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AB INITIO MO STUDY OF THE HALOGEN CATION BASICITIES OF SOME ORGANIC BASES

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Hartree–Fock calculations were performed to investigate the structure and relative stabilities of complexes between halogen cations and first- and second-row bases. It is shown by means of both a qualitative perturbation molecular orbital treatment and a topological analysis of the electronic charge density that second-row bases present enhanced halogen cation basicities compared with first-row bases. In this respect the results predict that although the fluorine cation basicity of water is smaller than its proton affinity, the fluorine cation basicities of SH_2, thioether, phosphine and *trimethylphosphine* are considerably higher than their proton basicities. Similarly, phosphine and trimethylphosphine should have chlorine cation basicities greater than their proton affinities, in contrast with ammonia and trimethylamine. The results also show that fluorine and chlorine cation basicities are more sensitive to methyl substitution than proton affinities.

INTRODUCTION

Recent Fourier transform ion cyclotron resonance spectroscopy (FTICR) studies[1] have allowed the experimental determination of iodine cation basicities for a variety of organic n-donor bases in the gas phase. Iodine cation basicities are defined as the standard free-energy change, $\Delta G_{I^+}{}^{\circ}$, for reaction (1) in the gas phase:

$$B + I^+ \rightarrow BI^+ \qquad (1)$$

A comparison of the $\Delta G_{I^+}{}^{\circ}$ values so determined and the corresponding $\Delta G_{H^+}{}^{\circ}$ values for selected substituted pyridines showed that the ratio $\Delta G_{I^+}{}^{\circ}/\Delta G_{H^+}{}^{\circ} \approx 0{\cdot}44$ was slightly smaller than the ratio[2] $\Delta G_{Li^+}{}^{\circ}/\Delta G_{H^+}{}^{\circ}$. Similarly, it was found that tetrahydrothiophene (the weakest proton acceptor considered in that study) showed a high iodine cation basicity, comparable to that of tertiary amines such as Et_3N. These results indicated that the bonding between N and I^+ and between S and I^+ presents some peculiarities that need to be understood. This led us to start a systematic study, from the theoretical point of view, of the relative stabilities of the complexes involving different types of bases and halogen cations.

The aim of this paper is therefore to provide theoretical estimates of the complexation energies of a selected set of nitrogen, oxygen, phosphorus and sulphur bases and H^+, F^+, Cl^+ and Br^+ cations, in order to gain some insight into the characteristics of the corresponding acid–base interactions. In this respect we shall take advantage of the information provided by the topological analysis of the electronic charge density of some complex. Simultaneously, a perturbation molecular orbital (PMO) analysis will permit us to rationalize the variations in basicity when the reference acid changes from H^+ to Br^+ and when the reference base has first- or second-row basic centres. In particular, we have considered the following organic bases, ether, trimethylamine, thioether and trimethylphosphine. In order to analyse methyl substituent effects we also included the corresponding parent compounds OH_2, NH_3, SH_2 and PH_3.

COMPUTATIONAL DETAILS

The geometries of the different complexes included in this study, and also those of the neutral bases, were fully optimized at the Hartree–Fock level of theory employing suitable gradient optimization techniques.[3] These optimizations were carried out using the STO-3G* basis set,[4] which includes polarization functions in all second- and third-row atoms. Geometry

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optimizations at higher levels of accuracy are costly when considering Br^+ complexes. Nevertheless, and in order to check whether larger basis sets would yield different relative trends for the calculated complexation energies, the geometries of $O(CH_3)_2X^+$ and $S(CH_3)_2X^+$ ($X = H, F, Cl$ and Br) complexes were also fully optimized using the $3-21G^{(*)}$ basis set.[5] For the particular case of the complexes containing Br^+, this basis is that proposed by Dobbs and Hehre.[6] Analogously, for the complexes involving H^+ and Cl^+ we also carried out $6-31G^{*}$[7] single-point calculations for the STO-3G* and $3-21G^{(*)}$ fully optimized structures in order to check whether the inclusion of polarization functions, not only on second but also on first-row atoms, could affect part of our conclusions.

The characteristics of halogen cation–base interactions were also analysed by means of the Laplacian of the electronic density. As has been shown by Bader and co-workers[8–10], $\nabla^2\rho$ identifies regions of space wherein the electronic charge of a given system is locally concentrated or depleted. In the first situation $\nabla^2\rho(r) < 0$, whereas in the latter $\nabla^2\rho(r) > 0$. In general, negative values of $\nabla^2\rho$ are typical of covalent bonds, where charge is concentrated in the interatomic region leading to a lowering of energy associated with the predominance in this region of the potential energy density. In contrast, positive values of $\nabla^2\rho$ are associated with interactions between closed-shell systems, as in typical ionic bonds, hydrogen bonds or van der Waals molecules, where electronic charge is depleted in the interatomic region, leading to a predominance of the kinetic energy density. Therefore, an analysis of the topological properties of $\nabla^2\rho(r)$ will yield direct information on the nature of the interactions between the base and the X^+ ions. We have also localized the relevant bond critical points, i.e. points where the electronic charge density, ρ, has one positive curvature (λ_3) and two negative curvatures (λ_1, λ_2), because the values of ρ and $\nabla^2\rho$ at these points permit us to characterize quantitatively the bonding between the base and the attaching ion. For instance, the ratio between the two negative curvatures along axes perpendicular to the bond yield information[10] on the σ–π character of the bond. For single and triple bonds where the electronic density around the bond axis presents cylindrical symmetry, both curvatures are identical. However, they are not degenerate when the bond presents a double-bond character, since the charge density is preferentially distributed in a particular plane containing the bond axis. This is quantitatively measured by the ellipticity $\varepsilon = \lambda_1/\lambda_2 - 1$, which, according to the previous arguments, should be zero for single and triple bonds and different from zero for double bonds or single bonds with a given π character.

The non-bonded maxima in the valence-shell charge concentrations of a base may also provide information about its relative base strength.[9] These non-bonded maxima, which are associated with a lone pair of electrons, correspond to maxima in $|\nabla^2\rho|$. Therefore, and in an attempt to provide information on the 'hard' and 'soft' nature of the bases[9] included in this study, we shall also analyse the critical points of the Laplacian of the charge density of some of them and their corresponding halogen cation complexes.

The gradient and the Laplacian of the electronic charge density and also the Hessian matrix were programmed by M. Alcamí and implemented in the framework of the Gaussian-80 series of programs.[11]

RESULTS AND DISCUSSION

Structures

Figure 1 shows the structures of the complexes included in this work optimized at the STO-3G* level. For ether and thioether complexes the $3-21G^{(*)}$ optimized geometrical parameters are also reported. Although a detailed discussion of the structures of these complexes was not the main purpose of our study, some geometrical changes, which take place when the complex is formed, deserve attention since they bear some relation to the trends in the corresponding halogen cation basicities when compared with proton affinities.

When the OR_2X^+ or SR_2X^+ ($R = H, CH_3$) complexes are formed, the ROR (or RSR) angle opens and the degree of pyramidalization decreases from F^+ to Br^+, being significantly higher for sulphur than for oxygen bases. This can be easily rationalized using a qualitative perturbation molecular orbital picture. For this purpose and for the sake of simplicity, we shall limit our discussion to the OH_2X^+ and SH_2X^+ complexes. The conclusions are easily generalized to the corresponding methyl derivatives. As shown by Gimarc,[12] the MOs of ABH_2 systems evolve from a planar (C_{2v}) to a pyramidal (C_s) conformation as indicated in Figure 2, following AO overlap changes. The only exceptions are $3a_1 \rightarrow 3a'$, and $1b_1 \rightarrow 4a'$ which present an avoided crossing, mix and diverge, yielding a stabilized $3a'$ MO and a strongly destabilized $4a'$ MO. Since the complexes under investigation (OH_2X^+ or SH_2X^+, $X = F, Cl, Br$) are formally 14 valence electron systems, their highest occupied MO is $5a'$, which stabilizes considerably on pyramidalization.

