π-Electron "Donor–Acceptor" Complexes $B\cdots ClF$ and the Existence of the "Chlorine Bond"

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Abstract: Prereactive intermediates $B\cdots ClF$ isolated in mixtures of ClF with unsaturated or aromatic hydrocarbons B can be detected and characterised through their rotational spectra. Properties determined for the two series $B\cdots ClF$ and $B\cdots HCl$ run parallel for each of a range of prototype π-electron donors B, thereby allowing a "chlorine bond", the analogue of the hydrogen bond, to be postulated.

Keywords: chlorine • chlorine bonds • fluorine • hydrogen bonds • intermediates • pi interactions

Introduction

The hydrogen bond occupies a position of central importance in chemistry, biology and materials science. Its properties, which include well-defined directionality and a strength somewhere between those of normal chemical bonds and van der Waals interactions, lead to profound consequences for the structure of water and of proteins and for supramolecular chemistry in general. Although the hydrogen bond is generally accepted to be unique, a recent article[1] draws attention to a remarkable parallelism between the properties of the series of hydrogen-bonded complexes $B\cdots HCl$, involving simple Lewis bases B, and those of the corresponding series $B\cdots ClF$ in which HCl is replaced by chlorine monofluoride. The emphasis of the article was mainly (but not exclusively) on pairs of complexes $B\cdots HCl/B\cdots ClF$ in which the electron-donor region of B consisted of a nonbonding electron pair.

In particular, it was demonstrated that $B\cdots HCl/B\cdots ClF$ pairs with a given B are isostructural, have similar interaction strengths (as measured by the intermolecular stretching force constant k_σ), and are composed of subunits in which there is only minor perturbation of the electric charge distribution when the complex is formed. These similarities were explained in terms of a model common to both types of complex but originally proposed for the hydrogen-bonded series.[2] Thus, an interaction between unperturbed electric charge distributions was assumed and the observed geometry was explained by assuming that the Lewis acid (either $^{\delta+}HCl^{\delta-}$ or $^{\delta+}ClF^{\delta-}$) lies along the axis of a nonbonding electron pair carried by the acceptor atom in B, with the electrophilic end $\delta+$ sampling this region of greatest nucleophilicity.

In view of the assumed uniqueness of the hydrogen bond, it might seem controversial to refer to a "chlorine bond" in $B\cdots ClF$ that is analogous to the hydrogen bond in $B\cdots HCl$. However, such an approach can be justified in terms of an operational definition based on similarities among experimentally determined properties, as alluded to earlier.

In this article, we focus attention on some recent experimental results for another series of $B\cdots ClF$ complexes, namely one in which B is systematically varied from one unsaturated hydrocarbon to another, with each B chosen as the prototype π-electron donor of its class. Table 1 lists the molecules B and indicates in each case the class of π system for which B is the prototype. Included among the various classes are simple π and pseudo-π donors, conjugated but nonaromatic systems acting as π donors, cumulative π systems composed of two adjacent π bonds or an adjacent π and pseudo-π bond, aromatic and heteroaromatic π-electron donors. Questions to be addressed through the choice of B include: Is the notion of a "chlorine bond", analogous to the hydrogen bond, appropriate to complexes $B\cdots ClF$ in which B is a π-electron donor? Is the pair $B\cdots ClF/B\cdots HCl$ isostructural for a given B? Does a common model account for the properties of the π-donor complexes $B\cdots ClF$ considered? What is the result of competition for ClF when more than one π-donor centre is present in B? How do aromatic and nonaromatic π-electron donors differ? What is the result when B carries both π-bonding and nonbonding electron pairs?

A more comprehensive review, to be published elsewhere,[3] will deal in a similar manner with the more general series of complexes $B\cdots XY$ and $B\cdots HX$, where XY is one of the halogen or interhalogens F_2, ClF, Cl_2 and BrCl and X is F, Cl, CN, C≡CH, etc. The Lewis bases B will then include those chosen as simple examples of n-type and mixed n/π-type as well as π-type electron-pair donors. This review will not only

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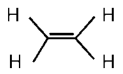
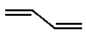
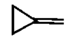
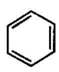
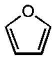
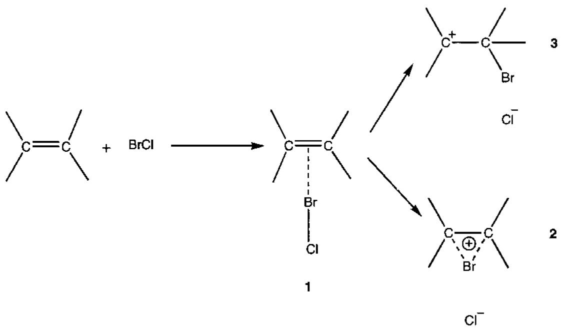
Table 1. π-Electron donors B used in the study of a series of B···ClF complexes, and the class of π system for which each B is the prototype.

Hydrocarbon	Type of π donor
H—≡—H	prototype simple π donor
	prototype simple π donor
	prototype pseudo-π donor
	prototype conjugated, nonaromatic π-π donor
	prototype cumulative,π–π donor
	prototype cumulative,π–pseudo-π donor
	prototype aromatic π donor
	prototype heteroaromatic (first row heteroatom)
	prototype heteroaromatic (second row heteroatom)

describe the relationship among the properties of the various series of complexes but will also indicate how to determine those properties for isolated complexes.

Discussion

Prereactive complexes: Definition and a method for their observation: The addition of halogen molecules to C=C double bonds constitutes an important class of chemical reaction. There is general agreement[4] that, in the dark and in polar solvents, these reactions proceed via a mechanism of the type shown in Scheme 1, where the example of BrCl is used. Complexes such as **1**, which involve a weak interaction, were called the *outer* type by Mulliken[5] while those involving extensive electric charge rearrangement, as in **2**, were classified as the strong, *inner* type. It seems reasonable to define **1** as a *prereactive intermediate* because it precedes reaction and it exists at a potential energy minimum. If it is accepted that a prereactive complex **1** is formed when a halogen and an alkene first interact, before charge separation occurs to give the halogenium ion **2** or the ion pair **3**, it is clearly a matter of general interest in chemistry to characterise species of the type **1** in detail experimentally. To do this requires the answers to the following questions: What is the molecular point group? What are the radial and angular geometries of the complex? What is the strength of the interaction? What is the extent of electric charge redistribution on formation of **1**? Is it significant, thereby indicating some incipient inner complex character, or is it minor?



