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Halogen Bonding With Phosphine: Evidence For Mulliken Inner Complexes And The Importance Of Relaxation Energy

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Abstract

Intermolecular halogen bonding in complexes of phosphine and dihalogens has been theoretically investigated using explicitly correlated coupled cluster methods and symmetry adapted perturbation theory. The complexes $H_3P\cdots ClF$, $H_3P\cdots BrF$ and $H_3P\cdots IF$ are demonstrated to possess unusually strong interactions that are accompanied by an increase in the induction component of the interaction energy and significant elongation of the X–Y halogen distance on complex formation. The combination of these factors is indicative of Mulliken inner complexes and criteria for identifying this classification are further developed. The importance of choosing an electronic structure method that describes both dispersion and longer range interactions is demonstrated, along with the need to account for the change in geometry on complexation formation via relaxation energy and overall stabilisation energies.

Introduction

Complexes involving intermolecular halogen bonds have been synthesised since as early as 1814,[1,2] but it was relatively recent systematic rotational spectroscopy investigations and applications within crystal engineering that have prompted an intense effort towards developing an understanding of the underlying interaction and possible applications.[3,4] An extensive history and review of the properties of inter- and intramolecular halogen bonds has recently been published,[5] hence only the most relevant information is detailed herein. The IUPAC definition of a halogen bond states that "a halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity".[6] The same IUPAC recommendation also lists as a typical feature (amongst others) that "the forces involved in the formation of the halogen bond are primarily electrostatic, but polarization, charge transfer, and dispersion contributions all play an important role. The relative roles of the different forces may vary from one case to the other". The definition that this type of interaction is primarily electrostatic is key as it differentiates between halogen bonds and more generic interactions that feature a halogen atom, for example, an interaction that is primarily dispersion bound. The electrostatic component of the halogen bond can be rationalised through the presence of a σ-hole located on the halogen bond donor; this cap of depleted electron density often results in an area of positive charge that can form attractive interactions with nucleophilic sites such as Lewis bases.[7,8]

While it is clear that the underlying mechanism of the halogen bond must be primarily electrostatic, the IUPAC features of a halogen bond listed above carefully indicate that the exact composition of the forces involved may vary. This allows for a variation in the strength of the interaction between the sub-units of a halogen bonded complex and hence the possibility of tuning the interaction for specific purposes. Although the changes in the underlying mechanism of halogen bonding may be subtle in many cases, there is evidence for unusually strong interactions with significantly different compositions of the forces responsible. This includes the "chlorine-shared" bonds investigated by Del Bene and co-workers,[9–11] and "Mulliken inner complexes" that feature a halogen bond.[5,12–16] Mulliken's classification of complexes is based on charge transfer between an electron donor D and an electron acceptor A.[17] A typical halogen bonding interaction that is almost entirely electrostatic in nature would be presented in the form $\mathrm{D}\cdots\mathrm{XA}$ and denoted as an "outer complex". Inner complexes are more strongly bound and may be written in the form $[\mathrm{D\text{-}X}]^+\cdots\mathrm{A}^-$. It is important to emphasise that this representation is purely notational; indicating significant charge transfer on complex formation, but not implying a requirement for the complete transfer of X^+.

Experimental evidence for the charge transfer typical of a Mulliken inner complex has been garnered from rotational spectroscopy studies of $\mathrm{H_3N}\cdots\mathrm{ClF}$ and $\mathrm{(CH_3)_3N}\cdots\mathrm{ClF}$, where various experimentally measured properties, such as the centrifugal distortion constant and changes in the nuclear quadrupole constants, indicate that the complexes have approximately 10 and 60% contributions (respectively) from valence bond structures of the $[\mathrm{D\text{-}Cl}]^+\cdots\mathrm{F}^-$ ionic type.[18,19] Surprisingly, the $\mathrm{(CH_3)_3N}\cdots\mathrm{F_2}$ complex should also be described with a significant contribution from $[(CH_3)_3NF]^+ \cdots F^-$,[20,21] contrary to the expectation that halogen bonds involving F_2 will be very weak. As halogen bonds are highly directional, tapping into stronger interactions in the form of Mulliken inner complexes is likely to be important in fields such as crystal engineering and nano-materials. However, the criteria for differentiating between inner and outer halogen bonded complexes are not well defined beyond an importance placed upon charge transfer.