The degree of pyramidalization is, however, a function of the electronegativity of X. If X is more electronegative than O (or S), perturbation arguments show that the contribution from the p orbitals of X must be larger in $1b_1$ π-type molecular orbitals, while p_o (or p_s) has the larger weighting in $2b_1$ MOs. Since upon pyramidalization $2b_1$ becomes $5a'$, where mixing with 1s hydrogen orbitals is possible, the degree of pyramidalization should increase with the difference

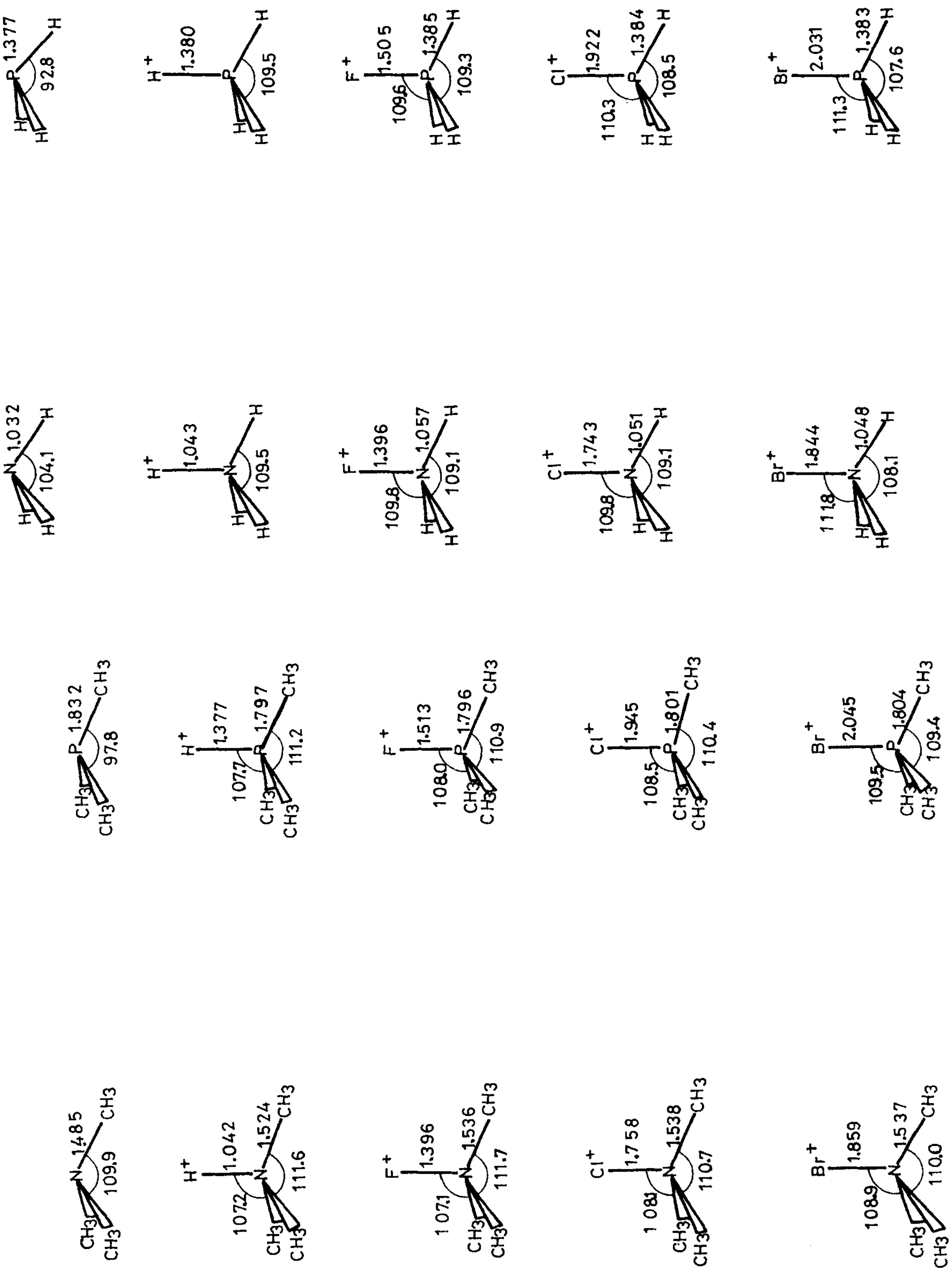


Figure 1. STO-3G* optimized geometrical parameters of the systems included in this study. Values in parentheses were obtained using the 3–21G$^{(*)}$ basis set

Figure 1. *(Continued)*

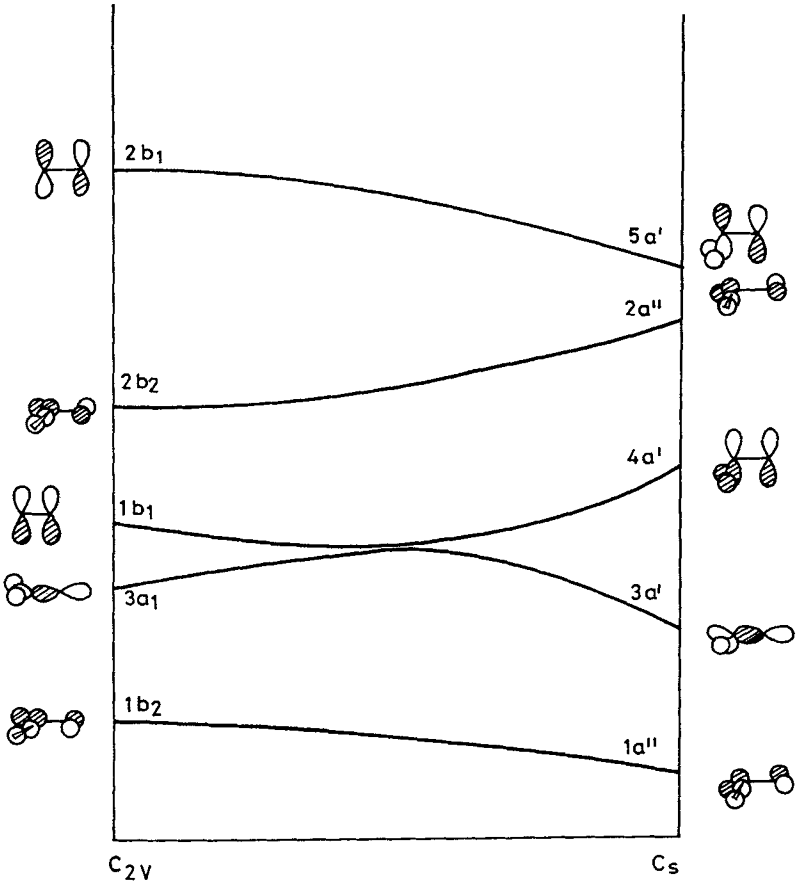
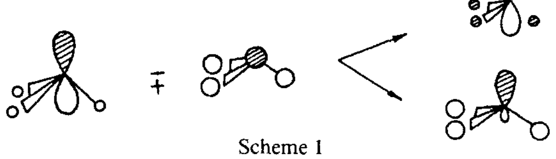


