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Expansion of the σ-hole concept

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Abstract The term "σ-hole" originally referred to the electron-deficient outer lobe of a half-filled *p* (or nearly *p*) orbital involved in forming a covalent bond. If the electron deficiency is sufficient, there can result a region of positive electrostatic potential which can interact attractively (non-covalently) with negative sites on other molecules (σ-hole bonding). The interaction is highly directional, along the extension of the covalent bond giving rise to the σ-hole. σ-Hole bonding has been observed, experimentally and computationally, for many covalently-bonded atoms of Groups V–VII. The positive character of the σ-hole increases in going from the lighter to the heavier (more polarizable) atoms within a Group, and as the remainder of the molecule becomes more electron-withdrawing. In this paper, we show computationally that significantly positive σ-holes, and subsequent noncovalent interactions, can also occur for atoms of Group IV. This observation, together with analogous ones for the molecules $(H_3C)_2SO$, $(H_3C)_2SO_2$ and Cl_3PO, demonstrates a need to expand the interpretation of the origins of σ-holes: (1) While the bonding orbital does require considerable *p* character, in view of the well-established highly directional nature of σ-hole bonding, a sizeable *s* contribution is not precluded. (2) It is possible for the bonding orbital to be doubly-occupied and forming a coordinate covalent bond.

Keywords Electrostatic potentials · Group IV atoms · Noncovalent interactions · σ-hole · σ-hole bonding

Background

The σ-hole concept was introduced by Clark et al. [1] in the context of halogen bonding, which is a well-established noncovalent interaction between some covalently-bonded halogens and negative sites on other molecules, e.g., lone pairs of Lewis bases. (For reviews, see Metrangolo et al. [2, 3] and Politzer et al. [4].) Since bonded halogens are commonly viewed as being negative in character, such "negative-negative" interactions were puzzling, until Brinck et al. [5], and subsequently others [6, 7], showed that the halogen atoms X in some molecules RX have regions of positive electrostatic potential on their outer surfaces, on the extensions of the R—X bonds. The remainder of the halogen surface is usually negative.

Halogen bonding could thus be explained as the electrostatic attraction between the positive potential of the halogen and the negative site on the other molecule. But what is the origin of such positive potentials, and why are they found on some bonded halogens and not others? The interpretation given by Clark et al. [1] was that when a half-filled *p* orbital on the halogen participates in forming a covalent bond, there results an electron deficiency in the outer (noninvolved) lobe of that *p* orbital. This was called a σ-hole. If the electron deficiency is sufficient, a positive electrostatic potential is associated with the σ-hole, creating the possibility of an attractive electrostatic interaction with a negative site. This explanation also accounts for the remarkable directionality of halogen bonding, which is essentially along the extension of the R—X bond; the angle R—X- - -base is usually close to 180°.

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σ-Holes tend to be more positive as the halogen atom is more polarizable, i.e., F < Cl < Br < I. Thus positive σ-holes are uncommon (but not unknown [8, 9]) on bonded fluorines. A second important factor is the electron-withdrawing power of the remainder of the molecule; the greater it is, the more positive is the σ-hole. The strengths of halogen bonding interactions with a given negative site correlate, in general, with the magnitudes of the positive electrostatic potentials associated with the σ-holes [8, 10].

It is now recognized that covalently-bonded atoms of Groups V and VI can also participate in noncovalent interactions through positive σ-holes [11, 12]. (We refer to such interactions as σ-hole bonding, which of course includes halogen bonding.) This can similarly be interpreted in terms of electron deficiencies (σ-holes) in the outer lobes of the half-filled *p* (or nearly *p*) orbitals that are involved in the covalent bonds. Since Group V and VI atoms have three and two half-filled *p* orbitals, respectively, they can have three and two σ-holes on their surfaces, on the sides opposite to the covalent bonds. If these σ-holes have sufficiently positive electrostatic potentials, they can interact with negative portions of other molecules. This will again be highly directional, approximately along the extensions of the covalent bonds to the atoms.

As with Group VII, the magnitudes of the Group V and Group VI σ-hole potentials increase with the polarizability of the atom (N < P < As < Sb; O < S < Se < Te) and with the electron-withdrawing ability of the remainder of the molecule. Thus, while the sulfur in $H_3C—S—OCH_3$ has σ-holes on its surface on the extensions of both the C—S and the O—S bonds, only the second is positive, reflecting the greater electron withdrawal by the OCH_3 group [13]. In $H_3C—Se—OCH_3$, however, the more polarizable selenium has positive σ-holes on the extensions of both bonds (the σ-hole due to the $Se—OCH_3$ being the more positive). The first example illustrates the fact that σ-holes do not always have positive electrostatic potentials; they may simply be less negative than their surroundings.

