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σ-hole bonding between like atoms; a fallacy of atomic charges

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Abstract Covalently bonded atoms, at least in Groups V–VII, may have regions of both positive and negative electrostatic potentials on their surfaces. The positive regions tend to be along the extensions of the bonds to these atoms; the origin of this can be explained in terms of the σ-hole concept. It is thus possible for such an atom in one molecule to interact electrostatically with its counterpart in a second, identical molecule, forming a highly directional noncovalent bond. Several examples are presented and discussed. Such "like-like" interactions could not be understood in terms of atomic charges assigned by any of the usual procedures, which view a bonded atom as being entirely positive or negative.

Keywords σ-hole bonding · Noncovalent interactions · Electrostatic potentials · Like-like interactions

Introduction

The qualitative idea that some atoms in a molecule are more positive or more negative than others, i.e., the concept of electronegativity, has been very useful in rationalizing and predicting chemical behavior. However, attempts to quantify this idea have had mixed success. Neither electroneg-

ativity nor atomic charge is a physical observable, and thus neither has a unique mathematical formulation. Instead, numerous procedures have been, and continue to be, proposed for assigning numerical values to atomic electronegativities and charges. For some overviews, see Allen [1], Meister and Schwarz [2], Bergman and Hinze [3] and Politzer et al. [4].

The difficulties associated with electronegativity and atomic charge not being physical observables are well known, and we do not intend to discuss them further. We wish, rather, to draw attention to a common fallacy related to atomic charges: they are typically viewed as global. The entire atom is assigned a single numerical positive or negative charge; in effect, it is being treated as a point charge. While this is valid for monatomic ions, it is in general not true for atoms in molecules. The charge distributions on their surfaces and the resulting electrostatic potentials are not uniform. The potential is nonuniform even if it is all positive or all negative; however, it is often not limited to being one or the other. We and others have found many examples of covalently bonded Group V, VI and VII atoms that have regions of both positive and negative electrostatic potential on their surfaces [5–13]. It should be possible for such an atom in one molecule to interact electrostatically with its counterpart in another molecule of the same type to form a noncovalent bond. In terms of global atomic charges, such an interaction would be repulsive, because it would be "like attracting like."

In this paper, we will look in detail at the electrostatic potentials on the surfaces of several covalently bonded atoms, and at the electrostatically driven noncovalent bonds that can be formed between like atoms. Our focus will be specifically upon such "like-like" interactions; accordingly, we will not specifically look for others that may be possible between the same molecules.

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Procedure

Our analytical tool is the molecular electrostatic potential, V($\mathbf{r}$), defined by Eq. 1:

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \tag{1}$$

V($\mathbf{r}$) is the electrostatic potential created by the nuclei and electrons of a molecule at the point $\mathbf{r}$; Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the molecular electronic density. V($\mathbf{r}$) will be positive or negative in a given region depending upon whether the contribution of the nuclei or that of the electrons is dominant there. V($\mathbf{r}$) is a physical observable; it can be obtained experimentally [14, 15] as well as computationally.

For studying interactive tendencies, we normally compute V($\mathbf{r}$) on the surface of the molecule; the result is labeled $V_S(\mathbf{r})$. While a molecular surface is not a physical observable, an effective representation of it has been found to be the 0.001 au (electrons/Bohr^3) contour of $\rho(\mathbf{r})$, as suggested by Bader et al. [16]. The most positive and most negative values of $V_S(\mathbf{r})$ are designated $V_{S,max}$ and $V_{S,min}$. There may be several such local maxima and minima on a molecular surface.

The $V_S(\mathbf{r})$ of the individual molecules considered were obtained with the density functional B3PW91/6–31G(d,p)// B3PW91/6–31G(d,p) procedure. Interaction energies were calculated at a higher computational level, MP2-FC/6-311+ +G(3df,2p)//B3PW91/6–311G(3df,2p). The use of such large basis sets should minimize basis set superposition error, which was accordingly not evaluated. The interaction energies are the differences in the energy minima, products minus reactants, at 0 K. (Our experience with σ-hole-bonded complexes has been that MP2-FC/6-311++G (3df,2p) and B3PW91/6-311G (3df,2p) interaction energies, with the same geometries, are generally within 1–2 kcal mol^{-1} of each other [12, 13].)

