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Categorizing Halogen Bonding and Other Noncovalent Interactions Involving Halogen Atoms

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CATEGORIZING HALOGEN BONDING AND OTHER NONCOVALENT INTERACTIONS INVOLVING HALOGEN ATOMS

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**Objective**

To take a comprehensive look at intermolecular interactions involving halogens as electrophilic species and classify them. To give a modern definition of halogen bonding, which takes into account all current experimental and theoretical pieces of information on both gaseous and condensed halogen-bonded systems in chemical and biological systems.

**Description**

Halogen atoms in organic compounds typically can be found at the periphery of molecules. For this reason, they are ideally positioned to be involved in intermolecular interactions. In fact, thanks to the large number of halogenated drugs and inhibitors, interactions involving halogen atoms are frequently observed in protein-ligand complexes. Halogens also occur naturally in biological systems. The best-known examples of this are probably the iodinated thyroid hormones, such as thyroxine. The crystal structure of the transport protein transthyretin complexed with thyroxine showed multiple iodine to carbonyl oxygen contacts involved in hormone binding. It is well-known that the electron density around the halogen nucleus is highly anisotropic so that halogens can serve both as electron-acceptors and -donors. While we acknowledge that the terminology used to name noncovalent interactions given by halogen atoms has to be as unifying as possible, it is our opinion it has always to be done in keeping with the electrophile/nucleophile role the halogen atom plays. The term halogen bonding has been introduced for describing any noncovalent interaction involving halogens as acceptors of electron density. The general scheme D···X-Y thus applies to halogen bonding (XB), wherein X is the halogen (Lewis acid, XB-donor), D is any electron-donor (Lewis base, XB-acceptor), and Y is carbon, halogen, nitrogen, etc. The definition itself sheds light on the nature of XB, which possesses numerous similarities with hydrogen bonding (HB), wherein hydrogen functions as the acceptor of electron density. In our opinion, the use of the term halogen bonding has to be limited to those interactions wherein halogens function as acceptors of electron density. Its use also to address interactions in which halogen atoms functions as electron-donors is conceptually misleading and contrasts with the clear tendency, well-documented in the literature, to name such -X···H-Y interactions differently (i.e. hydrogen bonds).

This project will attempt to give a modern definition of halogen bonding that is as inclusive as possible. Also, intermolecular interactions will be categorized logically considering the physical forces involved.

Project announcement in *Chem. Int. March-Apr 2010* (vol. 32 No. 2)
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ORAL PRESENTATIONS
SESSION I– Theoretical Modelling

Chairman: Gautam R. Desiraju
Perspectives on Halogen Bonding:

*lex parsimoniae* - Select the hypothesis that makes the fewest new assumptions
(Occam’s Razor)

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Abstract

Covalently-bound halogen atoms have anisotropic charge distributions; their radii are shorter along the extension of the bond than in the directions perpendicular to it. This often gives rise to a significant positive electrostatic potential (a positive $\sigma$-hole) on the outer side of the halogen, through which it can interact attractively with negative sites. This noncovalent interaction is called halogen bonding. It is highly directional, along the extension of the covalent bond to the halogen, and is often competitive with hydrogen bonding. For a given negative site, the strengths of the interactions have been shown to correlate with the magnitudes of the $\sigma$-hole potentials.

This electrostatic interpretation of halogen bonding (which emphasizes some mutual polarization of the halogen atom and the negative site) is based only upon physical observables – the electrostatic potential, interaction energies and geometries. The weakness of this interpretation is that it is simple and straightforward, and is therefore viewed by some with suspicion. More elaborate interpretations, involving less physically-based methods and models, are sometimes advanced. Our objective in this presentation shall be to address and if possible reconcile some of the apparent differences in these interpretations.
A number of studies have examined intermolecular interactions arising from hydrogen bond (HB) and halogen bond (XB) formation [1]. Such studies have demonstrated that the nature of the HB may vary significantly, being either traditional, proton-shared, or ion-pair. In contrast, the vast majority of halogen bonds appear to be traditional bonds.

Recently, we carried out a theoretical study of XB complexes formed between isocyanate derivatives (XNC) with FCl (Figure 1) [2]. To our surprise, the halogen bonds with these carbon bases do span the range of halogen-bond type from traditional, to halogen-shared, to ion-pair. These bonds have been characterized based on binding energies, geometries, and nuclear spin-spin coupling constants.

![Figure 1. Examples of traditional, halogen shared, and ion-pair halogen bonds in the FCl:CNX complexes. The structures were optimized at the MP2/aug-cc-pVTZ computational level.](image)

To further understand the nature of the XB bond in these complexes, we have compared them to halogen bonds formed by cyanate derivatives (XCN) [3]. This comparison led to the identification of the factors which govern the type of halogen bond which is formed.

References
Computational analysis of I$_3^-$···I$_3^-$ halogen bonds

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Iodide ions have a strong affinity to iodine molecules, forming polyiodide species such as triiodide (I$_3^-$), where the I$^-$···I$_2$ interaction is extremely strong (~180 kJ.mol$^{-1}$) [1]. These triiodide species can then form further interactions to neighbouring I$_3^-$ ions, often forming infinite chains of ions.[2] These I$_3^-$···I$_3^-$ interactions are surprisingly common, as seen from the number of crystal structures that contain this motif in the Cambridge Structural Database (CSD).[3] Although the most commonly observed chains are linear, or contain the triiodide ions oriented at 90$^\circ$ with respect to each other, as would be expected from the sigma-hole model of halogen bonding [4], a wide deviation from these angles has been observed. In this work we describe a detailed analysis of the relative orientations of I$_3^-$ ions involved in interactions with neighbouring I$_3^-$ ions, which we show with the aid of MP2 and density functional theory calculations is the result of the bending potential in I$_3^-$···I$_3^-$ interactions being very low. Furthermore, we have found that the chemical environment of the ions plays a major role in stabilising the interactions. Although I$_3^-$ is calculated as being stable in the "gas-phase", the presence of a surrounding electric field, as found in ionic crystals, is necessary for the stabilisation of I$_3^-$···I$_3^-$ interactions.

References

SESSION II – Experimental Techniques

Chairman: Pui Shing Ho
Intermolecular complexes in the gas phase: a comparison of halogen bonds, hydrogen bonds and other interactions.

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Some generalizations will be presented concerning the properties of various types of binary gas-phase complex. The properties have been determined from the rotational spectra of the complexes. In particular, we shall focus on those complexes in which the two component molecules are held together by a halogen bond, a hydrogen bond, or another (possibly related) type of interaction. The generalizations have been established in the case of the hydrogen-bonded series B···HX by the systematic variation of the Lewis base B (e.g.: OC, HCN, HCCCH, H₂CCH₂, H₂O, H₂S, NH₃, PH₃, etc.) and the hydrogen donor HX (X = Cl, etc.). For halogen bonding, the complexes to be discussed will be mainly those in series of the type B···XY, where B is one of the Lewis bases already defined and XY is a dihalogen molecule (ClF, Cl₂, BrCl, Br₂ or ICl). By including some results from recent work on gas-phase, halogen-bonded complexes of the type B···ICF₃, a comparison of ICl and ICF₃ as iodine donors in halogen bond formation will be possible and will allow comment effect of the electronegativity of Y = Cl or CF₃ on the halogen-donor ability of X = I. In addition to the results for the hydrogen- and halogen-bonded systems, a summary recent results for molecules of the type B···MX, where M is a Group 11 coinage (Cu or Ag) metal and X is a halogen atom, will be presented. The B···MX are novel compounds that have been synthesized in the gas phase by a laser-ablation technique. Similarities to and differences from their hydrogen-bonded and halogen-bonded analogues will be considered.
Halogen bonding from charge density analysis

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Directional intermolecular interactions of diverse strengths[1,2] are favorite tools of crystal engineering, since the orientation of molecules in the solid state can be predicted with a reasonable degree of accuracy. Two such interactions stand out: hydrogen bonding and halogen bonding. The marked directionality of the hydrogen bond (HB) is well established and is the basis for efficient and reliable topologies of intermolecular motifs. The strength of the hydrogen bond can be estimated from high resolution X-ray diffraction as proposed by our group[3,4] and this method based on the topological analysis of the electron density \( \rho \) at the HB critical point is now widely used. On the other hand, the halogen bonding interaction has been much less investigated. It occurs in the systems C−Hal···X (X = L, Hal) where an organic halogen atom approaches either a Lewis base (L) or a halogen atom (Hal). Halogen bonding can be as effective as hydrogen bonding for driving highly specific crystal packing motifs, as synthons. It finds its origin in the anisotropy of \( \rho \) around the halogen nucleus, leading to a smaller effective atomic radius along the extended C−Hal bond axis than in the direction perpendicular to this axis, a feature called polar flattening. In a recent experimental charge density analysis of hexachlorobenzene (C₆Cl₆)[5] we have confirmed the anisotropy of the electron distribution around the chlorine nuclei, leading to the formation of electrophilic and nucleophilic sites in the valence-shell charge concentration of chlorines. In the crystal structure of C₆Cl₆, main halogen···halogen interactions are thus electrophilic-nucleophilic in nature, being established between oppositely polarized regions in front of each other within a Cl₃-synthon. The Atoms in Molecules theory[6] has been applied to crystalline C₆Cl₆, demonstrating these features (Fig. 1) and indicating that the electron density properties at Hal···Hal bond critical points correlate with the strength of the observed interactions.

Figure 1: \( \Delta \rho \) and \( -\nabla^2 \rho \) maps showing the electrophilic-nucleophilic interactions in the Cl₃-synthon.

