

π -Hole Halogen Bonds Are Sister Interactions to σ -Hole Halogen Bonds

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Cite This: *Cryst. Growth Des.* 2024, 24, 7789–7807

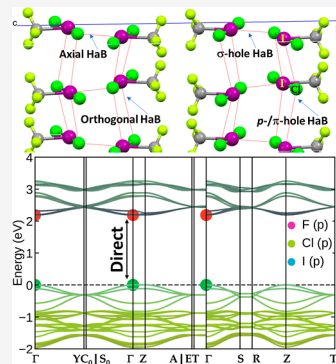
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ABSTRACT: Halogen's σ -hole interactions are found throughout the chemical, biological, and crystal engineering literature. These interactions are directional and may be of van der Waals type, weak, strong, or even very strong, with binding energies ranging between -0.01 and -100 kcal mol $^{-1}$. When occurring between interacting neutral molecular entities, the energy range is often between -0.01 and -8.0 kcal mol $^{-1}$. This study was undertaken to show there is crystallographic evidence that a covalently bonded halogen in a molecule can present with p/π -holes that are capable of engaging in attractive interactions with nucleophiles on an identical, or dissimilar, neighboring molecule, and that the strength of the interaction between the p/π -hole halogen bonded dimers can vary between -4.0 and -12.0 kcal mol $^{-1}$ depending on the mode of that interaction and whether other interactions are involved. To this end, density functional theory at the M06 level with and without the effect of dispersion, in conjunction with the aug-cc-pVTZ (aug-cc-pVTZ-PP for iodine) basis set, suggested for the study of halogen bonding, was employed. Various charge density-based models were applied and the results of bonding modes are elucidated. Analysis of molecular electrostatic surface potentials revealed the electrophilicity of the σ - and p/π -holes on the surfaces of covalently bonded halogens in molecules, which were useful indicators for the formation of σ - and p/π -holes halogen bonding interactions in the dimers studied. Individual interactions identified may be weak, but since they are collective, they strengthen the geometry of the dimers formed. Furthermore, periodic calculations of two crystalline systems (CF_3ICl_2 and CF_3IClIF) reveal that they are direct bandgap materials, indicating the importance of halogen bonding in the design and subsequent growth of such materials for application in optoelectronics.



1. INTRODUCTION

Crystal growth and design is an important aspect of the engineering of chemical systems,^{1–5} which is an active field in the broad area of materials nanoscience and technology.⁶ It deals with the study of crystals as chemical systems, their geometry, shape and physical properties in both amorphous and crystalline forms. Molecular entities (viz. neutral molecules and ions in molecular and/or atomic forms) are their building blocks, which are self-assembled by a variety of intermolecular forces. The forces are adhesive in nature, and when properly engineered between atomic/molecular basins, result in ordered, functional materials. They are widely recognized as intra- or intermolecular interactions and are key chemical synthons that appear largely as σ -,^{7,8} p -,^{9,10} and/or π -hole interactions.^{11–14}

σ - or π -holes in molecules are generally understood to be electron density deficient (electrophilic) regions on covalently bonded atoms in a molecule, but they can be electron density rich as well. When the former, they are capable of donating σ - or π -holes as electrophiles, and when the latter, they can be regarded as electron density donors (for example, the negative σ -hole on F in the HF molecule¹⁵).

A σ -hole appears on the opposite side of the R–A bond extension of the covalently bonded atom A, whereas a p/π -hole

appears on the surface of atom A perpendicular to the R–A bond axis, or in the junction region between close-lying unbound atoms, or around the bond region, or in the plane of the molecule; R is the remainder part of the molecule. For example, the σ -hole is electrophilic on the side of atom X opposite the X–X bond in a dihalogen molecule X_2 (X = F, Cl, Br, I), and nucleophilic on the side of F opposite the C–F bond in CH_3F and HF. Similarly, an electrophilic p/π -hole can be observed on the surface of N in substituted NO_2 ,¹⁶ and in PnX_3 molecules (Pn = P, As, Sb, Bi),^{17–19} around the $\text{N}\equiv\text{N}$ triple bond in N_2 ,²⁰ in the junction region in between a pair of two neighboring C–F bonds and on the centroid portion of the C_6 ring in in C_6F_6 . Bauzá and co-workers have shown that nitromethane and nitrobenzene are able to interact favorably with electron-rich molecules by means of the p/π -hole that is located above and below the C–N bond.¹⁶ Similarly, B in BF_3

Received: March 30, 2024

Revised: August 25, 2024

Accepted: August 26, 2024

Published: September 9, 2024



is widely known to have a pair of π -holes on its outer surface orthogonal to the plane of the molecule, yet Tarannam et al.⁹ and Taylor¹⁰ passionately asserted that the designation “p-hole” is far more apt, as the existence of an empty p-orbital embodies a concept that is profoundly distinct from the origin of a π -hole.

A nucleophilic p/ π -hole (or p/ π -belt) can be observed on many arene moieties, as well as around the C $\equiv$ C triple bond in acetylene and on the planar centroid portion of the C₆ ring in C₆H₆. These and perusal of the noncovalent chemistry literature clearly suggest that the electrophilic and nucleophilic strengths of these “holes”, or “belts”, depend on many factors, including the type of atom(s), the periodic table group to which it (they) belongs, its (their) electronegativity, polarizability, and the nature of the electron-withdrawing group R to which it (they) is covalently bonded. Since either of these (p or π) holes/belts emerge from a p-type orbital (or even p-type Rydberg valence orbitals) orthogonal to the covalent bond axis in a molecular entity, we, hereafter, refer to them as p/ π -hole (or p/ π -belt).

Typical binding energies for many dimer systems involving σ -hole interactions in neutral molecules have been reported to range from -0.01 to -8.0 kcal mol⁻¹.^{21–28} If the σ -hole on atom A in the R–A molecule is stronger and the remainder R is very polarizable, the binding energies of the resulting complexes will be larger. Indeed, if an anion binds to the σ -hole of a neutral molecule, the strength of the interaction may exceed the so-called covalent bonding limit of -40.0 kcal mol⁻¹.^{1,29,30} The ion-pair adduct formed by the involvement of the σ -hole on the cation is characterized by very large interaction energies,^{31,32} and a significant portion of this energy arises from point-charge interactions driven by Coulombic forces. This concept may also be applicable to the energies of p/ π -hole (or p/ π -belt) interactions in complexes.

Electrophilic π -holes have been visualized experimentally using Kelvin probe force microscopy.³³ They have also been reported on the electrostatic surface of elements of groups 14, 15, 16 and 18. When belong to these particular groups, they can be referred to as a π -hole tetrel bond,³⁴ pnictogen bond,^{35,36} chalcogen bond,³⁷ and aerogen bond,³⁸ respectively. The π -hole bond donating proficiency exhibited by groups 14 and 18 are not rare, but that due to a halogen derivative (group 17) in molecules is very rare,^{14,38,39} although halogen can be involved in counterintuitive interactions has been demonstrated by Murray and Politzer.²⁶ Zierkiewicz et al.¹⁴ have speculated that halogen atoms in molecular entities may host a π -hole in hypervalent bonding situations. This was exemplified by showing that a crystal formed from the BrOF₂⁺ cation was stabilized in the presence of two KrF₂ and one AsF₆[−] anion moiety as building blocks. Although the Lewis bases in the latter three molecules appear to interact through a σ -hole on the covalently bonded Br atom in BrOF₂⁺, it was suggested that the existence of a π -hole site on the BrOF₂⁺ cation, which has the strength to attract another Lewis base, cannot be ruled out, a result similar to that found by one of us in a recent study.⁴⁰

We have recently revisited the definition of the halogen bond (HaB) (IUPAC recommendations 2013⁴¹)⁴² and have put forward an ambitious revision inspired by a multitude of groundbreaking studies employing cutting-edge computational and experimental techniques. Our proposed updates encompass an extensive array of detailed annotations and distinctive

features, supplemented by a rich tapestry of examples showcasing various donors and acceptors engaged in HaB formation. We have also curated a selection of illustrative crystal systems that vividly demonstrate the nuances of halogen bonding, including the intriguing possibility of interactions involving p/ π -holes or p/ π -belts.

Although the views given in ref 14 concerning p/ π -holes and their involvement in halogen bonding may be speculative, it would be interesting to verify whether hypervalent halogen derivatives in molecules other than cations generally exhibit p/ π -holes and whether they can form p/ π -hole HaBs with the nucleophiles with which they interact. If so, what is the strength of the interaction that determines the stability of the complexes so formed? What are the current state-of-the-art theoretical methods for revealing this? Do they follow the guidelines and recommendations of the IUPAC working group⁴¹ for identifying halogen bonding in molecules, crystals, and crystalline systems? To this end, we have surveyed the Cambridge Structural Database (CSD)^{43–45} and Inorganic Crystal Structure Database (ICSD)^{46–48} and identified several crystal systems to address these fundamental questions.

We undertook an extensive exploration using density functional theory (DFT) calculations on a selection of dimers in the gas phase, chosen from specific crystalline systems. Our analysis delved into various descriptors to elucidate the nature of halogen's p/ π -hole capability for forming noncovalent bonds, employing three sophisticated theoretical frameworks: molecular electrostatic surface potential (MESP),^{49,50} quantum theory of atoms in molecules (QTAIM),^{51,52} and independent gradient model (IGM).^{53–55} A central aim of this endeavor was to ascertain whether the findings from the first model align seamlessly with those derived from the subsequent two models. To advance our investigation, we conducted precise halogen substitutions on the parent molecules, fabricating an array of model dimers to computationally uncover chemical systems that may be useful for future synthetic endeavors. As we bring our study to a conclusion, we provide a succinct overview of the periodic calculations performed on two experimentally known crystal systems, with a focus on their bandgap properties. The insights garnered may pave the way for innovations in materials design and discovery, particularly through the intriguing phenomena of σ - and p/ π -hole halogen bonding.

2. CRYSTAL AND MOLECULAR SYSTEMS AND COMPUTATIONAL DETAILS

CF₃IF₂, CF₃ICl₂, and CF₃IClF are members of the (trifluoromethyl)iodine dihalide, F₃C–I–X₂ (X = halogen), family. Crystals of trifluoromethyl iodine difluoride (CF₃IF₂) (ICSD ref 408935),⁵⁶ and (dichloro-trifluoromethyl)iodine (also called (trifluoromethyl)iodine dichloride (CF₃ICl₂)) (CSD ref COXYIX),⁵⁷ have been known since 1998 and 1999, respectively, yet their materials properties (viz. bandgap features) have not been explored to date. The crystal of chloro-fluoro-(trifluoromethyl)iodine (CF₃IClF) was reported in 2001 (CSD ref WOWYUC).⁵⁸ Both CF₃ICl₂ and CF₃IClF crystallize in the orthorhombic space group *Cmca*, but CF₃IF₂ (ICSD ref 408935) crystallizes in the *I*_{42d} space group. The molecular form of each of them, as a building block, features a T-shape structure, and this is taken into account in this study.

All geometric and energy stability calculations for the dimers were performed using Gaussian 16,⁵⁹ including geometric optimization and subsequent frequency calculations. The latter

resulted in positive eigenvalues of the Hessian (second derivatives) of the energy with respect to the atom fixed nuclear coordinates, confirming that the geometries of the dimers reported in this study are a true stationary point at the applied M06⁶⁰ level of theory. The use of the DFT-M06 functional was based on its appreciable performance to describe halogen bonded systems compared to other DFT functionals and MP2, as reported in a recent benchmark study.⁶¹ The aug-cc-PVTZ basis set was used for all atoms except iodine, for which the pseudopotential basis set, aug-cc-PVTZ-PP, obtained from the EMSL basis set library^{62–64} was used.

The electrophilic and nucleophilic nature of various regions on the surfaces of atoms in the monomer molecules were examined using the MESP model,^{49,50} based on the electrostatic potential, $V(r)$. Murray and Politzer^{65,66} have already demonstrated the usefulness of the model and the underlying theoretical details several times, showing how suitable is the physical observable, $V(r)$, in describing the origin of non-covalent interactions formed by chemical systems comprised largely of main group elements of the periodic table. When an appropriate isoelectronic density envelope of the molecule under investigation is used on which to compute the potential, two descriptors emanate from the MESP model. They are the local most minimum and maximum of potential ($V_{S,min}$ and $V_{S,max}$, respectively). Their positive and negative signs are the determinants of surface electrophilicity and nucleophilicity, respectively, and their magnitudes are the determinants of their strengths. The $V_{S,max}$ and $V_{S,min}$ are often (but not always!) seen on the side of atom A along and around the covalent bond extension in R–A, respectively.