The strengths of σ-hole bonds, in themselves, usually correlate approximately with the magnitudes of the σ-hole potentials. However the overall interaction energies may be significantly influenced by secondary interactions involving other portions of the molecules, as will be seen.

Our objectives in the present work have been two fold: (1) to show that covalently-bonded atoms of Group IV, as well as those of Groups V–VII, can have positive σ-holes and through them interact electrostatically to form complexes with negative sites, and (2) to expand the original interpretation of how σ-holes come to exist. The need for the second objective is a consequence of achieving the first, as well as our recent computational analysis of dimethylsulfoxide, $(H_3C)_2SO$, and dimethyl sulfone, $(H_3C)_2SO_2$ [14]. We found that σ-holes can result not only from half-filled *p*-type orbitals participating in covalent bonds but also from doubly-occupied orbitals forming coordinate covalent bonds.

The electrostatic potential on a molecular surface

The nuclei and electrons of a molecule produce an electrostatic potential V(**r**) in the surrounding space, which is given by

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

In Eq. (1), Z_A is the charge on nucleus A, located at R_A, and ρ(**r**) is the molecule's electronic density. V(**r**) is a physical observable, which can be obtained experimentally by diffraction methods [15, 16], as well as computationally. Its sign in any region depends upon whether the positive contribution of the nuclei or the negative one of the electrons is dominant there.

To use V(**r**) in analyzing noncovalent interactions, we customarily compute it on the surfaces of the molecules and label it $V_S(\mathbf{r})$. While any definition of a molecular surface is necessarily arbitrary, we have found an effective one to be the three-dimensional 0.001 au (electrons/bohr^3) contour of the electronic density ρ(**r**), as suggested by Bader et al. [17]. This has the advantage that it reflects the specific features of each molecule, e.g., lone pairs, π electrons, strained bonds, etc.

Earlier, we have demonstrated that a variety of physical properties that depend upon noncovalent interactions can be expressed analytically in terms of certain quantities that characterize the respective molecular surface electrostatic potentials $V_S(\mathbf{r})$ [18–20]. These quantities include the most positive and most negative values of $V_S(\mathbf{r})$ (denoted by $V_{S,max}$ and $V_{S,min}$), its average deviation, its positive and negative variances, etc. In the present context, it is particularly relevant that the $V_{S,max}$ of hydrogens and the $V_{S,min}$ of Lewis bases have been found to correlate with empirical measures of hydrogen bond donating and accepting tendencies [21].

Electrostatic potentials and noncovalent interactions of group IV molecules

We have optimized the geometries and computed the molecular surface electrostatic potentials $V_S(\mathbf{r})$, with the density functional B3PW91/6-31G(d,p) procedure, for a series of molecules containing the Group IV atoms C, Si and Ge. We also included one phosphorus derivative, Cl_3PO, which will be discussed later.

For some of these molecules, we then determined the interaction energies ΔE with Lewis bases; for this purpose, we optimized all geometries at the B3PW91/6-311G(3df,2p) level and used these to calculate ΔE, both B3PW91/6-311G (3df,2p) and MP2-FC/6-311++G (3df,2p), via Eq. (2),

$$\Delta E = E_{complex} - \sum (E_{reactant}) \tag{2}$$

$E_{complex}$ and $E_{reactant}$ are the respective energy minima at 0 K. The very large basis sets should minimize any basis set superposition error [22], which was accordingly not considered. We want to emphasize that our primary purpose in computing ΔE is simply to establish that stable interactions are occurring.

In Table 1 are listed the most positive electrostatic potentials (the $V_{S,max}$) on the surfaces of the Group IV atoms as well as on any halogens that may be present. These $V_{S,max}$ are all associated with positive σ-holes, and are located essentially on the extensions of the indicated covalent bonds to these atoms. (Hydrogen $V_{S,max}$ are not given.) For example, Fig. 1 shows the positive σ-holes on the silicon and the chlorines of $SiCl_4$. Also included in Table 1 are the most negative potentials (the $V_{S,min}$) on the Group IV atoms and the halogens.

