cases where only homeotropic textures were observed, the SmA phase was characterized by preparing homogeneously aligned samples on slides coated with nylon. Compounds 1-4 and 1-6 differed in displaying a monotropic nematic phase, whose texture was again highly homeotropic, although schlieren areas could be observed at the edge of the samples and the characteristic flashing was observed on mechanical disturbance. Compound 1-6 also showed a transition to a (monotropic) SmA phase prior to crystallization. All of the thermal behavior was reproducible, even after several excursions into the isotropic phase.

For the purpose of comparison, complex **2** was targeted in which the Lewis base was bromopentafluorobenzene. Here, despite several attempts, we were never able to obtain evidence that we had prepared the complex and the thermal behavior mirrored that of the free stilbazole.<sup>10</sup> It is argued<sup>4</sup> that the strength of the donor–acceptor interaction depends on the polarizability of the halogen atom which decreases as I > Br > Cl (e.g. N···Br interactions tend to be >3 Å in the solid state).<sup>4c</sup> Hence, the behavior of **2** suggests that the N···Br interaction is simply not strong enough for the complex to exist at temperatures significantly above ambient. That no complex forms is further evidence that quadrupolar interactions are not responsible for the mesomorphic behavior in these systems; there was similarly no evidence of complex formation with C<sub>6</sub>F<sub>6</sub>.

Finally, and for the purposes of comparison, we obtained complexes **3** and **4** as examples of materials more closely related

**Table 1.** Transition Temperatures for the New Complexes

compound	transition	T/°C	compound	transition	T/°C
1-4	Cr-I	85	1-10	Cr-SmA	70
	(N-I)	(76)		SmA-I	81.5
1-6	Cr-I	78	1-12	Cr-SmA	81
	(N-I)	(76)		SmA-I	84
	(SmA-N)	(70)	3	Cr-I	96
1-8	Cr-SmA	77		(SmA-I)	(94)
	SmA-I	80	4	Cr-SmA	104
				SmA-I	127

to the hydrogen-bonded mesogens described previously, yet still containing the pentafluorophenyl group.

Using optical microscopy, a monotropic SmA phase was observed for **3**, while for **4** it was enantiotropic.

One of the more interesting observations that can be made with these latter complexes relates the transition temperatures of **3** to those of **1** (see Table 1). Our previous work with stilbazoles hydrogen-bonded to electron-poor phenols<sup>7</sup> has shown that mesophases can be stabilized up to around 125 °C. This means that the hydrogen bond must be stable to at least this temperature. In **3**, the SmA phase is observed at 94 °C, and as neither component is mesomorphic, this represents a minimum temperature up to which the hydrogen bond exists. Consideration of **1** then shows that the highest temperature to which a mesophase of these complexes is stable is 84 °C. These last two temperatures are comparable, which suggests that the halogen bond in the fluid, liquid crystal phase of these systems has an appreciable strength, similar to that seen in hydrogen-bonding systems.

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**Supporting Information Available:** Full crystallographic data (cif file), molecular structure employing thermal ellipsoids (TIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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