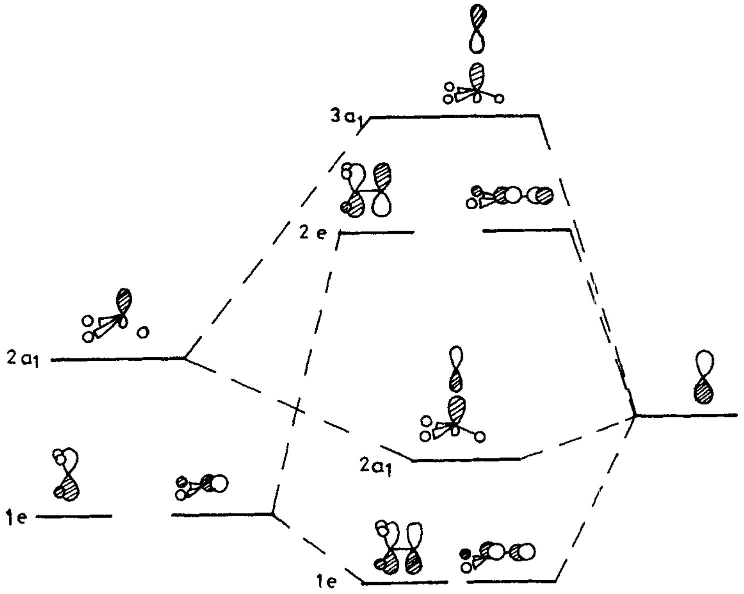
Figure 2. Qualitative MO correlation diagram for planar (C_{2v}) and pyramidal (C_s) H_2AB molecules

between the electronegativity of X and O (or S). This explains both why the degree of pyramidalization decreases from F^+ to Br^+ and why it is considerably greater for sulphur- than for oxygen-containing compounds.

Let us consider now the case of NR_3X^+ or PR_3X^+ complexes. In this case it is apparent that the degree of pyramidalization of the neutral base decreases when the complex is formed, and this decrease is greater for phosphorus than for nitrogen bases. This effect is again the larger the greater is the electronegativity of X. AH_3 systems present C_{3v} symmetry, and it is well known that their degree of pyramidalization[13] and also their inversion barriers[14] increase as the electronegativity of the central atom, A, decreases. This is a consequence of the strong mixing (see Scheme 1) between the $2a_1$ and $3a_1$ molecular orbitals which are closer in energy the lower the electronegativity of A. Therefore, for PH_3 the s character of $2a_1$ MOs is very high and the system is strongly pyramidal. When the complex AH_3X^+ is formed, the $2a_1$ MO (see Scheme 2) yields in-phase and out-of-phase linear combinations with one of the p AOs of X. The in-phase combination is responsible for the new A—X σ-type bond and it results in a decrease in the s character of the $2a_1$ MO of the AH_3 fragment and therefore in a decrease in its degree of pyramidalization. Obviously this effect increases with the electronegativity difference between X and A, explaining why the loss of pyramidalization is greater in PH_3 than in NH_3. Similar arguments can be generalized for the particular case of the corresponding methyl derivatives.



Scheme 1



Scheme 2

Halogen cation basicities

The calculated complexation energies are summarized in Table 1. As is well known,[15] absolute complexation energies are overestimated at the SCF level, in particular when the STO-3G minimal basis set is used. Relative basicities of bases containing first-row atoms are reasonably well reproduced, although those involving S or P bases are overestimated by at least 7 kcal mol^{-1} (see Table 1). Nevertheless, these limitations will not affect our conclusions in a significant way since, as we shall show later, the changes in the calculated complexation energies of N or O bases with respect to P or S bases are considerably greater than 10 kcal mol^{-1}. This is clearly illustrated in Figure 3 for OH_2 and SH_2 and in Figure 4 for NH_3 and PH_3. Figure 3 shows that F^+ is predicted to be a weaker acid than H^+ when the reference base is water, but considerably stronger when the reference base is SH_2. Similar results are found for Cl^+ and Br^+; both cations

Table 1. Calculated complexation energies (kcal mol^{-1}) obtained at the STO-3G* level

Compound	H^+	F^+	Cl^+	Br^+
OH_2	228·8 (30·7,[b] 36·7[c])	225·8	178·4	162·7
SH_2	239·4 (20·1,[b] 32·9[c])	306·3	233·9	213·5
$O(CH_3)_2$	247·7 (+11·5,[b] + 12·9[c])	257·1	202·9	178·6
	(215·8)[a]	(246·5)[a]	(158·5)[a]	(133·8)[a]
$S(CH_3)_2$	263·1 (−3·6,[b] + 4·9[c])	339·2	263·3	235·4
	(201·2)[a]	(311·2)[a]	(180·8)[a]	(150·2)[a]
NH_3	259·5	270·8	213·5	194·6
PH_3	250·3 (+9·2,[b] + 16·0[c])	351·9	268·2	244·2
$N(CH_3)_3$	280·0 (−20·3,[b] − 21·2[c])	305·3	241·2	212·9
$P(CH_3)_3$	288·8 (−29·3,[b] − 22·5[c])	397·0	313·5	283·5

[a] Values obtained at the 3–21G$^{(*)}$ level. At the 6–31G*//STO-3G* level $O(CH_3)_2H^+$ is predicted to be 65·1 kcal mol^{-1} more stable than $O(CH_3)_2Cl^+$ and $S(CH_3)_2H^+$ 32·6 kcal mol^{-1} more stable than $S(CH_3)_2Cl^+$. The corresponding values at the 6–31G//3–21G$^{(*)}$ level are 62·3 and 29·1 kcal mol^{-1} respectively.

[b] Calculated basicity with respect to NH_3 in kcal mol^{-1}.

[c] Experimental basicity relative to NH_3, taken from Ref. 19.

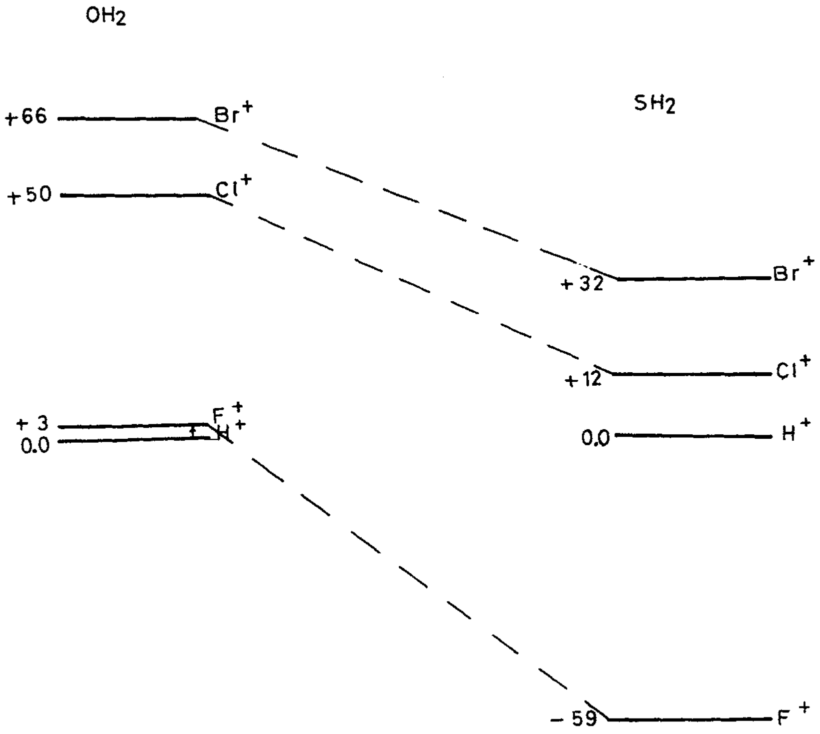


Figure 3. Calculated halogen cation basicities of OH_2 and SH_2 relative to their proton basicities

yield complexes less stable than the corresponding protonated species, but on going from water to SH_2 the stability gap decreases by about 40 kcal mol^{-1}. This agrees well with the experimental results of Abboud *et al.*,[1] which show, as indicated in the Introduction, that tetrahydrothiophene presents a very high iodine cation basicity although it is a weak proton acceptor.