Table 1 confirms that covalently-bonded Group IV atoms, just as those of Groups V–VII, can indeed form positive σ-holes. The trends in the magnitudes of their potentials, the $V_{S,max}$, follow the patterns observed for Groups V–VII. Within a given Group, the $V_{S,max}$ increase with the polarizability of the atom (C < Si < Ge, F < Cl < Br, etc.) and the degree of electron withdrawal by the remainder of the molecule, particularly by the partner in the covalent bond producing the σ-hole. Thus the carbon in CH_4 has no positive σ-holes, whereas the silicon in SiH_4 has a $V_{S,max}$ of 13.0 kcal/mole on the extension of each H—Si bond and germanium in GeH_4 has four $V_{S,max}$ of 14.0 kcal/mole. Carbon still does not have a $V_{S,max}$ in CH_3Cl, while the silicon in SiH_3Cl has one of 31.0 kcal/mole on the extension of the Cl—Si bond and three of 17.7 kcal/mole due to the three H—Si bonds. The analogous values in GeH_3Cl are 36.1 and 18.5 kcal/mole. In CCl_4, however, carbon does have four $V_{S,max}$ of 8.5 kcal/mole, which increase to 20.0 kcal/mole when the more electronegative fluorine is the substituent, in CF_4. The $V_{S,max}$ in the corresponding silicon and germanium tetrahalides are of course more positive, reaching 46.4 kcal/mole in GeF_4.

Looking at the halogens in Table 1, none of the fluorines have positive σ-holes, even when the rest of the molecule is the potent electron-withdrawer CF_3. In the past, we found positive $V_{S,max}$ on fluorines in only a few cases, including N≡C—F, F—C≡C—F, N≡C—C≡C—F [8] and F_2 [23]. However chlorine, being more polarizable, does have positive $V_{S,max}$ in CCl_4, $SiCl_4$ and $GeCl_4$.

Table 1 Most positive and most negative computed electrostatic potentials, $V_{S,max}$ and $V_{S,min}$, on surfaces of some covalently-bonded Group IV atoms and halogens

Molecule	Atom	$V_{S,max}$	Bond producing $V_{S,max}$	$V_{S,min}$
CH_4	C	None	None	−3.5 (4)
$H_3C{-}CH_3$	C	None	None	−2.9, −2.5 (3)
CH_3Cl	C	None	None	none
	Cl	None	None	−16.6
CCl_4	C	8.5 (4)	Cl—C	none
	Cl	18.3	C—Cl	−3.5
CF_4	C	20.0 (4)	F—C	none
	F	None	None	−2.1
SiH_4	Si	13.0 (4)	H—Si	none
$H_3C{-}SiH_3$	C	None	None	none
	Si	11.7 (3)	H—Si	none
		7.1	C—Si	
SiH_3Cl	Si	31.0	Cl—Si	none
		17.7 (3)	H—Si	
	Cl	None	None	−12.9
$SiCl_4$	Si	20.2 (4)	Cl—Si	none
	Cl	9.3	Si—Cl	−1.7
SiF_4	Si	43.8 (4)	F—Si	none
	F	None	None	−7.2
GeH_4	Ge	14.0 (4)	H—Ge	none
$H_3C{-}GeH_3$	C	None	None	none
	Ge	12.6 (3)	H—Ge	none
		7.5	C—Ge	
GeH_3Cl	Ge	36.1	Cl—Ge	none
		18.5 (3)	H—Ge	
	Cl	None	None	−14.7
$GeCl_4$	Ge	21.1 (4)	Cl—Ge	none
	Cl	9.9	Ge—Cl	−2.0
GeF_4	Ge	46.4 (4)	F—Ge	none
	F	None	None	−7.4
Cl_3PO	P	21.6	O—P	none
		19.4 (3)	Cl—P	
	Cl	17.0	P—Cl	none
	O	None	None	−26.7

One phosphorus derivative, Cl_3PO, is also included. When a given $V_{S,max}$ or $V_{S,min}$ is present more than once on a particular atom, this is indicated in parentheses. Calculations were at B3PW91/6-31G(d,p) level, and values are in kcal/mole.

