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Strength, Character, and Directionality of Halogen Bonds involving Cationic Halogen Bond Donors

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Abstract

Halogen bonds involving cationic halogen bond donors and anionic halogen bond acceptors have recently been recognized as being important in stabilizing the crystal structures of many salts. Theoretical characterization of these types of interactions, most importantly in terms of their directionality, has been limited. Here we generate high-quality symmetry adapted perturbation theory potential energy curves of a $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ model system in order to characterize halogen bonds involving charged species, in terms of contributions from electrostatics, exchange, induction, and dispersion, with special emphasis on analyzing contributions that are most responsible for the directionality of these interactions. It is found that, as in the case of neutral halogen bonds, exchange forces are important contributors to the directionality of charged halogen bonds, however, it is also found that induction effects, which contribute little to the stability and directionality of neutral halogen bonds, play a large role in the directionality of halogen bonds involving charged species. Potential energy curves based on the $\omega\text{B97X-D/def2-TZVP/C-PCM}$ method, which includes an implicit solvation model in order to mimic the effects of the crystal medium, are produced for both the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ model system and for the 4-bromoanilinium... Cl^- dimer, which is based on the real 4-bromoanilinium chloride salt, whose crystal structure has been determined experimentally. It is found that, within a crystal-like medium, charged halogen bond are significantly weaker than in the gas phase, having optimum interaction energies up to approximately -20 kcal/mol.

Graphical abstract

Introduction

For the past decade halogen bonds have been recognized as playing important roles in many aspects of chemistry, material science, and biochemistry.^{1–9} These noncovalent interactions have been observed in protein-ligand complexes,^{9–13} crystal structures of neutral molecules,^{14–16} and crystals composed of molecular ions.^{17, 18} A halogen bond is an interaction of the type $RX \cdots YZ$, where X is a halogen (chlorine, bromine, or iodine) that is part of the molecule, or molecular ion, RX , and YZ is a Lewis base. Most commonly Y is an atom, such as oxygen, nitrogen, or sulfur, that has a lone pair.⁶ The electrostatic attraction between the σ -hole, a region of positive potential located along the extension of the $R-X$ bond, and the negative Lewis base is the origin of halogen bonding (see Figure 1).

In many ways, halogen bonds can be said to be very similar to their more ubiquitous counterparts, hydrogen bonds (of the form $RH \cdots YZ$). The strengths of halogen bonds are generally similar, if somewhat weaker, than those of hydrogen bonds. The most important similarity between hydrogen bonds and halogen bonds is their directional nature. A halogen bond of the $C-X \cdots O$ type, for example, reaches its potential energy minimum at a $C-X \cdots O$ angle of 180° . These interactions quickly become weaker as the $C-X \cdots O$ angle is rotated away from linearity.^{19–22}

Halogen bond directionality was long held to be attributable to electrostatic forces. This view is intuitively reasonable, as one may picture that as the halogen σ -hole rotates away from the negative Lewis base, the strength of the electrostatic interaction would tend to decrease. Several recent studies have called this view into question, pointed to exchange repulsion forces as being responsible for halogen bond directionality.^{19–21} In a recent work, Stone systematically investigates the effect of halogen bond rotation for several small halogen bonding complexes, such as $F-Cl \cdots F-H$, considering both the $F-Cl-F$ and $Cl-F-H$ angles, on the SAPT interaction energy terms (other complexes are also studied).¹⁹ In this study it is found that the exchange-repulsion term varies strongly as a function of $F-Cl-F$

bending while the electrostatic term is almost completely flat. The reason for the strong involvement of exchange-repulsion effects in halogen bond directionality involves the oblate shape of a bound halogen's electron density envelope (a phenomenon known as polar flattening), with the halogen's radius in the direction of its covalent bond being smaller than its radius perpendicular to the bond. Rotation of the halogen bond geometry away from linearity results in a higher amount of overlap between the electron densities of the halogen and the halogen bond acceptor, bringing about a larger exchange-repulsion contribution.

