

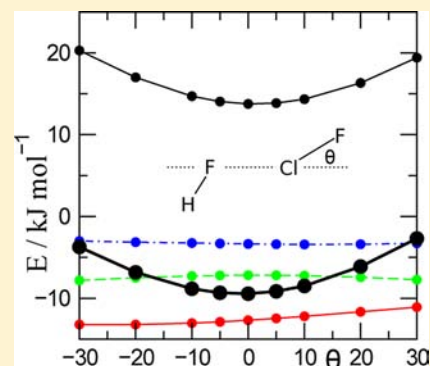
Are Halogen Bonded Structures Electrostatically Driven?

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S Supporting Information

ABSTRACT: Halogen-bonded complexes $B \cdots XY$, where B is a Lewis base and X a halogen atom, have been described as electrostatically driven, largely because of the close analogy between their structures and those of corresponding hydrogen-bonded complexes. Analysis of the components of the binding energy using symmetry-adapted perturbation theory suggests that while the main contribution to the binding is usually the electrostatic energy, the geometries are not always determined by electrostatics alone. In particular, the strong tendency to linearity of the $B \cdots XY$ bond is a consequence of exchange–repulsion, not electrostatics.



1. INTRODUCTION

The phenomenon of the halogen bond has aroused a good deal of interest in the past decade or two. It is an intermolecular bond between a Lewis base B and a molecule XY in which X is a halogen atom and Y is another X atom or a more electronegative halogen or some other electronegative group. There are strong analogies in structure between a halogen-bonded complex $B \cdots XY$ and the hydrogen-bonded complex $B \cdots HX$, as documented by Legon following extensive spectroscopic work by him and his research group.^{1,2} The electrostatic potential around the X end of the XY molecule is positive, because the X atom carries a positive quadrupole moment and also a positive charge if Y is more electronegative than X. This positive region, called a σ hole by Politzer et al.^{3,4} and illustrated for ClF and F₂ in Figure 1, can evidently interact favorably with the regions of high electron density around a Lewis base.

Consequently it is widely accepted that the binding in these complexes is electrostatically driven, in Politzer's phrase, though it is acknowledged that induction and dispersion interactions also contribute, often substantially.⁵ The close

analogy between the structures of hydrogen-bonded and halogen-bonded complexes has been assumed to extend to the underlying mechanism determining the structures. It is well established that the structures of hydrogen-bonded complexes can be attributed to electrostatic interactions alone. Buckingham and Fowler showed clearly that those structures can be predicted very successfully using a model comprising accurate distributed multipole electrostatics and a simple hard-sphere repulsion,^{6–8} and the strong analogies in structure between corresponding halogen-bonded and hydrogen-bonded complexes have led to a general assumption that the structures of the halogen-bonded complexes can also be attributed to electrostatics alone.

However this assumption has not been directly tested. This paper seeks to address the issue by studying a number of halogen-bonded complexes, mostly involving ClF, using symmetry-adapted perturbation theory based on density functional theory (SAPT(DFT)) to evaluate the components of the interaction energy. There are two aspects to consider. First, it is clear that the angle at Cl of $B \cdots Cl-F$ is very close to linear, closer than that in the corresponding $B \cdots H-Cl$. Is this due to electrostatics or something else? Second, the direction of the ClF molecule relative to the structure of the Lewis base B is similar to the direction of HCl in the hydrogen-bonded complex. What determines that direction?

We shall see that the linearity of $B \cdots Cl-F$ arises from exchange–repulsion—from the oblate shape of bonded Cl atoms. This property of bonded halogen atoms was noted by Legon,¹ though used by him only to explain why the $B \cdots Cl$ distances are shorter than the sum of standard van der Waals radii. Adhikari and Scheiner⁹ showed that the energy of

Figure 1. Electrostatic potential (volt) on the $vdW \times 1.5$ surface of ClF (left) and F₂ (right).