Scheme 1. Accepted mechanism of addition of halogen molecules to C=C double bonds in the dark and in polar solvents shown by the example of BrCl. Complex **1** is called the outer type; halogenium ion **2** the inner type.

There is a particular problem in attempting to observe prereactive complexes B···ClF when B is an unsaturated hydrocarbon. Chlorine monofluoride undergoes violent chemical reactions with substances such as ethyne and ethene, even in the gas phase. One way to observe complexes B···ClF is in cryogenic matrices[6] but the level of detailed geometrical information obtained is unfortunately not high. A method is required which allows B···ClF to be formed and then rapidly isolated, while remaining in the gas phase and before reaction can occur. Then the rotational spectrum of the complexes, which is a rich source of detailed information, can be observed. The approach outlined below shows how to achieve this and employs the so-called fast-mixing nozzle.[7]

A diagram of this device is shown in Figure 1. It consists of a pair of concentric, approximately coterminal tubes that issue into a vacuum. Ethyne, for example, flows continuously into the vacuum chamber from the central capillary (glass, 0.3 mm internal diameter). The solenoid valve produces short pulses of a ClF/argon mixture (ca. 2% ClF) which issue into

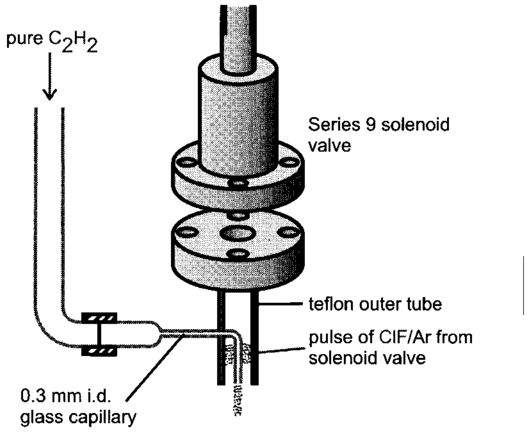


Figure 1. Schematic diagram of the fast-mixing nozzle used to create complexes B···ClF but avoiding chemical reaction of B and ClF.

the outer tube. Each pulse meets the ethyne gas only as the two flows simultaneously expand into the vacuum. Complexes are formed at the cylindrical interface of the flows and soon achieve collisionless expansion in their lowest rotational and vibrational energy states, all of which occurs within 10 µs or so and in the absence of surfaces. After this stage no chemical reaction, either unimolecular or bimolecular, can occur until the gas pulse meets the wall of the vessel. The complexes in this frozen state can then be probed spectroscopically.

This approach has two advantages. First, prereactive complexes formed from components of high mutual reactivity can be isolated. Secondly, we can be confident that the properties of a species B···ClF determined in this way are free of perturbation through lattice or solvent effects. In view of the weak interactions between B and ClF that are discussed here (typically, the intermolecular stretching force constant k_σ is only 5–10 N m^{-1}), this is an important consideration, especially when making comparisons within series of complexes in the search for systematic behaviour.

All the results summarized in this article have been obtained by using rotational spectroscopy as the means of probing the supersonically expanded gas pulse. The technique involved is called pulsed-nozzle, Fourier-transform microwave spectroscopy and was originally developed by Flygare and coworkers.[8] The particular version of the spectrometer employed has been described.[9] This technique leads to precise values of some important properties of the complex B···ClF, including the angular and radial geometry, the strength of the weak interaction (via k_σ) and the extent of electric charge redistribution within ClF on complex formation, all of which usually refer to the electronic and vibrational ground state. They are obtained, through simple models, from the rotational constants, centrifugal distortion constants and Cl nuclear quadrupole coupling constants, respectively. Details of the routes from spectroscopic constants to molecular properties are discussed elsewhere;[1,3,10,11] only the results will be considered here.

π-Electron donor complexes B···ClF: Are they of the Mulliken outer or inner type? This question has been answered by considering the Cl nuclear quadrupole coupling constants and the intermolecular stretching force constants k_σ of the complexes B···ClF under discussion here. When the complex is formed, the electric field gradient (efg) at the Cl nucleus is modified because of the response of the ClF electrons to the electric charge distribution of B. Nuclear quadrupole coupling constants for Cl are proportional to the efg at the Cl nucleus, and hence their changes on complex formation provide evidence about the redistribution of the ClF charge. If equilibrium values were available they could be interpreted by using a simple model (Townes–Dailey model[12]) in terms of the fraction δ of an electron transferred from Cl to F.

In fact, the measured coupling constants refer to the zero-point state, and it is necessary to correct them for the effects of the zero-point motion. A method for doing this was first developed for the more straightforward B···Cl$_2$ systems,[11,13] with the conclusion that only about 0.02 e is transferred from the inner (Cl$_i$) to the outer (Cl$_o$) chlorine atom when C_2H_4···Cl$_2$[13] and C_2H_2···Cl$_2$[14] are formed. Experience with the B···Cl$_2$ series then suggested an approach suitable for B···ClF, the details of which are given elsewhere.[1] It was found that, when B = C_2H_2, C_2H_4, cyclopropane or methylenecyclopropane, the charge transfer from Cl to F when forming B···ClF was 0.01 e or less, which is smaller than for B···Cl$_2$ complexes and is as expected in terms of general polarizability. This provides clear evidence that the B···ClF species under consideration are weak, Mulliken complexes of the outer type and is a conclusion reinforced by the values of the intermolecular stretching force constant k_σ, none of which exceeds ≈10 N m^{-1}.

Evidence of weak perturbation of electric charge, and other evidence based on experimentally observed moments of inertia, suggests that the geometries of the components B and ClF can be assumed to a good approximation to be unchanged by complex formation. On this assumption, the angular geometry of B···ClF is readily derived from the observed moments of inertia of various isotopomers. Such an approach was used for all cases considered below.