The theoretical partitioning of intermolecular interactions into separate contributions such as charge transfer, dispersion, induction (also referred to as polarisation) etc. has proved somewhat controversial. It is possible to argue that electrostatic forces and their polarisation encompass all other contributions,[22–24] yet these other concepts do provide a level of insight into why some interactions are stronger than others and, indeed, are mentioned in the IUPAC features of a halogen bond. Shaik and co-workers meanwhile argue that polarisation arrises from electron excitations within the sub-units of a complex and as charge transfer is associated with excitations between the sub-units the two must be physically distinct.[25,26] This discussion is further complicated by different energy decomposition schemes and partitioning methods giving results that are often incomparable. A more detailed account of this controversy can be found in a recent review of computational modelling of halogen bonding.[27] Herein, Symmetry Adapted Perturbation Theory (SAPT)[28] is used to probe the underlying mechanism of halogen bonding within a number of complexes with the goal of rationalising trends observed in interaction energies. This methodology has been successfully used to highlight that quantum mechanical exchange-repulsion is responsible for the increased linearity of halogen bonds when compared to analogous hydrogen bonds,[29–31] and has suggested that Mulliken inner complexes show an increase in induction and decrease in dispersion relative to outer complexes.[14]

The interactions of simple Lewis bases B with homo- and hetero-dihalogen molecules XY have been systematically studied by rotational spectroscopy over an extended period,[3,32] and the properties of $B \cdots XY$ determined in these investigations are those of the isolated complex in the gas phase. This makes for a natural comparison with high-level *ab initio* calculations and a recent investigation has demonstrated excellent agreement between experimental equilibrium structures and those calculated using the explicitly correlated coupled cluster with single, double and perturbative triple excitations [CCSD(T)-F12b][33] method.[31] Experimentally the strength of the interaction in $B\cdots XY$ has been measured in terms of the intermolecular stretching force constant k_σ and for a given Lewis base the strength increases in the order $F_2 < Cl_2 < Br_2 < ClF < BrCl < ICl$.[3] It has also been shown that the intermolecular charge transfer (as a fraction of an electron δ_i) from a donor centre within B to the halogen X can be extracted from the changes in the halogen nuclear quadrupole coupling constants on complex formation.[34] Plotting δ_i against the "appropriate" ionisation energy I_B of B produces a roughly exponential decrease of the form $\delta_i = A\exp\{-bI_B\}$, where A and b are coefficients fitted to experimental data.[34,35] As phosphine has a low ionisation energy it follows that the amount of electron transfer should be large and hence result in strong interactions, particularly with the hetero-dihalogens. Experimental rotational spectroscopy studies of complexes of phosphine with Cl_2, Br_2, BrCl and ICl confirmed these trends, with 0.144 of an electron transferred in the $H_3P\cdots ICl$ case.[35–38]

In the present article, benchmark quality calculations for $H_3P\cdots XY$ are presented. The aim is to examine if this shows agreement with experimental data both in terms of geometry and trends in the strength of interaction, and to extend the study to complexes involving dihalogens that have not yet been investigated through rotational spectroscopy. The low ionisation energy of phosphine suggests that some of the molecular complexes may be of the Mulliken inner type, which is explored further through SAPT calculations. Finally, the high-accuracy *ab initio* results are compared with those from more computationally affordable quantum chemical methods in order to determine the suitability of the latter for describing Mulliken inner complexes.

Computational procedure

Geometry optimizations and single point energy calculations were carried out at the explicitly correlated coupled cluster level with single, double and perturbative triple excitations,[39,40] using the 3C(Fix)[41] explicit correlation Ansatz and approximation c [CCSD(T)-F12c][42] with the MOLPRO package of *ab initio* programs.[43,44] This method is also referred to as CCSD(T)(F12*) by some groups. The correlation consistent cc-pVTZ-F12 basis set was used for all elements except Br and I, where the cc-pVTZ-PP-F12 basis and Stuttgart-Cologne small-core relativistic pseudopotentials were used.[45–48] For simplicity, this combination will be referred to as cc-pVTZ-F12 herein. The fitting of the Fock and exchange matrices used the cc-pVQZ/JKFit auxiliary basis set (ABS) and def2-QZVPP/JKFit ABS for the lighter and heavier (Br and I) elements, respectively.[49,50] Density fitting of the remaining two electron integrals used the aug-cc-pwCVQZ/MP2Fit ABS for lighter elements along with cc-pVTZ-PP-F12 for the heavier elements.[46,51] The complementary ABS+ (CABS+) procedure as implemented in MOLPRO used the OptRI ABSs specifically matched to the orbital sets,[40,46,52–54] and CABS singles relaxation of the Hartree-Fock energy was included throughout. The geminal Slater exponent was set to 1.0 a_0^{-1} for all explicitly correlated calculations.