Electrostatic potentials on the surfaces of some covalently bonded atoms

Consider first a free, spherically symmetrical neutral atom. On any surface at a radial distance r from the nucleus, $V_S(\mathbf{r})$ is positive [17] and uniform over that surface. Negative $V_S(\mathbf{r})$ develop through interactions with other atoms to form molecules.

Figure 1 presents the $V_S(\mathbf{r})$ of 2-chloropropane, $(CH_3)_2C(H)Cl$. The chlorine surface is entirely negative; however, its outer portion, centered around the extension of the C–Cl bond, is less so. In the middle of this outer region, $V_S(\mathbf{r})$ is −5.7 kcal mol^{-1}, which is its least negative value

Fig. 1 Calculated electrostatic potential on the surface of 2-chloropropane, $(CH_3)_2C(H)Cl$. The chlorine is on the right. Color ranges (kcal mol^{-1}): *purple* more negative than −10, *blue* between −10 and 0, *green* between 0 and 6, *yellow* between 6 and 12, *red* more positive than 12
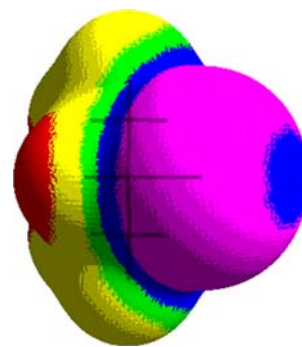
(and therefore $V_{S,max}$), whereas $V_S(\mathbf{r})$ reaches a $V_{S,min}$ of −18.5 kcal mol^{-1} on the sides (Table 1). Thus, this chlorine is globally negative, but not uniformly so; its most negative values are on its sides, becoming less so toward the outer tip and toward the carbon.

Now let's look at chlorine in another molecule, SCl_2, in Fig. 2a and Table 1. Here, each chlorine's outer tip has actually become positive, with a $V_{S,max}$ of 13.3 kcal mol^{-1}. The angle S−Cl−$V_{S,max}$ is 178°, confirming that the $V_{S,max}$ is essentially on the extension of the S−Cl bond. The sides of the chlorines are negative, $V_{S,min}$=−5.9 kcal mol^{-1}. The chlorines in SCl_2 clearly cannot be described as either globally positive or globally negative.

This is also true for the sulfur in SCl_2, Fig. 2b. It has *two* buildups of positive potential on its surface, one along the extension of each Cl−S bond. The $V_{S,max}$ are 25.1 kcal mol^{-1}, the Cl−S−$V_{S,max}$ angles are 180°. However, the sides of the sulfur are negative, $V_{S,min}$=−5.9 kcal mol^{-1}.

Proceeding to another halogen, the bromine in BrOH, Fig. 3 and Table 1 show it to have a positive outer portion, with a $V_{S,max}$ of 30.6 kcal mol^{-1} very close to the point where the extension of the O−Br bond intersects the bromine surface. The O−Br−$V_{S,max}$ angle is 178°. The sides of the bromine are negative, as can be seen in Fig. 3.

Table 1 Most positive ($V_{S,max}$) and most negative ($V_{S,min}$) electrostatic potentials on the surfaces of the indicated Group V, VI or VII atoms, in kcal mol^{-1}, computed at the B3PW91/6-31G(d,p) level. The $V_{S,max}$ are in all instances approximately along the extensions of the bonds

Molecule	$V_{S,max}$ along extension of bond[a]			
	Atom	Bond	$V_{S,max}$	$V_{S,min}$
$(CH_3)_2C(H)Cl$	Cl	C-Cl	−5.7 (1)	−18.5 (2), −18.4 (1)
SCl_2	Cl	S-Cl	13.3 (1)	−5.9 (2)
	S	Cl-S	25.1 (2)	−5.9 (2)
BrOH	Br	O-Br	30.6 (1)	−[b]
AsH_2F	As	F-As	37.2 (1)	−5.3 (1)
	As	H-As	15.9 (2)	