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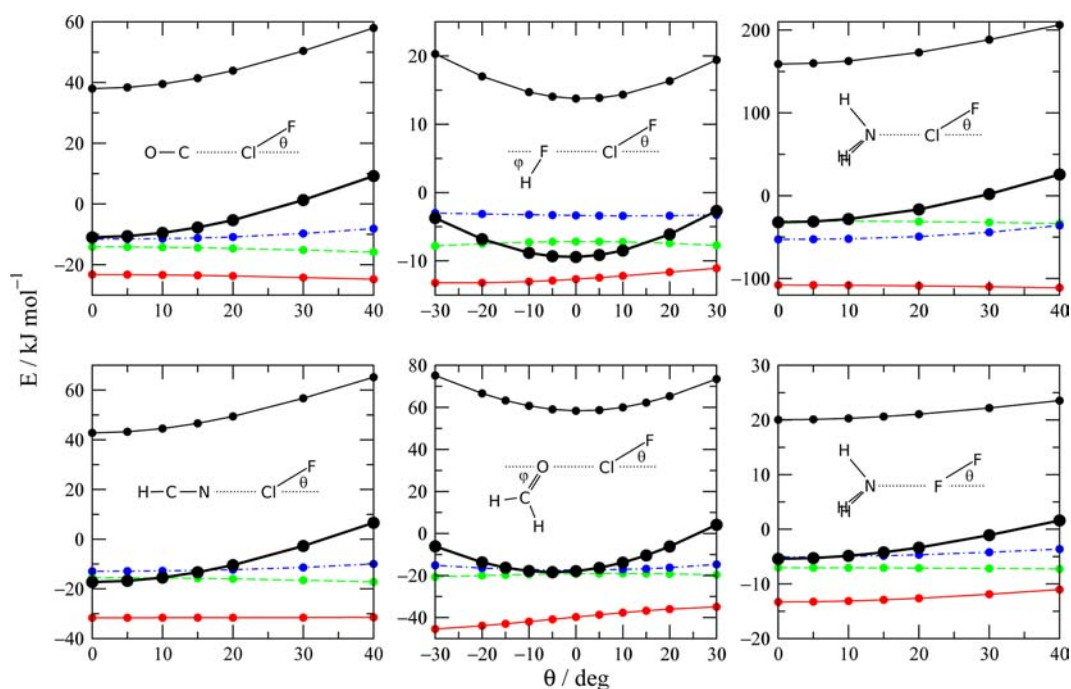


Figure 2. Variation of energy components with tilt angle θ of $B\cdots X-Y$ away from linear. The angle φ was held at 55° for $\text{HF}\cdots\text{ClF}$ and 69° for $\text{H}_2\text{CO}\cdots\text{ClF}$. The components are black, exchange–repulsion; red, electrostatic; green dashed, dispersion; blue dash-dot, induction; heavy black, total.

bending the $\text{N}\cdots\text{XY}$ angle in a number of $\text{H}_3\text{N}\cdots\text{XY}$ complexes, where X can be S or P or a halogen, correlates with the exchange–repulsion energy and not with the electrostatic energy and that this can be understood by reference to the shape of the electron density envelope. On the other hand, Shields et al.¹⁰ attribute the linearity in $\text{B}\cdots\text{BrCN}$ complexes to electrostatic interactions involving the nonbonding Br electrons.

The reasons for the direction of the halogen bond relative to the geometry of the base B are less clear-cut but are not always attributable to electrostatics alone.

2. METHODS

Calculations were carried out using the SAPT(DFT) method^{11,12} as implemented in the CamCASP program of Misquitta and Stone.¹³ Basis sets used were Sadlej or aug-cc-pVTZ, in both cases with the aug-cc-pVTZ density-fitting basis. There was very little difference between the results from the Sadlej and aug-cc-pVTZ basis sets, but the Sadlej basis is smaller and faster. The CamCASP program provides a breakdown of the interaction energy into the first-order electrostatic and exchange–repulsion energies and the second-order induction, exchange–induction, dispersion, and exchange–dispersion. In addition it can provide the δ_{HF} estimate of the higher-order induction terms.¹⁴ Any charge-transfer effects appear as part of the induction energy, but no attempt has been made to separate them out in this work. In the figures, we show the total of induction, exchange–induction, and δ_{HF} as the induction term and the total of dispersion and exchange–dispersion as the dispersion term.