Among the properties distinguishing halogen bonds from hydrogen bonds is their strong dependence on dispersion interactions. As halogens are large atoms with large polarizabilities, especially when compared to hydrogen atoms, it is not surprising that dispersion plays a large role in stabilizing halogen bonds.²³ As with hydrogen bonds, halogen bond acceptors are not always of the "standard" Lewis base type. Most notably, it has been recognized that aromatic species can serve as halogen bond acceptors, with the resulting interaction often referred to as R-X... π interactions (analogous to R-H... π interactions).^{22, 24, 25}

There are two ways in which the strength of a halogen bond is modulated: by changing the identity of the halogen and by controlling the halogen's chemical environment. Larger halogens tend to have larger σ -holes (I > Br > Cl), and thus form stronger halogen bonds.^{1, 6, 7} The size of the σ -hole can also be strongly modified by its chemical environment, with substitution of electronegative groups into neighboring positions having the largest impact.^{6, 23} Thus, F₃C-Br will have a much larger σ -hole than H₃C-Br, and will generally form stronger halogen bonds with a Lewis base. This ability to modulate or "tune" halogen bond strengths is a property that makes these interactions very promising in the design of new supramolecular structures and pharmaceutical ligands.

Halogen bonds involving neutral species have been the subjects of many experimental and theoretical investigations, those involving charged chemical moieties are much less common and, thus, have not been characterized as extensively as their neutral counterparts. Halogen bonds have been used in the design of several new salts in which the halogen is contained within the molecular cation structure.^{17, 18} As an example, Rissanen and coworkers, developed several crystal structures composed of haloanilinium and halopyridinium cations along with chloride, bromide, and dihydrogen phosphate anions.¹⁷ Here our goal is to use computational techniques to characterize the properties of halogen bonds involving cationic halogen bond donors and the chloride anion, which serves as the simplest anion commonly found in these types of salts. The most important property considered here is halogen bond directionality, as it is reasonable to expect that the ionic character of both members of the interacting pair, and especially that of the halocation, might have a dramatic impact on the angular dependence of the halogen bond strength.

Here we use the SAPT method to characterize halogen bonds involving charged species in terms of contributions from electrostatics, exchange, induction, and dispersion.^{26–29} SAPT potential energy curves, as functions of intermolecular separation, as well as C-X...Cl[–] angles, are generated in order to investigate the factors influencing the strength and directionality of charged halogen bonds. The density functional-based, ω B97X-D/def2-

TZVP/C-PCM method, incorporating an empirical dispersion function and an implicit solvation model, is used to investigate the effects that a salt's solid-state medium might have on the strength of halogen bonds involving a cationic halogen bond donor and an anionic halogen bond acceptor. In most studies reported here the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ dimer is used as a model system. $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+$ is taken to be the smallest cation that can reasonably mimic the behavior of larger cations, such as haloanilinium and halopyridinium. In a more limited set of computations, based on the $\omega\text{B97X-D/def2-TZVP/C-PCM}$ method, we investigate the strength and directionality of the Br^+-Cl^- halogen bond in 4-bromoanilinium chloride, a salt whose crystal structure has been determined experimentally (Figure 2).

Results and Discussion

Electrostatic potentials for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+$, 4-bromoanilinium, and bromoethyne are given in Figure 1. Bromoethyne is representative of a typical, neutral, halogen bond donor in which a ring of negative potential exists on the halogen perpendicular to the C-X bond axis and a positive σ -hole is found along the extension of the C-X bond. The fact that $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+$ and 4-bromoanilinium are cations results in electrostatic potentials that are significantly distinct from those of neutral species, with electrostatic potentials that are positive at all points on these surfaces. Nonetheless, a belt of potential that is *less* positive than the surrounding potential exists on the bromines, on a plane perpendicular to the C-Br bond axis, with both molecules showing distinct σ -holes, with *increased* positive potentials (relative to the remaining potential on Br), along the extension of their C-Br bonds. The presence of these σ -holes indicates that halogen bonds involving these two cations as halogen bond donors will have the same type of directionality exhibited by halogen bonds involving purely neutral species.