[a] Number of each $V_{S,max}$ and $V_{S,min}$ given in parentheses
[b] Negative potential on sides of bromine merges with that of oxygen, and no $V_{S,min}$ can be identified on the former
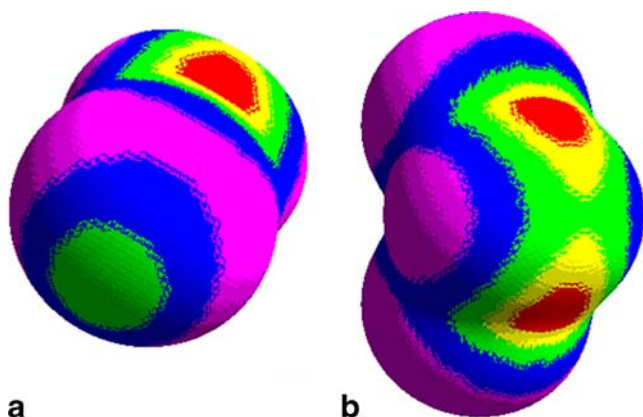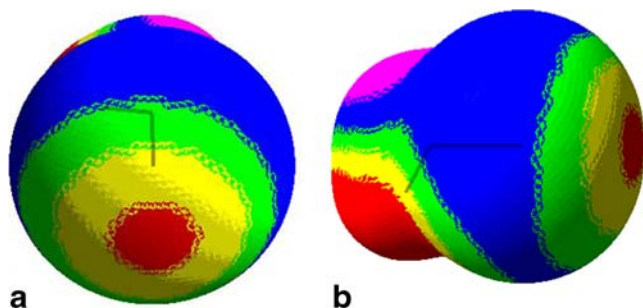
Fig. 2 Calculated electrostatic potential on the surface of SCl_2. Two views are shown: **a** one of the chlorines is in the foreground, **b** the sulfur is in the foreground, the chlorines are at the back. Color ranges (kcal mol^{-1}): *purple* negative, *blue* between 0 and 8, *green* between 8 and 15, *yellow* between 15 and 20, *red* more positive than 20
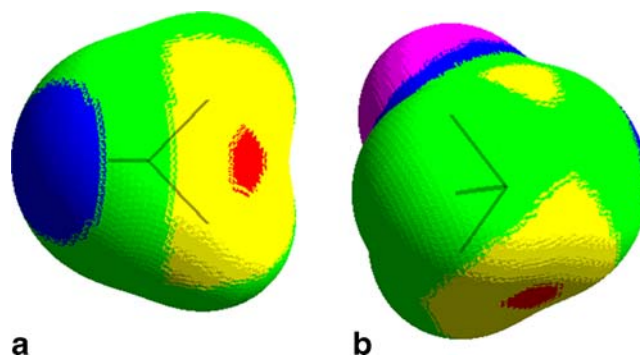
Therefore it cannot be described as globally positive or negative.

Our final example is the arsenic atom in AsH_2F. It has three $V_{S,max}$. The strongest, 37.2 kcal mol^{-1}, is roughly along the extension of the F−As bond, (Fig. 4a, Table 1). The F−As−$V_{S,max}$ angle is 159°. Next to this is a negative region, $V_{S,min} = -5.3$ kcal mol^{-1}. The other two, weaker, $V_{S,max}$ are near the extensions of the H−As bonds; their magnitudes are 15.9 kcal mol^{-1}, with H−As−$V_{S,max}$ angles of 152°. One of these $V_{S,max}$ can be seen in Fig. 4b, along with another view of the strong $V_{S,max}$. The fact that the F−As−$V_{S,max}$ and H−As−$V_{S,max}$ angles deviate more from 180° than the corresponding angles in SCl_2 and BrOH can be attributed to the greater proximity, and thus interactions, between the three atoms bonded to the arsenic compared to the two to sulfur and one to bromine.