An important point that is brought out by Table 1 is that some covalently-bonded atoms have regions of both positive and negative electrostatic potential on their surfaces. (Note, for instance, the chlorines in Fig. 1.) They can accordingly interact attractively with both electrophiles and nucleophiles. This has in fact been observed crystallographically for halides [24] and for sulfides [25], and has been examined computationally by Politzer and Murray [26]. It follows that the common practice of modeling electrostatic interactions between atoms, whether inter- or intramolecular, by means of single point charges can be quite misleading [7, 26].

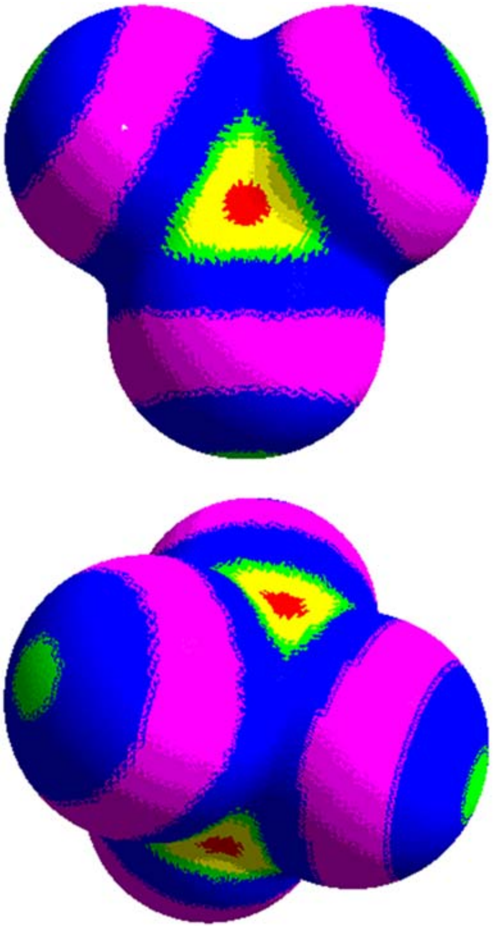

Fig. 1 Two views of the calculated electrostatic potential on the 0.001 au molecular surface of $SiCl_4$. Color ranges, in kcal/mole, are: purple, negative; blue, between 0 and 8; green, between 8 and 11; yellow, between 11 and 18; red, more positive than 18. The top view shows three of the four chlorines. In the center is the σ-hole due to the fourth Cl—Si bond, its most positive portion (red) being on the extension of that bond. In the bottom view are visible two of the σ-holes on the silicon. In both views can be seen the σ-holes on the chlorines, on the extensions of the Si—Cl bonds; their most positive portions are green

Some of the molecules in Table 1 have several possibilities for interacting with negative sites on other systems. For example, $SiCl_4$ can do so through the positive σ-holes on the silicon and/or those on the chlorines. For molecules with sufficiently positive hydrogens, these represent yet another option.

Since our immediate interest is in Group IV, we will proceed now to look at complexes involving σ-holes on some of the silicon and germanium atoms in Table 1 interacting with the nitrogen lone pairs of NH_3 and HCN. Seven examples are presented in Table 2. For each of these is given the optimized N—Si or N—Ge distance, the interaction angle and the interaction energy ΔE, computed by both B3PW91 and MP2-FC procedures.

The N- - -Si and N- - -Ge distances can be compared to the sums of the van der Waals radii of the respective atoms, which give a rough indication of the maximum separation for a noncovalent interaction. For N- - -Si, this sum is 3.65 A [27]; we do not have a value for N- - -Ge, but it can be expected to be 3.70–3.75 A, by analogy to Groups V–VII. The relevant separations in all of the complexes in Table 2 are well below these van der Waals distances, sometimes considerably so, with the exception of HCN- - -$SiCl_4$, in which N- - -Si is greater by about 0.3 A; this is also the most weakly-bound complex.

The interaction angles are all 180°, which means that the nitrogen of NH_3 or HCN is literally on the extension of the covalent bond to the Si or Ge that produced the σ-hole. While it is one of the characteristic features of σ-hole bonding that such angles are close to 180°, they often deviate somewhat due to the effects of other portions of the molecules [11, 12, 26]. In the complexes in Table 2, such deviations are avoided because both reactants are, in each instance, symmetric with respect to the N- - -Si or N- - -Ge axis.