QTAIM^{51,52,67–69} produces a molecular graph, composed of bond path and bond critical point topologies of the charge density, a theoretical approach that has been extensively applied to molecular and intermolecular systems to provide insight into the nature of the chemical bonding between bonded atomic basins based on its unique space partitioning approach that relies on the zero-flux boundary condition. There are many descriptors of the model, but three crucial descriptors are the charge density (ρ_b), the Laplacian of the charge density ($\nabla^2\rho_b$), and the total energy density (H_b). The evolution of these properties rely on the existence of a bond critical point between interacting atomic basins; failure of the model to do so may mislead in identifying the presence of an attractive interaction.^{70–73} On the other hand, the IGM model^{53–55} has been demonstrated to reveal both intra- and intermolecular interactions in and between the interacting molecules via two its descriptors, IGM- δg^{intra} and IGM- δg^{inter} . They are represented by colored isosurface domains in low density regions between noncovalently bonded atomic moieties computed using low isovalues (typically around 0.01 au). The isosurfaces generated using the model are generally colored red, blue, cyan, and/or green; the former represents repulsion and the latter three represent attraction depending on the decreasing nature of their energy strengths. AIMAll,⁷⁴ Multiwfn⁷⁵ and VMD⁷⁶ software were used.

The uncorrected and BSSE-corrected interaction energies of the dimers were computed using eqs 1 and 2, where BSSE refers to the basis set superposition error accounted for by the counterpoise procedure of Boys and Bernardi,⁷⁷ and E_T refers to the total electronic energy of individual species.

$$\Delta E(\text{dimer}) = E_T(\text{dimer}) - E_T(\text{sum of monomers}) \quad (1)$$

$$\Delta E(\text{BSSE}) = \Delta E(\text{dimer}) + E(\text{BSSE}) \quad (2)$$

The effect of dispersion was considered at the level of Grimme's DFT-D3 (hereafter GD3) that accounts for the original D3 damping function.⁷⁸ The dispersion-incorporated uncorrected and BSSE-corrected interaction energies are referred as $\Delta E(\text{GD3})$ and $\Delta E(\text{GD3-BSSE})$, respectively.

Crystals of CF_3ICl_2 (CSD ref COXYIX),⁵⁷ and (CF_3IClF) (CSD ref WOWYUC)⁵⁸ were also examined using periodic boundary conditions at the Perdew–Burke–Ernzerhof (PBE)⁷⁹ level of theory. The Vienna Ab Initio Simulation Package (VASP 5.3)^{80–84} was used. The pseudopotentials invoked emerged from the projector-augmented-wave (PAW) method.^{85,86} The cutoff criterion for force on ions, energy for plane-waves, and self-consistent loops were 0.01 eV $\text{\AA}^{-1}$, 520 eV and 10^{-6} eV, respectively. A k -mesh of $6 \times 6 \times 4$ was used to sample the Brillouin zone. Since there were no metals involved, nonspin polarized calculations were performed. The electronic band structures and density of states (DOS) were plotted using the Sumo⁸⁷ and pyband⁸⁸ codes, respectively.

3. RESULTS AND DISCUSSION

3.1. Crystal Geometries and DFT Calculations.

3.1.1. (Trifluoromethyl)iodine Dichloride (CF_3ICl_2) CRYSTAL. Our analysis of the geometry of the CF_3ICl_2 crystal revealed some close intermolecular contacts between the CF_3ICl_2 molecular building blocks as shown in Figure 1a. The key chemical synthon that holds the CF_3ICl_2 molecules together is the I...Cl contact. They are either shorter, or even longer, than the sum of the van der Waals (vdW) radii of atomic I and Cl, 3.86 Å ($r_{\text{vdW}}(\text{I}) = 2.04$ Å and $r_{\text{vdW}}(\text{Cl}) = 1.82$ Å⁸⁹). Some of them are consistent with IUPAC's distance-based feature,⁴¹ while others are not. This means that the recommended IUPAC feature fails to fully identify and characterize HaBs. However, as we^{34,35} and others^{90,91} have suggested before, and which also appeared in our recently proposed relook at the definition of the HaB (feature d),⁴² the reported vdW radii of atoms of the periodic table may be accurate within an error of ± 0.20 Å. Taking this into account, both the I...Cl close contacts shown in Figure 1a could be regarded as HaBs.

The covalently bonded I atom in each CF_3ICl_2 building block is noncovalently bonded to the six nearest Cl atoms of six other identical molecules, forming six I...Cl close contacts (Figure 1a). Four of these are p/π -hole HaBs and the remaining two are σ -hole HaBs. The σ -hole HaBs are quasilinear, with $\angle \text{C–I} \cdots \text{Cl} = 162.2^\circ$ (and 148.0°) and $r(\text{I} \cdots \text{Cl}) = 3.324$ (and 4.345) Å. The latter contact is substantially longer than the vdW radii sum of I and Cl [$r_{\text{vdW}}(\text{I}) + r_{\text{vdW}}(\text{Cl}) = 3.86$ Å]. Similarly, a pair of p/π -hole HaBs occur on one side of the C–I covalent bond axis and is 3.926 Å, while the other pair appears on the other side with a length of 3.838 Å; the former violates the IUPAC's geometric feature for a HaB.⁴¹ All four of these close contacts are directional and nonlinear. The directionality arises from the Coulombic nature of these interactions, i.e., positive sites interact with negative sites, although the importance of exchange repulsion cannot be discounted. The sum of the six noncovalent bonds and three covalent bonds results in a pseudo-9-coordinate iodine in CF_3ICl_2 . This scenario may be reminiscent of the pressure-induced formation of the neutral fluoride compound IF_8 , composed of 8-coordinate iodine, that was recently reported by Luo and co-workers.⁹² Similar chemical environments of iodine in molecular entities have been reported by others,^{93,94}

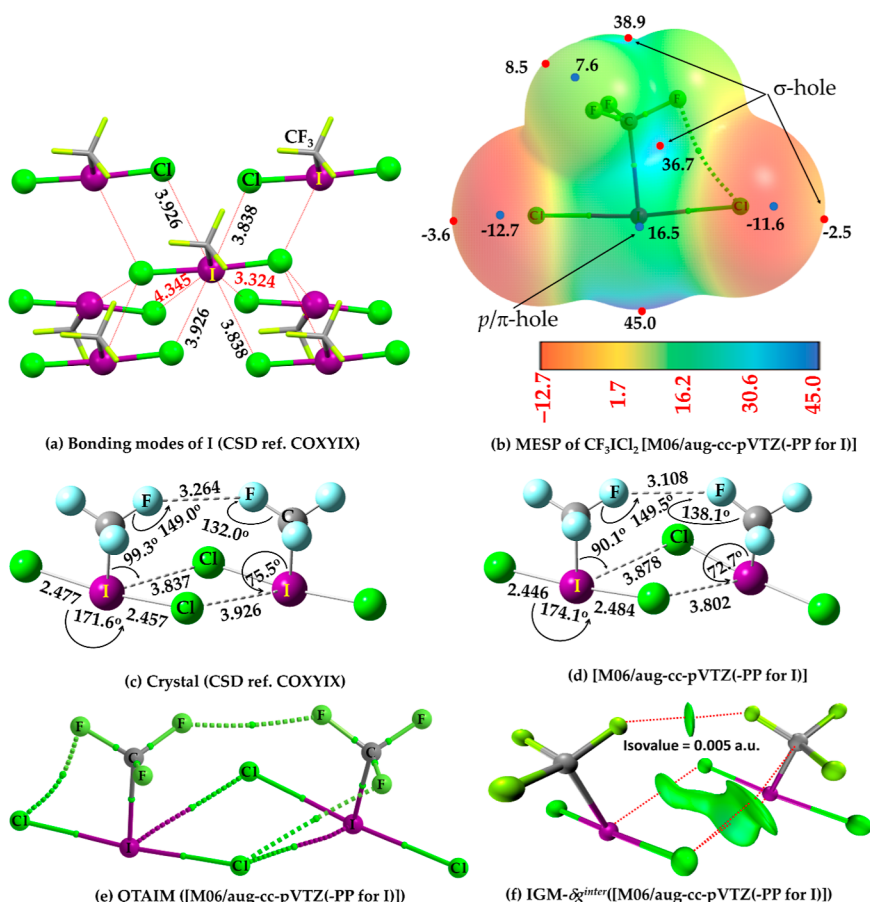


Figure 1. (a) Geometry-based identification of the intermolecular bonding environment around the covalently bonded I in the crystal of CF_3ICl_2 (CSD ref shown as uppercase letters), showing possible σ - and p/π -hole halogen bonded contacts. (b) The 0.0015 au (electrons bohr⁻³) mapped potential (kcal mol⁻¹) on the electrostatic surface of the CF_3ICl_2 molecule, depicting various electrophilic and nucleophilic regions. (c,d) Comparison of selected bond distances (Å) and bond angles (degrees) of a dimer extracted from the crystal with that of the geometry optimized with [M06/aug-cc-pVTZ]. The tiny blue and red circles in (b) represent the local most minima and maxima of potential, respectively, and the MESP plot is superimposed with QTAIM's molecular graph of the molecule; the tiny green sphere between bonded atomic basins in (e) represent the bond critical points and the solid and dotted lines between atomic basins represent the covalent and noncovalent interactions, respectively. Shown in (f) is the IGM- δg^{inter} isosurface plot, displaying attraction between the atom basins.

for example, highlighting the occurrence of 9- and 12-coordinate iodine.

The plot of the molecular electrostatic potential surface of the CF_3ICl_2 monomer, Figure 1b, reinforces the view developed above. As can be seen, the outer surface of the covalently bonded I in CF_3ICl_2 is completely electrophilic along and around the outermost extension of the $(\text{F}_3)\text{C}-\text{I}$ bond. The σ -hole resides on the side of I along the outer portion opposite to the $\text{C}-\text{I}$ covalent bond, characteristic of $V_{\text{S,max}} > 0$ ($V_{\text{S,max}} = 45.0$ kcal mol⁻¹). Similarly, there are two regions on the outer surface of I, each characterized by $V_{\text{S,min}} > 0$ ($V_{\text{S,min}} = 16.5$ kcal mol⁻¹); they lie above and below the plane formed by the Cl_2IC fragment of the molecule, and that are orthogonal to the $\text{C}-\text{I}$ covalent bond. Each of these two electrophilic regions are what we call iodine's p/π -hole, and originate from a p-type valence accepting orbital. It is worth noting that electrophilic σ - and p/π -holes on bonded atomic surfaces in molecular entities are typically characterized by $V_{\text{S,max}} > 0$. The electron-density deficient electrophilic regions on the iodine atom in CF_3ICl_2 are characterized by $V_{\text{S,min}} > 0$, but since they are orthogonal to the $\text{C}-\text{I}$ bond axis, we refer to them here as the p/π -holes. It is this p/π -hole in the CF_3ICl_2 molecule that is attractively engaged with the negative lateral

part of a pair of covalently bonded Cl atoms ($V_{\text{S,min}} = -11.6$ or -12.7 kcal mol⁻¹) of two neighboring molecules to form two orthogonal $\text{I}\cdots\text{Cl}$ contacts (p/π -hole HaBs). They are not equivalent (Figure 1a).

The geometry of a dimer of CF_3ICl_2 extracted from the crystal, and that optimized using [M06/aug-cc-pVTZ], is compared in Figure 1c,d. As can be seen, the nature of the intermolecular interactions in these dimers do not deviate significantly from each other, and the chosen theoretical level faithfully preserves the geometry of the dimer observed in the crystal. Discrepancies are particularly striking when the $\angle \text{C}-\text{I}\cdots\text{Cl}$ angles, rather than the intermolecular distances, are the primary concern. This is reasonable because packing and other forces between the building blocks play an important role in shaping the crystal lattice, which is absent in the gas phase dimers.⁹⁵ However, both dimer geometries indicate that orthogonal HaBs between the building blocks are present in the crystal.

From Figure 1b, it may be seen that the covalently bonded F and C atoms of the CF_3 group in CF_3ICl_2 are also electrophilic, and the latter more so than the former. For example, the $V_{\text{S,max}}$ is 8.5, 38.9 and 36.7 kcal mol⁻¹ for the $\text{C}-\text{F}$, $\text{I}-\text{C}$, and $\text{F}-\text{C}$ bond extensions, respectively, indicating that the σ -hole on C

is considerably stronger than that on F. Due to the anisotropy of the charge density along and around the axial portions of the covalently bonded F atoms, the two neighboring F atoms facing each other (Figure 1c,d), each from a CF_3ICl_2 , form a quasilinear σ -hole centered $\text{F}\cdots\text{F}$ close contact in the dimer's equilibrium geometry. The same occurs in the crystal geometry [$r(\text{F}\cdots\text{F})$ values 3.264 Å (crystal) vs 3.108 Å (DFT-M06)].