In this section, we have presented examples of four covalently bonded atoms—one in Group V (As in AsH_2F), one in Group VI (S in SCl_2) and two in Group VII (Cl in SCl_2, Br in BrOH)—that have both positive and negative electrostatic potentials on their surfaces, the former being
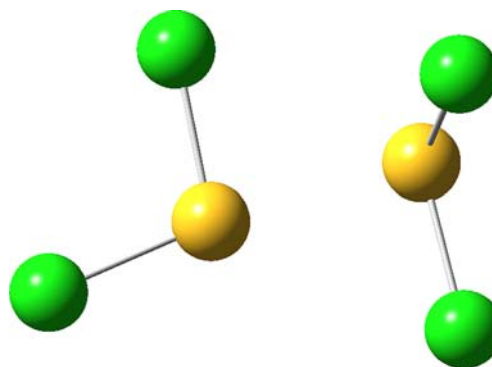

Fig. 4 Calculated electrostatic potential on the surface of AsH_2F. Two views are shown. In both views, the arsenic is in the foreground. Color ranges (kcal mol^{-1}): *purple* more negative than −10, *blue* between −10 and 0, *green* between 0 and 13, *yellow* between 13 and 33, *red* more positive than 33

approximately along the extensions of the covalent bonds to these atoms. It would accordingly not be valid to assign a global positive or negative charge to any of these atoms. Even if this charge were designed to be the net result of the positive and negative contributions, it would hide the fact that the atom can interact electrostatically through both the positive and the negative regions separately. That this is indeed possible will be demonstrated in the next section.

"Like can attract like"

Figures 5, 6 and 7 illustrate the complexes formed by the interactions of two SCl_2 molecules through their sulfur atoms, two BrOH through their bromines, and two AsH_2F through their arsenics. The computed interaction energies and the atom–atom separations are listed in Table 2, along with the sums of the respective van der Waals radii [18].

In the complex $Cl_2S\cdots SCl_2$, it can be seen in Fig. 5 that one of the positive $V_S(r)$ regions on the sulfur at the left, along the extension of the Cl−S bond, is interacting with the negative potential on the side of the sulfur at the right (see Fig. 2). The Cl−S−S angle is 169°, just 11° away from exact linearity. The S—S separation of 3.17 Å is much less

Fig. 3 Calculated electrostatic potential on the surface of BrOH. Two views are shown: **a** bromine in the foreground, **b** bromine to the right. Color ranges (kcal mol^{-1}): *purple* more negative than −12, *blue* between −12 and 0, *green* between 0 and 10, *yellow* between 10 and 25, *red* more positive than 25


Fig. 5 Complex between two SCl_2 molecules interacting through the two sulfur atoms, $Cl_2S\cdots SCl_2$

than the sum of two sulfur van der Waals radii, 3.66 Å, confirming the occurrence of a noncovalent interaction.

The HOBr---BrOH system, shown in Fig. 6, has the interesting feature that there are two interactions. One is very clearly between the positive potential on the outer portion of the bromine at the right and the negative region on the side of the bromine at the left (Fig. 3). The Br---Br distance is 3.21 Å, compared to 3.70 Å as the sum of the van der Waals radii. The second interaction is a hydrogen bond, involving the hydrogen of the molecule on the left and the negative potential on the side of the bromine at the right; their separation is 2.64 Å, which is 0.38 Å less than the sum of their van der Waals radii. The positive nature of the BrOH hydrogen is quite apparent in Fig. 3b; its $V_{S,max}$ is 56.1 kcal mol^{-1}. The total interaction energy is −3.5 kcal mol^{-1}.

The FH$_2$As---AsH$_2$F complex in Fig. 7 also has a notable feature in that it appears to be a double interaction. The positive region on the extension of each F−As bond is interacting with the negative potential on the other arsenic atom; see Fig. 4a and structure below:
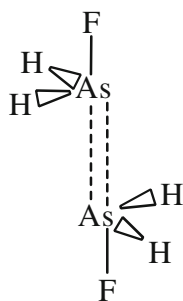

The As---As distance of 2.90 Å is well below the sum of the arsenic van der Waals radii. Figure 7 brings out particularly well the directional aspect of the interactions being discussed in this paper.

