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Methyl Substituent Effects in $[H_nX\therefore XH_n]^+$ Three-Electron-Bonded Radical Cations (X = F, O, N, Cl, S, P; $n = 1-3$). An ab Initio Theoretical Study

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Abstract: The effects of methyl substitution on the geometries and bonding energies of a systematic series of three-electron-bonded radical cations of the type $[H_nX\therefore XH_n]^+$, covering all possible symmetrical three-electron bonds that may take place between atoms of the second and third rows of the periodic table, have been investigated at the level of Møller−Plesset perturbation theory. Methyl substitution leads to significant weakening and lengthening of the $X\therefore X$ bond when X is a second-row atom. The effects increase with the number of substitutions and are more and more important in the series X = N, O, F. By contrast, methyl substitution leaves the bonding energies between third-row atoms practically unchanged but leads to a surprising bond shortening in the $S\therefore S$ and $P\therefore P$ cases. These seemingly contradictory effects are rationalized through a qualitative analysis based on an elementary molecular orbital description of three-electron bonding.

Introduction

Two-center three-electron (2c-3e) bonds have attracted considerable attention in recent years. In this type of bonding, first described by Linus Pauling[1] in the 1930s, two electrons occupy the σ orbital of a dimer and one single electron occupies the corresponding σ^* one, hence the alternative name of σ^*-bond for this interaction.[2−4] Such species have been the subject of considerable recent experimental and theoretical interest, and their importance as major intermediates is nowadays well recognized.[5,6−19] They can be encountered in many different areas such as free-radical chemistry[7−11] or biochemistry,[12−16] organic reactions,[17−24] radiation studies,[25−34] intrazeolite photochemistry,[35,36] and bioinorganic enzymology.[37,38] Three-electron bonds

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are preferentially observed in cations but can also be detected in neutral[12,19,23a,26,27,34] and anionic[11,15,19,23b,24,26,30−32] adducts. Here we will restrict ourselves to cationic radicals, which are by far the most frequently observed.

As a result of their radical nature, experimental information on three-electron bonded species is limited. In solution, the complexes are easily formed and give rise to distinctive ESR[6a] and visible[6c] spectra from which only indirect information on the nature of the 2c-3e bond can be extracted. Thus, although such species are often detected, their structural features cannot always be probed, and thermochemical data are difficult to obtain. During the past decade, such species have also been the subject of extensive gas phase, experimental[39,40−42] or mixed mass spectrometry and computational[43−47] studies, which provided, in particular, thermodynamical data on the three-electron bond energies. Nevertheless, the three-electron-bonded species cannot always be characterized unambiguously. The most extensively studied group of three-electron-bonded species is that of sulfur-centered radical cations; however, this type of bonding can be observed in many other linkages of the type $N\therefore N$,[21,22,35,39a,48] $P\therefore P$,[19,20] $Se\therefore Se$,[5c,36,49] $I\therefore I$,[40,47b,50] and more generally all kinds of $X\therefore Y$ (X, Y = N, S, P, halogen, etc.).

On the theoretical side, the most frequently studied species are the rare gas dimer cations,[51−54] dihalogen anions,[55−57] and disulfide ions,[58−62] which have long been experimentally identified. These molecules have been studied by means of ab initio calculations,[51−53,56−62] and semiempirical potential energy curves were generated by combining different experimental data.[54,55] In two landmark papers, Clark[3] and Gill and Radom[4] extended the investigations to all the model systems of the type $[H_mX\therefore YH_n]^+$ and attempted to rationalize the existence of σ^*-bonds. The same species have been used in several methodological analyses that provided a better insight into the nature of this peculiar type of bonding.[57,61,63−65]

More recently, the possible existence of various others three-electron-bonded cations,[66] anions,[67] and neutral[68] molecules was explored. One point of interest is the competition that often occurs between hydrogen-bonded and σ^*-bonded adducts and may condition the stability of the latter species.[3,59,69,70] In the past few years, the number of computational studies have gradually increased, often as a complement to experimental work.[15,27,43,46,54,55,62] As far as methodology is concerned, studies on model systems have established that although the most commonly used density functional theory methods are generally inappropriate for studying this type of bonds,[71] the Møller−Plesset perturbation theory is on the contrary adequate, provided the molecules are symmetrical and the geometries that are investigated are not too stretched relative to equilibrium.[57,65] Now the three-electron-bonded systems of interest in chemistry or biochemistry are most of the time parts of big hydrocarbon chains or cycles, and one may wonder if the properties that have been found for model systems carry over to substituted systems. As such systems can be featured by alkyl-substituted models, it is essential to know to what extent alkyl substituents may

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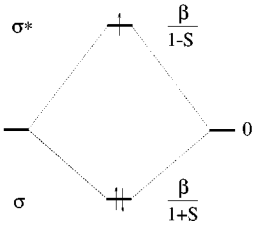
affect the geometries and bonding energies of three-electron-bonded systems.