Differences between first- and second-row bases are quantitatively more significant when comparing NH_3 and PH_3 (see Figure 4). According to our theoretical estimates, F^+ should be a stronger acid than H^+ when the reference base is either NH_3 or PH_3, but the $F^+{-}PH_3$ complex should be about 70 kcal mol^{-1} more stable than the $H^+{-}PH_3$ complex in relative terms. This is especially relevant when considering Cl^+, since our results indicate that the NH_3Cl^+ complex is considerably less stable than NH_4^+ with respect to the isolated reactants, whereas PH_3Cl^+ is about 10 kcal mol^{-1} more stable than PH_4^+. Similarly, the difference between the bromine cation basicity and the proton affinity is 50 kcal mol^{-1} smaller for PH_3 than for NH_3.

These results can be explained in the light of simple perturbation molecular orbital arguments. Let us take as suitable examples the NH_3X^+ and PH_3X^+ complexes. In these cases the analysis becomes simpler since there is no symmetry change on complex formation, but a similar one could be carried out for OH_2X^+ and SH_2X^+ systems. The MOs of the AH_3X^+ complex are formed, as indicated in Scheme 2, by in-phase and out-of-phase linear combinations of the $1e$ and $2a_1$ MOs of the AH_3 subunit with the p AOs of the halogen cation. Therefore, the greater relative stability of the PH_3X^+ complexes must be related to quantitative differences between these MO interactions and the analogous ones in NH_3X^+ species. We shall show that π-type interactions leading to the formation of $1e$ and $2e$ MOs of the complex are more stabilizing when A is a second-row atom while no significant differences from the σ-type interactions leading to the $2a_1$ and $3a_1$ MOs should be expected.

Consider two MOs, ϕ_A and ϕ_B, with energies $\varepsilon_A < \varepsilon_B$, which interact through a perturbation, h'. A perturbation treatment to second order, neglecting overlap for simplicity, yields[13] an in-phase combination whose energy lies

$$\beta^2/(\varepsilon_A - \varepsilon_B), \text{ where } \beta = \int \phi_A^* h' \phi_B \, d\tau \qquad (2)$$

below ε_A, and an out-of-phase combination which destabilizes with respect to ε_B by the same amount. According to this, in the π-type MO interactions

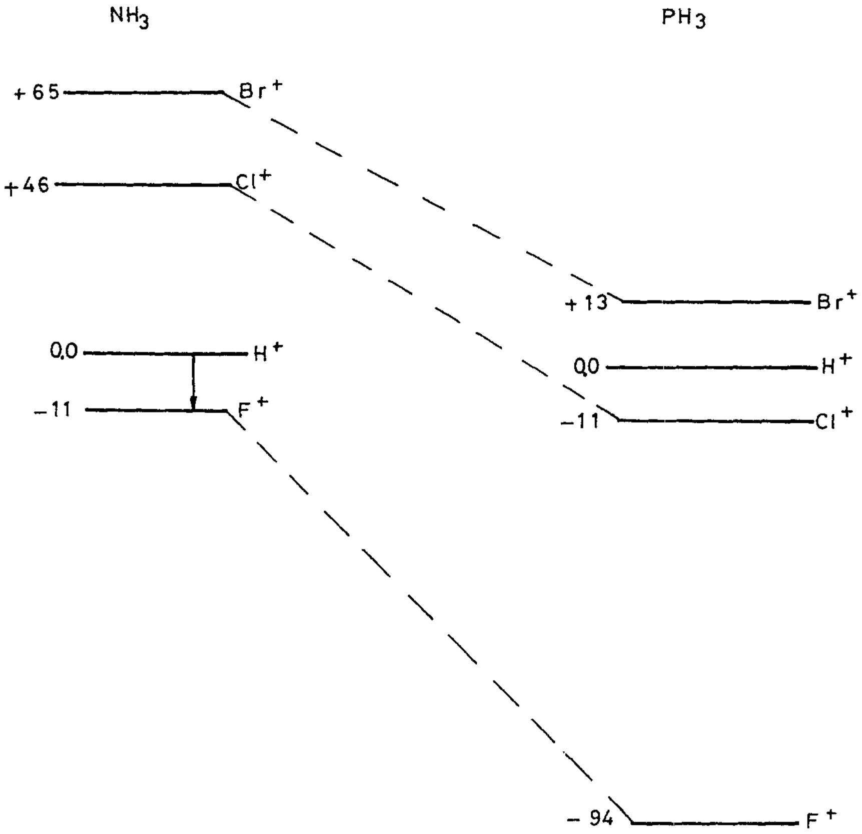


Figure 4. Calculated halogen cation basicities of NH_3 and PH_3 relative to their proton basicities

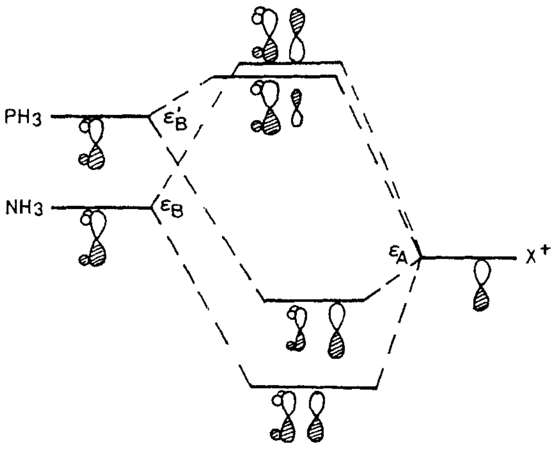
depicted in Scheme 3 for NH_3X^+ and PH_3X^+ complexes, the 1*e* in-phase combination of NH_3X^+ stabilizes with respect to the 1*e* MO of the NH_3 subunit by

$$(\varepsilon_A - \varepsilon_B) + \beta^2/(\varepsilon_A - \varepsilon_B) \tag{3}$$

while the stabilization undergone by the 1*e* of PH_3 will be

$$(\varepsilon_A - \varepsilon'_B) + \beta'^2/(\varepsilon_A - \varepsilon'_B) \tag{4}$$

Since the 1*e* MO of PH_3 lies about 3 eV above that of NH_3, $\varepsilon_A - \varepsilon'_B > \varepsilon_A - \varepsilon_B$. Therefore, the first term of equation (4) is greater than that of equation (3) whereas the second term of equation (4) is smaller than that of equation (3). Hence, the relative stabilization undergone by the 1*e* orbitals of NH_3 and PH_3 subunits are about the same, with the result that the energy gap between them does not change appreciably upon complex formation. The situation is completely different when the out-of-phase combinations, 2*e*, are considered. The destabilization undergone by the 1*e*



Scheme 3

orbitals to yield the $2e$ MOs are $\beta^2/(\varepsilon_A - \varepsilon_B)$ for NH_3X^+ complexes and $\beta'^2/(\varepsilon_A - \varepsilon'_B)$ for PH_3X^+ systems, the former being considerably greater than the latter. Since the $2e$ MOs are occupied in the complex, the overall effect considerably stabilizes PH_3X^+ complexes with respect to NH_3X^+ complexes. Following similar arguments, one may conclude that the contributions of the σ-type interactions, leading to the $2a_1$ and $3a_1$ MOs, to the stabilization of these complexes must be similar for both NH_3X^+ and PH_3X^+ systems, because in both cases the $3a_1$ MO is empty. This simple scheme also explains the quantitative differences between the relative stabilities of F^+ and Cl^+ or Br^+ complexes. It is clear from Scheme 3 that the gap between the $2e$ MOs of NH_3X^+ and PH_3X^+ complexes should be greater the greater is the electronegativity of X^+.