For SiF_4 and $SiCl_4$, Table 2 includes their complexes with both NH_3 and HCN, which permits a comparison of the interactions with two different Lewis bases. Those with NH_3 are distinctly more stable (more negative ΔE) and have much shorter N- - -Si separations. One reason is that the nitrogen lone pair in NH_3 has a considerably more negative potential ($V_{S,min}$=−46.3 kcal/mole) than does that in HCN ($V_{S,min}$=−32.9 kcal/mole) [23]. Thus the positive σ-holes of the silicons in SiF_4 and $SiCl_4$ interact more strongly with NH_3.

An additional factor is the secondary interactions between the reactants. In Table 3 are listed some relevant intermolecular atomic separations for all of the systems; they are compared to the sums of the respective van der Waals radii. Note that in H_3N- - -SiF_4 and H_3N- - -$SiCl_4$, there are six H- - -F and six H- - -Cl hydrogen bonds (as indicated by the distances being shorter than the van der Waals). These provide additional stabilization. (In H_3N- - -$SiCl_4$, the hydrogens face the negative lateral sides of the chlorines, not the positive σ-holes.)

In the HCN complexes, on the other hand, any interactions other than N- - -Si would be repulsive: N- - -F and N- - -Cl. This prevents the closeness of approach that would result from the N- - -Si interactions alone; the N- - -F and N- - -Cl distances need to be kept longer than the sums of the van der Waals radii.

Thus the stabilities of these systems depend upon both the magnitudes of the $V_{S,max}$ and $V_{S,min}$ that give rise to the σ-hole bonding and also upon any existing or potential secondary interactions. The interplay of these factors is seen again in H_3N- - -SiH_3Cl and H_3N- - -GeH_3Cl. The germanium has a more positive $V_{S,max}$ (Table 1), but N- - -H hydrogen bonding is more significant in H_3N- - -SiH_3Cl. The result is that ΔE is approximately the same for the two systems.

Table 2 Computed properties of σ-hole-bonded complexes[a]

Complex	Separation, A	Interaction angle, deg	*ΔE, kcal/mole*	
			B3PW91	MP2-FC
H_3N- - -SiH_3Cl	N- - -Si: 2.49	N-Si-Cl: 180	−7.1	−6.4
H_3N- - -GeH_3Cl	N- - -Ge: 2.77	N-Ge-Cl: 180	−6.6	−6.3
H_3N- - -SiF_4	N- - -Si: 2.10	N-Si-F: 180	−9.4	−11.4
H_3N- - -GeF_4	N- - -Ge: 2.12	N-Ge-F: 180	−19.2	−23.1
H_3N- - -$SiCl_4$	N- - -Si: 2.07	N-Si-Cl: 180	−3.6	−6.3
HCN- - -SiF_4	N- - -Si: 3.27	N-Si-F: 180	−1.6	−3.5
HCN- - -$SiCl_4$	N- - -Si: 3.93	N-Si-Cl: 180	−0.4	−2.5

[a] Geometry optimizations are at the B3PW91/6-311G(3df,2p) level; ΔE values are B3PW91/6-311G(3df,2p) and MP2-FC/6-311++G(3df,2p).

Three of the complexes in Tables 2 and 3 — H_3N- - -SiF_4, H_3N- - -GeF_4 and H_3N- - -$SiCl_4$ — feature remarkably close approaches between the reactants (Table 2). A possible factor is that each of them has six hydrogen bonds, compared to three in the other NH_3 complexes. In H_3N- - -SiF_4 and H_3N- - -GeF_4, the hydrogen bonds are rather long and presumably weak, but on the other hand, the Si and Ge $V_{S,max}$ involved in the σ-hole bonding are the highest in Table 1. It is relevant to mention a computational study by Ignatyev and Schaefer of fluorosilane and chlorosilane complexes with NH_3 and H_2O, the latter acting as nucleophiles [28]. Several of these appear to involve σ-hole interactions, along the extensions of the F—Si and Cl—Si bonds; among these, the fluorosilane ones are the more stable, just as in Table 2. For H_3N- - -SiF_4 and H_3N- - -$SiCl_4$, the N- - -Si distances are also very short, between 2.01 and 2.05 A by various computational procedures [28].

Expanded interpretation of the origins of σ-holes

A σ-hole was originally viewed as the electron-deficient outer lobe of a half-filled *p* orbital that is involved in a covalent bond [1, 4, 11, 12]. It was initially believed that one of the prerequisites for a strong σ-hole is minimal mixing of *s* character into the *p* orbital; the more nearly it is pure *p*, the more positive the σ-hole.