The energy of the interaction between the subunits is presented as both interaction energy and stabilisation energy. The former of these is defined as the difference in energy between the optimised geometry of the complex and the energies of the two subunits fixed in their interacting geometry. The stabilisation energy is formed by calculating a relaxation energy; the energy of the subunits in their interacting geometries with an artificial separation of 1000 Å subtracted from the sum of the energies of the subunits in their isolated geometries. This relaxation energy is then subtracted from the interaction energy. In this way, a bound complex should have a negative interaction energy and the associated stabilisation energy will be smaller in magnitude as it includes the energy required to distort the subunits relative to their isolated equilibrium geometries. These definitions correspond to those proposed by

Szalewicz and Jeziorski,[55] and it should be noted that the resulting stabilisation energy cannot be directly compared with experiment. Addition of the difference in vibrational zero-point energies to the stabilisation energy would give the dissociation energy, but as intermolecular vibrations are usually highly anharmonic, and hence very expensive at the CCSD(T) level, the calculation of zero point energies has not been attempted in the present investigation. Interaction energies were corrected for basis set superposition error with the counterpoise method of Boys and Bernardi.[56]

DFT calculations using either the M06-2X functional of Zhao and Truhlar,[57] or the long range corrected ωB97X-D functional that includes a modified dispersion correction,[58,59] were performed using the Gaussian 09 program.[60] These two functionals have been recently recommended for the investigation of halogen bonds based on the benchmarking of 42 functionals for both energies and geometries.[61] All of the DFT calculations used the diffuse augmented aug-cc-pV(T+d)Z basis set,[62–64] which includes an additional set of "tight" d-functions for second row elements, and an integration grid with 99 radial shells and 590 angular points per shell (a so-called UltraFine grid). A number of density fitted Møller-Plesset second order perturbation theory (MP2) calculations were also carried out using the aug-cc-pV(T+d)Z basis set in MOLPRO. Density fitting at the MP2 level used the aug-cc-pV(T+d)Z/MP2Fit ABS,[65] with density fitting of the Hartree-Fock reference facilitated by the aug-cc-pVTZ/JKFit ABS.[49]

Symmetry adapted perturbation theory calculations were performed using the SAPT2012[28,66,67] program interfaced to MOLPRO. The SAPT2+(3)δMP2 truncation was used (where a counterpoise corrected MP2 correction is applied) along with the aug-cc-pV(T+d)Z basis set.[68] For Br and I the aug-cc-pVTZ-PP basis sets and Stuttgart-Cologne pseudopotentials were used,[47,48] and herein this level of theory will be referred to simply as SAPT. To aid with interpretation, the individual SAPT terms were collected into electrostatic, exchange, induction and dispersion contributions following the established "chemist's grouping":[69]

$$\begin{aligned}
E_{\text{electrostatic}} &= E^{(10)}_{\text{elst}} + E^{(12)}_{\text{elst,resp}} + E^{(13)}_{\text{elst,resp}} \\
E_{\text{exchange}} &= E^{(10)}_{\text{exch}} + E^{(11)}_{\text{exch}} + E^{(12)}_{\text{exch}} \\
E_{\text{induction}} &= E^{(20)}_{\text{ind,resp}} + E^{(20)}_{\text{exch-ind,resp}} + E^{(30)}_{\text{ind}} + E^{(30)}_{\text{exch-ind}} + {}^{t}E^{(22)}_{\text{ind}} + {}^{t}E^{(22)}_{\text{exch-ind}} + \delta E^{(3)}_{\text{HF}} + [\delta E_{\text{MP2}}] \\
E_{\text{dispersion}} &= E^{(20)}_{\text{disp}} + E^{(30)}_{\text{disp}} + E^{(21)}_{\text{disp}} + E^{(22)}_{\text{disp}} + E^{(20)}_{\text{disp-exch}}.
\end{aligned}$$

The individual SAPT components are fully defined in Ref. 28.

Results and Discussion

The interaction energies, stabilisation energies and selected optimised geometrical parameters of the $H_3P\cdots XY$ complexes calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level are shown in Table 1. Focusing momentarily on the interaction energies, it can be seen that ClF, BrF and IF all appear to have very strong interactions with H_3P. Significantly, $H_3P\cdots ClF$ possessing the strongest interaction contradicts previously observed trends in halogen bonding, whereby less electronegative halogens in the X position form stronger bonds,[8,13,27,70] and the experimental intermolecular stretching force constant increases in the order $F_2 < Cl_2 < Br_2 < ClF < BrCl < ICl$.[3] The binding energy for $H_3P\cdots ClF$ has previously been reported at the MP2/aug-cc-pVTZ (with diffuse functions removed from H atoms) level of theory as -12.2 kcal mol^{-1}, with a $P\cdots Cl$ distance of 2.182 Å.[11] Whilst the latter is in excellent agreement with the present, higher level results, this binding energy underestimates the interaction energy and overestimates the stabilisation energy. The distance $R(P\cdots I)$ for $H_3P\cdots ICl$ is 0.02 Å shorter than that previously obtained at the CCSD(T)-F12c/cc-pVDZ-F12 level,[71] reflecting changes due to the increased size and flexibility of the basis set. The interaction energies of Table 1 can also be compared with those for $H_3N\cdots XY$ that have been calculated at the approximately equivalent CCSD(T)-F12b/CBS level of theory,[70] where it is clear that the majority of $H_3P\cdots XY$ interactions are significantly weaker (generally 30–50%) than the analogous $H_3N\cdots XY$. Again, the exceptions are ClF and BrF, where the interaction with phosphine is stronger than with ammonia, and IF, where the two interactions are roughly of the same strength. An inspection of the optimised geometries indicates that the $H_3P\cdots ClF$, $H_3P\cdots BrF$ and $H_3P\cdots IF$ complexes all have relatively short intermolecular $P\cdots X$ distances, suggesting that these complexes possess some of the characteristics of the "chlorine-shared" bonds studied by Del Bene and co-workers.[9–11] However, in the present case unexpectedly strong interaction energies and short intermolecular distances are also found for $P\cdots Br$ and $P\cdots I$ and hence the more general "Mulliken inner complex" terminology is used herein. Halogen bonded complexes of phosphine were also previously designated as Mulliken inner complexes by Ramasami and Ford based upon the results of lower-level MP2 calculations,[13] but this study did not distinguish between inner and outer complexes involving phosphine, and used a smaller subset of halogen bond donors than the present work.