Simple π-donor complexes: Figure 2 compares the experimentally determined angular geometries, the distances $r(\circ\cdots\text{Cl})$, where $\circ$ is the midpoint of the π bond, and the intermolecular stretching force constant k_σ for the complexes B···ClF and B···HCl, where B is one of the two simplest π-electron donors ethyne[15,16] or ethene.[17,18] Also included in Figure 2 is the value of δ, the fraction of an electronic charge presumed transferred from Cl to F when B···ClF is formed.

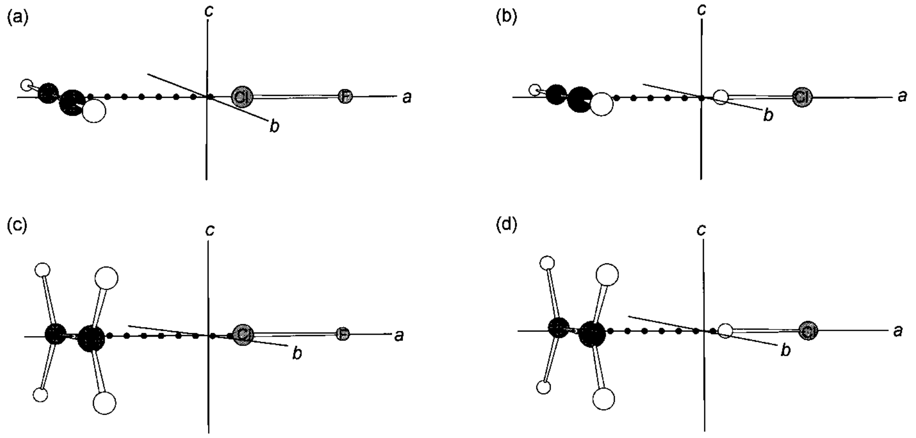


Figure 2. The angular geometries of complexes formed by ClF and HCl with simple π-electron donors. The shading code for the atoms is white for H and grey for carbon, with all other atoms labelled with the symbols for the element. The principal inertial axes a, b and c are indicated for each of the four complexes shown. All diagrams in this article are drawn to scale. a) Ethyne···ClF: geometry is planar C_{2v}; $r(\circ\cdots\text{Cl}) = 2.873$ Å; $k_\sigma = 10.0$ N m^{-1}; $\delta = 0.016\,e$; b) Ethyne···HCl: geometry is planar, of symmetry C_{2v}; $r(\circ\cdots\text{Cl}) = 3.699$ Å; $k_\sigma = 6.4$ N m^{-1}; c) Ethene···ClF: C_{2v} symmetry; $r(\circ\cdots\text{Cl}) = 2.768$ Å; $k_\sigma = 11.0$ N m^{-1}; d = 0.010 e; d) Ethene···HCl: C_{2v} symmetry; $r(\circ\cdots\text{Cl}) = 3.724$ Å; $k_\sigma = 5.9$ N m^{-1}.

The equilibrium angular geometries have all been demonstrated to belong to the point group C_{2v}, are clearly isomorphous within the pair $\mathrm{B\cdots ClF/B\cdots HCl}$ for a given B, and can be understood by the following rule, originally enunciated[2,19] for hydrogen-bonded complexes involving π-electron donors: *In the equilibrium geometry of a π-electron donor complex* $B\cdots XY$*, the XY axis lies along the symmetry axis of a π-bonding orbital of B, with* $X^{\delta+}$ *closer to the π system than* $Y^{\delta-}$ *(XY = HCl or ClF).*

Simple pseudo-π donor complexes: The chemical behaviour of cyclopropane led to a description of the molecule (due to Coulson and Moffitt[20]) in which its unsaturated character was reflected in a pseudo-π C–C bond (or "banana bond") formed by overlap of sp^3 hybrid orbitals on adjacent C atoms. The symmetry axis of this pseudo-π orbital coincides with a median of the cyclopropane equilateral triangle. According to the rule set out above, the angular geometries of cyclopropane···ClF/HCl complexes should therefore have the ClF/HCl internuclear axis coincident with a median of the cyclopropane triangle, leading to a C_{2v} geometry. Figure 3 shows that this is indeed the case for both the HCl[21] and ClF[22] complexes and that evidently the rule is also appropriate for pseudo-π donors.

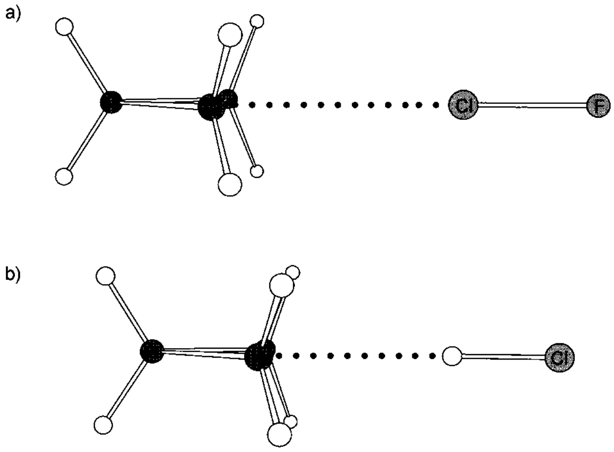


Figure 3. Angular geometries of complexes formed by ClF and HCl with the prototype pseudo-π-electron donor cyclopropane. a) Cyclopropane···ClF: geometry has C_{2v} symmetry; $r(\circ\cdots \mathrm{Cl}) = 2.958$ Å; where ○ is the centre of a C–C bond, $k_\sigma = 9.8\ \mathrm{N\,m^{-1}}$; $\delta = 0.010\ e$; b) Cyclopropane···HCl; C_{2v} symmetry; $r(\circ\cdots \mathrm{Cl}) = 3.567$ Å; $k_\sigma = 8.0\ \mathrm{N\,m^{-1}}$.