References
Multinuclear Solid-State Magnetic Resonance Studies of Halogen Bonding Environments

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Halogen bonding, RX-B, is the result of a non-covalent interaction between a halogen X and a negative site B (e.g., Lewis base or π electrons). The halogen, X, is typically part of an RX molecule where R can be another halogen, an organic or an inorganic electron-donating-group.[1] Our research group has been actively developing the solid-state nuclear magnetic resonance (SSNMR) spectroscopy of $^{35/37}$Cl, $^{79/81}$Br, and $^{127}$I. [2,3] These are all quadrupolar nuclei ($I > \frac{1}{2}$) which typically give rise to broad NMR powder patterns. While the spectroscopy of covalently-bound halogens remains generally impractical, we discuss the promising results of a series of SSNMR experiments on halide ions involved in halogen bonding environments in a series of 18 haloanilinium halide salts. These experiments were facilitated by the use of an ultrahigh magnetic field of 21.1 T (900 MHz $^1$H frequency) at the National Ultrahigh-Field NMR Facility in Ottawa (www.nmr900.ca). We discuss the relationships we have observed between the halide ion environment and the halide electric field gradient (EFG) and chemical shift (CS) tensors. Secondly, we have used SSNMR to study thiocyanate and selenocyanate moieties which are halogen-bonded with iodine atoms.[4] The main objective is to understand the possible correlation between halogen bonding and the NMR parameters. We are studying the effects of this interaction on the NMR tensors of nuclei involved directly and indirectly in halogen bonding, such as $^{13}$C, $^{77}$Se, and $^{14/15}$N. Static, cross-polarization magic angle spinning (CPMAS), and Hahn-echo SSNMR experiments allowed for the measurement of $^{13}$C and $^{15}$N CS tensors for compounds of the form $(R_4N(S/Se)CN)_x(o- or p-C_6H_4I_2)_y$. Results are compared with those for simple thiocyanate and selenocyanate salts. Also, gauge-including projector-augmented wave (GIPAW) density functional theory was used to compute the shielding and EFG tensors of the synthesized compounds in order to corroborate experimental findings and to determine trends. We describe the relationships that we have elucidated between the EFG and CS tensors for various nuclei and the local halogen bonding environment.

![Solid-state $^{81}$Br NMR spectrum of 3-chloroanilinium bromide at 21.1 T.](image)

References
Halogen Bonding in Crystal Engineering

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The unusual behavior of halogens in their intermolecular contacts in crystals has been noted for more than 50 years. The anomalous layered crystal structures of the solid halogens Cl₂, Br₂ and I₂ have elicited much comment. One of the earliest “rules” in crystal engineering, the 4Å chloro rule of Gerhard Schmidt invoked the presence of a chloro substituent in an aromatic molecule. The pioneering work of Hassel and Kochi relies on the use of electrophilic halogen. Our early forays in this area systematized the crystal structures of the dichlorophenols and a substantiation of the Type-I and Type-II classification of Sakurai, Sundaralingam and Jeffrey. A distinction between these two types of halogen···halogen interactions is clearly illustrated in an analysis of unsymmetrical X₁···X₂ halogen···halogen interactions, that is where X₁ ≠ X₂. The Type-I contacts are normal van der Waals interactions of the dispersion–repulsion type while the Type-II contacts are of the electrophile–nucleophile type. That the halogen atom potentials are anisotropic is without doubt as judged from the experience of participants in the Crystal Structure Prediction blind tests. Evidence for the anisotropic nature of the Type-II Cl···Cl interaction appears from very accurate charge density studies on hexachlorobenzene and mechanical nanoindentation studies on the same compound. The behavior of fluorine seems to be different. Halogen bonding has many similarities with hydrogen bonding as can be seen from the analogy between halogen atoms and the ethynyl group. The use of electrophilic halogen in crystal engineering is only beginning and more interesting applications are expected.

References

An exciting research challenge in supramolecular chemistry is to design, synthesize, and characterize nano-sized architectures with applications in chemistry, materials science and biology. Predicting and designing non-covalently bound supramolecular complexes and assemblies is difficult because of the weakness of the interactions involved, thus the resulting superstructure is often a compromise between the geometrical constraints of the building blocks and the competing weak intermolecular interactions.

Our research interest has been focused on the studies of weak non-covalent intermolecular, viz. supramolecular interactions as the driving force in solid state self-assembly and molecular recognition, especially by single crystal X-ray diffraction. The lecture will highlight some of our recent studies on system showing concerted hydrogen bonding and hydrogen bonding in some porous and XBOF (halogen bonded organic framework) solid state structures and solar cell dyes [1].

Figure 1. XB-based porous lattice [2h] (left) and XB and HB in solar cell dye [1g].

References

Halogen Bonds in Inorganic Chemistry

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Terminally bound halogen atoms exhibit anisotropic charge distributions and electrostatic potentials leading to directional intermolecular interactions that can vary in nature. Halogens in organic compounds (C−X) can engage both in interactions with electrophiles and nucleophiles. The former, such as hydrogen bonds are rather weak, but nevertheless directional [1]. The latter, known as halogen bonds, can be appreciably stronger and highly directional. Halogens bound to metal centres (M−X) exhibit the same anisotropic charge distributions as their organic analogues, except that they carry an overall larger partial negative charge. This renders their interaction with nucleophiles repulsive and enhances their interaction with electrophiles [1]. Thus, M−X groups form strong, directional hydrogen bonds [1,2] and provide excellent Lewis basic partners for halogen bond donors. The resultant halogen bonds (C−X⋯X−M) have provided excellent scope for tuning halogen bond strength and assessing the importance of different energetic contributions to halogen bonding [3]. The combination of halogen bonds and hydrogen bonds has enabled a series of halopyridinium halometallates to be studied in the solid state and in particular their solid state reactions involving HX gases [4], where we have recently extracted mechanistic information that depends upon the difference in strength of interactions involving different halogens [4c]. Metal fluorides, in particular, form very strong halogen and hydrogen bonds and 19F NMR provides a mean of determining the energetics of these interactions in solution [5]. The talk will extend the development of these systems to look at halogen bonds in which small pseudohalide ligands in metal complexes act as halogen bond acceptors [6] and examine the broader scope for halogen bonding in inorganic chemistry.

References

SESSION IV – Donors & Acceptors

Chairman: Marc Fourmigué
Expanding the Halogen Bonding Periodic Table: Heavier Congener Acceptors

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Halogen bonding involving organohalogens as donor and either nitrogen or oxygen as the acceptor is well known. Cocrystals involving heavier congeners of these acceptors have received much less attention. Most of the known examples involving sulfur and selenium acceptors were reported in the 1950’s and 60’s by Hassel and coworkers2 with only a few papers focused on these interactions appearing in the current decade3,4.

Nitrogen and oxygen Lewis bases serve as excellent acceptors for both hydrogen and halogen bonding, and numerous reports comparing the strength and occurrence of these two interactions have appeared5. Competition between these two interactions is often counterproductive for effective crystal design applications, where the construction of supramolecular assemblies often depend on the use of diverse and selective synthons. Coexistence of the two interactions within a given crystal has been reported, but only recently has a systematic approach to combining them, based on a hierarchy of potential H-bonding and X-bonding interactions, been proposed6. This approach is similar to the very successful use of hydrogen bonds of varying strengths for the construction of binary and ternary co-crystals7.

We are developing an alternate approach employing sulfur as an acceptor for both H- and X-bonds, in a complementary rather than competitive fashion, based thioamides as the acceptor system. Thioamides having an E-configuration about the C-N bond reliably form N-H···S linked dimers with an eight-membered $R_2^{2(8)}$ ring. Thiodiamides, such as thiourea and derivatives form infinite ribbons of these $R_2^{2(8)}$ rings. In addition to N-H···S hydrogen bonding, the sulfur atoms can also act as halogen bond acceptors, with one or more S···I interactions, oriented in roughly orthogonal positions to the N-H···S ribbon plane.

We will also report on a number of new halogen bonding systems involving selenium and phosphorus as acceptors, and discuss the relative strengths and potential applications of these X-bonding synthons.

1 K. Rissanen, CrystEngComm 2008, 10, 1107.

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It is well known that the reaction between a L=E (L = organic framework; E = S, Se) chalcogenone donor and a di-halogenic molecule X$_2$ (X = Cl, Br, I) can afford two types of adducts, i.e. linear charge-transfer (C.T.) or “T-shaped” adducts, characterized by two different linear tribody systems (E–X–X and X–E–X, respectively) in which the central atom is in a hypervalent state. Both types of systems are characterized by linearity and a total bond length greater than the sum of the covalent radii of about 10-12%; this entity of elongation is typical of a 3c-4e bond. A peculiar characteristic of these systems is the possibility to be frozen in the solid state in practically endless situations spanning from balanced (0.5 bond order for each bond) to very unbalanced bonds (one bond order approaching to 1 and the other to 0, always keeping the total bond order roughly equal to 1). By studying in the density functional theory (DFT) context the possible mechanisms involved in the reactions between 1,3-dimethylimidazoline-2-thione and -2-selone and di-halogens X$_2$ (X = Cl, Br, I) to form both types of adducts, a surprising result was that no direct formation of the T-shaped adduct from the reactants was possible, while its formation resulted possible from the C.T. adduct through a trigonal bipyramidal transition state in which the two halogen atoms occupy an axial and an equatorial position. Therefore, the formation of the cation [LEX]$^+$ is not necessary to explain the inter-conversion between the two types of adducts; however, the formation of such cation seems to be very important to explain the origin of other archetypes of solid products, such as dications [LE]$_2$$^+$ bearing a chalcogen-chalcogen single bond, monocations [(LE)$_2$X]$^+$ in which X$^+$ is formally coordinated by two donor molecules or other oxidation products in which a complete electron transfer from the donor to the halogen occurs with a consequent formation of a very great variety of polyhalide counter-anions. In this paper, only some selected archetypes of products will be considered, namely those containing a linear tribody system: C.T. adducts (E–X–X), hypervalent chalcogen compounds bearing the linear X–E–X group, compounds in which a central halogen is co-ordinated by two chalcogen atoms [E–X–E]$^+$ and trihalides [X–X–X], which together with X$^+$ and X$_2$ represent one of the three fundamental building blocks able to generate all the polyhalides. The discussion will be centred mainly on the structural features of these tribody systems on the grounds of structural data from a search of the Cambridge Structural Database (CSD) in order to point out not only the close analogy of the chemical bond in all these systems, but also the analogy between these species and trichalcogenide species characterized by the [E–E–E]$^{n}$ (n varying from -4 to +2) linear arrangement. The information obtained from this kind of analysis will be considered for the interpretation of the nature of the halogen bond in its more wider definition in A\textsuperscript{--}X$^+$B systems (A, B elements, X halogen).

References
Iodoacetylenes were among the first halogen bond donors studied in solution in the early 1980s by Laurence [1]. These behave as strong Lewis acids and their properties have been successfully linked to several spectroscopic (IR, $^{13}$C NMR) and electronic (Taft’s factors $\sigma_I$ and $\sigma_R$) characteristics. In spite of these properties, they have been mostly ignored in supramolecular chemistry until relatively recent applications in the design of conducting organic crystals by Yamamoto and coworkers [2] and the synthesis of highly organised conjugated polymers by Goroff, Lauher and coworkers [3].