Figure 3 gives gas-phase SAPT potential energy curves for the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ complex, as a function of the Br...Cl distance, at C-Br...Cl angles of 90° , 120° , 150° , and 180° . The directionality of this charged halogen bond can clearly be seen in this figure, with the strongest interaction of -78.7 kcal/mol occurring at a Br...Cl separation of $2.64\text{\AA}$ along the $a(\text{C}-\text{Br}\dots\text{Cl}) = 180^\circ$ curve. Initially, as the C-Br...Cl angle decreases the potential minimum interactions are destabilized, with values of -71.7 kcal/mol ($R(\text{Br}\dots\text{Cl}) = 2.73\text{\AA}$) and -62.8 kcal/mol ($R(\text{Br}\dots\text{Cl}) = 3.06\text{\AA}$) for the $a(\text{C}-\text{Br}\dots\text{Cl}) = 150^\circ$ and $a(\text{C}-\text{Br}\dots\text{Cl}) = 120^\circ$ curves, respectively. Interestingly, this trend does not continue and the interaction energy at the potential energy minimum along the $a(\text{C}-\text{Br}\dots\text{Cl}) = 90^\circ$ curve is lower than that on the $a(\text{C}-\text{Br}\dots\text{Cl}) = 120^\circ$ curve, with a value of -66.8 kcal/mol.

The reason for this observation has to do with the increased exposure of the chloride ion to the very positive region of potential located within the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+$ ammonium group as the C-Br...Cl angle approaches 90° , leading to an enhanced electrostatic attraction. The differences between distance dependences of the potential energy curves at various angles gives an indication of the stronger influence of electrostatics in stabilizing the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ complex at smaller C-Br...Cl angles. Here the $a(\text{C}-\text{Br}\dots\text{Cl}) = 90^\circ$ curve is much more attractive and the $a(\text{C}-\text{Br}\dots\text{Cl}) = 120^\circ$ curve is slightly more attractive than the large-angle curves at long distances, especially beyond $R(\text{C}-\text{Br}) \approx 4.5\text{\AA}$. As electrostatic forces act over a longer range than dispersion, induction, and exchange forces, it seems clear that

electrostatics play a larger role in stabilizing the $\alpha(\text{C-Br}\dots\text{Cl}) = 120^\circ$ and, especially, $\alpha(\text{C-Br}\dots\text{Cl}) = 90^\circ$ complexes.

Figure 4 shows SAPT interaction energy terms, as functions of $R(\text{Br}\dots\text{Cl})$, for interactions at $\alpha(\text{C-Br}\dots\text{Cl}) = 180^\circ$ and $\alpha(\text{C-Br}\dots\text{Cl}) = 90^\circ$. There are two very important features of the data depicted here that should be further explored. The first of these is the dominance of electrostatics, for interactions at both $\text{C-Br}\dots\text{Cl}$ angles, at distances beyond approximately $4.5\text{\AA}$. To emphasize this point, it will be noted here that at a range of $5.5\text{\AA}$ the contributions from electrostatics, dispersion, induction, and exchange are -39.13 , -0.17 , -1.24 , and 0.04 kcal/mol, respectively, for the $\alpha(\text{C-Br}\dots\text{Cl}) = 180^\circ$ curve, and -47.37 , -0.24 , -1.18 , and 0.06 kcal/mol, respectively, for the $\alpha(\text{C-Br}\dots\text{Cl}) = 90^\circ$ curve. Thus, the only appreciable contributions to interaction, both attractive and repulsive, are attributable to electrostatic forces, with the *difference* between the interaction energies of the two curves (at $5.5\text{\AA}$) also being attributable to electrostatics.

The second notable feature of the data depicted here is the substantial differences that exist, when comparing the $\alpha(\text{C-Br}\dots\text{Cl}) = 90^\circ$ and $\alpha(\text{C-Br}\dots\text{Cl}) = 180^\circ$ curves, in the exchange and induction terms that are observed at small $R(\text{Br}\dots\text{Cl})$ distances. The difference in the exchange term curves are consistent with results reported by Stone and others, as described above. When this halogen bond is rotated away from linearity, the oblate shape (polar flattening) of the halogen leads to a higher amount of overlap between the bromide and chloride electron density envelopes, resulting to a larger amount of exchange repulsion.