We note from a comparison of Figures 2 and 3 that the order of k_σ is B = ethene < ethyne < cyclopropane for the HCl series but is reversed for the ClF series. This behaviour is reflected in $r(\circ\cdots \mathrm{Cl})$, which has the order B = ethene > ethyne > cyclopropane in the HCl series but is again reversed for the ClF series. Detailed arguments, set out elsewhere,[22] ascribe these relationships to a secondary hydrogen bond interaction between the $\mathrm{C{-}H^{\delta+}}$ of the hydrocarbon and $\mathrm{Cl^{\delta-}}$ of HCl, which is greatest in cyclopropane. The corresponding secondary interaction with $\mathrm{F^{\delta-}}$ in the $\mathrm{B\cdots ClF}$ complexes is much less important because the $\mathrm{H\cdots F^{\delta-}}$ distances are much larger than the $\mathrm{H\cdots Cl^{\delta-}}$ distances.

Complexes in which B carries two π bonds: What happens when the electron donor B carries more than one π system? If we consider a donor B with two equivalent π bonds, there are two possibilities consistent with the rule: Either the HCl/ClF interaction with a π bond will be localised (if the potential energy barrier between equivalent sites is high enough) or there will be tunnelling between equivalent sites.

The prototype conjugated, nonaromatic π donor is 1,3-butadiene. The geometry of the complex[23] formed by ClF with this Lewis base is shown (drawn to scale) in Figure 4.

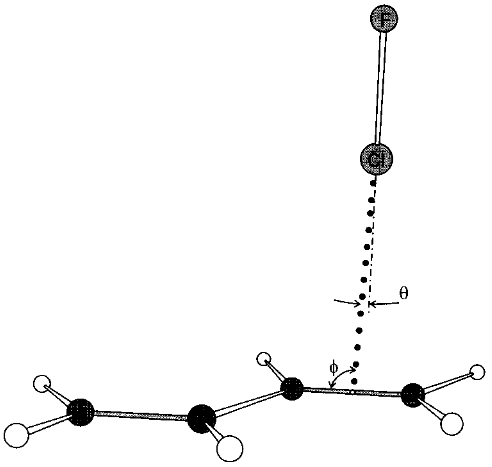


Figure 4. Angular geometry of the complex formed by the prototype conjugated, nonaromatic π donor 1,3-butadiene with ClF. The geometry has C_1 symmetry, and the ClF subunit is perpendicular to the plane of the 1,3-butadiene nuclei; the angle $\phi = 95.0°$; the system $\circ\cdots\mathrm{Cl{-}F}$ deviates from collinearity by $\theta = 2.7°$; the distance $r(\circ\cdots \mathrm{Cl}) = 2.736$ Å; $k_\sigma = 6.2\ \mathrm{N\,m^{-1}}$.

There was no evidence from the ground-state rotational spectrum of this complex to indicate tunnelling and evidently the $\pi\cdots\mathrm{ClF}$ interaction is localised (on the timescale of the experiment) at one site. We note that the ClF molecule lies perpendicular to the plane containing the nuclei of 1,3-butadiene and that the local geometry defined by the angle $\phi = \mathrm{C_2}{-}\circ\cdots\mathrm{Cl}$, where ○ marks the midpoint of the C=C bond, is as predicted by the rule. Although we have observed the rotational spectrum of the analogous complex in which HCl is the Lewis acid,[24] it has not yet been fully analysed because it deviates from the usual semirigid-rotor behaviour, possibly as a result of a significant tunnelling rate between the four equivalent sites at which HCl can interact with a π bond.

The prototype π donor carrying two cumulative double bonds is allene. The geometries of allene···HCl[25] and allene···ClF[26] determined from analyses of their rotational spectra are shown drawn to scale in projection in the principal inertial planes *ab* in Figure 5. Although all angles of rotation ψ about the C=C=C axis are consistent with the observed moments of inertia, it seems chemically reasonable to choose $\psi = 0$ (i.e. that illustrated), for then $^{\delta+}\mathrm{H}$ or $^{\delta+}\mathrm{Cl}$ interacts with a π orbital rather than its nodal plane.

The two geometries displayed in Figure 5 are remarkably similar. Because, at most, the complexes have only a plane of symmetry (*ab*), it is possible to locate the HCl or ClF subunit

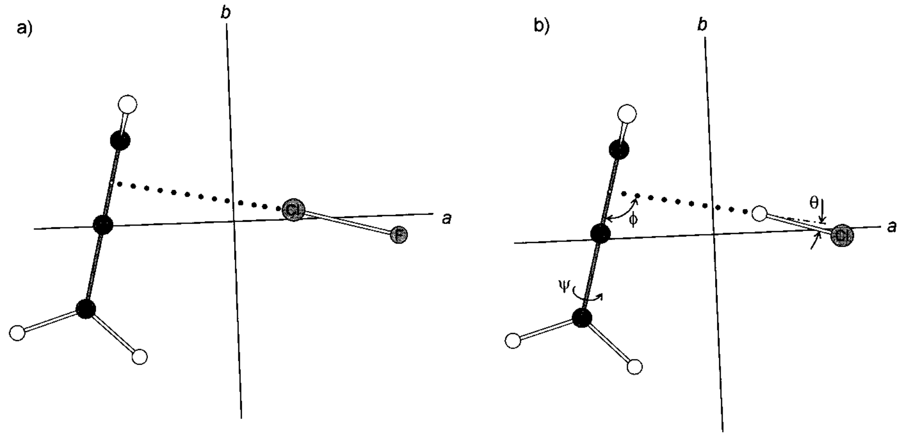


Figure 5. Angular geometries of complexes formed by the prototype cumulative $\pi-\pi$-electron donor allene with ClF and HCl. Each geometry is planar, of C_s symmetry, and is shown in projection in the principal inertial plane *ab*. The angle ψ defines the rotation of allene about its local C_2 axis. The structure shown defines $\psi = 0$. a) Allene $\cdots$ ClF. The angle $\phi = 92.5°$ and the $\circ\cdots$Cl–F system deviates from collinearity by $\theta = 4.9°$; $r(\circ\cdots\text{Cl–F}) = 2.774$ Å; $k_\sigma = 8.8\ \text{N m}^{-1}$. b) Allene $\cdots$ HCl. The angle $\phi = 94(3)°$ and the $\circ\cdots$H–Cl system deviates from collinearity by *ca.* 7°; $r(\circ\cdots\text{Cl}) = 3.55(5)$ Å; k_σ is not known.