QTAIM predicts possible intermolecular interactions in $(\text{CF}_3\text{ICl}_2)_2$, based on its molecular graph depicted in Figure 1e. The long and short $\text{I}(\text{p}/\pi\text{-hole})\cdots\text{Cl}$ HaBs in the dimer are characterized by ρ_b (and $\nabla^2\rho_b$) values of 0.0064 (0.0173) and 0.0073 (0.0193) a.u., respectively. The bond paths generate a pseudorhombic geometric architecture locally, consisting of a pair of $\text{I}-\text{Cl}$ covalent bonds and a pair of $\text{I}\cdots\text{Cl}$ noncovalent bonds. The total energy densities, H_b , were 0.00079 and 0.00081 au at the corresponding bond critical points (bcps), respectively. The small values of ρ_b indicate weak interactions, and the signs of $\nabla^2\rho_b$ and H_b indicate that these interactions are of the closed-shell type with recognizable depletion of charge density around the $\text{I}(\pi\text{-hole})\cdots\text{Cl}$ bcps. (1 au of $\rho_b = e/a_0^3 = 6.748 \text{ e}\text{\AA}^{-3}$; 1 au of $\nabla^2\rho_b = e/a_0^5 = 24.10 \text{ e}\text{\AA}^{-5}$; 1 au of $H_b = 1 \text{ hartree} = 627.5095 \text{ kcal mol}^{-1}$). Similarly, the $\text{F}(\sigma\text{-hole})\cdots\text{F}$ HaB is typified by ρ_b , $\nabla^2\rho_b$ and H_b values of 0.0026, 0.0146, and 0.0080 au, respectively.

QTAIM reveals $\text{F}\cdots\text{Cl}$ closeness in the dimer. This may not be surprising since the lateral portion of the covalently bonded F in CF_3 is weakly electrophilic and the covalently bonded Cl is fully nucleophilic (cf. Figure 1b). The surface properties provide a rational basis to appropriate the $\text{F}\cdots\text{Cl}$ closeness, which may be a consequence of a Coulombic interaction and is also a HaB. The ρ_b , $\nabla^2\rho_b$ and H_b values at the $\text{F}\cdots\text{Cl}$ bcp are 0.0046, 0.0174 and 0.0081 au, respectively. Furthermore, the $\text{F}\cdots\text{Cl}$ intramolecular interaction that appears in the monomer (see the dotted line between the F and Cl atoms in Figure 1b) persists in one monomer, but is absent in the other monomer of the dimer due to changes in electronic structure during dimer formation that cause the development of the $\text{F}\cdots\text{F}$ close contact (vide supra). The ρ_b , $\nabla^2\rho_b$ and H_b values at the $\text{F}\cdots\text{Cl}$ bcp in the monomer (dimer) are 0.0129 (0.0129), 0.0553 (0.0556), and 0.0022 (0.0022) au, respectively. The intermolecular interactions revealed by QTAIM may be in agreement with IGM- δg^{inter} 's isosurface plot, Figure 1f. Furthermore, the latter method discloses the possibility of a $\text{F}_3\text{C}\cdots\text{F}$ tetrel bond; this is supported by the MESP model-based chemistry (Figure 1b).

3.1.2. Chloro-Fluoro-(Trifluoromethyl)iodine (CF_3IClF) Crystal. The nature of intermolecular halogen bonding in the crystal of chloro-fluoro-(trifluoromethyl)iodine (CF_3IClF), Figure 2a, did not change appreciably compared to that observed in the crystal of CF_3ICl_2 (Figure 1a). There are four p/π -hole and two σ -hole HaBs formed by each hypervalent iodine atom in CF_3IClF with five nearest neighbors, which are expected because of the positive nature and anisotropy of the charge density profile on the surface of the I atom in the molecule (Figure 2b). One of the σ -hole HaBs is substantially longer than the other, $r(\text{I}(\sigma\text{-hole})\cdots\text{F}) = 2.870 \text{ \AA}$ and $r(\text{I}(\sigma\text{-hole})\cdots\text{Cl}) = 3.602 \text{ \AA}$, and the former is somewhat more directional than the latter, with $\angle\text{C}-\text{I}\cdots\text{F} = 156.7^\circ$ and $\angle\text{C}-\text{I}\cdots\text{Cl} = 146.0^\circ$ (and 148.0°). On the other hand, the two p/π -hole HaBs formed between I and Cl are somewhat shorter than the remaining two p/π -hole HaBs formed between I and F ($r(\text{I}(\pi\text{-hole})\cdots\text{Cl}) = 3.790 \text{ \AA}$ and $r(\text{I}(\pi\text{-hole})\cdots\text{F}) = 3.826 \text{ \AA}$), with the former being less directional than the latter ($\angle\text{C}-\text{I}\cdots$

$\text{Cl} = 74.2^\circ$ and $\angle\text{C}-\text{I}\cdots\text{F} = 98.0^\circ$). These results are not only in agreement with the description that emerged from the MESP model (Figure 2b), but also unequivocally demonstrate that the bond distances associated with the two p/π -hole HaBs formed between I and F do not conform with IUPAC's recommendation⁴¹ for HaBs that states "(i) The interatomic distance between (halogen) X and the appropriate nucleophilic atom of Y tends to be less than the sum of the vdW radii; and (ii) The angle $\text{R}-\text{X}\cdots\text{Y}$ tends to be close to 180° , i.e., the HaB acceptor Y approaches X along the extension of the $\text{R}-\text{X}$ bond." This rationalization is in agreement with the note 9 and feature *f* that appeared in our revised definition of the HaB.⁴²

The results of our DFT calculations showed that the $(\text{CF}_3\text{IClF})_2$ dimer extracted from the crystal structure did not retain its crystalline shape when energy minimized in the gas phase. The interacting CF_3IClF molecules in the crystal (Figure 2c) are rearranged in the gas phase so that the region of maximum molecular potential could interact favorably. As shown in Figure 2d, the covalently bonded F atom of one CF_3IClF molecule has come closer to the σ -hole of the I atom on the extension of the $\text{C}-\text{I}$ bond in another same interacting CF_3IClF . At the same time, in addition to the formation of the $\text{I}(\pi\text{-hole})\cdots\text{Cl}$ HaB, the covalently bonded Cl atom moves slightly to attract the nearest most positive carbon of the $-\text{CF}_3$ group, creating a σ -hole tetrel bond.³⁴ Both the $\text{F}-\text{C}(\sigma\text{-hole})\cdots\text{Cl}$ tetrel bond and $\text{I}(\sigma\text{-hole})\cdots\text{F}$ HaB are directional and quasilinear, the former more so than the latter because the lateral side of the covalently bonded F atom in CF_3IClF is simultaneously forming another close contact, $\text{F}\cdots\text{Cl}$, with the nearest Cl atom of a neighboring molecule. The appearance of this secondary contact is caused by the $\text{I}(\sigma\text{-hole})\cdots\text{F}$ HaB because it is strong ($r(\text{I}(\sigma\text{-hole})\cdots\text{F}) = 2.800 \text{ \AA}$); even though the lateral portion of the F atoms is negative in the monomer, its surface is polarized during the course of forming the $\text{I}(\sigma\text{-hole})\cdots\text{F}$ interaction.

Twelve other configurations of the dimer were manually constructed by displacing slightly the monomers from each other, away from I's σ -hole region in CF_3IClF . Once energy-minimized, three of them adopted the same geometry; one is shown as Conf6 (Figure 2i). Seven of them are shown as Conf1–Conf7, and the remaining three, Conf8–Conf10, are shown below (see Figure 3). As can be seen, the I's p/π -hole in both the interacting CF_3IClF monomers has indeed formed $\text{I}(\text{p}/\pi\text{-hole})\cdots\text{F}$ and $\text{I}(\text{p}/\pi\text{-hole})\cdots\text{Cl}$ HaBs in the dimers in Conf2 and Conf3 (Figure 2e,f), respectively, including Conf6 (Figure 2i). The intermolecular geometry of Conf6 resembles the dimer extracted from the crystal (Figure 2c), but its intermolecular bonding pattern is not as uniform as in the crystal probably because of the packing forces present in the latter. This can be explained by the shift of the covalently bonded F and Cl atoms in both the monomers in the gas-phase so they can simultaneously engage in an attractive engagement with the nearest C's σ -hole of the CF_3 group; this highlights the noninnocent bonding character of covalently bonded carbon and hence the development of directional $\text{C}(\sigma\text{-hole})\cdots\text{Cl}$ and $\text{C}(\sigma\text{-hole})\cdots\text{F}$ tetrel bonds in Conf6. The topology of intermolecular interactions in Conf6 is similar to that in Conf2, where the two tetrel bonds are of the $\text{C}(\sigma\text{-hole})\cdots\text{F}$ type. The distances of the $\text{C}(\sigma\text{-hole})\cdots\text{Cl}$ and $\text{C}(\sigma\text{-hole})\cdots\text{F}$ tetrel bonds in Conf6 are 3.712 and 3.158 Å, respectively, whereas in Conf2 they are 3.154 and 3.260 Å. They are all directional and quasilinear, as can be seen from the values of $\angle\text{F}-\text{C}\cdots\text{F}$ and $\angle\text{F}-\text{C}\cdots\text{Cl}$.

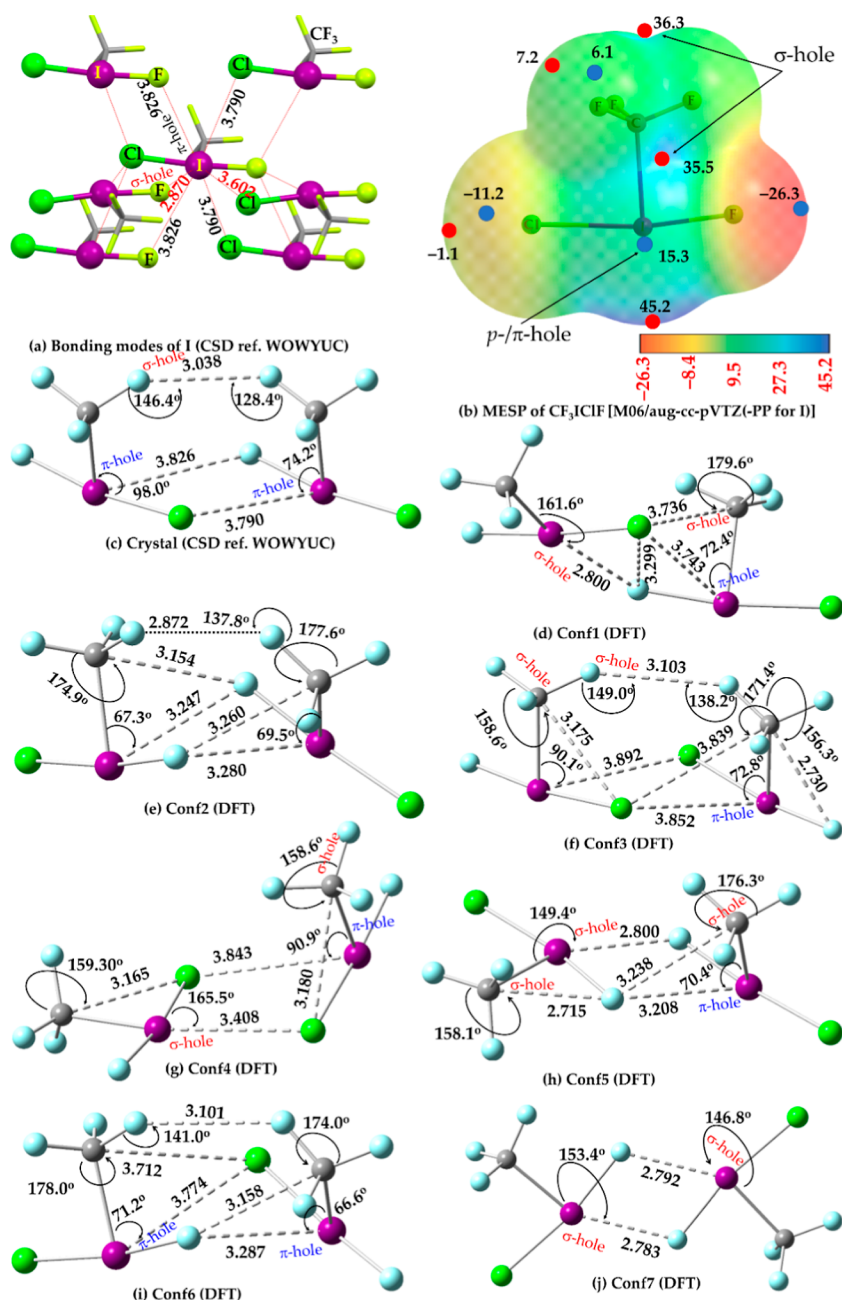


Figure 2. (a) Distance-based speculative nature of the 6-fold noncovalent interaction topologies around the iodine atom in CF_3ICIF in crystalline CF_3ICIF (CSD reference shown in uppercase letters). (b) The 0.0015 au isoelectronic density mapped potential of the same molecule, showing the local minima and maxima (filled tiny circles in blue and red, respectively). (c) A dimer geometry extracted from the crystal, showing the nature of intermolecular bonding environment between a pair of molecular building blocks. (d–j) DFT-[M06/aug-cc-pVTZ] optimized geometries of the dimer (Conf1–Conf7) in the conformational space, with selected bond distance (Å) and bond angles (degrees) shown in geometries (a,c–j). Locations of selected p/π - and/or σ -hole regions on covalently bonded I in CF_3ICIF are marked in (c–j).