Overall, the induction contribution to stabilization in $\text{H}_3\text{N-C}\equiv\text{C-Br}^+\dots\text{Cl}^-$ is significantly larger than for typical (neutral) halogen bonds. For example, the induction contribution to the $\alpha(\text{C-Br}\dots\text{Cl}) = 180^\circ$ structure at $2.6\text{\AA}$ (very near the potential energy minimum) is -32.31 kcal/mol while the induction contribution for the (neutral) $\text{Cl}\dots\text{O}$ halogen bond in $\text{F-Cl}\dots\text{OH}_2$ is found by Stone to be approximately -3.0 kcal/mol. The most straightforward explanation for the larger role of induction in stabilizing this complex is the enhanced polarizability of the anion and the increased polarizing ability of the cation. It is also observed that induction plays a larger role in stabilizing the complex at a $\text{C-Br}\dots\text{Cl}$ angle of 180° than at 90° . This effect is directly related to the proximity of the anion to the bromide σ -hole; the halogen bond donor has its greatest polarizing ability at the point where it possesses the largest positive potential. Induction is a short-range effect, thus the fact that the anion is exposed to the very positive ammonium group in the $\alpha(\text{C-Br}\dots\text{Cl}) = 90^\circ$ structure has very little effect on the induction contribution.

SAPT contribution potential energy curves as a function of the $\text{C-Br}\dots\text{Cl}$ angle, at $R(\text{Br}\dots\text{Cl})$ separations of both $3.0\text{\AA}$ and $3.8\text{\AA}$, are given in Figure 5. At $R(\text{Br}\dots\text{Cl}) = 3.0\text{\AA}$ it can be seen that the exchange and induction terms become significantly more attractive (or less repulsive) and the electrostatic term become less attractive as the $\text{C-Br}\dots\text{Cl}$ angle rotates toward linearity; compared with the other three terms, dispersion can be said to be effectively flat across this rotation. As noted above, the reason for this increase in electrostatic attraction as the $\text{C-Br}\dots\text{Cl}$ angle approaches 90° is the exposure of Cl^- to the very positive ammonium group; supporting this assertion is the fact that the electrostatic curve is relatively flat in the range from 125° – 180° , becoming much more attractive at

angles smaller than 125° , indicating that short-range factors, which would be expected to vary continuously, are not responsible for enhanced electrostatic attraction at smaller angles. The SAPT interaction energy curve at this distance assumes a rather complex shape as a result of the counterbalancing terms, with the minimum occurring for the linear structure. At $3.8\text{\AA}$, as might be expected, it is seen that the electrostatics plays the largest role in stabilizing the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ complex; more importantly, at this distance, electrostatics are almost entirely responsible for variations in the interaction energy as a function of the $\text{C}-\text{Br}\dots\text{Cl}$ angle. Although the electrostatic and induction terms are still seen to become more attractive with increasing angle, these curves are relatively flat at this distance. As a result of the dominance of electrostatics, the potential energy minimum shifts to a 90° $\text{C}-\text{Br}\dots\text{Cl}$ angle.

Halogen bonds occurring between charged species are most commonly found, or, at least, are of most interest, in the crystal structures of molecular ionic salts. Detailed computational data on gas-phase charged halogen bonding complexes, such as the SAPT results presented above, can give us insight into the forces that stabilize these types interactions, however it should be kept in mind that, within the crystal environment, the magnitude of attraction and, importantly, the factors affecting halogen bond directionality can be quite different. Here we investigate the ways in which the crystal environment affect the strength and directionality of charged halogen bonds using the $\omega\text{B97X-D/def2-TZVP}$ method along with the C-PCM implicit solvent model. These models are meant to mimic the minimum effect that the crystal environment could have on halogen bond strength and directionality.