Geometries were based on those determined by Legon et al. using Fourier transform microwave spectroscopy. For each complex, two or more series of SAPT(DFT) calculations were carried out. In one series, the XY molecule was rotated about an axis through the X atom perpendicular to the $X-Y$ bond. This was repeated for the orthogonal rotation axis if it was not symmetry-equivalent. Similarly, one or two series of calculations were carried out in which the B molecule was rotated about the nearest atom or bond to the XY molecule. In addition the dependence on the $B\cdots X$ distance was explored in some cases. This is by no means an exploration of the full potential energy

surface, but it is enough to answer the questions posed above. The XY molecule was usually ClF , but a few calculations were done for Cl_2 and F_2 . Complexes of XY with N_2 , CO , HF , H_2O , NH_3 , HCN , H_2S , H_2CO , SO_2 , ethyne, ethene, and oxirane were explored. Again, this list is not exhaustive, but it is enough to show that the results are reasonably general.

3. RESULTS

3.1. $B\cdots X-Y$ Linearity. Figures 2 and 3 show the results of tilting the XY molecule about the X atom for a selection of B molecules. Following Legon,¹ we use θ to denote the angle of tilt of $B\cdots X-Y$ away from linear and φ to denote the tilt of the B molecule away from some reference orientation relative to the $B\cdots X-Y$ axis. The reference direction for $\text{HF}\cdots\text{ClF}$ corresponds to the linear complex, and the experimentally observed¹⁵ $\varphi = 55^\circ$ has the ClF approaching an HF lone pair in a structure analogous to the hydrogen-bonded HF dimer. Similarly, in $\text{H}_2\text{CO}\cdots\text{ClF}$, the experimental $\varphi = 69^\circ$ corresponds to ClF approaching an oxygen lone pair.¹⁶ These values of φ were kept fixed as θ was varied.

It is clear that the binding energy is dominated by the electrostatic term, although there are substantial contributions from induction and dispersion. However none of these terms varies much with θ , and such variation of the electrostatic energy as does occur does not favor the linear geometry, except in the case of $\text{H}_3\text{N}\cdots\text{F}_2$. The variation of binding energy with θ is dominated by the exchange–repulsion term. We can understand this easily in terms of the shape of the bonded halogen atom, which is well-known to be somewhat oblate, so that its radius in the direction away from the bond is smaller than the radius perpendicular to the bond.^{17,18} Consequently an increase of θ with the halogen nucleus fixed increases the overlap of the B and halogen electron densities and so increases the repulsion energy. This effect is less evident for $\text{H}_3\text{N}\cdots\text{F}_2$, since the bonded F atom is more nearly spherical than the bonded Cl atom.¹⁷ In this weakly bound complex, the repulsion