The qualitative picture outlined above is ratified by the corresponding SCF calculations. For instance, while the $1e$ MO of PH_3 lies 67·1 kcal mol^{-1} above that of NH_3, the $2e$ MO of PH_3F^+ complex is only 26·0 kcal mol^{-1} above that of NH_3F^+, favouring a greater stability of the former with respect to the isolated subunits.

There is a secondary mechanism involved in the enhanced stability of complexes involving second-row bases. In these systems the basic centre has low-lying empty d orbitals which contribute to these π-interactions, through a typical $p\pi$–$d\pi$ back-bonding mechanism. This is mirrored in the high electronic population of the phosphorus (or sulphur) d orbitals, obtained using the Mulliken population analysis[17] (see Table 2). Of course, this mechanism is not likely to occur when the central atom is a first-row element.

It must also be emphasized that we found no significant variations in these trends on enlarging the basis set. When the basicity of ether and thioether are evaluated at the 3–21G$^{(*)}$ level, the results are qualitatively similar to those discussed for a STO-3G* basis set. Actually, the 3–21G$^{(*)}$ basis set predicts also a considerable increase in the relative stability of $S(CH_3)_2X^+$ complexes with respect to $O(CH_3)_2X^+$ complexes, which results in a much smaller difference between the acidic character of F^+, Cl^+ or Br^+ with respect to H^+ when the reference base is thioether. These conclusions do not change when we include polarization functions not only on the second- and third-row atoms but also on the first-row atoms. Our 6–31G*//STO-3G* and 6–31G*//3–21G$^{(*)}$ calculations on $O(CH_3)_2$, $O(CH_3)_2H^+$, $O(CH_3)_2Cl^+$, $S(CH_3)_2$, $S(CH_3)_2H^+$ and $S(CH_3)_2Cl^+$ (see Table 1) lead to the same trends as indicated above.

Table 2. Electronic population at the d orbitals of the second-row atom in complexes between sulphur and phosphorus bases with halogen cations

Complex	Population	Complex	Population
SH_2F^+	0·373	PH_3F^+	0·410
SH_2Cl^+	0·245	PH_3Cl^+	0·347
SH_2Br^+	0·236	PH_3Br^+	0·330
$S(CH_3)_2F^+$	0·416	$P(CH_3)_3F^+$	0·616
$S(CH_3)_2Cl^+$	0·280	$P(CH_3)_3Cl^+$	0·408
$S(CH_3)_2Br^+$	0·266	$P(CH_3)_3Br^+$	0·383

Table 3. Charge transferred (in electrons) from the base to the attaching ion

Compound	H^+	F^+	Cl^+	Br^+
OH_2	0·581	0·778	0·727	0·631
SH_2	0·790	0·965	0·982	0·874
$O(CH_3)_2$	0·635	0·863	0·808	0·729
$S(CH_3)_2$	0·833	1·007	1·049	0·957
NH_3	0·648	0·869	0·827	0·729
PH_3	0·883	1·029	1·081	0·993
$N(CH_3)_3$	0·711	0·957	0·942	0·851
$P(CH_3)_3$	0·938	1·070	1·156	1·001

We can conclude that when the complex is formed there is a strong charge transfer from the base to the halogen cation through the σ-interaction which yields the $2a_1$ MO. Simultaneously, there is a $p\pi$–$d\pi$ back-donation of charge from the halogen to the base which is not possible when the reference acid is an H^+ or when the basic centre is a first-row atom. This strong donation of charge from the base to the incoming ion, evaluated using the Mulliken population analysis,[17] is clearly illustrated in Table 3. It should be noted that for second-row bases the charge transferred is close to or even greater than 1 electron. There also exists a rough correlation between the amount of charge transferred and the calculated basicity. For instance, the charge transferred is greater for PH_3 than for SH_2 and for $N(CH_3)_3$ than for $O(CH_3)_2$. However, when considering protonation, PH_3 is an exception to this qualitative rule since the charge it transfers to the proton is greater than that transferred by NH_3, whereas the predicted intrinsic basicity is smaller. On the other hand, the relationship between charge transferred and basicity does not hold for different reference acids.

The perturbation MO picture presented above is also consistent with the characteristics of the Laplacian of the charge distribution of the different complexes. To illustrate this point, let us consider, for example, the complexes of ether and thioether. We present in Figures 5(a)–(e) the Laplacian of the charge density of neutral ether and that of its H^+, F^+, Cl^+ and Br^+ complexes evaluated at the COC plane. Figures 5(f)–(j) show the Laplacian of ρ evaluated in the plane which bisects the COC angle and which contains the C—X^+ bond. Figures 6(a)–(j) show similar plots for the particular case of thioether.

Several aspects should be singled out for comment.