Figure 6 gives $\omega\text{B97X-D/def2-TZVP/C-PCM}$ potential energy curves, as functions of $\text{R}(\text{Br}\dots\text{Cl})$ distance, at $\text{C}-\text{Br}\dots\text{Cl}$ angles of 90° , 120° , 150° , and 180° . The most conspicuous aspect of the data depicted in these curves is the destabilization of the complex that occurs upon inclusion of the implicit solvation model, with potential energy minimum interaction energies being roughly 20–25% as attractive as in the gas-phase. This is an expected result, as the strengths of noncovalent interactions, especially polar ones, are known to be significantly diminished within a medium, such as in solvent or within a crystal environment. It is also important to note that, upon gross inspection of Figures 3 and 6, the same general trends are observed, with optimum $\text{R}(\text{Br}\dots\text{Cl})$ distances increasing and interaction energies becoming less stable as the $\text{a}(\text{C}-\text{Br}\dots\text{Cl})$ angle is decreased from 180° to 120° , and with the $\text{a}(\text{C}-\text{Br}\dots\text{Cl}) = 90^\circ$ structure being slightly more stable, and having a slightly larger optimum $\text{R}(\text{Br}\dots\text{Cl})$ distance, than the $\text{a}(\text{C}-\text{Br}\dots\text{Cl}) = 120^\circ$ structure. Addition of medium (“solvent”) effects also results in potential energy minimum intermolecular separations that occur at significantly longer distances. This trend can more clearly be seen in Table 1, which gives potential energy minimum interaction energies and intermolecular separations as computed by SAPT (gas-phase), $\omega\text{B97X-D/def2-TZVP}$ in the gas phase, and $\omega\text{B97X-D/def2-TZVP/C-PCM}$. Here it is seen that, in terms of the location of the potential energy minima, the $\text{a}(\text{C}-\text{Br}\dots\text{Cl}) = 180^\circ$ and $\text{a}(\text{C}-\text{Br}\dots\text{Cl}) = 150^\circ$ curves exhibit the most pronounced increases in intermolecular separation, with increases of $0.6 - 0.7\text{\AA}$. For the two smaller angles the optimum intermolecular separation is not affected as strongly, with the optimum $\text{R}(\text{Br}\dots\text{Cl})$ distance increasing by approximately $0.3\text{\AA}$ upon introduction of medium.

For the purpose of validating the ω B97X-D/def2-TZVP method, with respect to the, very accurate, SAPT2+3- δ MP2/aug-cc-pVTZ method, potential energy minimum interaction energies and intermolecular separations have been computed at the ω B97X-D/def2-TZVP level in the gas-phase. Interaction energy and optimum R(Br...Cl) distances for all three computational methods considered here are given in Table 1. Here it is seen that ω B97X-D/def2-TZVP optimum interaction energies agree relatively well with the SAPT2+3- δ MP2/aug-cc-pVTZ reference, however, there is a tendency for the DFT method to overbind at larger α (C-Br...Cl) angles. The largest discrepancy between the two methods occurs for the α (C-Br...Cl) = 180° curve, for which ω B97X-D/def2-TZVP overbinds by 6.71 kcal/mol (8.5%). In terms of the location (intermolecular separation) of the potential energy minimum, the two methods are in relatively good agreement, meaning that optima are within 0.1 Å of each other for all four curves. Generally, in terms of both interaction energies and intermolecular separations, the agreement between ω B97X-D/def2-TZVP and the reference method are relatively good, and it can be said that results presented based on ω B97X-D/def2-TZVP/C-PCM calculations are semi-quantitative, indicating that the observed general trends are meaningful.