The remaining dimers Conf1, Conf4, and Conf5 consist of mixed $\text{I}(\sigma\text{-hole})\cdots\text{X}$ and $\text{I}(p/\pi\text{-hole})\cdots\text{X}$ bonds, and Conf7 is stabilized purely by a pair of $\text{I}(\sigma\text{-hole})\cdots\text{F}$ HaBs. In this case, the linearity is severely hampered by the competition between the interacting atomic domains in the process of making the HaBs. The other three dimers, Conf8–Conf10, which are geometrically very similar to Conf7, are driven by a pair of $\text{I}(\sigma\text{-hole})\cdots\text{F}/\text{Cl}$ HaBs that are also quasi-linear ($148.0^\circ < \angle\text{C–I}\cdots\text{Cl}/\text{F} < 170.0^\circ$) with $\angle\text{C–I}\cdots\text{F}$ is relatively more so than $\angle\text{C–I}\cdots\text{Cl}$ (see Figure 3).

QTAIM's molecular graphs for all the 10 dimers of are shown in Figure 3a–j. All types of HaBs in these dimers are

validated via the bond path and bcp topologies of the charge density, yet QTAIM missed all the topological features necessary for the recognition of the tetrel bonds. What appears to be a tetrel bond between monomers is captured as an $\text{F}\cdots\text{F}$ close contact between the -ICIF fragment in one molecule of CF_3ICIF and the F atom(s) of the CF_3 group in a similar molecule with which it interacts. These contacts are not unusual given that the electrostatic potential of F moieties of the functional group in the monomer are all weakly positive (Figure 2b) and can engage constructively with nearby nucleophiles (i.e., on F and Cl of the -ICIF fragment). Besides, QTAIM also predicted the possibility of $\text{F}\cdots\text{F}$ and $\text{Cl}\cdots\text{Cl}$ close

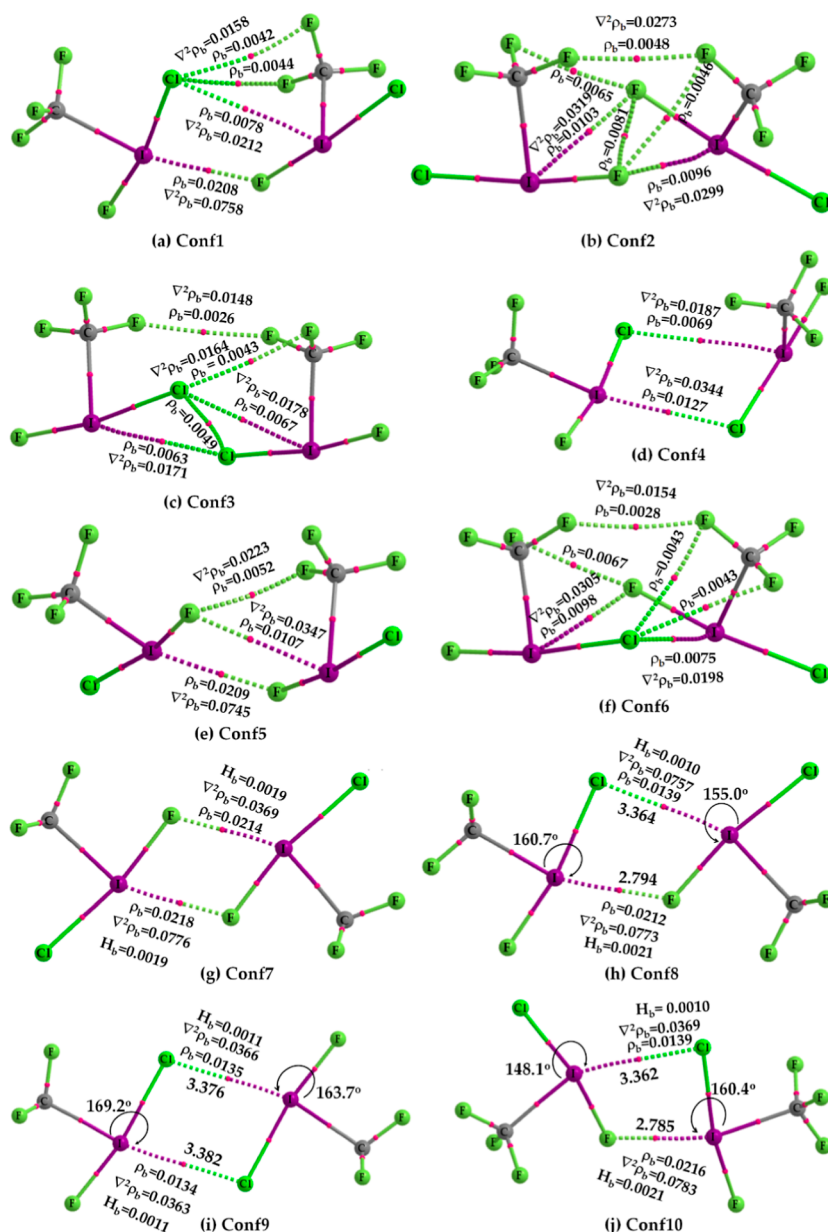


Figure 3. (a–j): QTAIM's molecular graphs for the ten $(\text{CF}_3\text{IClF})_2$ dimers, Conf1–Conf10, illustrating the bond path (solid and dotted lines in atom color) and bond critical point (tiny red spheres) topologies of charge density. Values of ρ_b and $\nabla^2\rho_b$ at selected bcps are in a.u. The intermolecular distances (Å) and angles (degrees) for Conf8–Conf10 are shown in (h–j), together with the total energy H_b density values in a.u. (see text for discussion). Selected HaB angles are shown for Conf8–Conf10 (see Figure 2 for the remaining dimers).

contacts in the dimer shown in Figure 3b,c, respectively; they are weak and can be gleaned upon performing an $\text{IGM}-\delta_g^{\text{inter}}$ analysis with an isovalue <0.005 au (see below). Regardless of the nature of the interactions involved in the 10 dimers, the following characteristics were found: H_b (0.0007 au $< H_b < 0.0021$ au) > 0 ; $\nabla^2\rho_b > 0$ and $\rho_b < 0.022$ au (see Figure 4 for ρ_b and $\nabla^2\rho_b$ values). These are typical of electrostatically driven (closed-shell) interactions, with no appreciable degree of covalency.^{69,96}

The $\text{IGM}-\delta_g^{\text{inter}}$ isosurface plots are shown in Figure 4a–f only for Conf1–Conf5 to provide evidence of the intermolecular interactions discussed above, an attempt to correlate with what was inferred from the MESP model. The tiny irregular isosurfaces (green volumes) associated with tetrel bonds in the dimers appear at lower isovalues and disappear when isovalues around 0.10 au were used. This was not the

case for the isosurfaces representing $\text{I}\cdots\text{Cl}$ and $\text{I}\cdots\text{F}$ HaBs, which are likely to lose their volumetric strength for isovalues larger than 0.10 au. This means that the tetrel bonds are secondary interactions while the $\text{I}\cdots\text{Cl}$ and $\text{I}\cdots\text{F}$ HBs are primary interactions. All the bond types coexist at isovalues around 0.008 au, indicating that the importance of the tetrel bond cannot be overlooked when considering the overall stability of the dimer. These bonds play a synergetic role in dimer formation, helping to explain, for example, why Conf6 (but not Conf1) resembles the dimer shown in Figure 2c. Similarly, the $\text{F}\cdots\text{F}$ close-contact in Conf3 persists at low isovalues around 0.006 au, disappears at isovalues of 0.008 au (Figure 4d), and has a reasonable volume at 0.005 au (Figure 4c). Furthermore, our assertion that the nonlinearity of the $\text{F}-\text{I}-\text{Cl}$ skeleton in the CF_3IClF monomer is the result of the involvement of intramolecular $\text{C}\cdots\text{F}$ and $\text{C}\cdots\text{Cl}$ tetrel bonds is

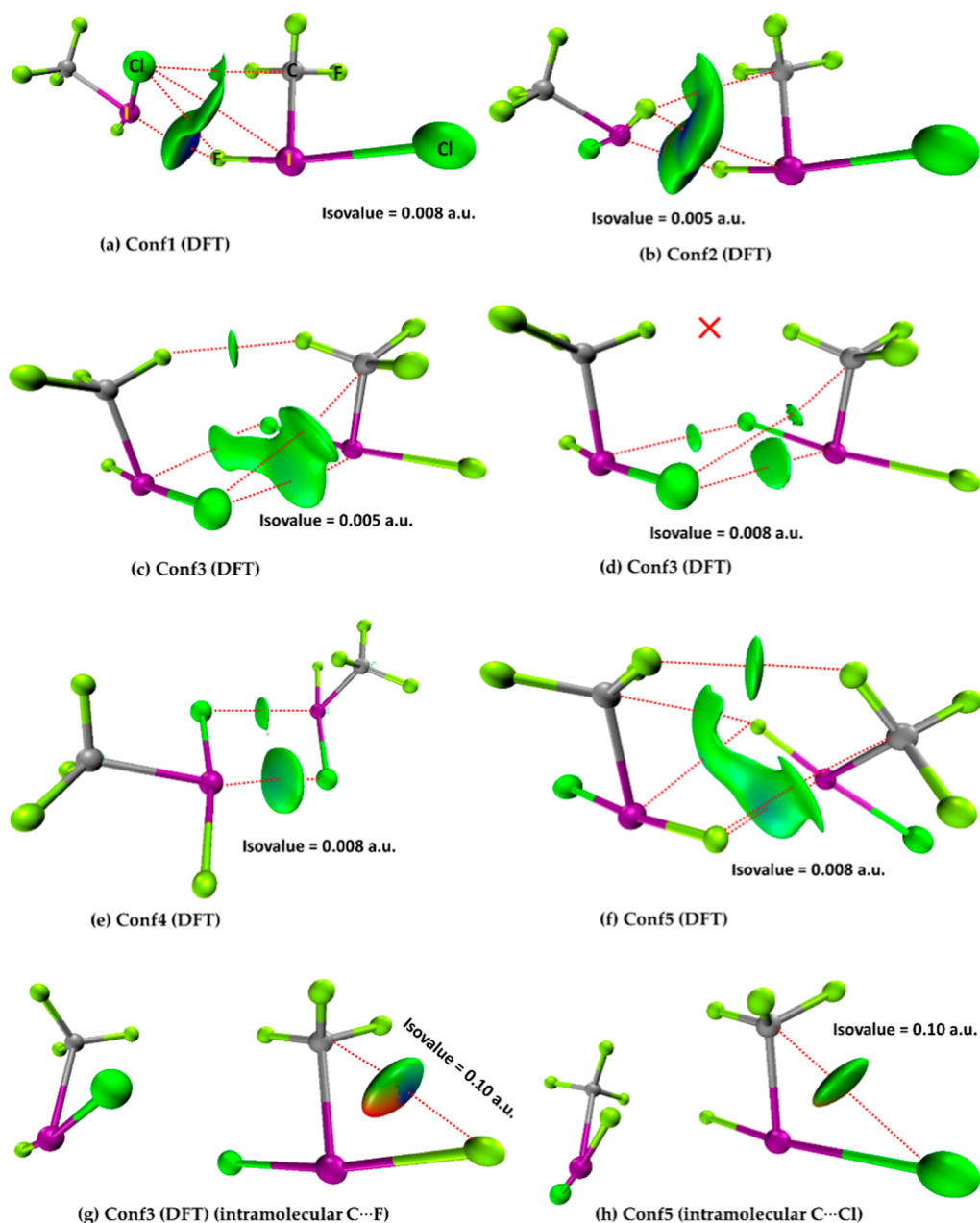


Figure 4. (a–f): IGM- δg^{inter} isosurface plots for five conformers of the $(\text{CF}_3\text{IClF})_2$ dimer, indicating the possible occurrence of $\text{C}\cdots\text{F}/\text{C}\cdots\text{Cl}$ tetrel and $\text{I}\cdots\text{Cl}/\text{I}\cdots\text{F}$ HaBs between the interacting monomer entities. Blue/green volumes between atomic basins are isosurfaces, indicating attraction, reddish areas repulsion. Shown in (g,h) are two representative dimers (Conf3 and Conf5), featuring intramolecular $\text{C}\cdots\text{F}$ and $\text{C}\cdots\text{Cl}$ tetrel bonds, respectively. Labeling of specific atomic basins is shown in (a), whereas the red cross in (d) indicates the loss of $\text{F}\cdots\text{F}$ contact with an isovalue of 0.008 au, and the red-dotted line indicates the interaction.

confirmed by the occurrence of the circular isosurface volumes between the respective atomic bases, shown only for Conf3 and Conf5 (Figure 4g,h), whose significance in shaping the backbone of the CF_3IClF molecule cannot be ignored. Similar intramolecular bonding features between halogen derivatives in halogenated molecules using isosurface topologies of the charge density that emanate from the IGM- δg^{inter} approach have been discussed previously.^{97–99}