Table 3 Some additional intermolecular atomic separations, optimized at the B3PW91/6-311G(3df,2p) level

Complex	Separation, A	Sum of van der Waals radii[a]
H_3N- - -SiH_3Cl	N- - -H: 2.62 (3)	2.75
H_3N- - -GeH_3Cl	N- - -H: 2.85 (3)	2.75
H_3N- - -SiF_4	H- - -F: 2.64 (6)	2.67
H_3N- - -GeF_4	H- - -F: 2.71 (6)	2.67
H_3N- - -$SiCl_4$	H- - -Cl: 2.84 (6)	2.95
HCN- - -SiF_4	N- - -F: 3.16 (3)	3.02
HCN- - -$SiCl_4$	N- - -Cl: 3.79 (3)	3.30

[a] Reference 26.

The number of times each one occurs in the complex is indicated in parentheses. The sums of the van der Waals radii of the respective atoms are also included.

The results in Table 1 show that this is not the case. All of the Group IV atoms are essentially sp^3-hybridized, meaning that their bonding orbitals have approximately 25% *s* contributions. This was confirmed by natural bond orbital (NBO) analyses [29] of SiF_4 and GeH_3Cl; the *s*/*p* ratios are 0.35 for the silicon and 0.37 and 0.25 for the germanium in the Ge—H and Ge—Cl bonds, respectively. Despite such sizeable levels of *s* character, some of the Group IV atoms in Table 1 have σ-hole $V_{S,max}$ that are among the highest that we have encountered.

We have recently studied two sulfur derivatives in which the sulfur is more than doubly-coordinated, $(H_3C)_2SO$ and $(H_3C)_2SO_2$ [14], and found that another aspect of our original interpretation of σ-holes also needs to be expanded. NBO descriptions of the O—S bonds in these molecules show them to be single and coordinate covalent, with both electrons being provided by the sulfur. The sulfur orbitals participating in these bonds have *s*/*p* ratios of 0.27 and 0.38 in $(H_3C)_2SO$ and $(H_3C)_2SO_2$, respectively. Thus these sulfur bonding orbitals do not have the characteristics originally believed to be associated with positive σ-holes in that they are doubly-occupied and have considerable *s* character. Nevertheless, there is a $V_{S,max}$ of 26.2 kcal/mole on the surface of the sulfur in $(H_3C)_2SO$ on the extension of the O—S bond, and there are two $V_{S,max}$ of 30.2 kcal/mole on the sulfur in $(H_3C)_2SO_2$, similarly on the extensions of the O—S bonds. These are clearly σ-holes.

We have now investigated a quadruply-coordinated Group V molecule: phosphorus oxide trichloride, Cl_3PO. The computational procedure was the same as for the Group IV molecules. The O—P bond in Cl_3PO is sometimes represented as double, O = P, as are often the O—S bonds in $(H_3C)_2SO$ and $(H_3C)_2SO_2$. However NBO analysis indicates that the O—P is also single and coordinate covalent, the electrons coming from the phosphorus. (The