We now have extended the scope of iodoacetylyl halogen bond donors to some heterocyclic compounds (Figure 1). Their crystal structures all show very short halogen bonds and the halogen bond capabilities will be discussed in the light of previous findings. We also characterised new adducts of the parent diiodoacetylene and compared it with other iodoacetylyl compounds.

Pentafluoroiodobenzene is the archetypal aromatic halogen bond donor and the starting compound for the synthesis of several 4-iodoperfluorophenyl derivatives [4]. We have determined the crystal structure of its adducts with a series of nitrogen bases and compared these with those of several other perfluorinated aromatic halogen bond donors (Figure 2), proposing also some general routes to their syntheses.

References

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The Symmetry of N-X^+-N Halonium Ion Complexes in Solution

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Halogen bonding (XB) has so far mostly been investigated with crystallographic or theoretical computational methods. Only few studies have been carried out in solution. An improved understanding of the behaviour of halogen bonds in solution is expected to provide useful insights for a wide variety of fields, e.g., synthetic chemistry, material science, and medicinal chemistry.

The strong resemblance of XB with hydrogen bonding (HB) is well known [1]. A classic concern regarding hydrogen bonds is their symmetry in solution [2]. For a molecular system where the hydrogen atom is located between two electron donating atoms (A and B) that both have the same proton affinity, there are two possibilities for its symmetry; symmetric with a single-well energy potential (A⋯H⋯B with H centrally located) or asymmetric with a double-well energy potential (A-H⋯B in equilibrium with A⋯H-B). The same question regarding the symmetry in solution may apply to halogen bonds. Molecular systems comprised of an electropositive halogen located between two identical electron donating nitrogen atoms or groups may either be symmetric (e.g., N⋯X^+-N) or asymmetric with tautomers (N^+-X⋯N and N⋯X-N^+) in rapid equilibrium. We expect that this will have important implications in the understanding of molecular recognition processes in biological contexts.

The symmetries in solution of N-X^+-N-type halonium ion complexes with various electronic properties have been investigated. In these complexes, the positively charged halogen atom (X = Br or I) is coordinated between two electron donating nitrogen atoms of two identical pyridine moieties. The symmetries of the N-X^+-N-complexes were determined by a combination of variable-temperature NMR and isotopic perturbation of equilibrium (IPE) solution NMR experiments. The latter uses equilibrium isotope effects to alter dynamically equivalent NMR chemical shifts [3]. From the chemical shift differences of the signals observed in the ^{13}C NMR spectrum of a mixture of deuterated and non-deuterated N-X^+-N-complexes the symmetry properties are revealed. Computational DFT calculations have been applied for confirmation of the experimental results.

References
SESSION V – Biomolecules

Chairman: Kari Rissanen
Halogen Bonding And In Silico Drug Design

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Noncovalent interactions play a key role in biochemistry and their description and subsequent understanding is of vital importance. The special role among noncovalent interactions is played by halogen bonding what is an electrostatic attraction between the positive σ-hole on the tip of the halogen atom and the negative Lewis base. The opening of the σ-hole is clearly a quantum effect and, consequently, halogen bonding cannot be described by current force fields using atom-centered charges.

Halogen bonding promise to be of a great importance in the design of novel drugs. In the present study we investigate complexes of CK2 protein kinase with halogenated inhibitors by means of advanced semiempirical QM PM6 method, properly covering hydrogen- and halogen-bonding as well as dispersion energy. The PM6-DH2X method provides reliable geometries of those CK2 protein kinase-inhibitor complexes involving halogen bonds that agree well with the X-ray structures. When AMBER empirical potential is used, this agreement become considerably worse. Similarly, the binding free energies determined with PM6-DH2X are much closer to the experimental inhibition constants than those based on the Amber empirical potential.
Anisotropic models for the structure-energy relationships of biological halogen bonds

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Halogen bonds are becoming increasingly recognized as relevant to recognition and binding in a number of biological systems (1), and have recently been observed in protein kinase inhibitors (2) that regulate alternative splicing (3) and protease inhibitors against Hepatitis C(4). The relationship between geometry (5) and stabilizing potentials (6) of biological halogen bonds are now becoming better understood, providing the structure-energy relationships required to develop accurate potential energy relationships for such interactions. We are deriving empirical models that treat both the electrostatic and van der Waals components as anisotropic interactions, as consistent with the sigma-hole model for halogen bonds (7). These directional potentials, when implemented into current force fields, will facilitate the design of new inhibitors and drugs, and potentially of new nanomaterials from biological molecules.

Figure 1: Structure of a four-stranded DNA Holliday junction stabilized by a bromine halogen bond (dots) (6).

References
Experimental Charge Density Analysis of the Nature of C-Br···N≡C Interactions in Biologically Active Compound

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(E)-3(6-bromopyridin-2-yl)-2-cyano-N(S0-1-phenylethyl)acrylamide, WP1066, is developed for the treatment of neoplasms expressing the JAK2 (Janus kinase 2) mutation. This mutation is responsible for the polycythemia vera disease which occurs when the bone marrow produces too many red blood cells [1]. The protein and nucleic acid structures reveal halogen bonds as potentially stabilizing inter- and intramolecular interactions that can affect the ligand binding and molecular folding [2].

Experimental charge density distribution in WP1066 has been established using high resolution X-ray diffraction data collected at 100K to evaluate quantitatively the nature of the C-Br···N≡C halogen bond in the molecular crystal. Moreover, the occurrence of the halogen bond and strong hydrogen bond in this structure gives the opportunity for comparison of the energy of electrostatic interactions.

The topological analysis of the total charge density was performed for the C(4)-Br(2)···N(5)=C(24) halogen bond and N(6)-H(6N)···O(2)x,.5+y,.1-z hydrogen bond. The ρ(r), υ2ρ(r) and ρ(r)3 values at the critical points of these interactions are: 0.055(2) eÅ⁻³, 0.525(2) eÅ⁻⁵ and 0.113(25) eÅ⁻³and 3.191(16) eÅ⁻⁵, respectively. The electrostatic interaction energy for the molecules interacting vis halogen bond is -49.7 kJ/mol and by hydrogen bond -184.7 kJ/mol. Electron density is anisotropically distributed around the bromine atoms in the crystal studied, Figure 1(b). The bromine atom exhibits electrophilic character along the axis of C-X bond and nucleophilic character perpendicular to this axis.

References

Figure 1: (a) ORTEP of WP1066 with 50% ellipsoid probability at 100K and H atoms are shown with anisotropic displacement parameters obtained from SHADE2 analysis. (b) 2D static deformation density map (c) laplacian maps for C-Br···N≡C bond from charge density modeling. The positive - solid blue lines and negative – broken red lines.
SESSION VI – Materials

Chairman: Jane Murray
Halogen Bonding Involving Substituted Pyridines – Liquid Crystallinity and Lability

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Halogen bonding is one of a number of non-covalent, specific intermolecular interactions that may induce liquid crystal phase behaviour from components that do not have such properties,\textsuperscript{1} and in 2004 we reported on the first instance of liquid crystallinity induced in this way.\textsuperscript{2} In collaboration with the Milan group\textsuperscript{3} and by ourselves,\textsuperscript{4} we have since reported several more examples, including, recently, a large and systematic study of some 90 new complexes.\textsuperscript{5}

Most closely related to halogen-bonded systems are liquid crystals formed by hydrogen bonding. Here we and others found that complexes can normally be realised either simply by mixing the components together in solution and removing the solvent or, where this did not lead to complete complex formation, melting the two components together.\textsuperscript{6} However, what we have found in halogen-bonded systems is that in order to ensure complete complex formation, it is necessary to crystallise the complexes and that where this is not possible, it is clear that complex formation is incomplete.\textsuperscript{5} Furthermore, we have observed that there is evidence for halogen bond rupture during heating in some 2 : 1 complexes of aromatic diiodo compounds,\textsuperscript{3b, 4a} in one case leading to some rather interesting liquid crystal behaviour.\textsuperscript{4a}

Consideration of these effects led us to investigate systematically issues of halogen bond strength.\textsuperscript{7} The presentation will take into account the results of all these studies and will draw some appropriate conclusions.

References

Halogen Bonding Induced Self-Assembly of Extreme Materials

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A new class of supramolecular materials assembled via a gas-solid reaction from rigid perfluorinated compounds and amorphous hydrophilic polyethers are described. Series of volatile iodo-terminated perfluoroalkanes have been complexed to a branched 4-arms poly(ethylene glycol) amine hydrochloride by halogen bonding between the iodine and the chloride anions. The disinclination of the perfluorinated and the polyether segments to mix endures in a lamellar motif, where the immiscible blocks segregate into layers joined by the intermolecular halogen bonds. Stringent fixation and stretching of the poly(ethylene glycol) termini caused by the constraints of the rigid perfluorinated residues limits the mobility of poly(ethylene glycol) chains and controls the supramolecular long-range alignment. Furthermore, this polymer network has demonstrated ability for controllable molecular actuations governed by a reversible displacement of the volatile perfluorinated tails. Vapor- and/or thermo- sensitive volume changes have been observed. However, a complete understanding of the actuator mechanisms certainly demands further theoretical and experimental examination.

The system suggests future strategies to create functional and responsive materials that are expected to be utilized for actuation or sensing.
Halogen Bonding towards Assembling Phosphorescent Cocrystals and Probing Specific Solvent Effect

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The abstract consists of two parts, one describes assembly of phosphorescent cocrystals by halogen bonding with other noncovalent interaction, and another is amid to exploring possible specific solvent effect as encountering halogenated solvent.

**Part one**: two supramolecular cocrystals 1, pyrene/1,4-diiodotetrafluorobenzene (1,4-DITFB) and 2, pyrene/1,2-diiodotetrafluorobenzene (1,2-DITFB) have been assembled by synergistical C-I⋯I interaction, π-π stacking and C-H⋯F contact. The x-ray single crystal diffraction data reveal the structural characteristics of two crystals and function of position of iodine atom in regulating cocrystal structure. Two cocrystals were also well characterized by element analysis, x-ray powder diffraction for homogeneity of samples, UV-vis absorption and FTIR. Furthermore, two cocrystals phosphoresce with well defined fine structure due to iodine acting as heavy atom perturber. They have 10³ to 10¹ s⁻¹ phosphorescence decay rate.

**Part two**: halide and a dual fluorescence molecule 4-dimethylaminobenzonitrile (DMABN) are used to probe possible specific solvent effect, halogen bonding between halogen donor part (Cl-C) of the solvent and acceptor group (cyano-N) of the probe molecule or halide. The experiment and calculation show cyano-N⋯Cl-C and halide⋯Cl-C are compatible to cyano-N⋯H-C (hydrogen donor part of the solvent) and halide⋯H-C. The results enlighten that the halogen bonding as one specific effect parallel to hydrogen bonding should be considered habitually in explaining interaction between solute and halogenated solvent molecule.