What we see in Figs 5, 6 and 7 and Table 2 are highly directional noncovalent interactions between the same atoms X in two identical molecules. The importance of the electrostatic factor in these interactions is indicated by their directional nature; they are always close to being along the extension of one of the covalent bonds to atom X, where the latter has a region of positive potential, and are
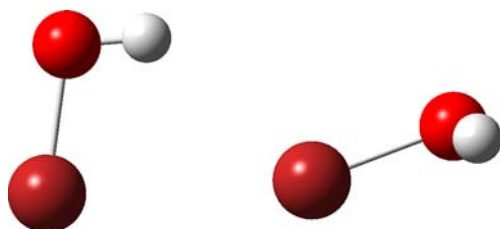
Fig. 6 Complex between two BrOH molecules, interacting through the two bromine atoms and also the hydrogen on the left with the bromine on the right

Fig. 7 Complex between two AsH$_2$F molecules interacting through the two arsenic atoms, FH$_2$As---AsH$_2$F
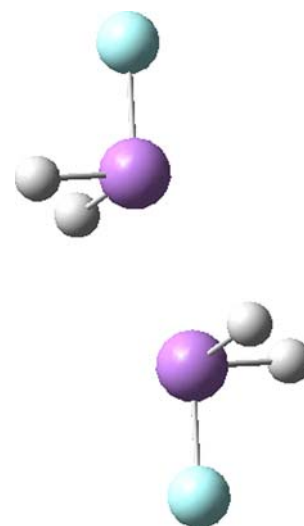
directed toward a negative region on the other atom X. We do not intend to discuss what fractions of the interaction energies may be due to other factors, such as dispersion, but it seems to be justified to describe the formation of these complexes as electrostatically driven. They could not be predicted in terms of global atomic charges, which would necessarily be the same for atom X in both molecules, resulting in electrostatic repulsion. Thus, in Figs 5, 6 and 7 we have "like attracting like" (referring to the atoms in the molecules, *not* charges or electrostatic potentials).

Noncovalent interactions between like bonded atoms have been observed earlier, both experimentally [19] and computationally [20, 21]. However, it was not recognized that these can be explained in terms of positive and negative potentials on an atom's surface.

The σ-hole concept

Why do the S, Cl, Br and As atoms in SCl$_2$, BrOH and AsH$_2$F have positive electrostatic potentials centered approximately along the extensions of the bonds to those atoms? What is the origin of these potentials and the reason for their directionality? Why does the Cl in (CH$_3$)$_2$C(H)Cl

Table 2 Computed interaction energies and separations in complexes, MP2-FC/6-311++G(3df,2p)//B3PW91/6-311G(3df,2p)

Complex	ΔE (kcal mol^{-1})[a]	Separation, Å	Sum, van der Waals radii, Å[b]
Cl$_2$S---SCl$_2$	−5.5	S---S: 3.17	S---S: 3.66
HOBr---BrOH	−3.5	Br---Br: 3.21	Br---Br: 3.70
		H---Br: 2.64	H---Br: 3.02
FH$_2$As---AsH$_2$F	−4.1	As---As: 2.90	As---As: 3.70

[a] Difference of energy minima at 0 K, product minus reactants
[b] Reference 18

have not a positive but only a weaker negative potential in this region?

These questions can be answered in terms of the σ-hole concept. This has been discussed in detail elsewhere [8, 9, 11–13, 22], and will be only briefly summarized here. Let's consider, for example, a Group VI atom X. In the free atom, its valence configuration is s^2, p_x^2, p_y^1, p_z^1. When present in the molecule R_1R_2X, the R_1-X and R_2-X bonds involve the half-filled p_y and p_z orbitals, probably with some level of s-p hybridization. If there is relatively little hybridization, so that the bonds are being formed by electrons in nearly pure p orbitals, then the outer lobes of these orbitals (which are not involved in bonding) should be deficient in electronic charge, possibly resulting in the development of positive potentials. These would of course be along the extensions of the R_1-X and R_2-X bonds. The σ-hole is the electron-deficient outer lobe of a half-filled p bonding orbital.

The σ-hole concept can readily be extended to Groups V and VII, and explains why Group V bonded atoms may have as many as three localized positive centers on their surfaces (arising from three half-filled p orbitals) and Group VII atoms only one. A key requirement is that the degree of s-p hybridization be low, since this introduces some s electronic charge into the outer lobe, reducing the electron deficiency. Natural bond orbital analyses have shown that s-p hybridization decreases rapidly and progressively in going from the lighter to the heavier elements within a Group [9, 12, 13].