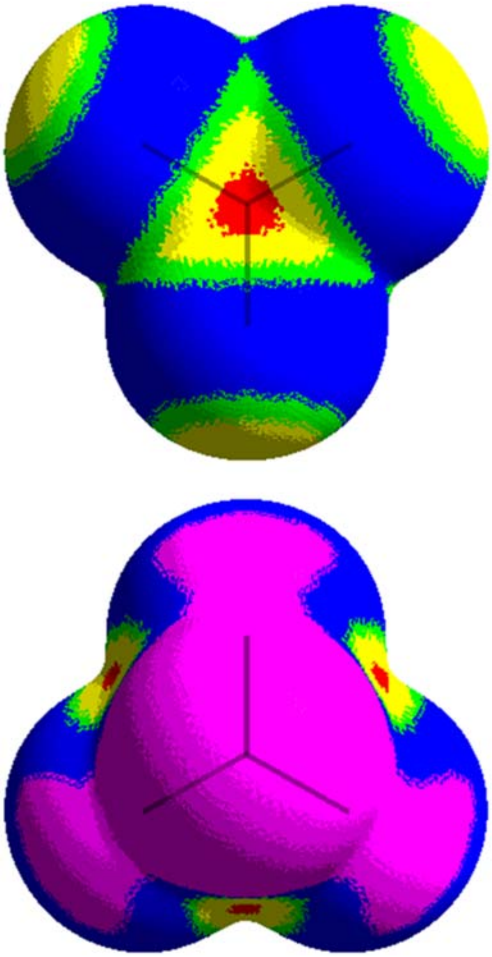

Fig. 2 Two views of the calculated electrostatic potential on the 0.001 au molecular surface of Cl_3PO. Color ranges, in kcal/mole, are: purple, negative; blue, between 0 and 8; green, between 8 and 11; yellow, between 11 and 18; red, more positive than 18. In the top view, the phosphorus is in the middle, the three chlorines are extending out from it, and the oxygen is hidden in the background; the positive σ-hole along the extension of the hidden O—P bond is apparent in the middle of this view (in red) and those associated with the chlorines are along the extensions of the three P—Cl bonds (the most positive portions being yellow). In the bottom view, the oxygen is facing the reader and is negative (purple); the three positive σ-holes on the phosphorus along the extensions of the Cl—P bonds can be seen (in red)

oxygen has three lone pairs.) The phosphorus orbital that is involved in the O—P bond has the very high *s*/*p* ratio of 0.55. On the phosphorus surface, however, on the extension of this bond, is a well defined σ-hole with a $V_{S,max}$= 21.6 kcal/mole (Fig. 2 and Table 1). So again, even though the phosphorus bonding orbital is doubly-occupied and more than 50% *s*, its bond to the oxygen does produce a positive σ-hole.

The phosphorus also has three other σ-holes on its surface, due to the Cl—P bonds (Table 1). These can be seen in Fig. 2, as can additional σ-holes with $V_{S,max}$ of 17.0 kcal/mole on the chlorines, on the extensions of the P—Cl bonds. With regard to the latter, it is noteworthy that crystalline Cl_3PO features chains of molecules linked through Cl---O interactions [30], which can now be explained as involving the chlorine σ-holes and the negative electrostatic potentials on the oxygens, $V_{S,min}$= −26.7 kcal/mole (Fig. 2 and Table 1).

Discussion and summary

The existence of σ-holes, giving rise to sites of positive (or at least less negative) electrostatic potential on the surfaces of covalently-bonded Group V–VII atoms, was initially attributed to the electron-deficient outer lobes of half-filled *p* (or nearly *p*) bonding orbitals [1, 4, 11, 12]. While this interpretation is quite satisfactory in a great many instances, the results presented in this paper demonstrate the necessity of expanding it. First, although the bonding orbital does need to have a great deal of *p* character, given the well-established directionality of σ-hole interactions, a sizeable *s* contribution is acceptable. Second, positive σ-holes can also be created by doubly-occupied orbitals forming coordinate covalent bonds.

Surface electrostatic potential plots such as those in Fig. 1 confirm that positive σ-holes can be found on covalently-bonded Group IV atoms. It might be anticipated, however, that the interactions of these σ-holes with nucleophiles would be hindered or even prevented by the proximity of other portions of the molecule. The tetrahedral structures of the molecules in Table 1 do make the σ-holes on the central atoms less accessible than is the case for Groups V – VII , and indeed, secondary interactions between the Group IV molecule and the nucleophile can be significant, as was discussed earlier. It was pointed out that these can affect (increasing or decreasing) the closeness of approach of the reactants. However the data in Tables 2 and 3 verify the occurrence of σ-hole bonding in these molecules. For example, the largest Si and Ge $V_{S,max}$, in SiF_4 and GeF_4 (Table 1), are associated with by far the most negative interaction energies with NH_3 (Table 2), and the H---F hydrogen bonds in these complexes are quite weak, judging by their lengths (Table 3). Perhaps the best proof that σ-hole bonding is taking place is the complexes with HCN, which have significant MP2-FC ΔE values of about −3 kcal/mole and the only possible secondary interactions would be repulsive, as already mentioned.

The discovery that covalently-bonded halogens can have localized regions of positive electrostatic potential on their surfaces [5] and the later concept of the σ-hole [1] resolved what some viewed as the enigma of halogen bonding: electronegative atoms, typically considered to be negative in character, interacting favorably with Lewis bases. The recognition that atoms of Groups VI, V and now IV can behave similarly was perhaps progressively less surprising, especially for Group IV, the members of which have only moderate electronegativities. However, even for Group IV, the σ-hole concept is needed to explain the marked directionalities of the interactions and their dependence upon (a) the position of the atom within the Group, and (b) the electron-withdrawing power of its partner in the covalent bond that leads to the σ-hole.

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