**Keywords**: halogen bonding, phosphorescence, specific solvent effect.

Authors thank the National Natural Science Foundation of China (No.20675009, No.90922023 and No.20801006) for the support.
Halogen bonding is a strong tool for constructing supramolecular network due to its strength and directionality. We have utilized crystalline anionic networks comprising halide anions and iodine-containing molecules for sheathing one-dimensional stack of conducting molecules. We co-crystallized the insulating supramolecular network with cation-radical of TTF derivative as counter cations. (TTF = tetrathiafulvalene) The TTF derivatives form one-dimensional conducting wire due to $\pi-\pi$ stacking, while the supramolecular network provides three-dimensional insulating sheath due to halogen bonding between halide anions and iodine-containing neutral molecules. For example, when EDT-TTF is electrochemically oxidized in the presence of bromide anion and tetraiodoethylene (TIE), the conducting EDT-TTF wire is confined in the channel formed inside the anionic network to form monocry stalline nanowire (EDT-TTF)$_4$BrI$_2$(TIE)$_5$. (Figure 1) The resistivity anisotropy of this crystal is about 2000. The extension of this supramolecular nanowire structure by replacing TIE with several different molecules has also been done. [Ref. 1, 2]

The directionality of the halogen-bonding donor makes the network firm, while the halogen-bonding acceptors such as halide anions exhibit flexibility in its coordination numbers and angles. This combination of somewhat opposing natures is a characteristic feature of halogen bonding network, and seems to be good for finding the same periodicity with the TTF moieties. In this presentation, some strategies for further crystal engineering will also be discussed. This work has been done in collaboration with Mr. J. Liefrig, Dr. H.-B. Cui, Dr. Y. Kosaka, Dr. J.-I. Yamaura, Dr. A. Nakao, Ms. R. Maeda, and Dr. R. Kato

Figure 1 : Crystal structure of supramolecular nanowire (EDT-TTF)$_4$BrI$_2$(TIE)$_5$.

References
Halogen Bonding in Organic Conductors: more than an Intermolecular Interaction

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The conductivity of organic metals finds its origin in the overlap interactions of the partially oxidized molecules into stacks or slabs, leading to the formation of partially filled bands. However, very small modifications of the exact interactions between molecules within these stacks (1D) or slabs (2D) can have a striking effect on the conductivity. In that respect, several approaches have been described toward modification/control of these 1D or 2D solid state arrangements by introducing weak interactions at the organic-inorganic interface, such as hydrogen bonding [1] or halogen bonding [2,3].

Upon oxidation of halogenated tetrathiafulvalenes such as EDT-TTF-I2, the partial charge on the iodine atom along the C–I direction is strongly enhanced, leading to characteristic recognition patterns, with halide [4], pseudo-halide (NCS-) [5], or more complex (ClO4-, organic sulfonates) anions. Different conducting phases involving iodo-tetrathiafulvalenes will be described and analyzed, revealing a strong enhancement of this halogen bond interaction in molecular conductors together with the contribution of the halogen atoms to the band dispersion. A specific point will be also addressed for the elaboration of chiral organic conductors, based on the halogen bonding interaction with chiral anions such as camphor sulfonate [6].

References
Dynamically Porous Materials Assembled by Halogen Bonding

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Organic porous networks and cages have revealed potential applications ranging from guest inclusion and gas absorption to molecular transport. Most of the above-mentioned properties are studied under external stimuli by exposing the porous solids to guest molecules at different temperatures and pressures. The dynamic properties upon external stimuli in nonporous crystalline organic solids have received far less attention, so far.

In this communication we report about the ability of the nonporous a,ω-bis(trimethylammonium)alkane dihalides to reversible encapsulate diiodoperfluoroalkanes (DIPFA)1 and dihalogen molecules2,3 through a size matching dynamic response under gas-solid and solution conditions. Metastable I$_4^{2-}$ anions and mixed trihalide species have been isolated thanks to cooperative halogen bond (XB) and cation templation effect. Despite a lack of porosity of the starting materials guest molecules are readily transported through the solid until a thermodynamically stable porous structure is achieved. In all cases XB prevails over hydrogen bond and guest molecules substitute for the hydration water of starting halide anions. The non-covalent nature of the XB allows the process to be reverted at high temperature and low pressure. Our results show the relevance of a supramolecular-templated assembly of dynamically porous materials. Hexamethonium halides are proven effective solids for the clathration and storage of molecular dihalogens, while DIPFAs can first be selectively complexed and then quantitatively evacuated, by using longer bis(trimethylammonium)alkanes, giving purified fluorinated telomers and a reusable ionic scaffold.

Figure 1: Crystal packing of hexamethonium iodide / I$_2$ adduct.

References
SESSION VIII – Supramolecules

Chairman: William T. Pennington
The Balance Between Hydrogen Bonds And Halogen Bonds

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The construction of molecular co-crystals has been achieved most commonly with hydrogen bonds and there are very few examples of structures where the initial supermolecules are constructed via hydrogen bonds, and their subsequent orientation is the result of directional halogen-bond interactions. The primary goal of this presentation is to examine how hydrogen bonds and halogen bonds can be combined in the deliberate design of co-crystals. In the process, we will address specific questions related to how the balance between different binding sites affects molecular recognition events:

1. Can hydrogen-bonds and halogen-bonds operate side-by-side in a hierarchical fashion in the assembly of co-crystals?
2. A hydrogen-bond donor and a Lewis acid will both be “interested” in N-heterocyclic moieties. At what point (if at all) will a strong XB donor win over HB donor?
3. Can we use calculated potential energy surfaces to predict the supramolecular outcome of these co-crystallization reactions with a reasonable degree of accuracy?

To probe the balance between different non-covalent interactions we have employed custom-designed molecules with the appropriate functionalities; this led us to develop a facile synthetic path to 2,3,5,6-tetrafluoro-4-iodobenzoic acid and 2,3,5,6-tetrafluoro-4-bromobenzoic acid.¹ These molecules combine two very powerful XB, and HB donors, respectively, and can be used in a range of crystal engineering efforts especially since they promote and facilitate supramolecular selectivity due to their built-in geometric differences.

We have also examined how ditopic structural probe molecules containing two sites (pyridyl and benzimidazole) that can act as either hydrogen-bond or halogen-bond acceptors respond to the presence of multiple hydrogen/halogen-bond donor moieties in a structurally competitive situation.²

References
Anion Templated Assembly of Halogen Bonded Supramolecular Networks

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The selective binding, extraction, and separation of anions are frequently invoked as potential solutions to a number of fundamental and applicative problems. As far as inorganic anions is concerned, their complexation is actually a major challenge in supramolecular chemistry and impacts in environmental, industrial, and health-related areas.

Similar to what happens for cations, the number of coordinated ligands which surround anions and form their coordination sphere, is usually greater that the anion charge, both in the solid state and in solution. Coordination to the cation, electrostatic interactions, hydrogen bonding, “anion-π” interactions, and combinations of these interactions commonly participate in the construction of the anion coordination sphere [1]. Halogen bond (XB), any noncovalent interaction involving halogens as the electrophilic species [2], is recently emerging as a new item in the toolbox for anion coordination and anion-templated assembly [3].

In this contribution, we report some examples of anion binding driven by halogen bonding wherein halide anions act as halogen bonding acceptors. We will present how XB directs the self-assembly of anions forming discrete adducts and 1D, 2D, or 3D supramolecular networks [4]. We will also describe how oxyanions can be used as new building block in crystal engineering based on halogen bonding.

Figure 1: (6,3)-network defined by Et₄P⁺I⁻ and C₆F₃I₃.

References

SESSION IX – IUPAC definition of halogen bonding

Chairman: Roberto Marquardt
The term ‘Hydrogen Bond’ has been used in the literature for nearly a century now. While its importance has been realized by physicists, chemists, biologists and material scientists, there has been a continual debate about what this term means. This debate has intensified following some important experimental results, especially in the last decade, which questioned the basis of the traditional view on hydrogen bonding. Most important among them are the direct experimental evidence for a partial covalent nature and the observation of a blue-shift in stretching frequency following X–H•••Y hydrogen bond formation (XH being the hydrogen bond donor and Y being the hydrogen bond acceptor). Considering the recent experimental and theoretical advances, an IUPAC task group chaired by me has proposed a new definition of the hydrogen bond, which emphasizes the need for evidence. The importance of halogen bonding analogous to hydrogen bonding has been realized in recent times. There are some similarities and some differences between hydrogen bonding and halogen bonding. These have to be considered carefully in choosing the definition for halogen bonding.

References

IUPAC Project no. 2009-032-1-100 “Categorizing Halogen Bonding and other Noncovalent Interactions Involving Halogen Atoms”

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Objective: To take a comprehensive look at intermolecular interactions involving halogens as electrophilic species and classify them. To give a modern definition of halogen bonding, which takes into account all current experimental and theoretical pieces of information on both gaseous and condensed halogen-bonded systems in chemical and biological systems

Description: Halogen atoms in organic compounds typically can be found at the periphery of molecules. For this reason, they are ideally positioned to be involved in intermolecular interactions. In fact, thanks to the large number of halogenated drugs and inhibitors, interactions involving halogen atoms are frequently observed in protein-ligand complexes. Halogens also occur naturally in biological systems. The best-known examples of this are probably the iodinated thyroid hormones, such as thyroxine. The crystal structure of the transport protein transthyretin complexed with thyroxine showed multiple iodine to carbonyl oxygen contacts involved in hormone binding. It is well-known that the electron density around the halogen nucleus is highly anisotropic so that halogens can serve both as electron-acceptors and -donors. While we acknowledge that the terminology used to name noncovalent interactions given by halogen atoms has to be as unifying as possible, it is our opinion it has always to be done in keeping with the electrophile/nucleophile role the halogen atom plays. The term halogen bonding has been introduced for describing any noncovalent interaction involving halogens as acceptors of electron density. The general scheme D···X-Y thus applies to halogen bonding (XB), wherein X is the halogen (Lewis acid, XB-donor), D is any electron-donor (Lewis base, XB-acceptor), and Y is carbon, halogen, nitrogen, etc. The definition itself sheds light on the nature of XB, which possesses numerous similarities with hydrogen bonding (HB), wherein hydrogen functions as the acceptor of electron density. In our opinion, the use of the term halogen bonding has to be limited to those interactions wherein halogens function as acceptors of electron density. Its use also to address interactions in which halogen atoms functions as electron-donors is conceptually misleading and contrasts with the clear tendency, well-documented in the literature, to name such -X···H-Y interactions differently (i.e. hydrogen bonds). This project will attempt to give a modern definition of halogen bonding that is as inclusive as possible. Also, intermolecular interactions will be categorized logically considering the physical forces involved.