Plots of the angular dependence of the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ interaction energy at several different R(Br...Cl) distances are given in Figure 7. The overall shapes of the curves depicted here strongly resemble the SAPT interaction energy curves shown in Figure 5, with the potential energy minimum corresponding to the linear structure for short R(Br...Cl) distances and to the α (C-Br...Cl) = 90° structure for long distances. Focusing on the shortest R(Br...Cl) distance given here (3.0 Å) it is seen that the amount by which the linear structure is favored, when compared to the α (C-Br...Cl) = 90° structure, is slightly greater when medium effects are taken into account (11.1 kcal/mol) than in the gas phase, as computed using SAPT (8.0 kcal/mol). This difference is relatively small and may be attributable to the different computational methods being used. Focusing on long R(Br...Cl) distances, it can be seen that the potential energy curves at distances of 5.0 Å and 7.0 Å are almost identical. Here the α (C-Br...Cl) = 90° structure is favored (over the linear structure) by 2.2 kcal/mol at R(Br...Cl) = 5.0 Å and by 2.0 kcal/mol at R(Br...Cl) = 7.0 Å.

Here we change focus from the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ model complex to the 4-bromoanilinium...Cl⁻ complex, a real system whose crystal structure has been determined (see Figure 2). Figure 8 gives ω B97X-D/def2-TZVP/C-PCM potential energy curves, as a function of R(Br...Cl), at α (C-Br...Cl) angles of 180°, 150°, 120°, and 90°. It will be noted here that, for these potential energy curve structures, the C-Br...Cl angle is modified in such a way as to rotate the Cl⁻ out of the plane defined by the aromatic group in 4-bromoanilinium, thus minimizing the effects of interactions that are not specifically being studied here (halogen bond and Cl⁻-NH₃⁺ electrostatic interaction). Comparing these curves to those produced for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$, the most immediately apparent feature of the data depicted here is the fact that the halogen bond in the 4-bromoanilinium...Cl⁻ complex is significantly weaker than that of the reference model complex, with the lowest interaction energy of -11.62 kcal/mol occurring along the α (C-Br...Cl) = 180° curve. Inspection of the electrostatic potentials in Figure 1 indicates that positive potential is more evenly distributed throughout the larger 4-bromoanilinium molecular ion than is the case for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+$, with an ammonium group that is marginally less positive and a bromide that is significantly

less positive (by about 100 kcal/mol). Comparing the $V_{S,\max}$ value, a measure of the most positive potential on the halogen (i.e. the most positive point on the halogen σ -hole), of the two molecules, it is seen that the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ bromide σ -hole ($V_{S,\max} = 428$ kcal/mol) is significantly more positive than that of 4-bromoanilinium bromide ($V_{S,\max} = 300$ kcal/mol).

This difference in positive potential results in weaker interaction whose intermolecular separations are significantly longer than those of the model complex, with potential energy minima for the four curves of -11.62 ($3.19\text{\AA}$), -9.94 ($3.48\text{\AA}$), -9.33 ($3.97\text{\AA}$), and -11.13 ($3.97\text{\AA}$) kcal/mol in order of decreasing C-Br...Cl angle. There are, most likely, two effects that result in longer intermolecular separations for the present system, namely decreased electrostatic attraction and increased exchange forces. A less positive potential on the bromide in 4-bromoanilinium indicates an increase in the electron density on the bromide, which would, in turn, result in increased exchange repulsion.

The 4-bromoanilinium... Cl^- curves shown in Figure 8 have general features that are very similar to those given for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$, with the major distinction between the two being the enhanced stabilization of the $\alpha(\text{C}-\text{Br}\dots\text{Cl}) = 90^\circ$ curve relative to the other three curves, with the potential energy minimum at this angle having an interaction energy of -11.13 kcal/mol, which can be compared to the potential energy minimum for the linear structure, which is -11.62 kcal/mol. In the case of $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$, potential energy minima for C-Br...Cl angles of 90° and 180° are -13.91 and -19.46 kcal/mol, respectively. Although the halogen bond in 4-bromoanilinium... Cl^- is weaker than in $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$, there is no reason to believe that the electrostatic interaction between Cl^- and the ammonium group would be significantly different in the two complexes (for a given Cl^- - NH_3^+ distance). Thus, the 4-bromoanilinium... Cl^- complex exhibits a larger degree of stabilization than $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ upon rotation to $\alpha(\text{C}-\text{Br}\dots\text{Cl})$ to 90° .