The electron deficiency, and hence the σ-hole, should be enhanced as the atom X becomes less electronegative and more polarizable. These two factors operate in the same direction as that of hybridization: if all else is the same, the σ-holes become stronger and the $V_{S,max}$ on the extensions of the bonds more positive in the orders N < P < As < Sb, O < S < Se < Te and F < Cl < Br < I. This prediction has been confirmed, as shall be discussed in the next section.

The potential along the extension of a bond R−X to a Group V – VII atom should also become more positive as R is more electron-withdrawing. This is why the $V_{S,max}$ due to the F−As bond in AsH_2F is much more positive than those arising from the H−As bonds, and the chlorine $V_{S,max}$ in SCl_2 are more positive than that in $(CH_3)_2C(H)Cl$ (Table 1).

σ-hole bonding

In a series of studies, we have examined the computed $V_S(r)$ on the surfaces of covalently bonded Group V – VII atoms in a large number of molecules [8–13, 22]. We have generally found indications of the presence of σ-holes on the extensions of the bonds to those atoms. Even when they are not strong enough to produce positive potentials, they do result in a less negative region, as in the case of $(CH_3)_2C(H)Cl$ (Fig. 1).

Table 3 lists the positive $V_{S,max}$ found on the extensions of the covalent bonds in a representative group of the molecules investigated. The trends observed fully confirm the predictions made in the last section. The lightest elements in a Group (N, O, F) typically do not have positive $V_{S,max}$ unless the remainder of the molecule is quite strongly electron-withdrawing; compare H_3CF and NC−C≡CF, or $(CH_3)_2O$ and $O(CN)_2$ in Table 3. For a given molecular environment, $V_{S,max}$ always increases progressively in going from the lightest to the heavier atoms in the Group; cf. $O(CN)_2$, $S(CN)_2$ and $Se(CN)_2$. The effect of the electron-withdrawing power of the group R in each R−X bond is quite evident, especially when the atom

Table 3 Positive $V_{S,max}$ on the surfaces of the indicated Group V, VI or VII atoms, in kcal mol^{-1}, computed at the B3PW91/6-31G(d,p) level. The $V_{S,max}$ are in all instances approximately along the extensions of the bonds

Molecule	Atom	Bond	Positive $V_{S,max}$[a,b]
CH_3F	F	C−F	None
CH_3Cl	Cl	C−Cl	None
CH_3Br	Br	C−Br	5.9
HC≡CF	F	C−F	2.3
HC≡CCl	Cl	C−Cl	20.4
HC≡CBr	Br	C−Br	27.0
NC−C≡CF	F	C−F	16.9
NC−C≡CCl	Cl	C−Cl	35.0
NC−C≡CBr	Br	C−Br	41.6
$(CH_3)_2O$	O	C−O	None
$(CH_3)FO$	O	F−O	11.9
	O	C−O	None
$(CH_3)_2S$	S	C−S	None
$(CH_3)FS$	S	F−S	28.8
	S	C−S	4.9
$(CH_3)_2Se$	Se	C−Se	None
$(CH_3)FSe$	Se	F−Se	34.8
	Se	C−Se	9.6
$O(CN)_2$	O	C−O	31.0 (2)
$S(CN)_2$	S	C−S	42.7 (2)
$Se(CN)_2$	Se	C−Se	46.9 (2)
$N(CH_3)_3$	N	C−N	None
$NF(CH_3)_2$	N	F−N, C−N	None
NF_3	N	F−N	14.5 (3)
	F	N−F	3.0
$P(CH_3)_3$	P	C−P	None
$PF(CH_3)_2$	P	F−P	20.0
	P	C−P	None
PF_3	P	F−P	27.8 (3)
$As(CH_3)_3$	As	C−As	7.7 (3)
$AsF(CH_3)_2$	As	F−As	25.4
	As	C−As	None
AsF_3	As	F−As	34.7 (3)

[a] When there is more than one $V_{S,max}$ of a given value, this is indicated in parentheses
[b] Group V $V_{S,max}$ are from reference [13], Group VI from reference [12] and Group VII from reference [11]

X is bonded to different partners; this was already seen for AsH_2F (Table 1, Fig. 4) but can be noted again in PF $(CH_3)_2$, CH_3FO, CH_3FS, CH_3FSe and $AsF(CH_3)_2$ (Table 3).