Our calculations suggests that Conf7 is the most stable and Conf4 the least stable dimer as determined from their relative interaction energies (Table 1). The order of stability in the BSSE corrected ΔE , $\Delta E(\text{BSSE})$, is: Conf7 > Conf10 > Conf8 > > Conf5 > Conf1 > Conf9 > Conf2 > Conf3 > Conf6 >

Conf4. The remarkable stability of Conf7, Conf10 and Conf8 is due to the sole involvement of σ -hole interactions and short bond distances, with $\Delta E(\text{BSSE})$ values of -11.52 , -9.93 and -9.65 kcal mol $^{-1}$, respectively. Conf5 and Conf1 have one σ -hole and one p/π -hole interaction, among other secondary interactions, thus ranked as the next set of stable dimers. The nature of halogen bonding environment in Conf1 is very similar to that in Conf4, but the latter lacks secondary interactions, resulting in an energy difference of -4.59 kcal mol $^{-1}$ between them. The synergy between many-fold intermolecular interactions in other dimers places them beyond the upper limit of weak bonding regime (~ -5 kcal mol $^{-1}$). As mentioned above, the dimers that contain a σ -hole

Table 1. Uncorrected and BSSE Corrected Interaction Energies (ΔE and $\Delta E(\text{BSSE})$), Respectively) of the 10 Dimers of CF_3IClF ^{a,b,c,d}

system	ΔE	$\Delta E(\text{BSSE})$	$E(\text{BSSE})$	$\Delta E(\text{GD3})$	$\Delta E(\text{GD3-BSSE})$	$\Delta E(\text{GD3-BSSE})-\Delta E(\text{BSSE})$
Conf1	−9.09	−8.60	−0.49	−9.55	−9.06	−0.46
Conf2	−6.70	−6.09	−0.61	−7.45	−6.83	−0.74
Conf3	−6.11	−5.71	−0.40	−6.57	−6.18	−0.47
Conf4	−4.52	−4.01	−0.51	−5.20	−4.69	−0.68
Conf5	−9.74	−9.26	−0.48	−10.25	−9.77	−0.51
Conf6	−6.07	−5.45	−0.62	−6.78	−6.16	−0.71
Conf7	−11.90	−11.52	−0.38	−12.30	−11.92	−0.40
Conf8	−10.01	−9.65	−0.36	−10.37	−10.01	−0.36
Conf9	−7.73	−7.39	−0.34	−8.03	−7.69	−0.30
Conf10	−10.28	−9.93	−0.35	−10.66	−10.30	−0.37

^aIncluded are also the dispersion-incorporated uncorrected and bsse-corrected energies ($\Delta E(\text{GD3})$ and $\Delta E(\text{GD3-BSSE})$, respectively) and the differential between $\Delta E(\text{GD3})$ and $\Delta E(\text{GD3-BSSE})$ ($\Delta E(\text{GD3-BSSE})-\Delta E(\text{BSSE})$). ^bSee Figure 3 for Conf1–Conf10. ^cValues are in kcal mol^{−1}. ^dSee eqs 1 and 2 for ΔE 's.

Table 2. Comparison of the [M06/aug-cc-pVTZ] and [M06-GD3/aug-cc-pVTZ] Level Uncorrected and BSSE Corrected Interaction Energies (ΔE and $\Delta E(\text{BSSE})$) of the 20 Binary Complexes Examined^a

Fig. 5/6	dimer ^b	ΔE	$E(\text{BSSE})$	$\Delta E(\text{BSSE})$	$\Delta E(\text{GD3})$	$E(\text{BSSE-GD3})$	$\Delta E(\text{GD3-BSSE})$	$\Delta E(\text{GD3-BSSE})-\Delta E(\text{BSSE})$
a	$\text{F}_3\text{CF}_2\text{Cl}\cdots\text{ClF}_2\text{CF}_3$	−4.25	0.60	−3.65	−4.89	0.60	−4.29	0.64
b	$\text{F}_3\text{CF}_2\text{Cl}\cdots\text{BrF}_2\text{CF}_3$	−4.35	0.55	−3.80	−4.96	0.55	−4.41	0.61
c	$\text{F}_3\text{CBr}_2\text{I}\cdots\text{BrF}_2\text{CF}_3$	−4.45	0.47	−3.98	−5.12	0.47	−4.65	0.67
d	$\text{F}_3\text{CCl}_2\text{Br}\cdots\text{BrCl}_2\text{CF}_3$	−4.72	0.61	−4.11	−5.50	0.60	−4.90	0.79
e	$\text{F}_3\text{CBr}_2\text{I}\cdots\text{BrCl}_2\text{CF}_3$	−4.82	0.55	−4.27	−5.58	0.54	−5.04	0.77
f	$\text{F}_3\text{CBr}_2\text{I}\cdots\text{BrBr}_2\text{CF}_3$	−4.89	0.57	−4.32	−5.69	0.57	−5.12	0.8
g	$\text{F}_3\text{CBr}_2\text{I}\cdots\text{IBr}_2\text{CF}_3$	−5.00	0.49	−4.51	−5.77	0.49	−5.28	0.77
h	$\text{F}_3\text{CCl}_2\text{I}\cdots\text{ICl}_2\text{CF}_3$	−5.09	0.55	−4.54	−5.86	0.55	−5.31	0.77
i	$\text{F}_3\text{CClBrI}\cdots\text{IBrClCF}_3$	−5.09	0.53	−4.56	−5.89	0.53	−5.36	0.8
j	$\text{F}_3\text{CClI}_2\cdots\text{I}_2\text{ClCF}_3$	−5.27	0.46	−4.81	−6.09	0.47	−5.62	0.81
k	$\text{F}_3\text{ClI}_2\cdots\text{BrBr}_2\text{CF}_3$	−5.30	0.52	−4.78	−6.13	0.51	−5.62	0.84
l	$\text{F}_3\text{CCl}_2\text{Br}\cdots\text{ClCl}_2\text{CF}_3$	−5.86	0.87	−4.99	−6.74	0.87	−5.87	0.88
m	$\text{F}_3\text{CF}_2\text{Br}\cdots\text{BrF}_2\text{CF}_3$	−5.87	0.39	−5.48	−6.32	0.40	−5.92	0.44
n	$\text{F}_3\text{CBr}_2\text{Br}\cdots\text{BrBr}_2\text{CF}_3$	−6.18	0.76	−5.42	−7.07	0.76	−6.31	0.89
o	$\text{F}_3\text{CBrI}_2\cdots\text{I}_2\text{BrCF}_3$	−6.36	0.54	−5.82	−7.27	0.54	−6.73	0.91
p	$\text{F}_3\text{Cl}_3\cdots\text{I}_3\text{CF}_3$	−6.66	0.46	−6.20	−7.57	0.46	−7.11	0.91
q	$\text{F}_3\text{CFBrI}\cdots\text{IBrFCF}_3$	−7.02	0.56	−6.46	−7.70	0.55	−7.15	0.69
r	$\text{F}_3\text{CFI}_2\cdots\text{I}_2\text{FCF}_3$	−7.07	0.48	−6.59	−7.79	0.48	−7.31	0.72
s	$\text{F}_3\text{CF}_2\text{I}\cdots\text{IF}_2\text{CF}_3$	−8.77	0.44	−8.33	−9.18	0.44	−8.74	0.41
t	$\text{F}_3\text{CClFI}\cdots\text{IFClFI}_3$	−9.09	0.49	−8.60	−9.55	0.49	−9.06	0.46

^aIncluded are also the bsse energy ($e(\text{bsse})$), the dispersion-incorporated uncorrected and bsse-corrected energies ($\delta e(\text{gd3})\Delta E(\text{GD3})$ and $\Delta E(\text{GD3-BSSE})\delta e(\text{gd3-bsse})$, respectively) and the differential between $\delta e(\text{gd3-bsse})$ and $\delta e(\text{bsse})\Delta E(\text{GD3})$ and $\Delta E(\text{GD3-BSSE})$ ($\Delta E(\text{GD3-BSSE})-\Delta E(\text{BSSE})$). Values in kcal mol^{−1}. ^bSee Figures 5 and 6 for a graphical representation of all the 20 dimers.

HaB, in addition to contributions from other secondary interactions, have an enhanced stability.

The inclusion of the effect of dispersion at the level of Grimme's DFT–D3 does not significantly increase the strength of the overall interaction (see $\Delta E(\text{GD3})$ and $\Delta E(\text{GD3-BSSE})$ values in Table 1), with contributions ranging between −0.30 and −0.74 kcal mol^{−1} [see $\Delta E(\text{DFT-D3-BSSE})-\Delta E(\text{BSSE})$ values] which are in the range of the correction made for the BSSE (−0.34 and −0.62 kcal mol^{−1}; see the $E(\text{BSSE})$ values). (The range is quantified by the difference, $\Delta E(\text{GD3-BSSE}) - \Delta E(\text{BSSE})$, which was the difference between the BSSE corrected interaction energies without and with the effect of dispersion [$\Delta E(\text{BSSE})$ and $\Delta E(\text{GD3-BSSE})$, respectively]. This means that the uncorrected interaction energy, ΔE , is a good approximation if neither BSSE nor dispersion is taken into account, suggesting that the formation of the dimers explored is electrostatically driven.

3.1.3. Design and Discovery of Molecules Featuring *p*-/*π*-Holes, and Their Dimers, Using DFT Calculations. Halogen substitution in $(\text{CF}_3\text{ICl}_2)_2$ led us to the manual design and computational discovery of several dimeric structures. We substituted the halogen derivative in the ICl_2 fragment of $\text{F}_3\text{C}-\text{ICl}_2$ (cf. Figure 1b for shape). This resulted in 18 new dimers that do not include pure σ -hole HaBs. These were fully relaxed using [M06/aug-cc-pVTZ], and their energy-minimized geometries based on their energy stabilities (see Table 2 for energies), including the two parent dimers, $(\text{CF}_3\text{ICl}_2)_2$ and $(\text{CF}_3\text{IClF})_2$, are shown in Figures 5a–j and 6k–t.

Physical insight into the regions of the atomic surfaces responsible for the interacting molecules to form the dimers is provided in Figure 7a–d. The MESP's for all monomers are not shown, but the systems of fundamental importance are considered. A major issue of concern, as Politzer and Murray noted previously,⁶⁶ is that the isoelectron density envelope for calculating the potential is arbitrary.^{25,100–102} The isoelectron

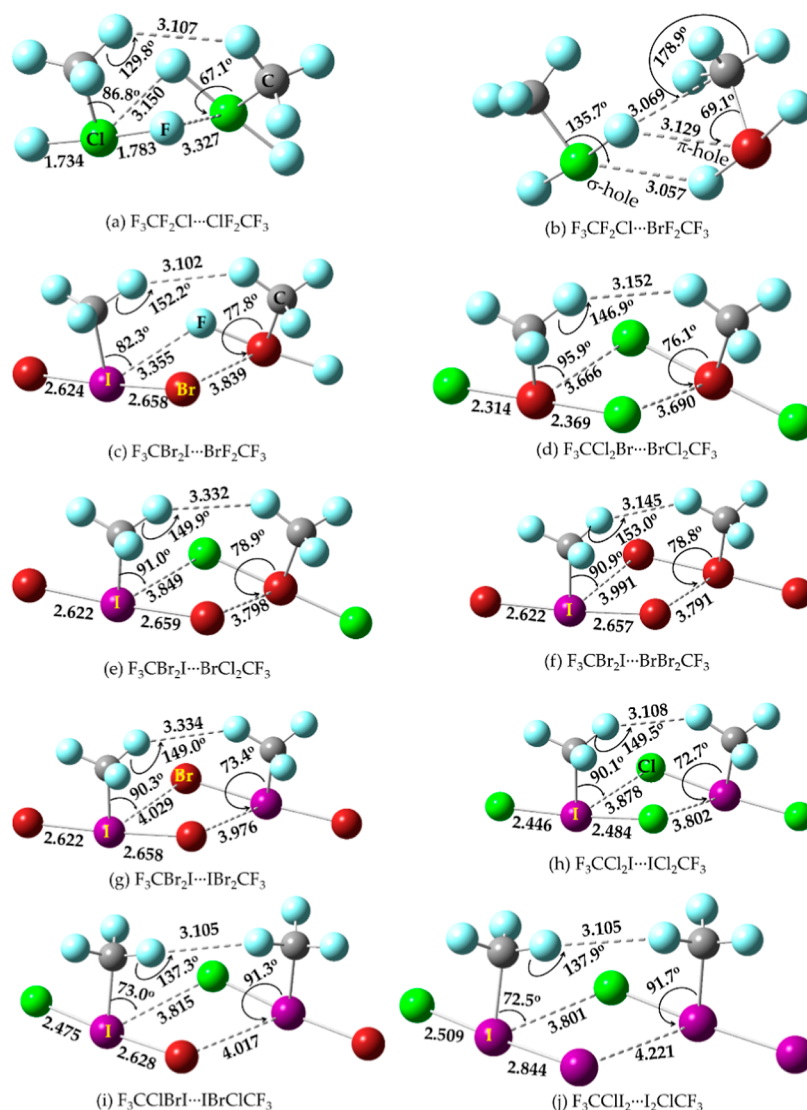


Figure 5. (a–j) [M06/aug-cc-pVTZ] relaxed geometries of 10 halogenated 1:1 complexes, featuring p/π-hole HaBs and other noncovalent interactions. Selected bond distances and bond angles are in Å and degrees. Atom labeling is shown only for cases (a,c).