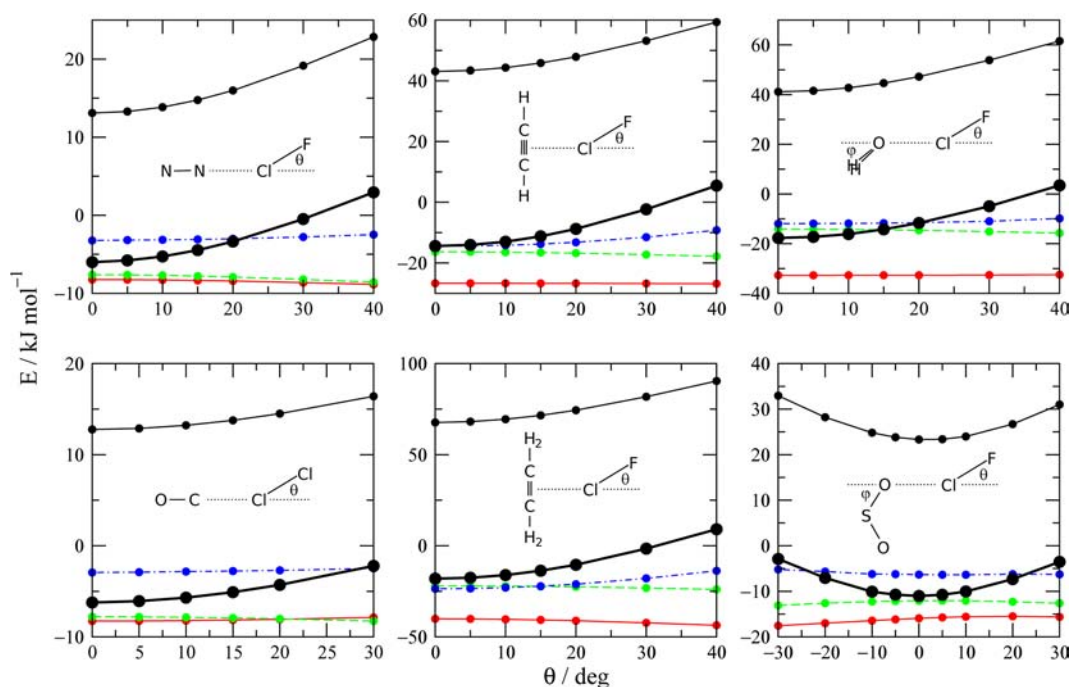


Figure 3. Variation of energy components with tilt angle θ of B...X–Y away from linear. The angle φ was held at 0° for $\text{H}_2\text{O}\cdots\text{ClF}$ and 48° for $\text{SO}_2\cdots\text{ClF}$. The components are black, exchange–repulsion; red, electrostatic; green dashed, dispersion; blue dash-dot, induction; heavy black, total.

increases by only about 4 kJ mol^{-1} at a tilt angle of 40° , compared with about 50 kJ mol^{-1} in $\text{H}_3\text{N}\cdots\text{ClF}$, and the electrostatic term does contribute to the linearity.

More examples are shown in Figure 3. For $\text{H}_2\text{O}\cdots\text{ClF}$, φ was held at 0° ; this is a floppy complex, not far from planar.¹⁹ For $\text{SO}_2\cdots\text{ClF}$, φ was fixed at 48° , the observed value.²⁰ Again, the energy variation with θ is entirely due to the exchange–repulsion in all of these examples.

One might argue that the geometry should be varied in such a way as to keep the exchange–repulsion constant, so taking account of the shape of the halogen atom, and that minimizing the electrostatic energy would then lead to the right structure. Indeed such an approach has been suggested,²¹ though not carried out. However it would be perverse to argue that the structure was determined by the approximately isotropic electrostatic attraction rather than by the anisotropic repulsion.

Another way to view this is to consider the contours of the attractive and repulsive terms, as functions of B...XY distance and the tilt angle θ , which are shown in Figure 4 for $\text{OC}\cdots\text{ClF}$. It is evident that the attractive terms are nearly independent of θ at all distances of interest, while the repulsion strongly favors $\theta = 0$.

3.2. Direction of the Halogen Bond Relative to the Lewis Base. Figure 5 shows, for several halogen-bonded complexes, the variation in energy component values as the direction of the halogen molecule XY is varied relative to the structure of the Lewis acid molecule B. In $\text{OC}\cdots\text{ClF}$, the total energy follows the electrostatic term quite closely, and this behavior is also seen in many other cases not illustrated.

In the other cases shown in Figure 5, however, the structure does not follow the electrostatic term. In $\text{HF}\cdots\text{ClF}$, the geometry found by spectroscopy¹⁵ has $\varphi = 55^\circ$, but the minimum in the electrostatic energy is at about 70° . The difference here, small though it is, can be attributed to the mildly nonspherical nature of the acceptor F atom, as shown by the increase in exchange–repulsion energy with increasing φ .

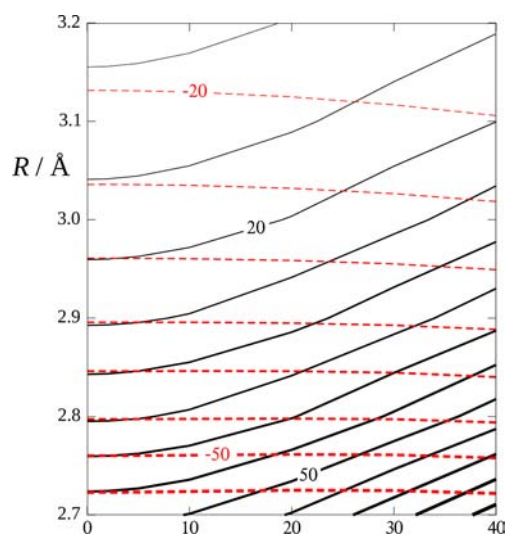


Figure 4. Contours of the exchange–repulsion (black) and the sum of the attractive terms (red, dashed) for $\text{OC}\cdots\text{ClF}$, as functions of the C...Cl distance R and the ClF tilt angle θ . Contour interval 5 kJ mol^{-1} .