Our focus in this paper is upon "like-like" interactions, involving the positive σ-hole $V_{S,max}$ on atom X in one molecule and a negative region on X in another molecule of the same type. However the σ-hole positive potential may of course interact attractively with any nucleophile, e.g., a Lewis base such as NH_3, pyridine, etc. This has been shown both experimentally [19, 23–28, and references therein] and computationally [8, 9, 11–13, 22, 29–32], although not always described in terms of the σ-hole concept. (One proposed explanation, offered for Group VII atoms, invokes reported anisotropies of their charge distributions [32]; however, this is fully consistent with the σ-hole concept, as we have pointed out [8].) The interactions involving Group VII atoms have commonly been labeled "halogen bonding;" however, we now view them as simply an example of what we call "σ-hole bonding."

The strengths of σ-hole bonds are, overall, comparable to hydrogen bonds [22]; indeed halogen bonding has been demonstrated experimentally to be competitive with hydrogen bonding [23, 24, 33]. This was also shown computationally for σ-hole bonding in general [22]. Typically, σ-hole bonding is stronger when it involves the heavier elements in Groups V–VII, which have the more positive $V_{S,max}$; for example, $\Delta E = -12.2$ kcal mol^{-1} for $H_3N\cdots SeF_2$ [12], and $\Delta E = -8.6$ kcal mol^{-1} for $HCN\cdots As(CN)_3$ [13]. For molecules within a given Group that differ only in the atom of that Group, e.g. $(CH_3)FO$, $(CH_3)FS$ and $(CH_3)FSe$, the magnitudes of their interaction energies with a particular nucleophile will normally increase as $V_{S,max}$ becomes more positive. However, there is not a general correlation between $|\Delta E|$ and $V_{S,max}$ when the molecules are from different Groups and/or have different components, due, at least in part, to the interactions between these components and the nucleophiles [22].

Another word of caution is that the presence of a positive σ-hole may not lead to a stable interaction with a nucleophile, if the $V_{S,max}$ and/or the $V_{S,min}$ of the nucleophile are too weak. An example is SCl_2 (Fig. 2, Table 1). While we did find like–like bonding between the sulfurs on two SCl_2 molecules, we did not obtain a stable $ClSCl\cdots ClSCl$ complex. The chlorines do have both positive σ-holes and negative regions on their sides, but these are (as a pair) too weak: $V_{S,max} = 13.3$, $V_{S,min} = -5.9$ kcal mol^{-1}.

It should be noted that, while the presence of a reasonably positive σ-hole permits noncovalent bonding with an appropriate nucleophile, it is not sufficient for like–like interactions such as have been discussed in this paper;

these require that the atom also has significant negative regions. If a Group V, VI or VII atom is bonded to strongly electron-withdrawing groups, it may be that its entire surface is positive, although the σ-hole(s) will still have the largest $V_{S,max}$ and can readily form σ-hole bonds to other nucleophiles. Such an atom cannot participate in like–like interactions (a special case of σ-hole bonding). This is the case, for example, for $As(CN)_3$ [13].

Summary

We have shown that the occurrence of a highly directional electrostatic interaction to form a noncovalent bond between an atom in one molecule and its counterpart in a second identical molecule can be explained by recognizing that a bonded atom can have regions of both positive and negative electrostatic potential on its surface. In terms of global atomic charges, assigned by any procedure, such an attraction could not occur.

The origin of localized positive regions of electrostatic potential on some bonded atoms, along the extensions of the covalent bonds to those atoms, can be understood on the basis of the σ-hole concept. The interactions of these with nucleophiles, known both experimentally and computationally, come under the heading of "σ-hole bonding." The interactions between like atoms mentioned above are a special case of σ-hole bonding, in which a given atom has both positive and negative regions.

We do not claim that σ-hole bonding is entirely electrostatic; there may well be other contributions. However, its highly directional nature, which coincides with the locations of the positive centers on the atoms' surfaces, does indicate that it is electrostatically driven.

A final point, brought up earlier by Auffinger et al. [7]: The fact that bonded atoms can sometimes have both positive and negative surface regions needs to be taken into account in designing force fields, e.g., in molecular dynamics. These often represent atoms by single point charges in calculating electrostatic interactions.

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