position precisely by consideration of the complete Cl nuclear quadrupole coupling tensor, as described in detail elsewhere.[27] As a result, the angles ϕ and θ as well as the distance $r(\circ\cdots\text{Cl})$ can be simultaneously determined, where $\circ$ is again the mid-point of the C=C bond involved in the interaction and θ is the deviation of the system $\circ\cdots$H–Cl or $\circ\cdots$Cl–F from collinearity. The angles ϕ are similar in the two complexes and close to 90°, as expected from the rule. The value of θ is $\approx 7°$ for allene $\cdots$ HCl and 4.9(15)° for allene $\cdots$ ClF, both in a direction that suggests a secondary interaction between $\text{Cl}^{\delta-}$ or $\text{F}^{\delta-}$, as appropriate, with the nearest H atom on C_3. Such secondary interactions have been observed for several B $\cdots$ HCl/B $\cdots$ ClF pairs when B is an n-pair donor.[1] In general, the $\text{Cl}^{\delta-}$ atom in B $\cdots$ HCl is closer to the centre of secondary interaction on B than is $\text{F}^{\delta-}$ in B $\cdots$ ClF and angular distortion in B $\cdots$ H–Cl bonds is less strongly resisted than in the somewhat stronger B $\cdots$ Cl–F bonds. Consequently, angles θ are in general larger for B $\cdots$ HCl than B $\cdots$ ClF. There is some evidence of this when B is allene, but the results for allene $\cdots$ HCl are preliminary in nature and refinement may change this.

Formally, at least, methylenecyclopropane can be viewed as the prototype Lewis base offering cumulative π- and pseudo-π bonds. The geometries of complexes of this molecule with HCl[28] and ClF[29] are shown in Figure 6 in projection in the *ab* principal inertial plane, which coincides with the symmetry plane in each of these C_s complexes. Clearly, the weak interaction is with the π rather than a pseudo-π bond and again the angle ϕ is very similar in both and close to 90°. Evidently, the rule is again obeyed. We note that the deviation θ of the $\circ\cdots$H–Cl system from collinearity (17.5°) is much larger than that (4.9°) of the $\circ\cdots$Cl–F system, reinforcing the conclusion, alluded to earlier, that hydrogen bonds can show significant deviations from linearity when symmetry allows. The origins of this effect are discussed in detail in ref. [1].

Complexes in which B is an aromatic π donor: The prototype aromatic π donor is benzene. Both benzene $\cdots$ HCl[30] and benzene $\cdots$ ClF[31] exhibit symmetric-top-type rotational spectra in the vibrational ground state. In the case of benzene $\cdots$ ClF, observation of a satellite associated with a low-lying vibrationally excited state in the rotational spectrum and evidence of a strong Coriolis interaction between this state and the ground state led to the conclusion that the geometry of the observed complex is as shown in Figure 7. The C_{6v} structure having $\theta = 0$ occurs at a potential energy maximum and the ClF subunit executes the motion indicated in Figure 7, that is the $^{\delta+}$Cl end samples the π electron density, with the motion in the coordinate ϕ corresponding to a nearly circular potential energy minimum around the maximum at $\theta = 0$. This is probably the case in benzene $\cdots$ HCl, but the distinction between this and a strictly C_{6v} equilibrium geometry ($\theta = 0$) could not be made on the basis of the observed spectrum. The geometry shown in Figure 7 applies to the zero-point state of benzene $\cdots$ HCl.

Several simple examples of molecules B that can in principle act as π-electron donors are available (namely, pyrrole, furan, thiophene, etc). Of these, only pyrrole does not carry a nonbonding electron pair on the heteroatom. So far, however, no gas-phase complexes of pyrrole with HCl or ClF

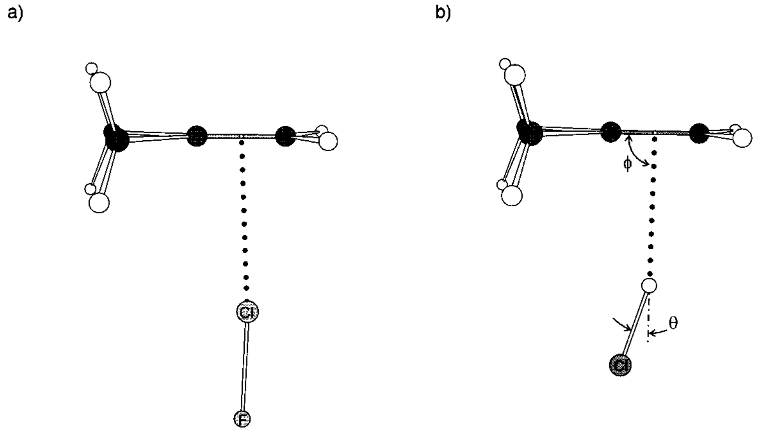


Figure 6. Angular geometries of complexes formed by the prototype cumulative π–pseudo-π electron donor methylenecyclopropane with ClF and HCl. Each geometry has C_s symmetry, with the principal inertial plane *ab* (not shown) coincident with the molecular symmetry plane. a) Methylenecyclopropane $\cdots$ ClF. The angle $\phi = 92.5°$ and the $\circ\cdots$Cl–F system deviates by $\theta = 4.9°$ from collinearity; $r(\circ\cdots\text{Cl}) = 2.675$ Å; $k_\sigma = 10.2\ \text{N m}^{-1}$; b) Methylenecyclopropane $\cdots$ HCl. The angle $\phi = 90.8°$ and the $\circ\cdots$H–Cl system deviates by 17.5° from collinearity; $r(\circ\cdots\text{Cl}) = 3.724$ Å; $k_\sigma = 5.8\ \text{N m}^{-1}$.