Table 1: Interaction energies (I.E. / kcal mol^{-1}), stabilisation energies (S.E. / kcal mol^{-1}) and some geometrical distances (Å) of the complexes $H_3P\cdots XY$ determined at the CCSD(T)-F12c/cc-pVTZ-F12 level of theory. ΔXY indicates the increase in the bond length on complex formation

XY	I.E.	S.E.	$R(P\cdots X)$	$R(X–Y)$	ΔXY
F_2	−0.85	−0.83	3.202	1.414	0.006
Cl_2	−2.40	−2.32	3.239	2.004	0.014
ClF	−19.61	−8.01	2.183	1.829	0.202
Br_2	−4.62	−4.15	2.993	2.328	0.039
BrCl	−6.27	−5.28	2.853	2.197	0.056
BrF	−17.82	−12.85	2.427	1.877	0.118
I_2	−4.63	−4.27	3.200	2.712	0.034
IBr	−7.35	−6.36	2.977	2.535	0.058
ICl	−9.33	−7.76	2.878	2.396	0.072
IF	−15.79	−13.34	2.693	1.981	0.072

It can be seen from Table 1 that the complexes with the strongest interaction energies also display a significant lengthening of the XY bond on complex formation (ΔXY), by as much as 0.202 Å in the case of ClF. Previous natural bond orbital (NBO)[72] studies of halogen bonding have suggested similar bond elongations are due to the donation of electron density from the lone pair on the Lewis base into an antibonding sigma orbital on XY,[11,13,14,73,74] but NBO calculations using the MP2/aug-cc-pV(T+d)Z or ωB97X-D/aug-cc-pV(T+d)Z density on the CCSD(T)-F12c/cc-pVTZ-F12 optimised geometry of $H_3P\cdots ClF$ partitioned the complex into H_3PCl^+ and F^- subunits, preventing such an analysis in the present case and lending some extra confidence to the designation of a Mulliken inner complex. The large distortions in X–Y on complex formation indicates relaxation energy is likely to be important, thus the relaxation energies are plotted in Figure 1 and included in the stabilisation energies of Table 1.

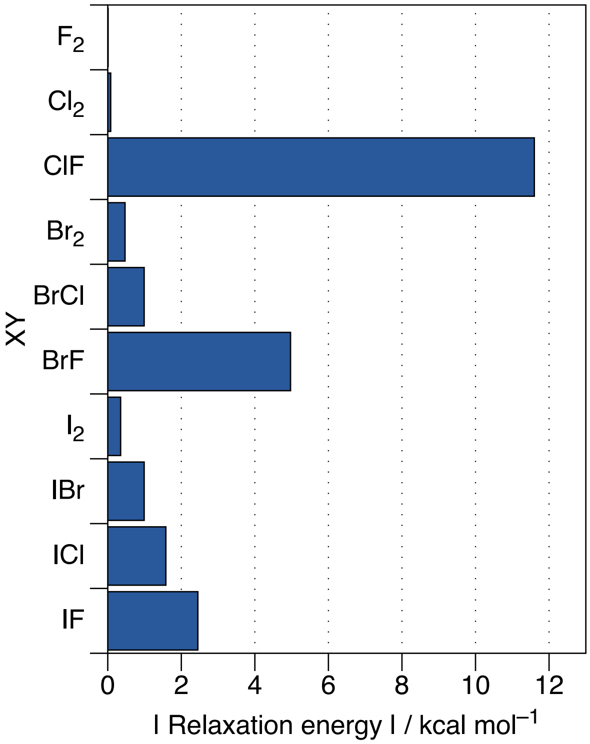

Figure 1: Magnitude of the CCSD(T)-F12c/cc-pVTZ-F12 relaxation energy of $H_3P\cdots XY$ halogen bonding complexes.