density envelopes commonly used to map potentials, 0.001 a.u.,^{8,90,103} can be a good approximation and often provide qualitative physical insight into regions on a surface suitable for the expression of directed, noncovalent interactions.⁸ However, this envelope is not suitable for all molecules because each molecule has its own isoelectronic density surface that roughly approximates its own vdW surface, and the 0.001 au isoelectronic density envelope is arbitrary⁶⁶ and hence may not adequately define all of them.⁶⁷

To obtain chemically intuitive maxima and minima of the potential on the surfaces of the F_3C-I-Y_2 ($Y = F, Cl, Br, I$) molecules, we used three other basis sets, Sadlej pVTZ, def2-TZVPPD, and 6–311G(d,p). This was prompted by the fact that the correlation-consistent pseudopotential basis set, aug-cc-pVTZ (-PP for I), failed to provide the expected features, especially for molecular entities involving the heavier halogen derivatives. The first two basis sets, like aug-cc-pVTZ (-PP for I), have also failed to give the expected maxima and minima of the potential on the surfaces of the covalently bonded I and C/ $F(-CF_3)$ atoms in F_3C-I-Y_2 , unless we used an electron density envelope close to, or higher than, 0.0014 au. The 6–311G(d,p) basis set, on the other hand, gave the expected

minimum of potential on the surface of covalently bonded I that characterizes its p/π-holes, but missed some minima and maxima of the potentials on the covalently bonded F and C atoms of the $-CH_3$ group of the molecule. We will address this issue elsewhere, but here we focus only on the results obtained using the 6–311G(d,p) basis set and the specific regions on the surface of the aforementioned molecules that are essential for understanding the chemical bonding features the monomers display toward the discovery of the dimers discussed below. It is worth noting that the use of higher isoelectronic density surfaces is necessary since the molecular entities investigated involve intramolecular interactions; the details of this has been discussed elsewhere.^{73,104}

As shown in Figure 7, the $V_{S,max}$ value on the surface of the hypervalent I atom in the F_3C-IX_2 ($X = F, Cl, Br, I$) molecules systematically decreases with the increasing the size of the halogen derivative in the $-IX_2$ fragment, with a systematic increase in the strength of I's σ-hole in the series. This is concordant with the electron-withdrawing power of the halogen derivative that increases as $F > Cl > Br > I$. There are also two $V_{S,min}$ on the surface of the same I atom that are characteristics of I's p/π-hole; they lie on either side,

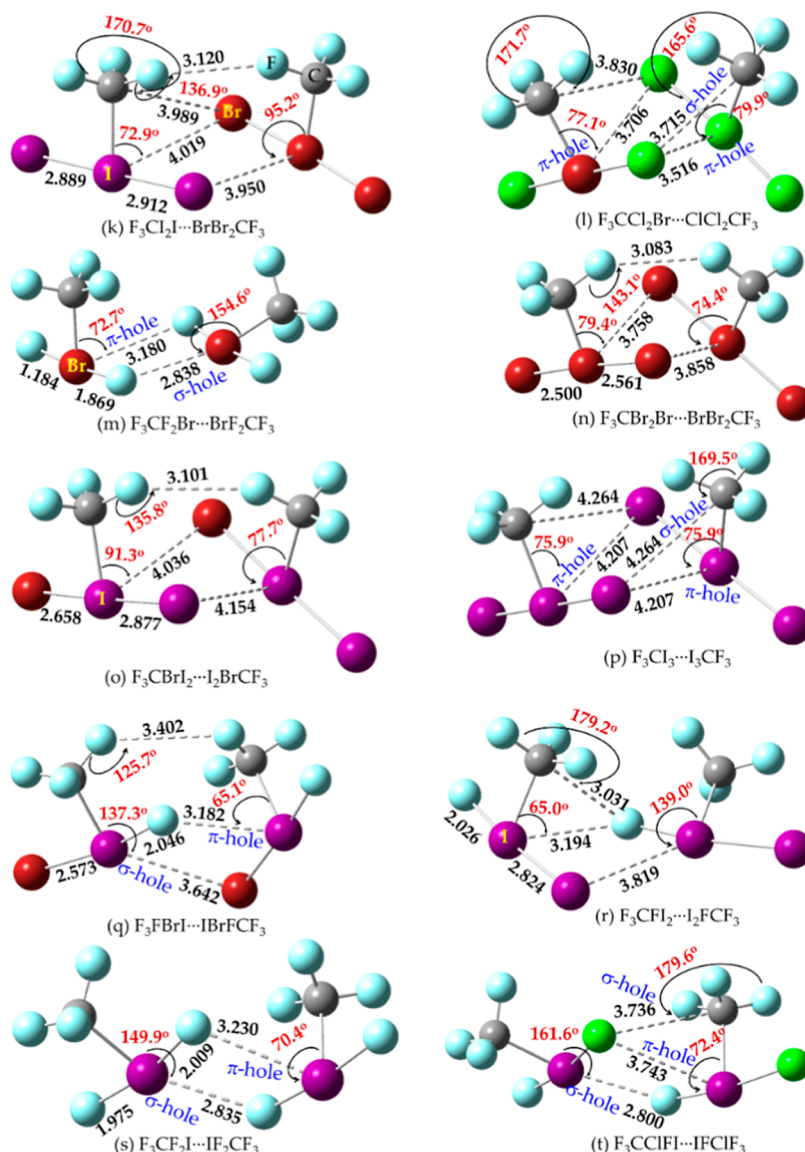


Figure 6. (k–t) [M06/aug-cc-pVTZ] relaxed geometries of another 10 halogenated dimers, featuring p/ π -hole HaBs and other noncovalent interactions. Selected bond distances and bond angles are in Å and degrees. Atom labeling is shown only for cases (a,c). For clarity, secondary interactions in most of the dimers are not shown (for example, the F–C(σ -hole)···F tetrel bond in (q) is not shown). The locations of p/ π - and σ -hole regions are marked.

orthogonal to the C–I covalent bond axis (one shown in Figure 7a–d). They are reasonably strong, with the $V_{S,\min}$ values that are positive and vary between 16.9 and 15.6 kcal mol^{−1}. We expected the stability of the p/ π -hole of I to have the same priority as found in the σ -holes of the series, but this was not the case. The stability preference is as follows: R–Cl > R–F > R–Br > R–I. Whether this alternation between F₃C–IF₂ and F₃C–ICl₂ is due to weak intramolecular interactions between the –CF₃ and –IX₂ groups for X = F where the electron density shift to the –CF₃ group is minimal is uncertain and requires further investigation. QTAIM does not predict any paths between two groups for X = F (Figure 7a), unlike for the other three members of the F₃C–IX₂ family (Figure 7b–d).

There is no discernible trend in the σ -holes on carbon atoms of the –CF₃ group along the series; they are highly electrophilic in all four cases. On the other hand, the X atom bonded to the hypervalent I atom in F₃C–IX₂ is more

nucleophilic for X = F and with the σ -hole on it neutralized, and more electrophilic when X = I. When comparing the strength of the σ -hole along the series, the observed trend was Cl < Br < I. The absence of the σ -hole on F along the I–F bond extensions in F₃C–IF₂ is due to a considerable buildup of electronic density in the σ -hole regions, causing the neutralization of the σ -hole on F, as observed in the case of molecular N₂.¹⁰³

The p/ π -hole HaB geometry seen in (CF₃ICl₂)₂, Figure 1d, is maintained in the eight dimers shown in Figures 5c–g and 6i–k. The same geometry in the remaining dimers is significantly deformed as a result of the breaking of the p/ π -hole HaB and the making of new or additional intermolecular interactions. For example, the dimer in Figure 5b, F₃CF₂Cl···BrF₂CF₃, does not have the pair of p/ π -hole HaBs observed in the crystal of CF₃ICl₂, Figure 1c. This is because one of the π -hole HaBs in F₃CF₂Cl···BrF₂CF₃ is ruptured upon halogen substitution and the interacting molecules rearrange to feature

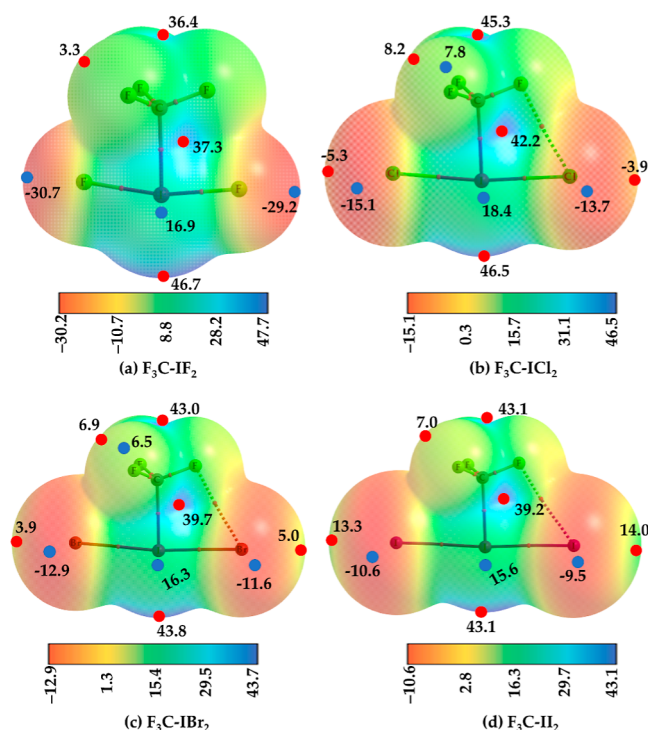


Figure 7. [M06/6-311G(d,p)] level MESP of F_3C-IX_2 ($X = F, Cl, Br, I$), obtained upon mapping with the 0.0015 au (electrons bohr⁻³) isoelectronic density envelope. The surface maxima and minima of potential (filled tiny circles in red and blue, respectively) are marked. Values in kcal mol⁻¹. QTAIM's bond paths (solid dotted lines in atom color) and bond critical point (tiny spheres between atoms colored red) topologies of the charge density are superimposed. Atoms as spheres are labeled.

a different scenario of chemical bonding. The stability of the newly formed dimer, $F_3CF_2Cl \cdots BrF_2CF_3$, results jointly from the $C-Cl(\sigma\text{-hole}) \cdots F$ and $C-Br(\pi\text{-hole}) \cdots F$ HaBs, and a $F-C(\sigma) \cdots F$ tetrel bond.³⁴ The first two are nonlinear ($\angle C-Cl(\sigma\text{-hole}) \cdots F = 135.7^\circ$) and bent ($\angle C-Br(\pi\text{-hole}) \cdots F = 69.1^\circ$), respectively, while the latter is markedly linear ($F-C(\sigma) \cdots F = 178.9^\circ$); nevertheless, they are all directional interactions.

The $C-Cl(\sigma\text{-hole}) \cdots F$ and $C-Br(\pi\text{-hole}) \cdots F$ HaBs in $F_3CF_2Cl \cdots BrF_2CF_3$, Figure 5b, is similar to the $C-X(\sigma\text{-hole}) \cdots Y$ and $C-X(\pi\text{-hole}) \cdots Y$ ($X, Y = \text{halogen}$) HaBs in $F_3CF_2Br \cdots BrF_2CF_3$ (Figure 6m), $F_3CFBrI \cdots IBrFCF_3$ (Figure 6q), $F_3CFI_2 \cdots I_2FCF_3$ (Figure 6r), $F_3CF_2I \cdots IF_2CF_3$ (Figure 6s) and $F_3CClFI \cdots IFClF_3$ (Figure 6t). They are all augmented by secondary interactions; their detailing is beyond the scope of this study. The last four dimers are the strongest of the 20 dimers in Figures 5a–j and 6k–t, with BSSE-corrected interaction energies, $\Delta E(\text{BSSE})$, of -6.46 , -6.59 , -8.33 and -8.60 kcal mol⁻¹, respectively. The energetic advantage of the strongest dimer $F_3CClFI \cdots IFClF_3$ (Figure 6t) over the next strongest dimer $F_3CF_2I \cdots IF_2CF_3$ (Figure 6s) occurs despite the presence of a longer $C-I(\pi\text{-hole}) \cdots Cl$ HaB and a longer $C-F(\sigma\text{-hole}) \cdots Cl$ tetrel bond in the former than in the latter. For example, the $F-C(\sigma\text{-hole}) \cdots Cl$ and $F-C(\sigma\text{-hole}) \cdots F$ tetrel bonds in the respective dimers have bond distances (angles) of 3.736 Å (179.8°) and 3.248 Å (176.7°). Similarly, the $C-I(\pi\text{-hole}) \cdots Cl$ bond distance of 3.743 Å in $F_3CClFI \cdots IFClF_3$ is longer than the $C-I(\pi\text{-hole}) \cdots Cl$ bond distance of 3.230 Å in $F_3CF_2I \cdots IF_2CF_3$. It is possible that secondary inter/molecular interactions involving, for example, $C \cdots F$, $F \cdots F/Cl \cdots$

$F(CF_2)$, or $I \cdots F(CF_2)$, etc., underlie the higher stability of $F_3CClFI \cdots IFClF_3$, but this has not been investigated here and requires further study.