Computational Methods

The SAPT2+36MP2/aTZ technique, a third-order SAPT method that includes third-order HF induction contributions and third-order MP2 contributions to induction and dispersion, is used to obtain accurate interaction energies that are divided into contributions from electrostatics, dispersion, induction, and exchange-repulsion terms.^{26–28} The SAPT2+36MP2/aTZ method has been shown to provide very accurate binding energies and is, among the family of SAPT techniques, among the optimal model chemistries for treating interactions between cations and anions.²⁹ All SAPT calculations are made using the Psi4 package.³⁰

Electrostatic potential maps are produced on the molecular ‘surface,’ taken to be the 0.001 electron/bohr contour of the molecule’s electron density. Molecular electronic densities are computed at the B3LYP/6-311G* level of theory. All molecular electrostatic potential maps are produced using Spartan molecular electronic structure program.³⁵

In order to investigate the effects of environmental factors on the strength and directionality of charged halogen bonds we produce potential energy curves for the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$

complex, as functions of both $R(\text{Br}\dots\text{Cl})$ and $a(\text{C}-\text{Br}\dots\text{Cl})$ using the $\omega\text{B97X-D/def2-TZVP}$ method along with the C-PCM implicit solvent model to mimic the crystal environment.^{31–34} The $\omega\text{B97X-D}$ functional includes an empirical dispersion correction term, which is important for describing halogen bonds, and are designed to yield improved results at long intermolecular separations, an issue that can be problematic for many DFT functionals. An additional reason for the use of a computational method that includes an empirical dispersion term is the fact that such methods are designed such as not to require the use of counterpoise corrections to account for the basis set superposition error. This is a critical point, as implicit solvation models, such as C-PCM, and counterpoise corrections are incompatible, meaning that they cannot be used together. The Spartan molecular electronic structure theory package was used for all $\omega\text{B97X-D/def2-TZVP/C-PCM}$ computations.³⁵

The C-PCM dielectric constant used for all calculations here is 4.33, corresponding to the dielectric constant of diethyl ether. To our knowledge, there are no known dielectric constants for halogen-containing molecular ionic crystals. Here we have chosen the, relatively low, dielectric constant value of 4.33 in order not to overestimate the effects of the environment on the energetic and geometric attributes of the charged halogen bonds being investigated. It is to be expected that higher dielectric constant values would serve to further destabilize the halogen bonding complexes. As a point of reference, we will note that the dielectric constants for ammonium bromide and sodium chloride salt crystals are 7.2 and 6.1, respectively.

Conclusions

Here we have shown that halogen bonds involving charged species, such as those observed in the crystal structure of 4-bromoanilinium chloride, are significantly stronger and equally as directional in nature when compared to their neutral halogen bonding counterparts. SAPT calculations have shown that, as might be expected for ionic pairs, attraction is largely attributable to electrostatic forces, meaning that these pairs form attractive interactions over much longer distances. For $\text{C}-\text{Br}\dots\text{Cl}$ angles at which the secondary interaction that occurs between Cl^- and the cation ammonium group (angles greater than $\sim 120^\circ$) enhanced exchange repulsion associated with the halogen's oblate shape can be said to be chiefly responsible for halogen bond directionality, as has been found for neutral halogen bonds. For these halogen bonds involving charged species, it has also been found that induction, which generally plays a very small role in the directionality of neutral halogen bonds, has a more pronounced impact in mediating halogen bond directionality in these charged systems.

It is worth mentioning here that the halogen bond found in the 4-bromoanilinium chloride crystal structure does not represent the ideal $a(\text{C}-\text{Br}\dots\text{Cl})=180^\circ$ configuration. This is not surprising, as the position and orientation of the 4-bromoanilinium molecular ion is not determined solely by a halogen bond, but by several noncovalent interactions. Based on curves in Figure 8 it can easily be estimated that the $\text{Br}^+\dots\text{Cl}^-$ halogen bond within the crystal structure, with an $R(\text{Br}\dots\text{Cl})$ distance of $3.59\text{\AA}$ and a $\text{C}-\text{Br}\dots\text{Cl}$ angle of 165.9° would have an interaction energy of roughly 10.5 kcal/mol .