In $\text{SO}_2\cdots\text{ClF}$, however, the experimental structure²⁰ has $\varphi = 48^\circ$, and while the calculated minimum is close to this, there is no sign of a minimum in the electrostatic energy there. The same behavior is seen in $\text{H}_2\text{CO}\cdots\text{ClF}$ ($\varphi_{\text{exp}} = 69^\circ$), $\text{H}_2\text{O}\cdots\text{ClF}$ ($\varphi_{\text{exp}} \approx 0^\circ$), and oxirane...ClF ($\varphi_{\text{exp}} = 67^\circ$).^{16,19,22} In these examples, the electrostatic energy is the largest attractive term, but the dispersion and induction energies contribute substantially, with a similar orientation dependence to the electrostatic term, and the geometry is the result of a balance between these attractive terms and the exchange–repulsion. Again, a contour diagram clarifies the position further. Figure 6 shows the contours of the repulsion (black) and the sum of the attractive terms (red, dashed) for $\text{SO}_2\cdots\text{ClF}$, $\text{H}_2\text{O}\cdots\text{ClF}$, and oxirane...ClF. In each case, the attractive terms draw the system

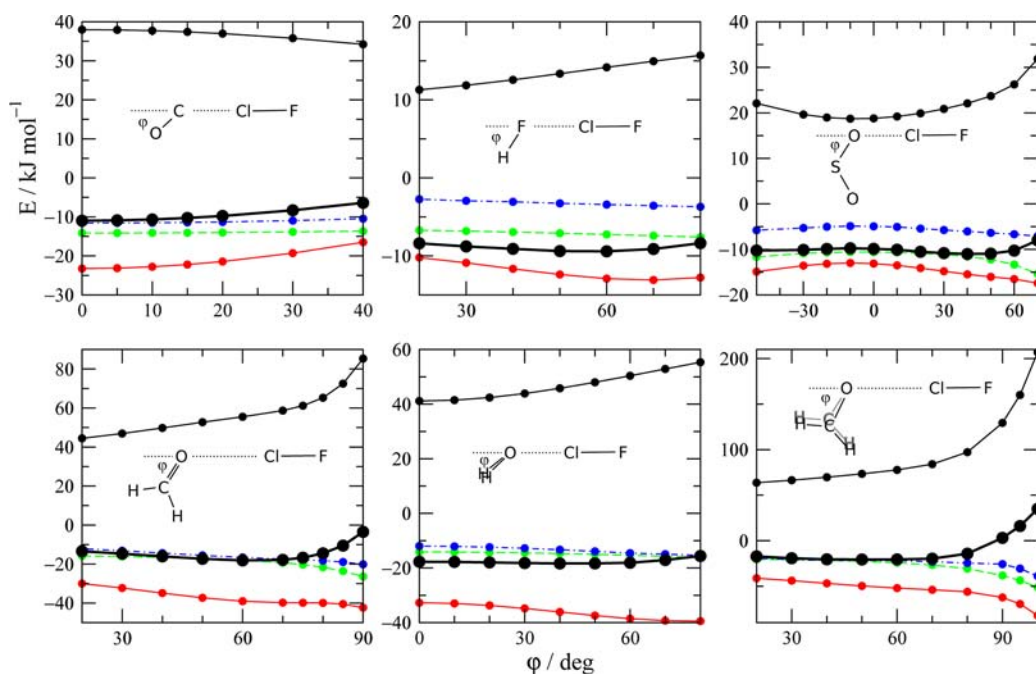


Figure 5. Variation of energy components with the tilt angle ϕ describing the direction of the XY halogen molecule relative to the structure of the Lewis acid B.