Both Table 1 and Figure 1 illustrate that, perhaps unsurprisingly, the complexes undergoing larger distortions on complex formation also have large relaxation energies. This is particularly pronounced in the case of ClF, where the relaxation energy of 11.60 kcal mol^{-1} is more than half the magnitude of the interaction energy. Indeed, when considering stabilisation energies $H_3P\cdots ClF$ is no longer the most strongly bound complex, which is instead $H_3P\cdots IF$. It is important to note that once the relaxation energy has been accounted for, the trend in the stabilisation energies now matches that of the interaction energies in $H_3N\cdots XY$ and less electronegative halogens in the X position lead to more strongly bound complexes.[70] However, the experimental trend observed for other Lewis bases were the halogen bond strength increases in the order $F_2 < Cl_2 < Br_2 < ClF < BrCl < ICl$ does not emerge as ClF forms the strongest interactions with phosphine from this subset of XY, suggesting that there is an unusually strong stabilisation energy in the $H_3P\cdots ClF$ case. In general, the magnitude of the stabilisation energies also increases with increasing difference of the electronegativities of X and Y. The electronic supporting information of Ref. 70 shows that the CCSD(T)-F12b/cc-pVTZ-F12 relaxation energy of $H_3N\cdots ClF$ is only around 1.1 kcal mol^{-1}, which is an order of magnitude smaller than that observed in the phosphine case but still larger than the established "chemical accuracy" of 1 kcal mol^{-1}.

In order to further investigate the effects of relaxation energy in halogen bonding systems, the geometries, interaction energies and stabilisation energies of $H_3N\cdots XY$, $H_2S\cdots XY$ and $H_2O\cdots XY$ have been calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level of theory, with results presented in Tables S1-S3 of the supporting information. Focusing on complexes with heteronuclear dihalogens (interhalogens), where the interactions are typically stronger, it can be seen that the mean average unsigned relaxation energy for $H_2O\cdots XY$ complexes is negligible at 0.09 kcal mol^{-1} (maximum of 0.13), larger yet still relatively small for $H_2S\cdots XY$ (average of 0.25 with a maximum of 0.47 kcal mol^{-1}), and somewhat appreciable for $H_3N\cdots XY$ (average of 0.76 with a maximum of 1.10 kcal mol^{-1}). The average for the $H_3P\cdots XY$ interhalogen complexes is 3.76 kcal mol^{-1}. It is thus apparent that accounting for the relaxation energy is important for Mulliken inner complexes that have undergone relatively large geometric changes on complex formation, and this is likely to make a significant difference when attempting to establish relationships between strengths of interactions and properties of either the halogen bond donor or acceptor. For example, Ramasami and Ford noted that most $H_3P\cdots XY$ interaction energies, which in their definition include zero point energy corrections, appear to be overestimated based upon the gas phase basicity of the acceptors,[13] yet plotting stabilisation energies against gas phase basicity (Figure S1 in the supporting information) produces a much clearer relationship for the interhalogens forming complexes with H_3P, H_3N, H_2S or H_2O. It is important to note that this is not a completely linear relationship, but the use of stabilisation energies means that $H_3P\cdots XY$ complexes are no longer obvious outliers.

Table 2: A comparison of geometries (Å) and intermolecular bond strengths of $H_3P\cdots XY$ between theoretical CCSD(T)-F12c/cc-pVTZ-F12 and experimental rotational spectroscopy. Theoretical bond strengths are presented as stabilisation energies (kcal mol^{-1}), experiment as intermolecular force constants k_σ (N m^{-1}).

	$R(P\cdots X)$		Bond strength	
XY	Theory	Expt.	S.E.	k_σ
Cl_2	3.239	3.240(15)[36]	−2.32	5.53[36]
Br_2	2.993	3.044[37]	−4.15	9.79[37]
BrCl	2.853	2.869(1)[38]	−5.28	11.56[38]
ICl	2.878	2.963(1)[35]	−7.76	20.7[35]

Phosphine complexes with Cl_2, Br_2, BrCl and ICl have been produced in the gas-phase and characterised using rotational spectroscopy.[35–38] Of particular interest to the present investigation is that these previous works determined intermolecular bond distances and the strength of the intermolecular bond in terms of intermolecular force constants. These experimental data are compared to theoretical results in Table 2. Excellent agreement of geometries from explicitly correlated coupled cluster and rotational spectroscopy has been noted in the past,[31] and this is generally the case for the small subset of $H_3P\cdots XY$ for which experimental data is available. The largest difference in $R(P\cdots X)$ of 0.085 Å occurs for $H_3P\cdots ICl$,[35] where the methodology used to produce the experimental value assumed the monomers were unperturbed by complex formation. Equation 10 of Ref. 35 proposes that an increase in the XY bond distance of ΔXY should decrease the intermolecular distance by approximately $1.50\Delta XY$, which, taking $\Delta XY = 0.072$ from Table 1, corresponds to a modified experimental P$\cdots$I distance of around 2.855 Å. This is in significantly better agreement with the theoretical value produced in the current investigation, and brings it more into line with the $H_3P\cdots BrCl$ experimental intermolecular distance that already accounts for BrCl elongation on complex formation.