The problem of substituent effects has been partially addressed in some pioneering articles by Asmus,[5b,5c] Radom,[4] and McKee.[43,61] The possibility that inductive effets of the substituents might play a leading role has been ruled out by Berthe-Gaujac,[72] who showed that both strong attractors such as fluorine susbtituents and strong donors such as silyl *both* have a weakening effect on three-electron bonds. Several attempts have been made to draw correlations between optical parameters and the strengths of various substituted three-electron bonds in solution[5b,c,7c,9d,61] or to study the influence of different alkyl chains on the strength of the sulfur−sulfur three-electron bond in the gas phase.[44,45,61] On one hand, both experimental and theoretical studies have shown that substituents such as methyl or ethyl do not significantly modify the nature of the three-electron bond between two sulfur atoms in radical cations. On the other hand, some preliminary theoretical studies[4,63b] of the tetramethyl-substituted analogue of $[H_2O\therefore H_2O]^+$ have led to the finding that methyl substitution reduces the $O\therefore O$ bond strength by one full third, a surprisingly large weakening effect as compared to the mild methyl substituent effects that are observed in two-electron bonds and to the quasi-absence of bond weakening in the $S\therefore S$ three-electron bond. These puzzling findings suggest that (i) the effects of methyl substitution do not follow the same logic in three-electron bonds as in two-electron ones and (ii) such effects can be considerable in some cases, so that standard three-electron bond lengths and/or bonding energies arising from model systems cannot be defined for large molecules before substituent effects are better understood and quantified. In this line, some efforts have dealt with the study of the comparative effects of different alkyl groups on some specific 2c-3e bonds (the $S\therefore S$ bond in general), but no systematic and general study on the substituent effects on all kind of three-electron bonds has been done so far. The present study aims at filling this gap in the case of methyl substitution, which has the advantage of modeling alkyl chains. Only symmetrical substitutions have been considered, i.e., substitutions that leave the two constituting fragments equivalent by symmetry, to avoid problems of symmetry breaking in the wave functions.[65]

The paper is organized as follow. First, the qualitative theory of three-electron bonds will be briefly recalled. Second, the effect of methyl substitution on the symmetric dimers of the type $[H_{n-p}(CH_3)_pX\therefore X(CH_2)_pH_{n-p}]^+$ ($X = F, O, N, Cl, S, P$; $n = 1-3$; $p = 0-n$) will be investigated at the Møller-Plesset perturbative level of theory. These systems cover all possible kinds of second- and third-row symmetrical three-electron-bonded radical cations. Then, the computational results will be interpreted by means of the concepts that arise from the qualitative model.

Qualitative Description of the Three-Electron Bond

In the elementary approximation of Molecular Orbital Theory, the formation of a three-electron bond between two equivalent fragments may be modeled by the perturbative interaction of the highest occupied molecular orbital (HOMO) of each fragment.[2a] The interaction leads to a bonding σ MO that is doubly occupied and to a singly occupied antibonding σ^* MO. Taking the initial energy of the fragment's HOMOs as the origin (i.e., setting the traditional α parameter to zero in the extended Hückel model), one gets the simpified diagram below that shows



that the three-electron bonding energy, D_e(3-e), is a simple function of S, the overlap between the two interacting fragment's orbitals, and β, the usual resonance integral in Hückel theory:

$$D_e(3\text{-e}) = \beta(1 - 3S)/(1 - S^2) \tag{1}$$

Assuming that β is proportional to S, as in the Wolfsberg−Helmholtz approximation,[73] one may further simplify the expression of D_e(3-e) to make it depend on a single parameter, the overlap S:

$$D_e(3\text{-e}) = KS(1 - 3S)/(1 - S^2); \quad \beta = KS \tag{2}$$

Equation 2 shows that the three-electron bond has the peculiar property that its bonding energy is approximately *quadratic* in S, instead of being linear in S as the two-electron bond. The equation also shows, by simple differentiation, that the interaction gets its greatest stabilization energy for an optimal value S_{opt} of the overlap S, which is equal to 0.17.[4] Last, since two electrons are bonding while only one is antibonding, the three-electron bond has a formal bond order of 0.5 and is expected to have half the strength of the corresponding two-electron bond. To summarize, the simple MO model predicts the three-electron bond to be a weak one, to prefer weak overlaps of the order of 0.17, and consequently to establish itself at rather large interatomic distances with respect to standard two-electron bonds.