Given the strength and strong directionality of the charged halogen bonds described here, it seems clear that these noncovalent interactions can play significant roles in stabilizing the crystal structures of salts and are likely to have a strong impact on determining the geometries of these crystal structures.

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Figure 1. B3LYP/6-31G* Electrostatic potential maps, in kcal/mol for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+$ (Left), 4-bromoanilinium (center), and bromoacetylene (right). $V_{S,\text{max}}(\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+) = 428$ kcal/mol; $V_{S,\text{max}}(\text{bromoanilinium}) = 300$ kcal/mol. Please note different potential scales for each of the molecules.

Figure 2.

Crystal structure of 4-bromoanilinium chloride. Halogen bonds, indicated with cyan dashed lines, have a Br...Cl distance of 3.59Å and a C-Br...Cl angle of 165.9°.

Figure 3. SAPT interaction energies as a function of Br...Cl distance for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\cdots\text{Cl}^-$ complex.

Figure 4.

SAPT interaction energy terms for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\cdots\text{Cl}^-$ complex. $a(\text{C}-\text{Br}\cdots\text{Cl}) = 180^\circ$ shown in solid, $a(\text{C}-\text{Br}\cdots\text{Cl}) = 180^\circ$ shown as dashed. Red = electrostatic, green = exchange, blue = dispersion, magenta = induction, black = $\Delta E(\text{int})$.

Figure 5. SAPT interaction energy terms for $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\cdots\text{Cl}^-$ complex in terms of $a(\text{C}-\text{Br}\cdots\text{Cl})$ angle. Top: $R(\text{Br}\cdots\text{Cl}) = 3.0 \text{ \AA}$; Bottom: $R(\text{Br}\cdots\text{Cl}) = 3.8 \text{ \AA}$.

Figure 6.
 $\omega\text{B97x-D/def2-TZVP/PCM}(\epsilon=4.33)$ potential energy curves $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ as a function of $R(\text{Br}\dots\text{Cl})$ distance.

Figure 7.
 $\omega\text{b97X-D/def2-TZVP/PCM}(\epsilon=4.33)$ interaction energy terms for $\text{H}_3\text{N-C}\equiv\text{C-Br}^+\cdots\text{Cl}^-$ complex as a function of $a(\text{C-Br}\cdots\text{Cl})$ angle.

Figure 8. $\omega\text{b97X-D/def2-TZVP/PCM}(\epsilon=4.33)$ interaction energy terms for $\text{H}_3\text{N-Benz-Br}^+\dots\text{Cl}^-$ complex as a function of $R(\text{Br}\dots\text{Cl})$ distance.

Table 1

SAPT, gas-phase ω B97X-D, and C-PCM($\epsilon=4.33$) potential energy minimum interaction energies (kcal/mol) and intermolecular separations ($\text{\AA}$, in parentheses) for the $\text{H}_3\text{N}-\text{C}\equiv\text{C}-\text{Br}^+\dots\text{Cl}^-$ complex at four different $\text{a}(\text{C}-\text{Br}\dots\text{Cl})$ angles.

	$\text{a}(\text{C}-\text{Br}-\text{Cl}) = 180^\circ$	$\text{a}(\text{C}-\text{Br}-\text{Cl}) = 150^\circ$	$\text{a}(\text{C}-\text{Br}-\text{Cl}) = 120^\circ$	$\text{a}(\text{C}-\text{Br}-\text{Cl}) = 90^\circ$
SAPT	-78.66 (2.64)	-71.74 (2.73)	-62.79 (3.06)	-66.78 (3.14)
ω B97X-D/gas	-85.37 (2.56)	-77.74 (2.71)	-66.87 (2.98)	-68.27 (3.18)
ω B97X-D/C-PCM	-19.46 (2.88)	-15.68 (3.11)	-12.56 (3.64)	-13.91 (3.82)