Examining the bond strengths in Table 2 reveals that experiment and theory produce the same general trend in the strength of the intermolecular interactions, lending further confidence to the theoretical description. This is perhaps unsurprising as a direct proportionality between intermolecular dissociation energy [calculated at the CCSD(T)-F12c/cc-pVDZ-F12 level] and intermolecular quadratic stretching force constants (k_σ) for a number of halogen bonding complexes has been previously established.[75] Experimental estimates of the fraction of an electron transferred from the Lewis base B to X (δ_i) were extracted from changes in the halogen nuclear quadrupole coupling constants when the complex is formed, which is based on the Townes-Dailey model.[76,77] The experimental values for XY = Cl_2, Br_2, BrCl and ICl are 0.01, 0.077(23), 0.100(5) and 0.144(7) e, respectively.[35,37,38,78] A comparison with Table 1 shows that as the experimental δ_i increases so does ΔXY (the bond elongation on complex formation), which appears logical based upon electron density being donated from the P lone pair to the XY antibonding orbital.

Further insights into the underlying mechanism of the halogen bonding in $H_3P\cdots XY$ are provided by using SAPT calculations to partition the interaction energies into a "chemist's grouping", with the results displayed in Table 3. A comparison of the SAPT interaction energies with those from counterpoise corrected CCSD(T)-F12c in Table 1 shows that overall is there is a very good level of agreement between the two methods, with the majority of interaction energies within 1 kcal mol^{-1}. The exceptions are $H_3P\cdots BrF$ where SAPT underestimates the strength of interaction by 1.15 kcal mol^{-1}, and $H_3P\cdots IF$ is underestimated by 1.46 kcal mol^{-1}. It should be noted that no attempt has been made to correct the SAPT decomposition for relaxation energy, but this will not affect the insights provided into the nature of the interactions.

Table 3: SAPT decomposition of the $H_3P\cdots XY$ interaction energy (kcal mol^{-1}).

XY	Electrostatic	Exchange	Induction	Dispersion	I.E.
F_2	-1.51	2.86	-0.95	-1.28	-0.89
Cl_2	-5.21	9.49	-3.23	-3.32	-2.27
ClF	-88.10	176.20	-86.42	-20.30	-18.62
Br_2	-13.94	21.14	-5.15	-6.22	-4.18
BrCl	-20.41	30.30	-8.05	-7.67	-5.83
BrF	-63.82	91.25	-28.47	-15.63	-16.67
I_2	-13.26	19.23	-3.88	-6.17	-4.08
IBr	-23.90	33.71	-7.69	-8.58	-6.46
ICl	-30.85	42.39	-10.10	-9.86	-8.41
IF	-48.89	64.11	-16.63	-12.92	-14.33

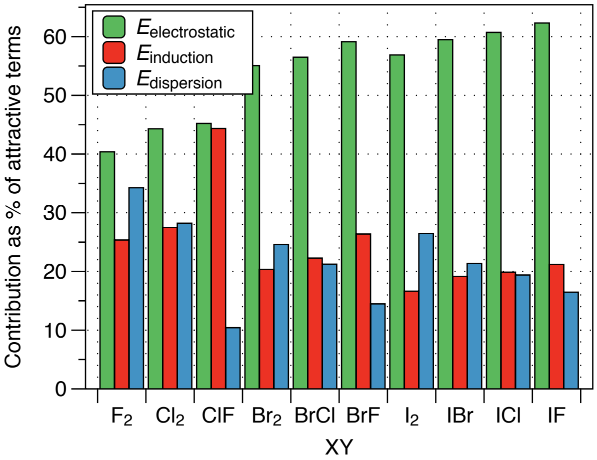

Figure 2: Individual attractive SAPT components of the $H_3P\cdots XY$ halogen bond interaction energy as a percentage of the total of the attractive terms.

Figure 2 plots the individual attractive SAPT components of the interaction in $H_3P\cdots XY$ complexes as a percentage of the total of the attractive terms. It is immediately apparent that the largest attractive component is due to electrostatics in all cases, and with larger halogens in the X position the percentage contribution from electrostatic forces increases. Placing more electronegative halogens in the Y position again increases the percentage contribution from electrostatics, as may have been anticipated from the σ-hole model. Also striking is the large increase in induction in the ClF case, which is accompanied by a decrease in the dispersion component. Indeed, induction contributes 44.36% to the attractive components in this case, compared with a mean average of 24.31% for all ten complexes considered.

Other complexes with a large degree of Mulliken inner-complex character ($H_3P\cdots BrF$ and $H_3P\cdots IF$) also have increased induction at the expense of dispersion, albeit at a level reduced from that seen in the ClF case. This appears to be entirely in line with the magnitude of the relaxation energies for these respective complexes. A similar increase in induction and decrease in dispersion was also noted for the thiirane$\cdots$ClF Mulliken inner complex,[14] and the reader is reminded that any charge transfer will be contained within the induction component of the SAPT methodology used.