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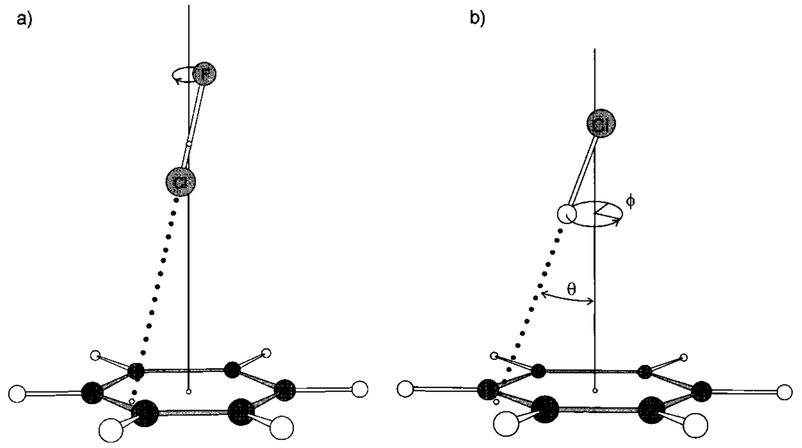

Figure 7. Angular geometries of complexes formed by the prototype aromatic π-electron donor benzene with ClF and HCl. Each geometry has effective C_{6v} symmetry in the zero-point state (i.e. the vibrational wavefunction has C_{6v} symmetry, even though there is a maximum at the C_{6v} conformation $\theta = 0$ for benzene ··· ClF and probably for benzene ··· HCl) and the $^{\delta+}$Cl and $^{\delta+}$H atoms sample the π system. The point ∘ represents the point of intersection of the extrapolation of the ClF or HCl internuclear axis with the plane of the benzene ring. a) Benzene ··· ClF: $r(\circ \cdots \mathrm{Cl}) = 3.313$ Å; $\theta = 14.4°$; b) Benzene ··· HCl: $r(\circ \cdots \mathrm{Cl}) = 3.903$ Å; $\theta = 23.0°$.

have been reported. Clearly, such investigations would be of interest in the present context. Presumably, when B = pyrrole the observed complexes B ··· HCl/B ··· ClF will be similar to the benzene analogues but possibly with the electrophilic end of HCl/ClF restricted to sample the π-electron density in the region of the CNC end of the molecule.

Complexes in which B can be both an n-pair and an aromatic π-pair donor: The conclusions established so far are that angular geometries of pairs of complexes B ··· HCl/B ··· ClF are isomorphous for a given B and that the rule for π-electron donors enunciated earlier has wide applicability. This rule is, in fact, the second of three that were originally developed for hydrogen-bonded complexes B ··· HX.[2,19] The first rule can be stated as: *In the equilibrium geometry of a complex B ··· XY in which B carries only nonbonding electron (n) pairs, the axis of the molecule XY lies along the axis of one of the n pairs.* This rule applies equally well when XY is HCl, ClF, and so on, as discussed in ref. [1]. The third rule states simply that: *If B carries both n pairs and π pairs, the n pairs are definitive of the B ··· XY angular geometry.* When the π pair is non-aromatic there have been no exceptions to rule 3 so far for either B ··· ClF or B ··· HCl complexes, as may be seen by examining refs. [1] and [32]. We therefore restrict interest here to molecules B that carry n pairs and aromatic π pairs.

The simplest molecule B that carries both an n pair and aromatic π pairs is furan. The geometry of furan ··· HCl[33] is shown in Figure 8. It has C_{2v} symmetry, and the HCl molecule lies along the C_2 axis of furan, forming a hydrogen bond to the n pair on oxygen. Thus, furan ··· HCl obeys rule 3. The experimentally determined geometry of furan ··· ClF,[34] which is also represented in Figure 8, is far from isomorphous with that of furan ··· HCl. In fact, the ClF axis points to near to the centre of one of the C_2–C_3 bonds of furan, but there is evidence of tunnelling between two such equivalent conformations, as manifest in a small splitting in *c*-type transitions in the rotational spectrum.[34] This result for furan ··· ClF is consistent with the generally accepted view that furans are much more like dienes, and less like six-electron aromatic systems, than are pyrroles and thiophenes.[35] The fact that the “soft” Lewis acid ClF interacts preferentially with the aromatic π system rather than the n pair, and vice versa for the “hard” acid HCl, is consistent with the soft/hard concept for acids and bases. It is usually assumed that aromatic π systems are soft Lewis bases while n pairs are hard bases and that soft bases interact more strongly with soft acids.

The case B = furan is the first example known where the pair of gas-phase complexes B ··· HCl/B ··· ClF have not been found to be isomorphous. What happens when furan is replaced by its congener thiophene? We first examine the behaviour of the electronic distributions by considering the molecular electric dipole and quadrupole moments of the series of pyridine, furan and thiophene,[36] all of which have an n pair carried by the heteroatom and lying along the C_2 axis. The electric dipole moments $\boldsymbol{\mu}$ have their negative ends at the heteroatom in each case and the magnitudes are 2.15, 0.68 and 0.54 D, respectively. The component of the electric quadrupole moment along the C_2 axis (z) is large and negative in pyridine, zero in furan but positive in thiophene. This set of dipole and quadrupole moments indicates that the n pair on the heteroatom becomes

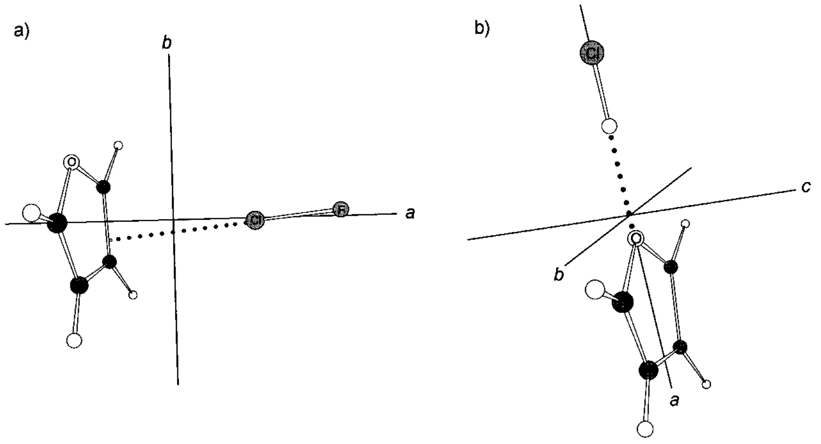

Figure 8. Comparison of the angular geometries of complexes formed by the prototype mixed n-type and aromatic π-type electron donor furan with ClF and HCl. a) Furan ··· ClF: geometry has C_1 symmetry. The principal inertial axes *a* and *b* are indicated; the axis *c* is perpendicular to the plane of the paper. The extension of the ClF internuclear axis intersects the plane of the furan ring at the point ∘ between C_2 and C_3. $r(\circ \cdots \mathrm{Cl}) = 2.826$ Å; b) furan ··· HCl: geometry has C_{2v} symmetry and is planar. The orientation of the principal inertial axes *a*, *b* and *c* has been arranged so that the attitude of the furan ring is similar to that in (a). The distance $r(\circ \cdots \mathrm{Cl}) = 3.267$ Å.