Project announcement in Chem. Int. March-Apr 2010 (vol. 32 No. 2)
Crystallographic Publication in the American Chemical Society Journal *Crystal Growth & Design* and Contentious Issues arising During Peer Review: An Editor’s Perspective (*so pay attention!*)

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Over the last decade *Crystal Growth & Design* has grown with such related fields as crystal engineering, metal organic frameworks, polymorphism, co-crystals, and several other important scientific fields related to the solid crystalline state. Many new scientists have begun publishing in these areas and many new concepts have been brought to the forefront. Some of these fields have also seen a transitional period from important early observational reports to now very complex theory and experiment driven fundamental understanding.

While I will attempt to provide “Scholarly and Pragmatic Aspects of Crystallographic Publication Practices” for the journal I edit, I could sum up most of what I would like for author’s to hear based upon a comment my neighbor used to make about life in general: “If you can read you can do anything.” In the specific case of scientific publishing, this most directly applies to thoroughly reading (and following) the Guidelines to Authors and the Ethical Guidelines for each journal.

This presentation will discuss my experiences with several contentious issues related to both rapid growth and transitional periods such as fractional publication, self plagiarism, referencing reviews rather than original works, and rejection without review. Nonetheless, ethical violations aside, in crystallographic publishing many of the disputes come down to whether a given crystallographic results is ‘good enough’ to support the science the author is reporting. This is where the fun begins.
CATEGORIZING HALOGEN BONDING AND OTHER NONCOVALENT INTERACTIONS INVOLVING HALOGEN ATOMS

POSTERS
Solids provide a convenient and generally stable format to store and deliver an active pharmaceutical ingredient (API) or a drug product. Within solids, crystalline solids and salts in particular are almost always the best approach for defining physical and chemical stability of a marketed drug.

Sibutramine, usually available in the form of the hydrochloride monohydrate salt, was marketed and prescribed as an adjunct in the treatment of exogenous obesity along with diet and exercise; being associated with increased cardiovascular events and strokes it has been withdrawn from the market in most countries. During the course of our studies on polymorphism and cocrystallization of APIs, we have re-determined the crystal structures of sibutramine hydrochloride anhydrous and monohydrate. The anhydrous form is only based on N-H⁺···Cl⁻ interactions that shape cation···anion pairs. Therefore, no extended hydrogen-bonding network is formed. The crystal packing of the monohydrate is based on halide-mediated hydrogen-bonding through N-H⁺···Cl⁻ that form anion···cation pairs and water molecules connect these pairs via O-H_water···Cl⁻ interactions, giving rise to two antiparallel hydrogen-bonded chains of API cations.

Gabapentin is a neuroleptic drug prescribed for the prevention of seizure, for the treatment of mood disorders, anxiety, tardive diskinesia, neuropathic pain and limb tremor. Besides its three polymorphic forms, a hydrochloride hemihydrate salt was also reported and we have disclosed a hydrochloride ester derivative of gabapentin [1]. Gabapentin ester aligns in two antiparallel chains connected through the anion by two N-H⁺···Cl⁻ interactions; a third N-H⁺···Cl⁻ bonding is used to form a layered structure of ester cations along a. In the hydrochloride hemihydrate supramolecular arrangement gabapentin cations interact directly with each other through N-H···O hydrogen bonds forming dimers that are reinforced by intermolecular interactions with the chloride anions. Chlorides support the dimers using N⁺-H···Cl⁻ charge-assisted hydrogen bonds and play a part in obtaining the anti-parallel chains as they act as acceptors for the water and the hydroxyl function of the carboxylic moiety.

References
Looking at the nature and strength of halogen bound complexes in the gas phase: molecular beam scattering experiment and ab-initio charge displacement calculations.

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The extent and role of charge-transfer (CT) effects in weak intermolecular interactions constitute a long debated and still unsettled question (see for example [1]). A full, detailed description of the nature of such interactions requires an account of the critical balancing of electrostatic, charge transfer, induction, dispersion, and exchange (or size) repulsion interaction components. This represents for long time a fundamental and broad field of research. Quantitatively identifying, among the others, the CT component is a particularly elusive task, but it is crucial in order to develop models founded on solid grounds and useful for the description of the force fields operating in complex systems of technological interest. Experimental and theoretical studies squarely aiming at this goal, starting with complexes of small molecules like water and ammonia, thus appear particularly desirable. On the basis of a combination of high resolution scattering experiment and ab-initio calculations we recently reported the definitive assessment of a measurable CT component in the weaker interacting complexes involving small hydrogenated molecules [2,3,4,5]. These investigations succeeded in casting light on the CT component of interactions which may be viewed as embryonic hydrogen bonds, in particular its extent and stereospecificity. The same type of combined experimental and theoretical analysis may be brought to bear on the halogen bond.

In this communication we present our preliminary results, employing molecular beam scattering experiments and charge displacement analysis obtained by high level ab-initio calculations, for the simplest halogenated molecules (CF₄ and CCl₄) interacting with water molecule. We show how a such combined experimental and theoretical study on simple halogenated molecules may reveal important details on the role of CT that may be of general relevance in halogen bound complexes.

Fluorinated organic compounds often show particular physical and chemical behaviour [1] that can be utilized in pharmaceutics and materials science. We studied the crystal structures of a systematically fluorinated organic Diels–Alder adduct [2]. The effects of the different degree of fluorination on the N-phenyl ring and the halogenation of the methylidene bound phenyl groups on the secondary interactions and on the packing arrangements of the molecules were investigated.

Isostructurality calculations and comparison of molecular conformations have been performed in order to structurally classify the compounds depending on the number and mode of fluorination. The fluorination of the N-phenyl ring, the molecular conformation and the packing arrangements can be well correlated. Four different types of molecular conformations can be distinguished characterized by the interplanar angles of the phenyl rings. The bromine substitution of the methylidene bound phenyl groups has a substantial increased space requirement which gives more freedom to the set of molecular conformations.

The effect of fluorine substitution on the solid state organization in competition with other weak intermolecular interactions was studied. A balanced interplay of C–H...O, C–H...F and especially C–H...π contacts is typical of the crystal packings. The fluorine atom is proved to be more specific than oxygen in making its choice to contact a hydrogen atom.

The placement of the molecule in the unit cell is mainly determined by the molecular conformation which is essentially governed by the mode of fluorine substitution of the N-phenyl ring. They are similar in the cases of the ortho and the ortho–para fluorine substituted molecules, and also in case of the meta substitution, while the ortho–meta–para perfluorinated compounds are the most different ones. Although the effects of halogenation of the molecules on the crystal structures are not strictly systematic, tendencies are revealed that may be useful in crystal structure prediction.

References
Weak Interactions Involving Aryl $\pi$ Systems and Halogen Atoms in the Crystal Structures of Phosphorus Derivatives of Betti Bases

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In connection with our research on synthesis and application of Betti bases [1], cyclic phosphonamides 1b-4b bearing three stereogenic centers were easily prepared by reacting chiral nonracemic aminobenzylnaphthols 1a-4a with chloromethylphosphonic acid dichloride (Figure 1).

The crystal structures of these intermediates were investigated by means of X-ray diffractometry. Besides hydrogen bonding and short contacts involving hydrogen and halogen atoms, two types of CH-$\pi$ interactions [2] were found: (i) an intra-molecular interaction between one hydrogen atom of the methylene group with the phenyl moiety; (ii) an inter-molecular interaction between one hydrogen atom of the methyl group of compounds 2b-4b with the naphthyl group bound to the oxygen atom. Furthermore, in the cyclic phosphonamides 3b and 4b, that are isostructural among themselves, we observed a halogen bonding [3] that involves the chlorine atom of the chloromethyl group and the $\pi$ system of the hydroxy naphthyl group [4].

References
Halogen bonds (X-bonds) result from an electrostatic attractive interaction between the electropositive crown of a polarized halogen, X, and an electron-rich Lewis base or accepting atom, A, resulting in an X—A distance closer than the sum of their traditional van der Waals radii. X-bonds have been shown to direct protein ligand recognition and binding [1] as well as the conformation of biological molecules [2]. We have demonstrated via high-resolution x-ray crystallography the ability of X-bonds to direct the isomeric conformation of DNA Holliday Junctions [2]. The stacked-X junctions can isomerize between two conformations; an X-isomer stabilized by X-bonding at the junction crossover, or the H-isomer stabilized by hydrogen bonding (H-bonding) at the junction crossover leaving the halogen on the outside strand. The structures of DNA Holliday junctions incorporating fluorine (F), chlorine (Cl), bromine (Br), or iodine (I) halogenated uracil were determined by single crystal x-ray diffraction from 1.6 to 2.2 Å resolution. DNA junctions that formed the X-isomer were found to have a junction stabilizing X-bond between the halogenated uracil and a phosphate oxygen. The angle of approach of the oxygen towards the halogen was near linear with respect to the halogen sigma bond, consistent with current halogen polarization and sigma hole theory. These structures show X-bonding interactions primarily with the π-orbital electrons of the phosphate oxygen, similar to interactions seen with proteins. The ratio of each isomer observed in the crystal structure was determined via occupancy titration calculations in which the halogen occupancy are varied to determine the percent of junction in the X- vs. H-isomer. We have shown that this ratio is correlated with the isomeric concentrations present in solution and therefore an indication of stabilization energy provided by either the X- or H-bonding. This conclusion is supported by differential scanning calorimetry of identical junctions in solution. We observe that halogen polarization, which increases from F > Cl > Br > I, affects both the X-bond structure and strength. The resulting structure and energy relationships of observed X-bonding interactions will be employed in development and parameterization of an anisotropic force field to accurately model the electrostatic and geometric treatment of halogens in current modeling programs. This will facilitate the applications of X-bonding interactions as a tool for biomolecular design and engineering.