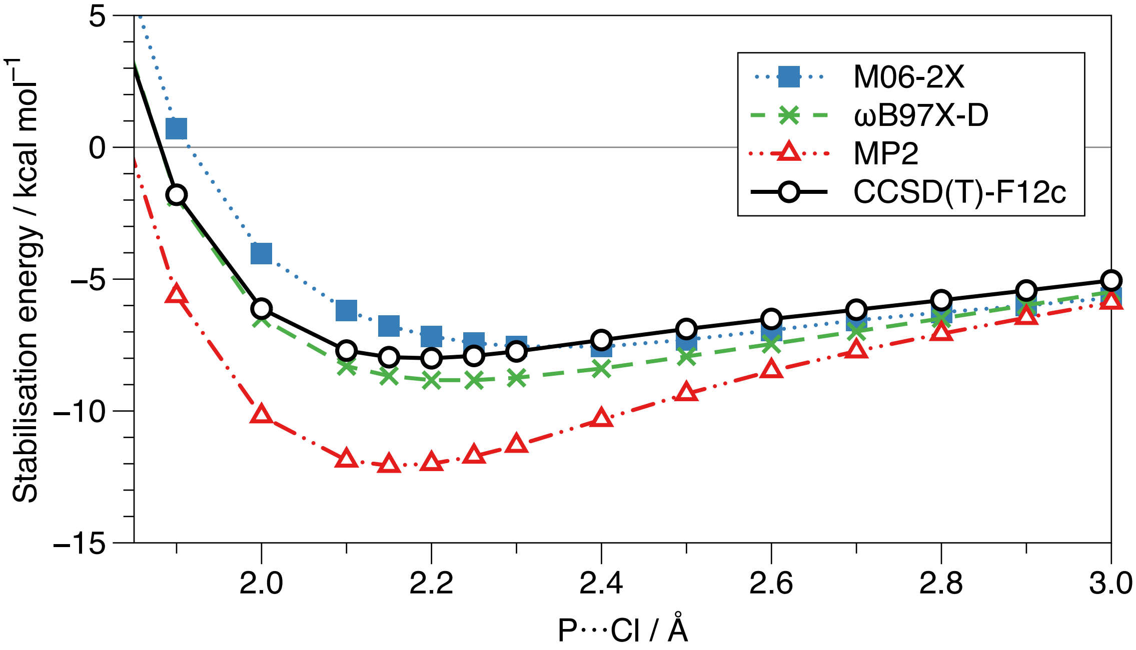

Figure 3: Relaxed scan of the intermolecular separation in the $H_3P\cdots ClF$ complex. All stabilisation energies are counterpoise corrected. See text for further details.

The CCSD(T)-F12c method improves the basis set convergence of the "gold standard" CCSD(T) method, yet the steep scaling with system size means that computationally cheaper methods such as DFT and MP2 remain attractive for the description of halogen bonding. In order to determine the suitability of these more affordable methods for describing Mulliken inner complexes, Figure 3 shows relaxed scans of the $H_3P\cdots ClF$ stabilisation energy calculated at the CCSD(T)-F12c/cc-pVTZ-F12, MP2/aug-cc-pV(T+d)Z, M06-2X/aug-cc-pV(T+d)Z and ωB97X-D/aug-cc-pV(T+d)Z levels of theory. In these scans the P$\cdots$Cl distance is fixed and all other internal coordinates are optimised before the counterpoise corrected stabilisation energy is computed. Full geometry optimisations were also carried out in order to obtain equilibrium geometries and stabilisation energies at each level of theory. It can be seen that while MP2 produces an intermolecular separation that is in reasonable agreement with CCSD(T) (underestimated by 0.043 Å), it significantly overestimates the stabilisation energy by 4.05 kcal mol^{-1} (roughly 50%). The shortening of the MP2 intermolecular separation relative to previously published MP2 data can be attributed to the use of the aug-cc-pV(T+d)Z basis for phosphorous in the current case, with aug-cc-pVTZ used in other investigations.[11,13] The popular M06-2X functional slightly underestimates the magntitude of the S.E., but performs quite poorly in terms of intermolecular separation where the P$\cdots$Cl distance is 0.158 Å longer than the benchmark CCSD(T). ωB97X-D produces somewhat better agreement, overestimating the separation by 0.041 Å and overbinding by 0.84 kcal mol^{-1} at the equilibrium geometries, while following the CCSD(T) scan to a reasonable extent. A thorough test of many different density functionals is beyond the scope of the current investigation, but it appears from these limited data that correctly describing halogen bonds such as that in $H_3P\cdots ClF$ is more challenging than for general halogen bonds.[61] One significant difference between M06-2X and ωB97X-D is that the latter includes long range corrections, which may be important in describing the electronic structure of Mulliken inner complexes.