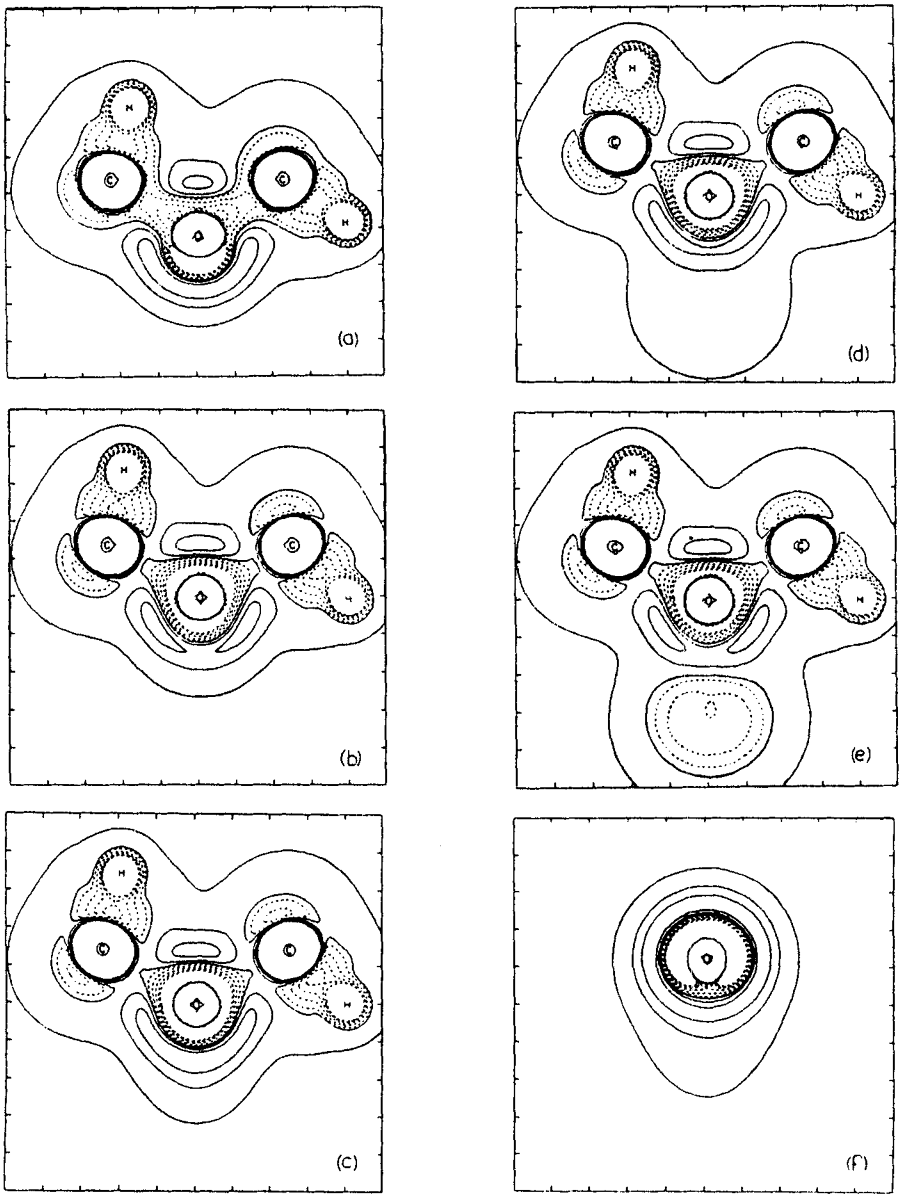


Figure 5. Laplacian of the charge density of: (a, f) ether; (b, g) ether–H$^+$; (c, h) ether–F$^+$; (d, i) ether–Cl$^+$; (e, j) ether–Br$^+$. Positive values of $\nabla^2\rho$ are denoted by solid lines and negative values by dashed lines. The contour values in au are ±0·05, ±0·25, ±0·50, ±0·75 and ±0·95. Maps (a), (b), (c), (d) and (e) were evaluated in the O—C—O plane; maps (f), (g), (h), (i) and (j) were evaluated in the plane which contains the O—X$^+$ bond and is perpendicular to the O—C—O plane

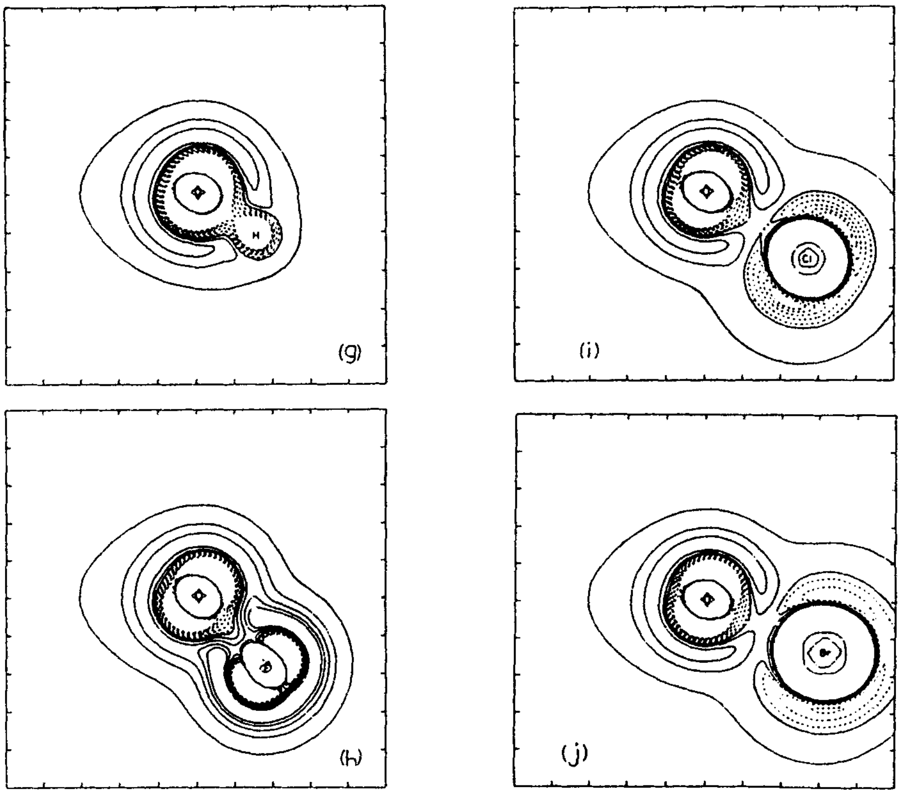


Figure 5. (*Continued*)

Figures 5(f)–(j) reveal that there is a strong charge transfer from the molecule of ether to the X^+ cation. As a consequence, a new strong O—X^+ covalent bond is formed. $\nabla^2\rho$ at the O—X^+ linkage is positive, with the only exception of the O—H^+ bond. In other words, in the new O—X^+ linkage the charge is concentrated within both atomic basins, a situation which is typical of bonds between highly electronegative atoms. Interestingly, the electronic distribution around the oxygen atom has not substantially changed with respect to that in the neutral molecule. In fact, the charge transfer from the base to the halogen cation strongly depopulates not the oxygen atom but the C—O bonds. This effect is clearly shown in Figures 5(a)–(e). The Laplacian of the charge density in the C—O bonding region of neutral ether, which is negative as in typical covalent bonds, becomes positive in the ether–X^+ complexes. This depletion is quantitatively shown by the decrease in the electronic density at the corresponding bond critical points (see Table 4). Therefore, the formation of the complex implies a noticeable weakening of the C—O linkages, which accordingly lengthen considerably.

The situation is different in thioether. Figures 6(f)–(j) show that, in contrast to what is found in ether complexes, the charge transfer from the base to the X^+ cation depopulates the valence shell of sulphur, but does not significantly affect the electronic charge in the C—S bonding region [see Figures 6(a)–(e)]. On the other hand, the depletion of the valence shell of sulphur is more important in S—H^+ complexes than in S—F^+, S—Cl^+ or S—Br^+ because in the latter three, part of the electronic charge which has been withdrawn through the σ-interaction is restored by a $p\pi$–$d\pi$ back-donation. In agreement with this, $\nabla^2\rho$ at the C—S—C plane [see Figures 6(a)–(e)] shows no significant depletion of the charge concentrated at the S—C linkages, but a polarization of it toward the sulphur atom. Accordingly, the bond critical point moves away from the latter [see Figures 6(a)–(e)] and its charge density slightly increases (see Table 4). In conclusion, the thioether–X^+ interaction does not imply a concomitant weakening of the C—S linkages of the base, which may be taken as another factor contributing to a greater relative stability of S– (P–) versus O– (N–)halogen$^+$ complexes. The existence of a $p\pi$–$d\pi$ back-bonding interaction between the halogen and the basic centre (S) is also shown by the ellipticity