References
Interactions between covalently bound halogen atoms (X) and Lewis bases (D) are known as halogen bonds (XB) [1]. The analogy with hydrogen bonding (HB) is withdrawn for several reasons. Both interactions are directional and essentially electrostatic in character, and in both of these hydrogen and halogen atoms are acceptors of electron density. But, while hydrogen bonds have been extensively studied so far, halogen bonding constitutes a rapidly growing area. Furthermore, while in HBs hydrogen atoms perform only one role (functioning as Lewis acid), halogen atoms in XBs can accept the electron density and act as electron donor as well. The origin of this dual halogen function is in the highly anisotropic electron density around the halogen nucleus known as 'polar flattening', which has its minimum along the extended C—X bond axis and its maximum perpendicular to that bond [2]. The preferences for the two distinct geometries involving halogen atoms, namely the interaction in the line of D—X bond and the interaction perpendicular to that bond, emerge consequently [3]. Having in mind similarities and differences between XB and HB, there arises the question whether the graph-set notation accepted in describing HB synthons be also used for describing halogen bonding motifs in supramolecular assemblies.

Therefore, we report the preparation and characterization of a series of molecular crystals of mono- and di-halopyridine complexes of copper(II) (where X ≠ F). The crystals are designed with intention to investigate the applicability of halogen bonding synthons for supramolecular construction, as well as to deduce the more common supramolecular architectures based on C—X···X—C and/or M—Cl···X—C halogen bonding synthons in CuCl₂—X-py and CuCl₂—X,X’-py systems.

References
Here we report on our investigations with tris(chloromethyl)phosphine oxide 1, which was chosen as starting material for the synthesis of new energetic materials. The substitution experiments of 1 with several nucleophilic energetic functionalities failed, however this failure was unexpected. Quantum chemical calculations - natural bond orbital (NBO) analysis [1] and electrostatic potential (ESP) calculation [2] at the B3LYP/cc-pVDZ level of theory [3, 4] - were carried out using the Gaussian G03W (revision B.03) program package [1] to explain the observed reactivity. The suitability of NBO and ESP method on molecules of this type will be emphasized. According to the ESP calculation the molecule 1 (Picture 1) shows an intramolecular interaction that induces steric hindrance at the carbon atoms and makes them consequently chemically inert towards nucleophilic attack.

![Picture 1: ESP of tris(chloromethyl)phosphine oxide](image)

Further ESP investigation were made for 1,3-Dichloro-2,2-dinitropropane 2 (Picture 2) to understand why this molecule is so unreactive towards nucleophiles. Also in this case the nucleophile cannot displace the Cl atoms, because the conformation of the molecule is locked. The driving force for the intramolecular interactions shown belowe are the positive σ-holes along the extensions of the C-Cl bonds and the negative potentials of the oxygens atoms of the nitro groups.

![Picture 2: ESP of 1,3-Dichloro-2,2-dinitropropane](image)

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Halogen bonding has been the subject of several experimental and theoretical studies [1,2,3]. Two possible geometries have been described: type I, van der Waals type interactions, involving the polar region of the electronic cloud of both atoms, and type II, $\delta^+...\delta^-$ interactions, involving the polar region of one of the halogen atoms and the equatorial region (with higher values of electron density) of another. Factors like polarizability and electronegativity affect the nature of the interactions involving halogens [4]. This work analyses the effect of the Cl position in the phenyl ring on the intermolecular bonds of chlorophenyl ferrocenoylmethyl thioether isomers. In the $\text{para}$ isomer the chlorine is involved in halogen-halogen bonds, while in both the $\text{meta}$ and the $\text{ortho}$ molecules it forms $\text{C}_\text{p}-\text{H}...\text{Cl}$ hydrogen bonds. The reasons for this behavior can be found in the lower electronic density on the $\text{meta}$-substituent that affects its ability to get involved in Cl-Cl bonds, while the absence of these contacts in the $\text{ortho}$ molecule can be explained by stereochemical reasons. These results are in good agreement with those of a search in the CCDC (38.3% of the $\text{para}$-Cl compounds display Cl-Cl bonds, while the values for $\text{meta}$-Cl- and $\text{ortho}$-Cl-substituted molecules are 4.5% and 4.7%, respectively).

Figure 1: Halogen bonding in (from top to bottom) $\text{p}$-, $\text{m}$- and $\text{o}$-chlorophenyl ferrocenoylmethyl thioethers

References
P9
Cation-templated synthesis of I$_4^{2-}$ using an extended viologen derivative

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The unstable halogen-bonded species I$_4^{2-}$ has been postulated to be the charge-transfer intermediate responsible for the charge-transport mechanism in I$^-$/I$_3^-$-based electrolytes of dye sensitized solar cells (DSSCs) [1], following a Grotthuss-like process [2].

The present communication will discuss our results on the use of an extended viologen derivative [(E)-4,4′-(ethene-1,2-diyl)bis(1-(2,3,5,6-tetrafluorobenzyl)pyridin-1-ium diiodide, 1•2I$^-$], for the cation-templated synthesis of the halogen-bonded complex 1•I$_4^{2-}$ by using the strategy of size-matching between anions and cations [3].

The bispyridinium derivative 1•2I$^-$ was found to selectively template the formation of 1•I$_4^{2-}$ via size-matching between the intramolecular N$^+$-N$^+$ separation in the cation, and the separation of the external iodine atoms in the dianion I$_4^{2-}$. 1•I$_4^{2-}$ was formed independently of the amount of iodine present in the crystallization solution, thanks to the cooperation between the above-mentioned anion-cation size-matching, as well as the space compartmentation produced by the bispyridinium cations. In the obtained crystal structure of 1•I$_4^{2-}$, the bis-benzyl bis(pyridinium)ethylene moieties adopt a Z-like conformation and stack via $\pi-\pi$ interactions affording supramolecular parallelepipeds wherein the metastable I$_4^{2-}$ anion is effectively caged (Figure 1).

Figure 1: Crystal packing of (E)-4,4′-(ethene-1,2-diyl)bis(1-(2,3,5,6-tetrafluorobenzyl)pyridin-1-ium) tetraiodide.

References
Weak Intermolecular Interactions between Iodine and Carbon in Organo-Iodine Compounds

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Weak interactions in the solid state involving large soft atoms like iodine represent a fascinating field of research and are of current interest.

Very intriguing are interactions of iodine with aromatic π-systems. There are very few reports in the literature about intermolecular interactions of iodine with the π-system of an aromatic compound.\(^1\) Most of the described interactions are those of iodine with the π-system of a triple bond, even in the presence of a phenyl substituent in the same molecule.\(^2,3\) Here we report for the first time the crystal structure of (E)-1,2-diiodo-1,2-diphenylethene (Figure 1), and (E)-(1,2-diiodovinyl)benzene which show intermolecular interactions between the iodine atoms and the aromatic π-systems of adjacent molecules. The interactions are discussed also with the help of quantum chemical calculations at B3LYP level of theory using cc-pVDZ basis sets.\(^3,4,5\)

References

Discotic liquid crystals (DLCs) have attracted special attention because of their high one-dimensional (1D) charge-carrier mobilities and self-healing properties, which are some of the most remarkable characteristics of these systems [1]. Columnar liquid crystals have become ideal candidates for molecular wires in several optical and electronic devices. The improvement of the functional capacity in these materials will be possible only with a new design of molecules and self-assembled systems. In this context, supramolecular chemistry has extended the horizon in the design of liquid crystals, capable of providing a huge number of new possibilities in the synthesis of dynamic molecules. In the liquid crystal assembly process, specific molecular interactions are involved. These can be used a priori in the design of the arrangement, such as: hydrogen bonds [2], ionic bonds, charge transfer interactions and halogen interaction, the latter being the most novel [3]. These non-covalent interactions have been recognized as key in the development of new dynamically functional materials.

This work suggests the synthesis of new columnar liquid crystals induced by halogen interactions. The building blocks have pyridine moieties derived from heterocycles as halogen-bond acceptors and iododerivatives as halogen-bond donors. The halogen interaction should be able to generate complementary structures that give rise to columnar phases.

![Figure 1: Units proposed for the complexes: pyridine units as a core and iodine derivatives for the side chains](image)

**References**

Halogen bonds are attractive non-covalent interactions between terminal halogen atoms in compounds of type R-X (X = Cl, Br, I) and Lewis bases. Strong halogen bonds are only obtained for very electronegative rests R. Although this interaction has been known for a long time, it has only started to get major attention since the early 1990s. Most of the investigations on halogens bonds to date have been performed for the solid state, based on x-ray structural analyses, while studies on the interaction in solution have been relatively sparse in comparison. The ubiquitous and much more common hydrogen bonds, on the other hand, have been studied extensively and have also been applied very successfully for organocatalysis and organic synthesis. Despite the various analogies between hydrogen bonds and halogen bonds, use of the latter in organocatalysis has only been reported for one case, namely the reduction of quinoline derivatives.\[1\]

The aim of our investigations is to find applications for halogen bonds in organocatalysis and organic synthesis. A special focus of our research efforts is on the rational design of novel (bidentate) halogen bond donors R-X.

Recently we could demonstrate that dicationic halogen bond donors of type 1 are able to activate the carbon-bromine bond of benzhydryl bromide (2) (and related substrates):

![Figure 1: Activation of benzhydryl bromide 2 by halogen bond donor 1; figure on the right: yield (in %) vs. reaction time (in h).](image)

In comparative experiments with non-iodinated compounds similar to 1 as well as with Broensted acids strong indications were obtained that the activation of the carbon-bromine bond can be ascribed to halogen bonding. Further investigations are in progress.

References
Dissecting Halogen Bonds: in Silico investigations on the Electronic Structure
Nature of Complexes between Iodoperfluoroarenes and Halide Anions

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In the last two decades, an increasing interest in halogen bonds has spurred numerous studies in several branches like supramolecular chemistry, materials science and related fields. Also, the role of halogen bonds (XBs) in biochemistry and drug design is increasingly recognized. Despite several analogies between XBs and the ubiquitous hydrogen bonds (HBs), subtle differences exist between these interactions, e.g. the high directionality of XBs and the nature of the interactions itself. In contrast to HBs, the exact electronic nature of XBs (i.e. the relative contributions of pauli, electrostatic, orbital and dispersion interactions to the overall interaction energy) is certainly not as well understood. While historically, XBs have generally been perceived as a charge-transfer-type interaction in recent years they have rather been viewed as being mainly based on electrostatics. Lately, a considerable amount of computational investigations on halogen bonds have been performed, and several of those calculations have included energy decomposition analyses. However, just a few theoretical studies have been based on selecting halides ions as Lewis base.