A question that arises from the present results is one of when should a stabilisation energy be calculated, given the increase in computational cost required relative to an interaction energy? With the established chemical accuracy of 1 kcal mol^{-1}, a guideline of half of this amount (0.5 kcal mol^{-1}) is suggested as a point above which the relaxation energy needs to be considered. Of course, it is desirable to have an *a priori* rule-of-thumb for when the relaxation energy approaches this guideline and examination of Tables 1 and S1–S3 shows that an increase in the XY bond length on complexation (ΔXY) of greater than 0.05 Å corresponds to relaxation energies of at least this magnitude. Investigations into extending this proposed diagnostic to halogen bond donors larger than diatomics are currently underway.

Conclusions

The classification of molecular complexes into Mulliken inner and outer types provides an important indicator of the strength of interaction and degree of charge transfer between the sub-units on complex formation. The present investigation proposes that the $H_3P\cdots ClF$, $H_3P\cdots BrF$ and $H_3P\cdots IF$ halogen bonded complexes are recognised as the stronger inner type complexes based upon a number of criteria. Firstly, benchmark quality interaction energies indicate very strong halogen bonding in these complexes, in a manner that contradicts previously observed trends in halogen bonds involving dihalogens. Secondly, the three complexes all have short $P\cdots X$ distances accompanied by a large increase in the interhalogen distance on complex formation. Finally, SAPT analysis reveals that for these complexes the percentage contribution of induction, which includes any charge transfer effects, to the the total attractive terms is increased relative to other halogen bonds. This is particularly striking in the $H_3P\cdots ClF$ case, where the component due to induction contributes almost as much as that from electrostatic effects. It is noted that all three of these complexes exhibit the above effects to a greater degree than $H_3P\cdots ICl$, where experimentally an electron transfer of 0.144 e has been obtained,[35] indicating relatively significant charge transfer.

Of the ten $H_3P\cdots XY$ complexes investigated six had a relaxation energy that was greater than 0.5 kcal mol^{-1} in magnitude, at which point this effect should be accounted for assuming a goal of producing chemically accurate data. The resulting stabilisation energies restore trends that appeared to be disrupted by considering only the interaction energy, such as less electronegative halogens in the X position forming stronger halogen bonds and trends in the strength of interaction relative to the gas phase basicity of the halogen bond acceptor. Including relaxation energy does not imply that the $H_3P\cdots ClF$, $H_3P\cdots BrF$ and $H_3P\cdots IF$ complexes should no longer be considered of the inner type, rather that it is compensating for the energy required to perturb the geometries of the sub-units as charge is transferred from the lone pair on phosphorous to the X–Y antibonding orbital. Indeed, the resulting stabilisation energy of $H_3P\cdots ClF$ is -8.01 kcal mol^{-1}, corresponding to an unusually strong halogen bond that breaks the experimentally observed trend for other Lewis bases; the strength of the interaction should increase as $F_2 < Cl_2 < Br_2 < ClF < BrCl < ICl$. It is proposed that if complex formation elongates the X–Y bond by greater than 0.05 Å then relaxation energy should be accounted for, and this may also serve as guideline for halogen bonded systems beginning to develop Mulliken inner complex character. SAPT based criteria to help identify inner complexes by comparison to analogous systems is also emerging; a reduction in the dispersion component is accompanied by an increase in the contribution from inductive effects, which is logical for an increase in charge transfer character.

Interestingly, it appears that halogen bonded Mulliken inner complexes are relatively difficult to correctly describe with a number of popular electronic structure methods. For $H_3P\cdots ClF$ the MP2 method produces stabilisation energies that are approximately 50% too strong, which may be related to the well-known tendency of this method to overestimate the effects of dispersion. Meanwhile, the M06-2X DFT functional that has previously been recommended for investigations of halogen bonding produces an intermolecular separation that is too long by 0.158 Å. NBO analyses partition the complex into H_3PCl^+ and F^- sub-units, which obscures chemical insights into the nature of the interaction but corresponds perfectly to the notation proposed by Mulliken for inner complexes. As the ωB97X-D functional produced relatively good agreement with benchmark quality CCSD(T)-F12c results for equilibrium geometry, stabilisation energy and potential energy scans, this appears to be a good choice of functional to use for halogen bonded complexes that are too large to be computationally tractable with CCSD(T) methods. This functional can describe both long range effects and dispersion, indicating that both are important in halogen bonded Mulliken inner complexes.

Supporting Information Available

Optimised geometries of all complexes investigated. Interaction energies, stabilisation energies and some geometrical distances of $H_2S\cdots XY$, $H_2O\cdots XY$ and $H_3N\cdots XY$ complexes, and a plot of stabilisation energies against gas phase basicities of the acceptor. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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