The dimer, $F_3CF_2Cl \cdots ClF_2CF_3$ (Figure 5a), does not represent an ordered structure. This view is based on the ordering observed in relation to the $C-Cl(\pi\text{-hole}) \cdots Cl$ halogen bonded pair and the $F \cdots F$ closeness in the $(CF_3ICl_2)_2$ dimer extracted from the crystal of CF_3ICl_2 (Figure 1c).

The bond distances associated with the $C-Cl(\pi\text{-hole}) \cdots F$ HaBs in $F_3CF_2Cl \cdots ClF_2CF_3$ are shorter, with $r[Cl(\pi\text{-hole}) \cdots F]$ of 3.150 and 3.327 Å. The nucleophiles on the covalently bonded F atoms in $-ClF_2$ in one monomer involved in the development of these HaBs are being simultaneously shared with the fluorine of the $-CF_3$ fragment in the other. The latter leads to the formation of two $Cl-F \cdots F(CF_2)$ close-contacts ($r(F \cdots F(CF_2)) = 2.896/2.847$ Å and $\angle(FCl)F \cdots F(CF_2) = 131.4^\circ/140.9^\circ$). They are quasi-linear and probably σ -hole centered.

The deductions made from considering the geometries are not consistent with QTAIM's molecular graph, Figure 8a. This indicates the possibility of five $F \cdots F$ close-contacts between the two $-CF_3$ groups and the $-ClF_2$ fragments of the interacting monomers. This led us to reinspect the geometry of the dimer, Figure 5a, and led to the conclusion that the F atom forming the $Cl(\pi\text{-hole}) \cdots F$ HaB ($r(Cl(\pi\text{-hole}) \cdots F) = 3.327$ Å) has close-contact distances of 2.847 ($F \cdots F$), 2.892 ($F \cdots F$) and 3.129 Å ($C \cdots F$) with the adjacent $-CF_3$ group. The latter is highly directional ($\angle F_3C(\sigma) \cdots F = 176.2^\circ$) (see Figure 8a) compared to the first two [$\angle(Cl-F(\sigma) \cdots F(CF_2)) = 140.9^\circ$ and $\angle Cl-F(\sigma) \cdots F(CF_2) = 120.9^\circ$]. The view that the tetrel bond exists is concordant with the positive electrostatic potential centered at the C atom that occurs along the outermost $F-C$ bond extension, which is the cause for the development of an attraction between the F atoms that contribute to formation of the dimer. The remaining two $F \cdots F$ close-contacts in $F_3CF_2Cl \cdots ClF_2CF_3$ occur between the two CF_3 groups ($r(F \cdots F) = 3.107$ Å and ($\angle(F_2C)F(\sigma) \cdots F(CF_2) = 133.4^\circ$), and between the $-ClF_2$ and $-CF_3$ fragments of the interacting molecules ($r(FClF \cdots F) = 2.896$ Å and ($\angle(FCl)F(\sigma) \cdots F(CF_2)/\angle(CF_2)F(\sigma) \cdots F(ClF) = 113.0^\circ$), and are not accompanied by any $C \cdots F$ tetrel bond. The inability of QTAIM to capture the tetrel bonds in chemical environments as here has been noted previously.^{105,106}

The $F_3-C(\sigma\text{-hole}) \cdots X$ tetrel bond is present in all dimers (see Figure 8a–t), with its singly or double occupancy, and is a quasi-linear directional interaction. Its bond distance varies with the size of the halogen derivative that shares its electron density rich site with the bonded carbon. The smallest bond distance is found for the dimer $F_3CFBrI \cdots IBrFCF_3$ (Figure 8q). It is comparable to the bond distance range, 3.023 – 3.248 Å, predicted for the dimers $F_3CF_2I \cdots IF_2CF_3$ (Figure 8s), $F_3CFI_2 \cdots I_2FCF_3$ (Figure 8r) and $F_3CF_2Br \cdots BrF_2CF_3$ (Figure 8m), $F_3CF_2Cl \cdots BrF_2CF_3$ (Figure 8b) and $F_3CF_2Cl \cdots ClF_2CF_3$ (Figure 8a); in these cases, the covalently bonded F in the $-CF_3$ fragment acts as an electron density rich center. The tetrel bond in all these six dimers is highly directional, with the angle of interaction ($\angle F-C \cdots F$) in the range from 175.8 to 179.1° . When the halogen derivative in the $-YYY'$ fragment of F_3C-XXX' in one molecule is involved in creating two $Y/Y' \cdots F$ contacts with the same participating fragment in a neighboring molecule, the tetrel bond becomes more directional; this is

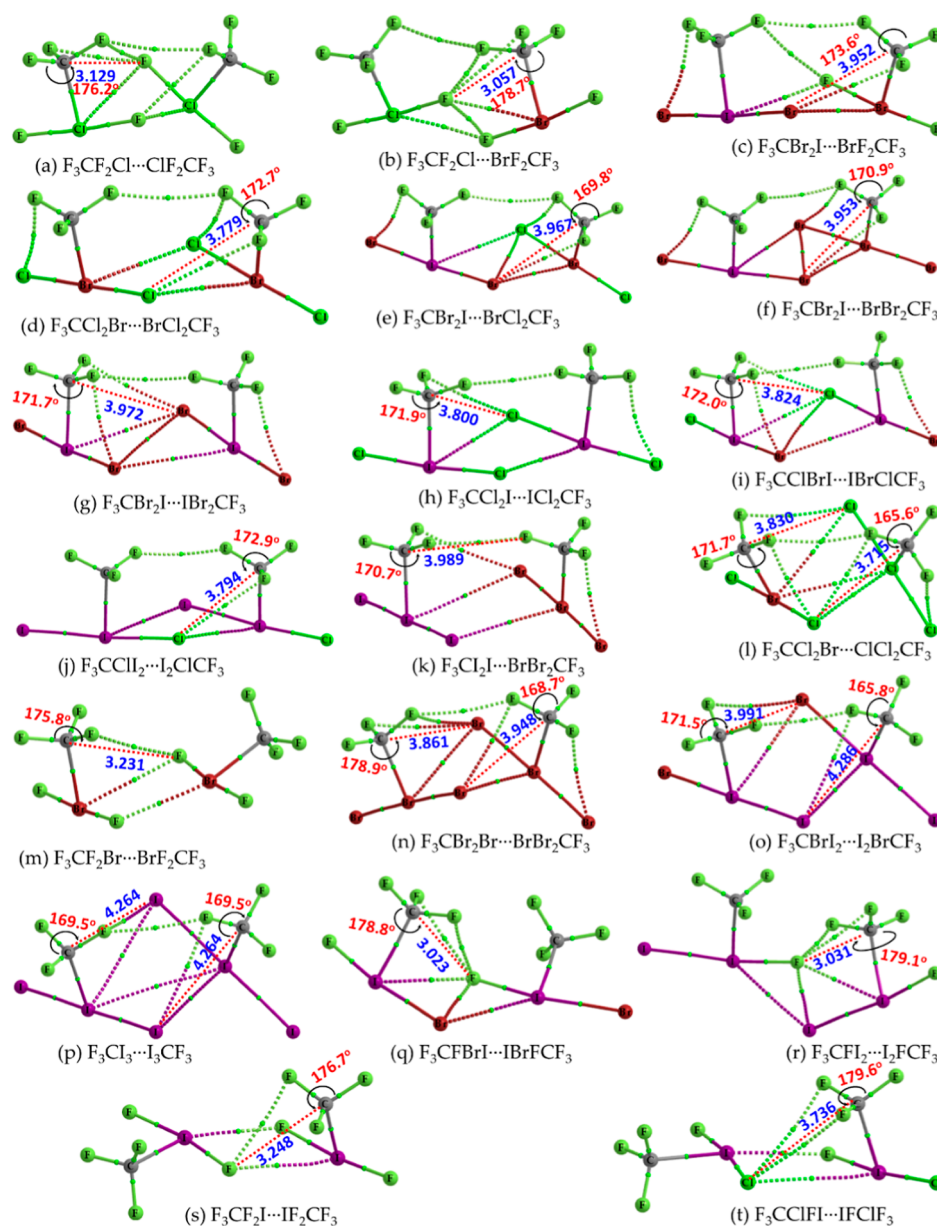


Figure 8. (a–t): QTAIM-based molecular graph of 20 dimers, showing possible bonding interactions between interacting monomer molecules via its bond path and bond critical point topologies of the charge density. The bonding paths between bonded atomic basins (large spheres) are indicated by atom color, with covalent and noncovalent interactions represented by solid and dotted lines, respectively. The tiny spheres between atoms in green are bond critical points. Atomic labeling is shown for each entry. The C...X (X = halogen) close contact distances in Å (dotted lines in red; manually drawn) and angles in degrees are shown, which are ubiquitous in the equilibrium geometry of dimers and are not predicted by QTAIM.

compared to dimers that feature single occupancy of the Y/Y'...F contact.

Depending on the size of the halogen derivative hosting the p/ π -hole in each molecule for the nucleophilic guest in the interacting monomer, the intermolecular distance of the p/ π -hole's HaB changes. Larger halogen derivatives feature longer bonds, as expected. For instance, the C–I(π -hole)...Cl and C–I(π -hole)...I π -hole HaBs in F₃CClI₂...I₂ClCF₃ (Figure 5j) are 3.801 and 4.221 Å, respectively, whereas each of the two C–I(π -hole)...I HaBs in F₃Cl₃...I₃CF₃ (Figure 6p) are 4.207 Å, which are certainly longer than those formed by Cl and F atoms in dimers shown in Figure 5a,b. Similarly, the IUPAC geometric feature has failed to describe the p/ π -hole HaBs in several dimers, viz. F₃CBr₂I...IBr₂CF₃ (Figure 5g), F₃CBr₂I...

BrBr₂CF₃ (Figure 5f) F₃CClBrI...IBrClCF₃ (Figure 5i), F₃CClI₂...I₂ClCF₃ (Figure 5j), F₃Cl₂I...BrBr₂CF₃ (Figure 5k). This recognition is not true for all C...X tetrel bonds given that the distance range 3.023–3.231 Å for the C...F tetrel bonds in some dimers (see Figure 8) is less than, or equal to, the sum of the vdW radii of the respective bonded atomic basins, 3.23 Å ($r_{\text{vdW}}(\text{C}) = 1.77$ Å and $r_{\text{vdW}}(\text{F}) = 1.46$ Å⁶⁰). Our reasoning is consistent with Murray et al.,^{90,91} and our previous comments,^{17,19,34,35,107} that one should expect favorable interactions in which close contacts can be significantly greater than the sums of the vdW radii of bonded atomic basins.⁴²

As shown in Table 2, the energy due to BSSE is less than 1.0 kcal mol^{−1} regardless of the dimers examined, with the E(BSSE), the energy due to the BSSE, varying between 0.39

Table 3. Comparison of Experimental and DFT-Calculated Lattice Constants (*a*, *b*, *c* and $\alpha/\beta/\gamma$) and Cell-Volumes of the Orthorhombic Crystals of CF₃ICl₂ (CSD Ref. COXYIX),⁵⁷ and CF₃IClF (CSD Ref. WOWYUC)⁵⁸

system	method	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\alpha = \beta = \gamma$ /degrees	cell-volume/Å ³
CF ₃ ICl ₂	Expt ⁵⁷	6.99	7.99	21.18	90°	1182.0
	PBE (this work)	7.68	8.05	22.39	90°	1383.4
	Expt ⁵⁸	6.90	7.31	20.13	90°	1014.9
CF ₃ IClF	PBE (this work)	7.57	7.44	20.86	90°	1173.8

and 0.87 kcal mol^{−1} (for F₃CF₂Br⋯BrF₂CF₃ (Figure 6m) and F₃CCl₂Br⋯ClCl₂CF₃ (Figure 6l) respectively). Thus, the BSSE corrected interaction energies, $\Delta E(\text{BSSE})$, vary between −3.65 and −8.60 kcal mol^{−1}, for F₃CF₂Cl⋯ClF₂CF₃ (Figure 5a) and F₃CClFI⋯IFClF₃ (Figure 6t), respectively, which are certainly smaller than the uncorrected interaction energies ΔE of the corresponding dimers. When the effect of dispersion was taken into account, the dispersion corrected interaction energy, $\Delta E(\text{GD3})$, increased compared to ΔE . This increase, after incorporating the effect of the energy due to BSSE ($E(\text{GD3-BSSE})$), amounted to between 0.41 and 0.91 kcal mol^{−1}. The largest dispersion contribution is notable for dimers that comprise the largest number of heavier halogen atoms [for example, F₃CBrI₂⋯I₂BrCF₃ (Figure 6o) and F₃ClI₃⋯I₃CF₃ (Figure 6p)], yet dispersion is not a major factor that confers stability to the dimers explored.