In this work we attempt to give a full in-depth analysis of the interaction between iodoperfluoroarenes (as typical XB donors) and halide anions. Density Functional Theory (DFT) has been used to evaluate the effect of several orientations of the Lewis base to pinpoint the origin of the highly directionality of the halogen bonds.
Although attractive interactions between terminal halogen atoms and Lewis bases (“halogen bonds”) have been known for almost 150 years, they have received relatively little attention from the scientific community until the late 1980s. In the last two decades, halogen bonds have been the subject of countless investigations and are now firmly established in supramolecular chemistry, materials science and related fields. Also, the role of halogen bonds (XBs) in biochemistry and drug design is increasingly recognized.

While historically, XBs have generally been perceived as a charge-transfer-type interaction, in recent years they have rather been viewed as being mainly based on electrostatics. Overall, a substantial number of theoretical investigations on halogen bonds have been performed, and several of those calculations have included energy decomposition analyses. However, only a small number of those computational studies concern charge-assisted halogen bonds, as is the case with halide anions as Lewis bases.

Understanding the intrinsic nature of these interactions is crucial in the design of novel materials, especially when halide anions might competitively form XBs or HBs in the crystal. In this work, we have used cutting-edge Density Functional Theory (DFT) decomposition analyses based on the Ziegler-Rauk approach to analyse the interaction of XB-bound complexes between iodoperfluoroarenes (as typical XB donors) and halide anions. In addition, the electronic nature of these interactions is compared to complexes with a neutral XB acceptor, ammonia.
Biologically Synthesized Amylose and Polyiodide Complex

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The blue color of starch-iodine test, discovered by Colin and de Claubry in 1814 [1], is a very important phenomenon in analytical chemistry. Amylose from starch is responsible for this deep blue polyiodide complex. Amylose is a linear α-1, 4-linked glucose polymer and is a minor component of starch. Inclusion complex formation of amylose with polyiodide and other guest molecules is an interesting feature of amylose and expected to be used in various industries. However, pure amylose has not been a practical material for industries, since the separation of amylose from starch is very difficult. We have developed enzymatic processes to produce synthetic amylose with essentially linear structure and strictly controlled molecular weight [2]. Synthetic amylose easily forms a very stable complex with polyiodides (Fig.1). K-edge EXAFS are employed to study the local structure of polyiodide in various molecular weight (MW=20K, 50K and 100K) of synthetic amylases at 20 K and room temperature. EXAFS Fourier transforms for polyiodide in synthetic amylose are shown in Fig. 2. Consequently, we assume that iodine is mainly present as I₃⁻ chain in the synthetic amylases.

Figure 1: Amylose Polyiodide Complex

Figure 2: XAFS Analysis

The complex was also found to be effective against microorganisms: gram-positive and gram-negative bacteria same as iodine [3]. Therefore the complex is expected to be one-part type solid iodophor which remains stable without liberating iodine during storage.

References

Multi-component supramolecular assemblies formed by halogen bonding

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We have already reported several nanowires where organic supramolecular insulting networks are sheathing conducting organic radical cations of TTF (tetrathiafulvalene) derivatives. In most cases, the sheath is formed by halogen bonding between halide ions and neutral molecules containing iodine atoms\cite{1}.

Enlargement of neutral molecules leads to thicker, and thus more insulting sheath. The most interesting issue of using enlarged neutral molecules is to solve the problem of the lattice defects. Indeed, it offers the possibility to obtain larger channel and thus “multiwires” in which several columns of conducting organic cations stay in the same sheath.

To the end, we have synthesized molecule 1 as a new material for insulating sheath. 1 can be co-crystallized with alkylammonium salts to form supramolecular assemblies. In the case of Et\textsubscript{4}NBr, the X-ray analysis clearly shows halogen bonding between 1 and bromide ions. In addition, Et\textsubscript{4}N ions are surrounded by the supramolecular assembly. Although the twist conformation of 1 is the same as in the pristine crystal, the co-crystallized structure and especially the channel are different in shape and size. This shows flexibility from the packing of the neutral molecule and gives serious hopes of compatibility with TTF derivatives, which leads to the formation of new nanowires. Optimization of conditions for electrochemical crystallization with several TTF derivatives is in progress. The synthesis of other similar iodine-containing molecules is also in progress. These molecules should lead to channels with different shapes and sizes. The wide range of channel structures expected from these molecules should show different compatibilities with different TTF derivatives and lead to unique nanowires.

Figure 1. sublattice of 1 in BPDT-TTF(1)Br crystal

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Electronic factors affecting the I-I bonds in the simplest polyiodides

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In the last decades, halogen bonding has acquired particular relevance for the building up of supramolecular patterns.[1] Heavier halides, especially iodines, are particularly sensitive to residual interactions, which allow formation of compounds of large nuclearities. In fact, anionic Iₙ⁻ᵐ species with n up 29 and m=-1,-2,-3 have been reported [2], the simplest one being obviously I₃⁻. Grouping of already electron rich atoms with similar, possibly with negative charge, is usually attributed to the high polarizability of the element. Calculations of the electron density are available, which highlight the points of its accumulation/depletion hence the capabilities of subsequent aggregations [3]. From the MO point of view, it is important to understand the electronic parameters which affect the stereochemistry of the higher nuclearity assemblies and, in particular, the variable strengths of the I-I interactions. The variability of the effects are already observed in the simplest linear systems I₃⁻ and I₄²⁻, of which there are numerous crystal structures available. The I-I distances significantly vary depending on the nature of the counterion(s) and the overall packing arrangement. Thus I₃⁻ has not always the expected Dₘ∞h symmetry but the two distances can become as different as 0.2 Å. Also for I₄²⁻, which in principle consists of a central I₂ molecule residually interacting with two external I⁻ anions, it is evident that the three I-I separations depend on the crystal environment with possible loss of the highest symmetry. Here, we present a simple model based on experimental and theoretical data, which highlights how the mixing of the key σ orbitals is affected by a different distribution of the positive charges in various crystals.[4] To determine the latter, the Hirshfeld surface approach has been applied to some selected experimental structures where the differences are most remarkable [5]. Systematic DFT calculations (in vacuum and solvent) confirm that variously localized positive charges around the polyiodide can significantly affect the geometries of even the smallest I₃⁻ and I₄²⁻ units. The satisfactory results are interpreted in terms of a simple qualitative MO model, which monitors the σ orbital mixing for different positive charge distributions, hence the variable strength of the I-I bonding. The reciprocal validation between experiment and calculations and the predictability of the trends are the interpretational key to predict the variability of the halogen bonding in the smallest polyiodides and possibly in those of higher nuclearity.

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Quantum chemical calculations have been carried out on halogen-bonded complexes between trifluoromethyl iodide and iodomethane and xenon. Halogen bonds to rare gases have the weakest binding energies reported [1] making it debatable as to whether they could be classified as halogen bonds. It is expected that the work presented here will provide some insight into the nature of these weakly bonded complexes where dispersion interactions are dominant.

Calculations have been carried out at high levels of theory, using both post Hartree-Fock and Density Functional Theory methods, with large basis sets to ensure sufficient accuracy. The performances of these methods have been compared and exchange-correlation functionals have been analysed based on their ability to include dispersion interactions. Counterpoise correction for the basis set superposition error has been used since the interaction is weak.

An alternative method of visualising (Figure 1) the $\sigma$-hole bonding model for halogen bonds, [2], involving the localised orbitals of the species, has been employed.

Figure 1: Localised orbitals for the lone pairs of xenon and iodine that can be used to visualise the presence of the $\sigma$-hole.

References
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Effects of Halogen Bonding in Ferromagnetic Chains Based on Co(II) Coordination Polymers

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Halogen bonds are directional interactions that have recently been widely applied in supramolecular chemistry as an alternative to hydrogen bonds to control solid-state structures.¹ However, the applications of halogen bonding in magnetic materials are more limited. Since 1D magnetic systems do not exhibit long-range order at finite temperature, the interchain interactions are crucial in this kind of low-dimensional system. Thus, halogen bonding can cause profound effects on the cooperative magnetic properties of the material. Here we present a strategy for the organisation of magnetic linear cobalt chloride chains in the solid state by using halogen bonds, which results in the modification of the magnetic properties of the 1D networks.

Two linear cobalt chloride ferromagnetic chains, trans-[CoCl₂(3,5-X₂py)₂] (X = Cl, Br), have been prepared and the influence of the halogen bonding on the interchain magnetic interactions has been investigated.² Halide bridged polymeric structures are promising candidates for the synthesis of single chain magnets, although the coexistence of ferromagnetic coupling within the chain with the interchain antiferromagnetic coupling results in an overall metamagnetic behaviour. We have successfully decreased the antiferromagnetic interchain interactions thanks to the use of halogen bonding to direct the packing of the chains, thus permitting the magnetic study of the isolated chains.

![Figure 1](image_url)

Figure 1. a) One dimensional network formed in trans-[CoCl₂(3,5-X₂py)₂] running parallel to the c axis; b) cyclic X₄ halogen bond synthon.

References
The investigation of weak non-covalent interactions is a recent and attractive trend in modern crystal engineering. Many reports can be found in recent times to establish the nature of halogen bonding. The role of chloro substituent on the crystal packing of some of the dichlorophenols has earlier been studied [1]. This work aims to identify the differences and similarities between the crystal structures after introduction of one more chloro substituent on the aromatic ring. In this context, we have described here the crystal structures of 3,4,5 and 2,3,4-trichlorophenols. To get an insight into the nature of halogen bonds, variable temperature studies have been done on 3,4,5-trichlorophenol [2]. Serendipitously, we got one solvate of 2,3,4-trichlorophenol too. To understand the nature of halogen bonding, we have compared the crystal structures of 2,4,6-tribromo and 2,4,6-trichlorophenol. Further, to explore the evolution and consistency of synthons we tried co-crystallization among different trichlorophenols. The co-crystallization experiments were performed between trichlorophenols and some of the N-bases to observe the structural insulation between the chloro groups and strong hydrogen bonding groups like –OH group.

References
In situ cryocrystallography study of liquid halogen-bonded complexes

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In situ cryocrystallography technique offers the possibility to study the structures of compounds that are liquids at ambient conditions. This allows to investigate the occurrence of weak and elusive interactions, e.g. CH···π hydrogen bonds, halogen···halogen contacts, etc. In fact, co-crystal structures of acetylene with different gaseous and liquid electron-donors and solvents have been reported [1-2]. Here, we report the first systematic study of supramolecular synthesis of liquid halogen-bonded complexes [3]. In this context, we used an OHCD (optical heating and cooling device) to obtain the crystal structure of 1,3-dibromotetrafluorobenzene (DBTFB), which is a liquid at room temperature, and its 1:1 molecular complexes with solvents like HMPA, DMSO, and DMF [4]. The weak Br···F interactions in the structure of DBTFB are replaced by Br···O=(P/S/C) halogen bonds. Strength and directionality of the halogen bonding observed depend on the electron donor ability of the used solvent. In this presentation, the salient features of halogen bonding, methodology followed, and IR and DSC data of the studied liquid halogen-bonded complexes will be discussed in detail.