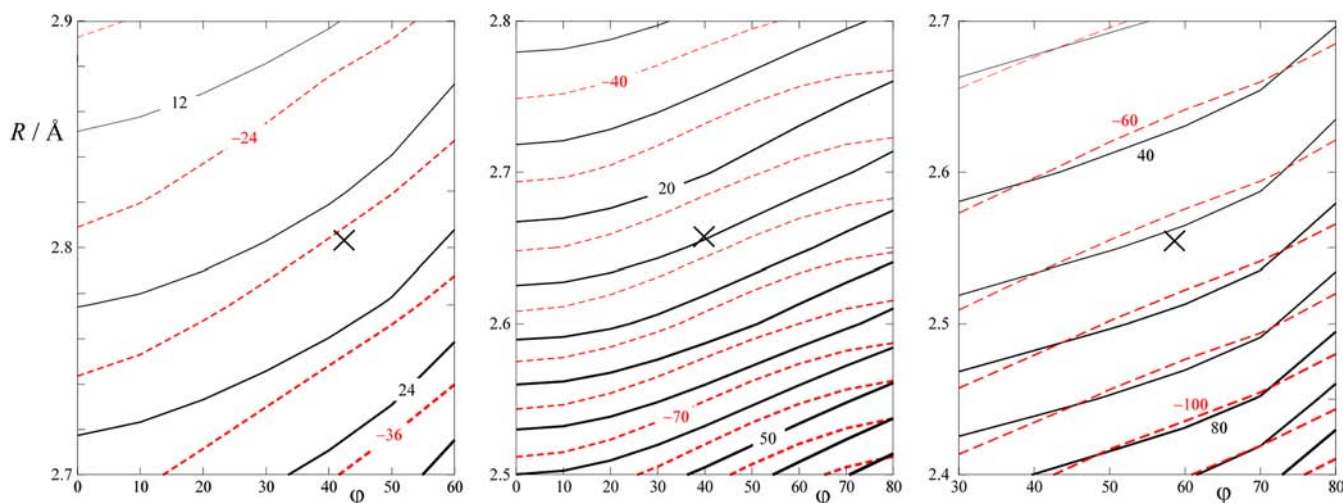


Figure 6. Contours of the exchange–repulsion (black) and the sum of the attractive terms (red, dashed) for $\text{SO}_2 \cdots \text{ClF}$, $\text{H}_2\text{O} \cdots \text{ClF}$, and oxirane $\cdots \text{ClF}$, as functions of the B \cdots Cl distance R and the B tilt angle ϕ (see Figure 5). Contour interval 4, 5, and 10 kJ mol^{-1} , respectively. The approximate position of the minimum in the total energy is shown by a cross.

to higher ϕ and smaller R , while the exchange–repulsion increases in approximately the same direction. There is a shallow minimum, arising from the balance between these effects, at approximately the position shown by the cross. The position of the minimum is sensitive to the details of the calculation and is not definitive, but it cannot be said that it is determined by the electrostatic interaction alone.

4. CONCLUSIONS

The conclusions of this work are threefold.

First, it is a justifiable generalization to say that the *binding* in halogen-bonded complexes $\text{B} \cdots \text{XY}$ is electrostatically driven, in that the electrostatic energy is usually the largest attractive term, but the dispersion and induction often contribute substantially.

Second, the linearity of the $\text{B} \cdots \text{X} \cdots \text{Y}$ unit is not due to electrostatics but is driven by the nonspherical character of bonded halogen atoms, which are oblate in shape, with a smaller radius in the direction away from the bond than perpendicular to the bond. Consequently tilting the XY molecule about the center of the X atom increases the overlap between the B and X atoms, and consequently the repulsion, while the change in electrostatic energy is much smaller.

Third, the electrostatic energy is undoubtedly a strong influence on the position of the halogen donor relative to the Lewis acid B in many, possibly most, cases. However there are cases where the electrostatic energy alone does not predict the structure, and where it is necessary to take account of the balance between the attractive terms, including induction and dispersion as well as electrostatics on the one hand and the

exchange–repulsion on the other. While it is helpful, as in complexes of polar molecules generally, to understand the influence of electrostatic interactions on the structure, one cannot expect to be able to predict the structures of halogen-bonded complexes in terms of electrostatics alone.

■ ASSOCIATED CONTENT

📄 Supporting Information

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Notes

The authors declare no competing financial interest.

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