progressively withdrawn into the ring along the series. On the other hand, the component of the quadrupole moment perpendicular to the ring plane is large and negative in each case, as expected from the extension of the π system above and below the plane of the ring, but is largest for thiophene. All of this evidence about the electronic distributions is consistent with the observed structures of furan $\cdots$ HCl[33] and pyridine $\cdots$ HCl,[37] which are as predicted by rule 3, but suggests that the π system may be more nucleophilic than is the n pair with respect to HCl, as well as to ClF, when the Lewis base changes to thiophene.

The experimental geometry of thiophene $\cdots$ HCl[38] is shown in Figure 9 in projection in the *ab* principal inertial plane. The complex either has C_s symmetry, with *ab* coincident with the molecular symmetry plane, or there is a low potential energy barrier at the C_s form separating two equivalent conformers of C_1 symmetry so that H of HCl lies slightly out of the plane at equilibrium. These two possibilities cannot be distinguished on the basis of ground-state spectroscopic constants alone. What is unambiguously clear is that the structure of thiophene $\cdots$ HCl is not planar of C_{2v} symmetry, with HCl forming a hydrogen bond to S, as in furan $\cdots$ HCl. Instead, thiophene $\cdots$ HCl resembles benzene $\cdots$ HCl more than it does furan $\cdots$ HCl. Preliminary results for thiophene $\cdots$ ClF also indicate a geometry in which the ClF samples the π-electron density rather than the n-pair density.[39]

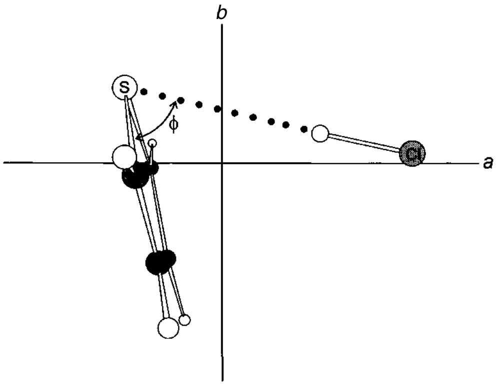

Figure 9. The geometry of thiophene $\cdots$ HCl. The principal inertial plane *ab* is either a plane of symmetry or nearly so for this molecule, which has effective C_s symmetry. For clarity, the thiophene subunit has been rotated slightly about its local C_2 axis to allow all the atoms to be shown. Another, similar geometry is also consistent with the observed spectrum; the positions of the thiophene subunit and Cl are essentially unchanged, but H takes on the small negative *b* coordinate required to change the sign of the angle between the HCl axis and the *a* axis while maintaining its magnitude. The HCl axis then points to the central region of the thiophene ring.

Summary and Outlook

A detailed comparison of the properties for a range of carefully selected complexes B $\cdots$ XY formed from prototype π-electron donors B and the Lewis acids XY, where XY is either ClF or HCl, has yielded some general conclusions. All of the complexes discussed in this article are of the Mulliken outer type, that is, their intermolecular binding is weak and there is only minor perturbation of electric charge distributions. Except in the case when B is the heteroaromatic π-donor furan, the angular geometries of the pair B $\cdots$ HCl/B $\cdots$ ClF are isomorphous for a given B. This suggests that a simple rule first proposed[2,19] for predicting the angular geometries of π-type hydrogen-bonded complexes B $\cdots$ HX applies equally well to the B $\cdots$ ClF series. Thus, the $^{\delta+}XY^{\delta-}$ molecule (XY is ClF, HCl, ...) lies along the local symmetry axis of a π or pseudo-π orbital in the equilibrium conformation, with $^{\delta+}X$ closer than $Y^{\delta-}$ to the π centre.

In view of the parallelism of the properties, especially angular geometries, in the π-type complexes B $\cdots$ HCl/B $\cdots$ ClF discussed here, as well as those previously noted for n-type interactions,[1] it is evidently possible to define operationally a "chlorine bond" in B $\cdots$ ClF complexes that is the analogue of the hydrogen bond in B $\cdots$ HCl. Of course, it requires a highly electronegative atom such as F to be attached to Cl to endow it with a net partial positive charge $\delta+$ and hence an electrophilic nature. Hydrogen has many more ways of achieving such a partial charge because of its low electronegativity and the hydrogen bond is accordingly very common. The main differences between the chlorine and hydrogen bonds arise from the relative sizes of Cl and H. There is the same magnitude of systematic shortening of $r(\circ\cdots\mathrm{Cl})$ in π-type complexes B $\cdots$ ClF relative to the corresponding B $\cdots$ HCl (see Figures 2–8) as was observed for the n-type complexes and was discussed in ref. [1]. In any given pair B $\cdots$ HCl/B $\cdots$ ClF, $^{\delta+}H$ is closer to the interaction centre (Z) of B than is $Cl^{\delta+}$ of ClF and correspondingly $Cl^{\delta-}$ of HCl is closer to any region of secondary interaction in B than is $F^{\delta-}$. This results in secondary interactions of greater significance in B $\cdots$ HCl and hence greater deviations θ of the nuclei Z $\cdots$ H–Cl in the hydrogen bonds from collinearity. Indeed, ClF is a more accurate probe of π bonding or n electron pair directions than is HCl for this reason.