Figure 1: Crystal packing of 1,3-dibromotetrafluorobenzene obtained by in situ cryocrystallization using an OHCD (optical heating and cooling device).

References
Halogen Bond Based Organic Frameworks (XOFs) with Solvent Induced Adaptation of Nano-sized Channels

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Five novel halogen bond based organic frameworks (XOFs) possessing large 1D channels have been obtained from co-crystals of hexamethylenetetramine with N-iodosuccinimide (Fig. 1). These XOFs rely on the formation of robust NHTA:NI (1:4) complexes via extremely strong (CO–)2N–I···N XB interaction. Indeed, the observed N–I···N bond distances, which vary in the range 2.486 Å to 2.586 Å are remarkably shorter (from 29.6 % to 26.7 %) than the sum of the standard vdW radii of nitrogen and iodine atoms [1]. According to our knowledge these distances are the shortest recorded so far in I···N XB systems [2]. It is worth noting that shorter distances lead to more linear N–I···N angles starting from 2.563 Å and 174.55° to 2.486 Å and 179.48°. Interestingly, the tetrahedral complex of [HMTA][NIS]4 forms stable framework structures with large channels. The volume (form 19.3 % [708 Å3] to 38.5 % [1790 Å3] of the unit cell volume) and the shape of channels are modulated by the guest molecule. The porous nature of these frameworks is proved by guest molecule exchange experiments, where CH2Cl2 are exchange with CCl4 via both solvent phase and gas phase. More importantly, the guest exchange reaction lead to a single-crystal to single-crystal conversion, i.e., from a crystal of [CH2Cl2]4[NIS4•HMTA] to a crystal of [CCl4]2[NIS4•HMTA].

![Figure 1: A view of XOF structure [CH2Cl2]4[NIS4•HMTA] with CH2Cl2 inclusion and the model of empty channels.](image)

A table of all five XOFs possessing similar structure but different channel size and shape (right).

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<tr>
<th>Structure</th>
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<tr>
<td>[MeNO2]4@ [NIS4•HMTA]</td>
<td>1180 (28.5 %)</td>
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<tr>
<td>[C2H5CH2]4@ [NIS4•HMTA]</td>
<td>708 (19.3 %)</td>
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<td>[CHCl3]2@ [NIS4•HMTA]</td>
<td>756 (20.5 %)</td>
</tr>
<tr>
<td>[CH2Cl2]4@ [NIS4•HMTA]</td>
<td>1790 (38.5 %)</td>
</tr>
<tr>
<td>[CCl4]2@ [NIS4•HMTA]</td>
<td>853 (36.7 %)</td>
</tr>
</tbody>
</table>

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2. Search of all intermolecular Br•••N contacts with distance range from 2.2 Å to 4 Å. Cambridge Structural Database (version 5.31, Nov 2009), The Cambridge Crystallographic Data Centre, Cambridge, UK.
Supramolecular Assembly through C-F\cdots F-C and C-F\cdots \pi interactions. Crystal Structure of L-(pentafluorophenyl)alanine hydrate.

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Highly fluorinated aminoacids have been reported as protein stabilizers [1]. In order to better understand the interactions involved in these aminoacids the structure of zwitterionic pentafluoro-L-Phenylalanine monohydrate (1) has been determined. The shortest and most directional ammonium\cdots carboxylate interaction found in the crystal forms pentafluoro-L-Phe dimmers that are then connected with a second ammonium\cdots carboxylate interaction forming molecular ladders. Ladders assembly occurs through ammonium\cdots water and ammonium\cdots carboxylate interactions that form molecular layers. Every two layers are assembled through a further water\cdots carboxylate hydrogen bond forming a bilayer with fluorinated nonpolar fragments pointing outside. Bilayer assembly depends on C_6F_5 groups packing and involves C-F\cdots F-C type I and C-F\cdots \pi interactions [2]. 3D assembly is compared to that found for other perfluorinated aromatic compounds. On the other hand, the structure of (1) is compared to that of L-Phe monohydrate where a bilayer supramolecular motive has also been found [3]. Both molecular bilayers, (1) and L-Phe-H_2O, present polar groups and water molecules in the inner part and non-polar groups pointing outwards, thus, generating hydrophobic surfaces. In the non-fluorinated hydrate the bilayer assembly occurs through C-H\cdots \pi interactions as in C_6H_6. Non-fluorinated versus perfluorinated aromatic compounds are discussed.

Crystal packing and asymmetric unit of L-(pentafluorophenyl)alanine monohydrate

References
3. G. Asensio, C. Andreu, A. Rodríguez-Gimeno, C. Ramírez de Arellano, communication to MISCA II, Oviedo, Spain, 2010.
Halogen bonds [1,2,3] play a crucial role in the inhibitor recognition processes in many biological systems. Due to their high directionality and specificity, halogen bonds can effectively be used in drug design to direct the binding of ligands to the target site [4]. Nonetheless, their modeling in-silico is currently troublesome, since existing molecular dynamics (MD) force fields do not account for the charge density anisotropy around the halogen atoms, making it impossible to correctly simulate the behaviour of halogenated molecules in biological systems. We propose here a new approach aimed at the correct description of halogen bonds in MD simulations, based on a reparametrization of AMBER force field. We show that, unlike the original package, the modified force field allows MD simulations of ligand-protein complexes involving halogen bonds to reproduce both crystallographic data and the results of QM/MM calculations on the complexes. We thus deem our work would be a significant improvement in the modeling of halogen bonds for drug design.

References
In this work we investigate the interactions of two iodine-containing ligands with thyroid receptor beta using several state of the art computational methods. Configurations of these protein-ligand complexes are generated using molecular dynamics based on a semi-empirical PM6-DH2X scheme, which explicitly incorporates dispersion corrections and halogen bonding corrections. Binding energies for these complexes are computed using the same semi-empirical method and binding free energies are estimated using a PM6-DH2X based scoring function. In order to determine the relative importance of the two halogen bonds exhibited in each of these complexes, we make dispersion corrected density functional theory (DFT-D) calculations on all ligand-residue interactions for amino acids within 6Å of the ligand. DFT-based symmetry adapted perturbation theory (DFT-SAPT) calculations are carried out on model systems derived from the protein-ligand complexes. DFT-SAPT analysis allows us to break the halogen bonding interactions into physically meaningful components (ie electrostatic, dispersion, etc.). The two thyroid receptor ligands investigated are the thyroid hormone (the native ligand, PDB: 1BSX) and [4-(4-Hydroxy-3-iodo-phenoxy)-3,5-diiodo- phenyl] acetic acid, a thyroid receptor inhibitor (PDB: 2PIN).
Halogen bonding between I$_2$ molecules and halogen containing metal complexes.

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Halogen bonding is a non-covalent interaction which can be used to construct molecular assemblies with different dimensionality. We have studied halogen bonding between bipyridyl based ruthenium complexes and I$_2$. In these structures we have found that I$_2$ and trans-[RuI$_2$(H$_2$dcbbpy)(CO)$_2$] (H$_2$dcbbpy = 4,4’-dicarboxylic acid-2,2’-bipyridine) form strong halogen bonds[1]. In addition to the halogen bond between the iodide ligand of the metal complex and I$_2$ there is also another halogen bond between two I$_2$ molecules which is supported by additional bifurcated hydrogen bonding with solvent methanol. This combined hydrogen and halogen bonding is a new combination of these two interactions. This shows that different interactions can be combined to provide new bonding modes, which allow formation of new compounds. Another system we have studied is so called N$_3$ ([Ru(H$_2$dcbbpy)$_2$(SCN)$_2$]) dye molecule, which is used as a sensitizer in dye-sensitized solar cells[2,3]. The interest in the halogen bonding of this molecule arises from the fact that I$^-$/I$_2$ acts as the reducing agent in the dye-sensitized solar cells and the mechanism of the reduction of the oxidized dye is still not completely understood. We have grown single crystals of the halogen bonded adduct of the N$_3$ and two I$_2$ molecules. As can be expected the halogen bonding occurs between the thiocyanate ligands and I$_2$. Both thiocyanate ligands form strong halogen bonds with I$_2$ molecules through the dangling sulfur atom. This shows clearly that the thiocyanate ligands can and do from halogen bonds with I$_2$, this result can help shed light on the regeneration mechanism of the dye sensitized solar cells and help design more effective dyes for the cells. Currently we are working with a series of halogen containing ruthenium complexes aiming to extended structures linked with halogen bonding to I$_2$.

The above examples show that I$_2$ and halogen containing metal complexes in can be used to construct new extended solid state system. Thus, use of halogen bonding provides another tool for crystal engineering of supramolecular entities.

References
Fluorine is a unique element. The question about the role of fluorine in intermolecular interactions is discussed controversially. Well known is the influence of fluorine on the electronic structure of aromatic backbones and therefore on the entire molecules. On the other hand, fluorine forms only weak intermolecular interactions and seems to have no influence on the crystal packing. Pauling’s definition of the hydrogen bond would imply that fluorine, as the most electronegative atom, should be a stronger hydrogen-bond acceptor than oxygen and nitrogen. But the C-F group, the so-called “organic fluorine”, does not form hydrogen bonds commensurate with electronegativity considerations in contrast to the C-O and C-N groups.

We investigated a range of partially fluorinated pyridines and analysed their crystal packings experimentally and theoretically. Low temperature in situ crystallisation on the diffraktometer was used to investigate crystal structures of low melting fluorinated pyridines followed by analysis of the crystallisation behavior. Interesting tendencies were observed in crystal packings depending on the fluorination degree.

![Figure 1: Difference between basic structural motives in the experimental (a) and theoretical (b) crystal packing of 3,5-difluoropyridine.](image)

But still the general question we are interested in, is: what determines the crystal packing in the absence of strong intermolecular interactions? Theoretical study of the energies of weak intermolecular interactions is an innovative method for research of the basic motives in the solid state. The comparison of our experimental and theoretical findings shows how fluorine atoms influence the aggregation of substituted pyridines.

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# Categorizing Halogen Bonding and Other Noncovalent Interactions Involving Halogen Atoms

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20-21 August 2011, Sigüenza, Spain