3.1.4. Electronic Structures, DOS and Band Structure Properties of the Crystalline Systems. The crystals of CF₃ICl₂ (CSD ref COXYIX),⁵⁷ and (CF₃IClF) (CSD ref WOWYUC)⁵⁸ were also examined using periodic boundary conditions at the PBE/PAW level of theory. The optimized lattice properties, summarized in Table 3, show the expected level of agreement between theory and experiment, even though the lattice is somewhat expanded compared to what was observed experimentally (see values of lattice volumes). As a result, the symmetry of the periodic lattice changed from *Cmca* to *Cmce*, yet both belong to the same orthogonal crystal system. The experimental I⋯Cl and I⋯F HaB distances in the crystals were slightly longer than that of the PBE calculated geometries (viz. the two inequivalent p/π-hole HaB bond distances in the crystals and PBE-relaxed geometries: 3.883 (3.926) vs 4.195 (4.290) Å for I⋯Cl in CF₃ICl₂ (CSD ref COXYIX);⁵⁷ 3.826 (3.790) vs 4.149 (4.110) Å for I⋯Cl (I⋯F) in (CF₃IClF) (CSD ref WOWYUC)⁵⁸). The small discrepancy is not very surprising since more accurate lattice properties can be obtainable upon invoking high *k*-mesh and cutoff criteria for forces on ions and self-consistent loops to converge, and using a high level of theory. We did not investigate this because of limited computational resources and the time required for such a calculation for a large cell containing 56 atoms. Nevertheless, and as highlighted above, the chemical bonding environment discussed in Sections 3.1.1 and 3.1.2 for these systems is not strikingly different from what was calculated using periodic boundary conditions. Some of the local interactions in the crystal geometries are illustrated in Figure 9a,b, respectively, for CF₃ICl₂ and CF₃IClF.

Although the details of the physical properties of the crystals are not known experimentally, our exploration of the band structures reveals that both the crystals feature a direct bandgap, E_g of 2.15 and 2.78 eV for CF₃ICl₂ and CF₃IClF, respectively. Clearly, the HaB, and other interactions, play an important role in these zero-dimensional crystals and suggest their possible application in optoelectronics, especially in the visible region. The valence band maximum (VBM) and

conduction band minimum (CBM) have respective energy strengths of −0.504 (−0.402) and 1.685 (2.381) eV at high-symmetry Γ -point for CF₃ICl₂ (CF₃IClF), where the character of the bandgap is direct. The detailed nature of the band structures of the corresponding crystals are shown in Figure 9c and d, respectively.

The semiparabolic and flat CBM appears far above the Fermi level for CF₃ICl₂ and CF₃IClF, respectively; the latter stands out as the boundary meeting the parabolic VBM. From DOS spectra (Figure 9e–f), we found that the VBM arises from the superposition of Cl and I's p-orbital states for CF₃ICl₂ (cf. Figure 9e and Table 4). This is not so in the case of CF₃IClF, in which case the VBM is composed equally of the Cl and I's p-orbital states, but that of F's p-orbitals is partially involved (Figure 9f). Contrarily, the orbital contribution to the CBM is of this order F(p) < Cl(p) ≤ C(p) < I(p) and Cl(p) < C(p) < F(p) < I(p) for CF₃ICl₂ and CF₃IClF, respectively, suggesting that the contribution from the p-orbital states between Cl, F and C is altered upon the replacement of Cl in CF₃ICl₂ by F that constitutes the halogen-bearing fragment Cl–I–X (X = F, Cl), so affecting the tetrel and halogen bonding environments in the crystal lattice. In both cases, the s-orbital contribution to the CBM is marginal (Table 4).

4. DISCUSSION AND CONCLUDING REMARKS

This study has revealed covalently bonded halogen's p/π- and σ-hole HaB donating features in the CF₃XY₂ (X, Y, Y' = halogen) series of molecules, showing their true combined involvement in the synthetic design principles toward the development of ordered crystalline materials. Three of these chemical systems have been known for the past two decades, and are prominent molecular building blocks toward the formation of crystalline CF₃IF₂, CF₃IClF and CF₃ICl₂. The remaining CF₃XY₂ models were designed manually via halogen substitution and computationally discovered as stable entities. They may be of interest to materials scientists for synthesis in the future. Periodic calculations with PBE have enabled us to show that CF₃IClF and CF₃ICl₂ are direct bandgap materials which may find application in the visible region of the electromagnetic spectrum.

Some dimers are shown to involve both the p/π- and σ-hole donors of the hypervalent halogen derivative to form HaBs. Depending on the size and type of hypervalent halogen derivative X in the two interacting CF₃XY₂ molecules, one type of HaB dominates over the other, contributing to the geometric stability to the dimers investigated. Those are stabilized by p/π-hole HaBs are relatively ordered and unaffected by a variety of secondary interactions. Distorted (or disordered) dimers, especially those involving fluorine and other mixed halogen environments, show a variety of secondary interactions, and form weak to moderately strong dimers. Those driven by both p/π- and σ-hole HaBs are found to be energetically more stable, an effect of the involvement of σ-hole HaB. The contribution of dispersion to the interaction

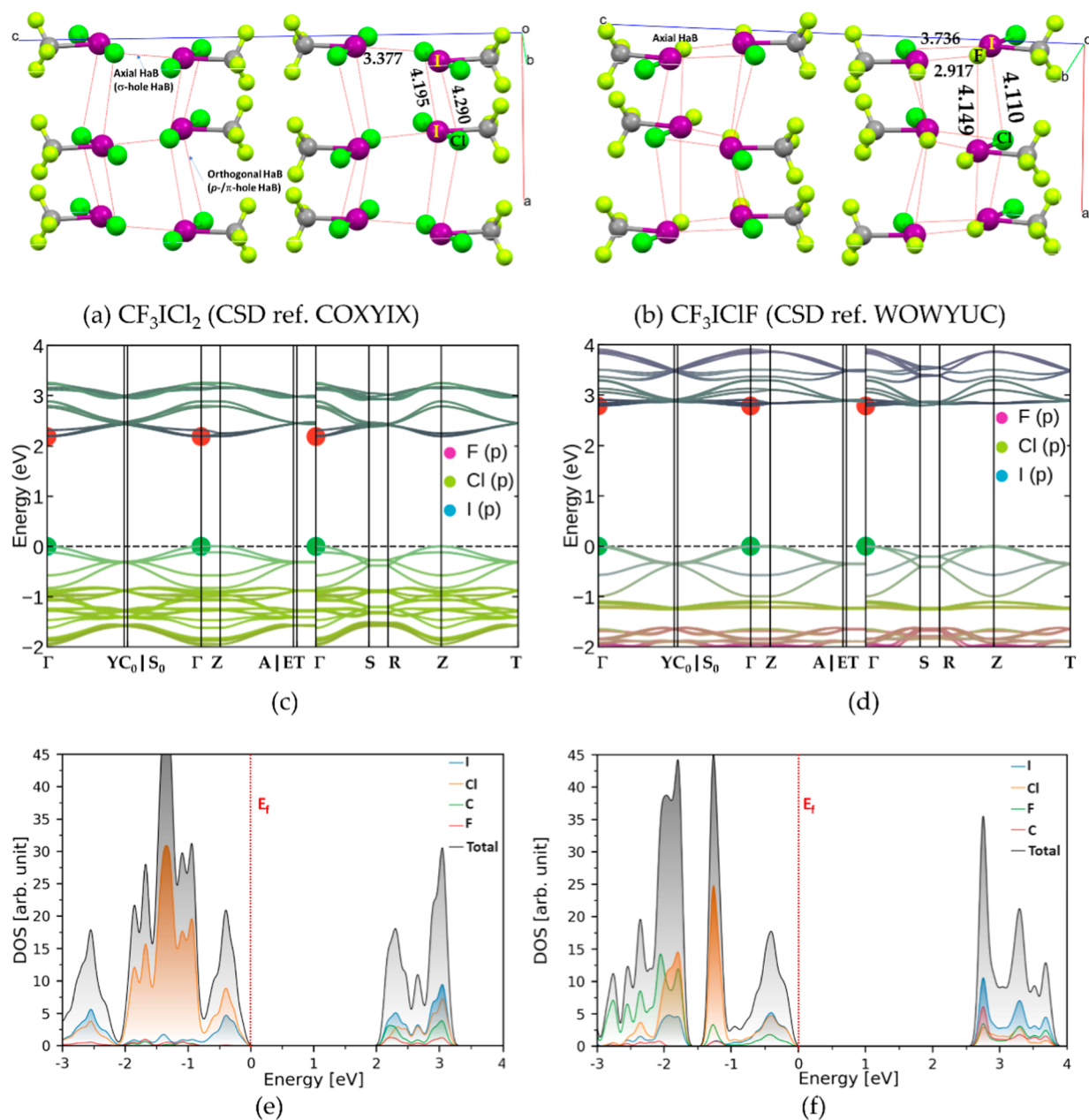


Figure 9. Ball-and-stick models of the PBE-relaxed crystal lattices of (a) CF_3ICl_2 and (b) CF_3ICIF . (c,d) represent the band structures, and DOS spectral features of the corresponding systems, respectively. The Fermi-level (E_f) is marked in (c–f) as a dotted line. Selected bond distances (Å) and bond angles (degrees) are shown in (a,b).

Table 4. Percentage of Various Orbital Contributions to the VBM and CBM of Crystals of CF_3ICl_2 (CSD Ref. COXYIX)⁵⁷ and CF_3ICIF (CSD Ref. WOWYUC)⁵⁸

CF_3ICl_2							CF_3ICIF						
VBM-character			CBM-character				VBM-character			CBM-character			
atom	s	p	d	s	p	d	atom	s	p	d	s	p	d
I	0	38.3	0.0	2.9	37.6	3.1	I	0	44.4	0	2.6	39.6	3.7
Cl	0	61.4	0.0	3.0	17.1	0	Cl	0	41.6	0	0.9	9.1	0
C	0	0.0	0.0	7.9	18.5	0	F	0	14.0	0	1.6	13.1	0
F	0	0.6	0.0	0.0	10.1	0	C	0	0.0	0	9.0	20.3	0

energy is less than 1 kcal mol^{-1} . While it cannot be totally overlooked, it is not a major stabilizing factor in shaping the dimers. In other words, electrostatic and polarization forces are probably sufficient to explain dimer stability. Murray and

Politzer have shown that a large degree of polarization occurs once the interaction energies are more negative than $-8.0 \text{ kcal mol}^{-1}$.¹⁰⁸

QTAIM recovered most of the halogen-centered intermolecular interactions in all the dimers, especially when p/π - and σ -hole HaBs between hypervalent halogen derivatives are the primary synthon. However, there is a major drawback, especially when correlating with the results of the electrostatic potential model, and this is most notably related to the tetrel bond. For instance, in the dimers studied, QTAIM did not reveal the presence of bond paths or bond critical point features between the carbon atom of the methyl fluoride group of the participating $F_3C\cdots XY'$ molecule and the halogen atom covalently bonded to the trivalent halogen derivative in a neighboring molecule. Rather, it predicted the bond paths and bond critical point features between the nearest F atom of the methyl fluoride group and the halogen atom covalently bonded to the trivalent halogen derivative. Although this result indicates the occurrence of potential $F\cdots F$ contacts, the number of these contacts depended on the size of the constituent halogen atoms forming the dimer. The aforementioned disagreement between the results of QTAIM and MESP is probably because QTAIM sometimes gives misleading results when analyzing the nature of noncovalent interactions.^{70–73} By carefully examining the positive potentials of the carbon atoms, and the directionality of the interaction, we were able to show that most of the dimers considered should have at least one $C\cdots X$ tetrel bond that is incorrectly predicted by QTAIM to be an $F\cdots F$ contact, a view that accords with previous observations.^{71,106} This is in agreement with IGM- δg^{inter} based isosurface topologies developed between bonded atomic basins.

■ ASSOCIATED CONTENT

Data Availability Statement

This research reported data in the manuscript itself.

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Conceptualization, project design, and project administration, P.R.V.; formal analysis and investigation, P.R.V.; software—P.R.V., H.M.M. and K. Y.; supervision, P.R.V.; writing—original draft, P.R.V.; writing—review, editing, and discussion,

P.R.V., H.M.M., A.V., and K.Y. All authors have read, understood and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was entirely conducted using various laboratory facilities provided by the University of Tokyo and the University of the Witwatersrand. P.R.V. is currently affiliated with the University of the Witwatersrand (RSA) and Nagoya University (Japan). A.V. is currently affiliated with Tokyo University of Science (Japan). K.Y. is currently affiliated with Yokohama City University (Japan). H.M.M. thanks the University of the Witwatersrand for funding. All authors thank Professors Jane S. Murray and Irek Grabowski, as well as the three reviewers, for their fruitful suggestions that have undoubtedly improved the scientific quality of this ms.

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