When two equivalent π bonds are carried by B, whether conjugated as in 1,3-butadiene or cumulative as in allene, the B $\cdots$ ClF complexes have relatively rigid geometries with ClF localised at one of the four equivalent sites of minimum potential energy. On the other hand, preliminary evidence for the corresponding B $\cdots$ HCl complexes suggests low potential energy barriers to tunnelling between equivalent conformers.

Although the similarities in behaviour of B $\cdots$ HCl and B $\cdots$ ClF extend to B = benzene, in which complexes the electrophile $^{\delta+}X$ samples the π electron density around the C atom skeleton, differences begin to occur when B is a heteroaromatic π donor that also has an n pair on the heteroatom. In cases where B carries nonaromatic π-donor and n-donor sites, the n pair is definitive of the angular geometry. This also appears to be so in the B $\cdots$ HCl series when B is one of the heteroaromatic molecules pyridine or furan but not when B is thiophene. This change within the heteroaromatic series can be understood in terms of a weakened nucleophilicity of the n pair in thiophene, as revealed by considering the molecular electric moments (and hence the electric charge distributions). Furan $\cdots$ HCl and furan $\cdots$ ClF provide the only example so far identified of a pair B $\cdots$ HCl/B $\cdots$ ClF that is not isostructural. Thus, it appears that the order of the nucleophilicities of the n pair on the heteroatom is pyridine > furan > thiophene and that for the furan there is a fine balance between the nucleophilicities of the π system and the n pair.

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[1] A. C. Legon, *Chem. Phys. Lett.* **1997**, *279*, 55–64.
[2] A. C. Legon, D. J. Millen, *Faraday Discuss. Chem. Soc.* **1982**, *73*, 71–87.
[3] A. C. Legon, *Angew. Chem.*, *Angew. Chem. Int. Ed.*, submitted.
[4] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd ed., G. Bell, London, **1969**, pp. 964–988.
[5] R. S. Mulliken, W. B. Person, *Molecular Complexes: A Lecture and Reprint Volume*, Wiley-Interscience, New York, **1969**, and references therein.
[6] See, for example, B. S. Ault, *J. Phys. Chem.* **1987**, *91*, 4723–4727.
[7] A. C. Legon, C. A. Rego, *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 1915–1921.
[8] T. J. Balle, W. H. Flygare, *Rev. Sci. Instrum.* **1981**, *52*, 33–45.
[9] A. C. Legon, in *Atomic and Molecular Beam Methods, Vol. 1* (Ed. G. Scoles), Oxford University Press, New York, **1992**, ch. 9, pp. 289–308.
[10] A. C. Legon, D. J. Millen, *Chem. Rev.* **1986**, *86*, 635–657.
[11] A. C. Legon, *Chem. Phys. Lett.* **1995**, *237*, 291–298.
[12] C. H. Townes, A. L. Schawlow, *Microwave Spectroscopy*, McGraw–Hill, New York, **1995**, ch. 9, p. 228–241.
[13] H. I. Bloemink, K. Hinds, A. C. Legon, J. C. Thorn, *Chem. Eur. J.* **1995**, *1*, 17–25.
[14] H. I. Bloemink, S. A. Cooke, K. Hinds, A. C. Legon, J. C. Thorn, *J. Chem. Soc. Faraday Trans.* **1955**, *91*, 1891–1900.
[15] K. Hinds, J. H. Holloway, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1996,** *92*, 1291–1296.
[16] A. C. Legon, P. D. Aldrich, W. H. Flygare, *J. Chem. Phys.* **1981**, *75*, 625–630.
[17] H. I. Bloemink, J. H. Holloway, A. C. Legon, *Chem. Phys. Lett.* **1996**, *250*, 567–575.
[18] P. D. Aldrich, A. C. Legon, W. H. Flygare, *J. Chem. Phys.* **1981**, *75*, 2126–2134.
[19] A. C. Legon, D. J. Millen, *Chem. Soc. Rev.* **1987,** *16*, 467–498.
[20] C. A. Coulson, W. E. Moffitt, *Philos. Mag.* **1949**, *40*, 1–35.
[21] A. C. Legon, P. D. Aldrich, W. H. Flygare, *J. Am. Chem. Soc.* **1982**, *104*, 1486–1490.
[22] K. Hinds, J. H. Holloway, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 373–378.
[23] S. A. Cooke, J. H. Holloway, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 2361–2365.
[24] Z. Kisiel, P. W. Fowler, A. C. Legon, unpublished results.
[25] A. J. Fillery-Travis, A. C. Legon, unpublished results.
[26] S. A. Cooke, J. H. Holloway, A. C. Legon, *Chem. Phys. Lett.* **1997**, *266*, 61–69.
[27] A. C. Legon, *Faraday Discuss. Chem. Soc.* **1994**, *97*, 19–33; A. C. Legon, J. C. Thorn, *Chem. Phys. Lett.* **1994**, *227*, 472–479.
[28] Z. Kisiel, P. W. Fowler, A. C. Legon, *J. Chem. Phys.* **1994**, *101*, 4635–4643.
[29] S. A. Cooke, J. H. Holloway, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 4253–4258.
[30] W. G. Read, E. J. Campbell, G. Henderson, *J. Chem. Phys.* **1983**, *78*, 3501–3508.
[31] S. A. Cooke, C. M. Evans, J. H. Holloway, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2295–2302.
[32] A. C. Legon, *Chem. Soc. Rev.* **1990**, *19*, 197–237.
[33] J. A. Shea, S. G. Kukolich, *J. Chem. Phys.* **1983**, *78*, 3545–3551.
[34] S. A. Cooke, G. K. Corlett, J. H. Holloway, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2675–2680.
[35] J. A. Joule, K. Mills, G. F. Smith, *Heterocyclic Chemistry*, 3rd ed. Chapman and Hall, London, **1995**, ch. 12, p. 227.
[36] For a summary of the electric dipole moments and electric quadrupole moments of pyridine, furan and thiophene, see S. A. Cooke, G. K. Corlett, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1565–1570.
[37] S. A. Cooke, G. K. Corlett, D. G. Lister, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 837–841.
[38] S. A. Cooke, G. K. Corlett, A. C. Legon, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1565–1570.
[39] S. A. Cooke, J. H. Holloway, A. C. Legon, unpublished results.