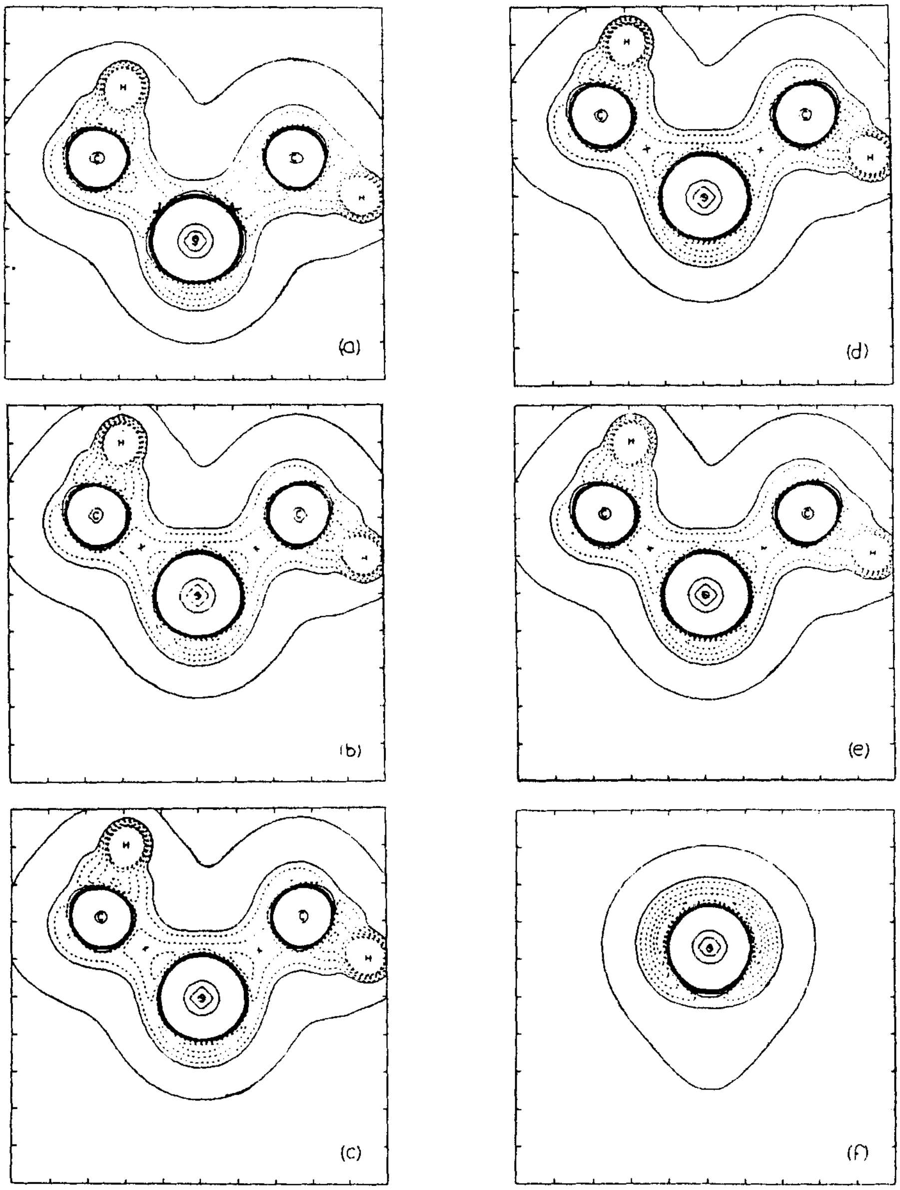


Figure 6. Laplacian of the charge density of: (a, f) thioether; (b, g) thioether–H$^+$; (c, h) thioether–F$^+$; (d, i) thioether–Cl$^+$; (e, j) thioether–Br$^+$. Conventions as in Figure 3. Maps (a), (b), (c), (d) and (e) were evaluated in the S—C—S plane; maps (f), (g), (h), (i) and (j) were evaluated in the plane which contains the S—X$^+$ bond and is perpendicular to the S—C—S plane; × indicates the position of the bond critical point

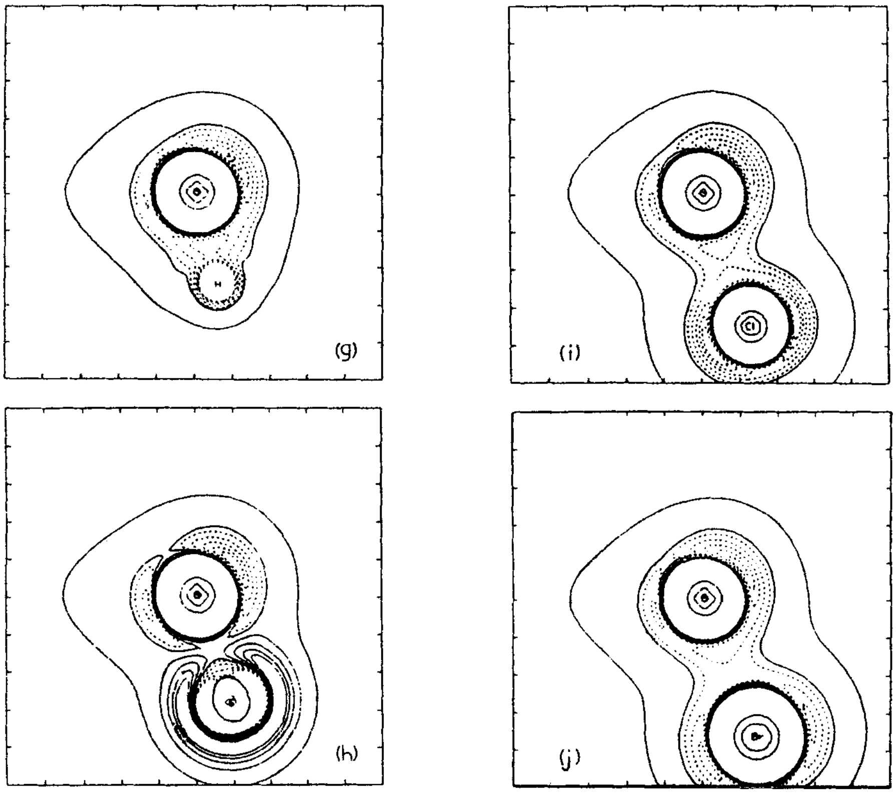


Figure 6. (*Continued*)

Table 4. Bond properties in complexes between ether and thioether with F^+, Cl^+ and Br^+ cations (all values in atomic units)

Compound	ρ	$\nabla^2\rho$	λ_1	λ_2	λ_3	ε
$O(CH_3)_2$						
O—C	0·2455	−0·3051	−0·4104	−0·3969	0·5022	0·0
$O(CH_3)_2F^+$						
O—C	0·1685	0·3284	−0·1066	−0·1037	0·5387	0·0
O—F^+	0·3387	0·0557	−0·8712	−0·8148	1·7417	0·0
$O(CH_3)Cl^+$						
O—C	0·1708	0·3024	−0·1155	−0·1145	0·5324	0·01
O—Cl^+	0·1794	0·0382	−0·0845	−0·0799	1·2027	0·0
$O(CH_3)_2Br^+$						
O—C	0·1757	0·3117	−0·1281	−0·1273	0·5672	0·01
O—Br^+	0·1472	0·3879	−0·0853	−0·0824	0·5556	0·0
$S(CH_3)_2$						
S—C	0·1852	−0·4084	−0·2943	−0·2449	0·1272	0·2
$S(CH_3)_2F^+$						
S—C	0·1907	−0·3804	−0·2738	−0·2674	0·1609	0·0
S—F^+	0·1904	0·8629	−0·2433	−0·1895	1·2957	0·2
$S(CH_3)_2Cl^+$						
S—C	0·1895	−0·3712	−0·2736	−0·2651	0·1675	0·0
S—Cl^+	0·1781	−0·3012	−0·2130	−0·1938	0·1056	0·11
$S(CH_3)_2Br^+$						
S—C	0·1893	−0·3723	−0·2737	−0·2654	0·1669	0·0
S—Br^+	0·1659	−0·2161	−0·1654	−0·1603	0·1096	0·0

of the S—X$^+$ bonds (see Table 4). As expected in the light of our previous discussion, this ellipticity is near zero for O—X$^+$ bonds whereas it is clearly different from zero in S—X$^+$ bonds showing, that these linkages present some double-bond character. The ellipticity of S—Cl$^+$ and S—Br$^+$ bonds is smaller than that of S—F$^+$ linkages, indicating a smaller extension of the pπ–dπ back-bonding interaction. This seems reasonable if one takes into account that F$^+$ withdraws a large amount of σ-charge and therefore is able to back-donate more electronic charge than chlorine or bromine, where the σ-withdrawing effect is less intense. The greater back-donation effect in the case of F$^+$ compounds is mirrored clearly in the electronic populations of the basic centre d orbitals (see Table 2).

Let us analyse briefly the non-bonded charge concentrations of ether and thioether associated with the oxygen and sulphur lone pairs, respectively. The corresponding maxima of $|\nabla^2\rho|$ are summarized in Table 5 for these two bases and their complexes. The maximum on oxygen is relatively tightly bound and of considerable magnitude. The maximum on sulphur is further away from the nucleus, of smaller magnitude and of much greater radial extent (see also Figures 5 and 6). Hence one would expect thioether to be a softer base than ether. For both kinds of complexes the charge concentration, and therefore the maximum value of $|\nabla^2\rho|$, is smaller than in the corresponding isolated bases. However, Table 5 shows that whereas in ether complexes $|\nabla^2\rho|$ decreases by about 34%, in thioether complexes it decreases by about 76%. This result also seems to be in agreement with a softer character of the latter and conforms with the discussion presented above. In particular, it should be noted that this effect is greater in the protonated form of thioether than in their halogen cation complexes, reflecting the pπ–dπ back-donation which takes place in the latter.

Table 5. Non-bonding charge maxima in complexes between ether and thioether with F$^+$, Cl$^+$ and Br$^+$ cations (all values in atomic units)

Compound	$\nabla^2\rho$	R[a]
$O(CH_3)_2$	−9·4044	0·59
$O(CH_3)_2H^+$	−6·1779	0·60
$O(CH_3)_2F^+$	−5·7182	0·61
$O(CH_3)_2Cl^+$	−6·2000	0·60
$O(CH_3)_2Br^+$	−6·9104	0·60
$S(CH_3)_2$	−1·1251	1·27
$S(CH_3)_2H^+$	−0·2674	1·36
$S(CH_3)_2F^+$	−0·3131	1·34
$S(CH_3)_2Cl^+$	−0·3016	1·35
$S(CH_3)_2Br^+$	−0·2908	1·35

[a] Distance in Å from the non-bonding charge maxima to the corresponding nucleus (O or S).

Substituent effects

As expected, methyl substitution implies a considerable increase in both proton and halogen cation basicities. This effect depends on the number of methyl substituents and therefore is greater for trimethylamine and trimethylphosphine than for ether or thioether. In fact, according to the polarizability parameter scale proposed by Hehre *et al.*,[18] an almost linear increase in the basicity as a function of the number of methyl substituents should be expected. Following analogous arguments, an average methyl effect of 6·1 kcal mol^{-1} on gas-phase basicities is found for amines, in good agreement with our results. It must be remarked, however, that methyl effects are noticeably higher when considering trimethylphosphine or thioether (*ca* 12 kcal mol^{-1}). This is also in agreement with the experimental evidence,[19] which shows, for instance, that $P(CH_3)_3$ is more basic than $N(CH_3)_3$ whereas PH_3 is a weaker base than NH_3. In general, our results show that methyl substituent effects are larger for second than for first-row bases. Taking into account that, as mentioned above, the theoretical values overestimate the experimental values we can reasonably estimate that each methyl group accounts for an increase in the proton affinity of about 10–12 kcal mol^{-1} for both sulphur and phosphorus bases. Methyl substituent effects on fluorine and chlorine cation basicities are considerably and systematically larger. In contrast, bromine cation basicities increase to a lesser extent than proton affinities on methyl substitution. In this respect, it should be noted that a similar finding was reported[1] for experimental iodine cation basicities. These results are directly related to the ability of methyl groups to accommodate the positive charge of the complex, behaving as π donors, through a typical hyperconjugative effect which is enhanced when the central atom is a second-row atom by the contribution of its d orbitals. Accordingly, the charge transfer to the incoming ion and also the d atomic population of the central atom, when it is a second-row element, are greater in methyl-substituted systems (see Tables 2 and 3). It should be noted, however, that the general trends in the halogen cation basicities discussed for the parent compounds do not change on methyl substitution. It can be seen, for instance, that both NH_3—Cl$^+$ and trimethylamine—Cl$^+$ complexes are less stable, with respect to the isolated reactants, than the corresponding protonated species. Similarly, both PH_3—Cl$^+$ and trimethylphosphine—Cl$^+$ complexes are more stable than the corresponding protonated systems.

CONCLUSION

We have shown by means of both a qualitative perturbation molecular orbital treatment and a topological analysis of the electronic charge density that second-row bases present enhanced halogen cation basicities with respect to the corresponding first-row counterparts. This is in good agreement with the experimental evidence,[1] which has recently shown that sulphur compounds present considerably higher iodine cation basicities than their proton affinities. According to our analysis, this is not exclusive to iodine cations but a rather general behaviour of halogen cations. On the one hand the π-type MO interactions between halogen cations and second-row bases tend to stabilize these complexes with respect to those involving first-row bases. On the other hand, halogen cations in the complex are able to back-donate charge through a typical $p\pi-d\pi$ mechanism which is only possible for second-row bases. In this respect, our results predict that although the fluorine cation basicity of water is smaller than its proton affinity, those of SH_2, thioether, PH_3 or trimethylphosphine are considerably higher than the corresponding proton affinities. This enhanced stability of complexes with second-row bases is particularly important for phosphorus-containing compounds. Therefore, according to our analysis, the enhanced stability of sulphur–I^+ complexes reported in the literature[1] should be even more evident for phosphorus bases. Similar findings are reported for Cl^+ and Br^+ cations, although there are quantitative differences. Essentially, the bromine cation basicities of the O-, N-, S- and P-bases investigated are always lower than the corresponding proton affinities, although the difference between the two sets of values is considerably smaller for second-row bases. The same applies to chlorine cation basicities of O- and S-bases, but not for N- and P-bases. Ammonia and trimethylamine present proton affinities notably larger than their chlorine cation basicities, but our results predict that both phosphine and trimethylphosphine should have chlorine cation basicities larger than their proton affinities.

Part of the enhanced stability of complexes involving second-row bases is related to the fact that the charge transfer from the base to the attaching ion comes essentially from the second-row atom valence shell, whereas for oxygen bases, for instance, owing to the high electronegativity of the basic centre, this charge transfer depopulates the C—O linkages, which accordingly become less bonding.

Methyl substituent effects on proton affinities and halogen cation basicities are stronger for second-row bases and in particular for phosphorus bases. Fluorine and chlorine cation basicities are more sensitive to methyl substituent effects than proton affinities. This explains, for instance, that whereas the fluorine cation basicity of water is smaller than its proton affinity, that of ether is considerably higher.

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