Theoretical Methods

Standard second-order Moller−Plesset perturbation theory (MP2) calculations were performed with the GAUSSIAN-98 suite of programs.[74] The unrestricted formalism was used throughout this study. The frozen-core approximation is applied in all cases. All the computational results displayed in Table 1 were performed with the 6-31G(d) basis set. Frequency calculations were carried out for each stationary point, to verify that they are true minima. The dissociation energies that are displayed in Table 1 were calculated in the 6-31G(d) basis set. Using the geometries optimized in the 6-31G(d) basis set, the dissociation energies were also recalculated in the 6-311G(2df,p)

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Table 1. Dissociation Energies (kcal/mol) for the Radical Cations As Calculated at the MP2/6-31G(d) Level. Parenthesized Values Refer to Single Point Calculations at the MP2/6-311G(2df,p) Level

	number of substitutions (*n*)			
	0	1	2	3
$[H_{1-n}Me_n\mathbf{F}\therefore\mathbf{F}Me_nH_{1-n}]^+$	48.1 (45.1)	15.2 (6.9)		
$[H_{2-n}Me_n\mathbf{O}\therefore\mathbf{O}Me_nH_{2-n}]^+$	46.3 (44.6)	37.8 (35.5)	29.3 (29.3)	
$[H_{3-n}Me_n\mathbf{N}\therefore\mathbf{N}Me_nH_{3-n}]^+$	40.1 (38.7)	33.6 (32.9)	29.3 (29.7)	26.5 (28.3)
$[H_{1-n}Me_n\mathbf{Cl}\therefore\mathbf{Cl}Me_nH_{1-n}]^+$	29.3 (32.1)	29.5 (32.3)		
$[H_{2-n}Me_n\mathbf{S}\therefore\mathbf{S}Me_nH_{2-n}]^+$	29.9 (31.7)	29.4 (31.5)	29.3 (32.3)	
$[H_{3-n}Me_n\mathbf{P}\therefore\mathbf{P}Me_nH_{3-n}]^+$	27.0 (29.5)	27.9 (30.9	28.8 (31.7)	29.7 (32.1)

Table 2. Overlaps between the Two Constituting Fragement Orbitals Involved in the Three-Electron Bond, at the EHMO Level

	number of substitutions (*n*)			
	0	1	2	3
$\langle H_{1-n}Me_n\mathbf{F} \mid \mathbf{F}Me_nH_{1-n}\rangle$	0.099	0.009		
$\langle H_{2-n}Me_n\mathbf{O} \mid \mathbf{O}Me_nH_{2-n}\rangle$	0.085	0.061	0.043	
$\langle H_{3-n}Me_n\mathbf{N} \mid \mathbf{N}Me_nH_{3-n}\rangle$	0.139	0.115	0.093	0.072
$\langle H_{1-n}Me_n\mathbf{Cl} \mid \mathbf{Cl}Me_nH_{1-n}\rangle$	0.141	0.132		
$\langle H_{2-n}Me_n\mathbf{S} \mid \mathbf{S}Me_nH_{2-n}\rangle$	0.176	0.173	0.174	
$\langle H_{3-n}Me_n\mathbf{P} \mid \mathbf{P}Me_nH_{3-n}\rangle$	0.309	0.303	0.294	0.295

basis set, a basis set of triple-ζ quality with d and f polarization functions of heavy atoms and p polarization functions on hydrogens. The corresponding values are also displayed in Table 1, in parentheses, for comparative purposes. The extended Hückel molecular orbital[75] (EHMO) analysis of the interactions were performed using the H_{ij} formula.[76] The parameters of each atom were taken from previous EHMO studies.[77] Calculations were made on all dimers, using the results of MP2 optimizations as geometrical parameters. The fragment orbitals that are involved in the three-electron bond are taken as the two contributors of the σ^* MO of the molecule, and the values of S (as defined in previous section) given in Table 2 are the overlaps between these two fragment orbitals.

Computational Results

Limiting ourselves to the second and third rows of the periodic table, the ensemble of symmetrical three-electron bonds that can possibly take place between heteroatoms in unsubstituted radical cations is covered by the series $[H_nX\therefore XH_n]^+$ (X = F, O, N, Cl, S, P; $n = 1-3$). Starting from these model systems, the substituted molecules are generated step by step, substituting one hydrogen for a methyl group (Me) on both sides of the $X\therefore X$ bond, then substituting a further pair of hydrogens, and so on up to full substitution. As a result, the series of 18 symmetric radical cations of the type $[H_{n-p}Me_pX\therefore XMe_pH_{n-p}]^+$ (X = F, O, N, Cl, S, P; $n = 1-3$; $p = 0-n$) was investigated. The optimized geometries of the 18 substituted molecules, as well as those of the unsubstituted model systems, together with the main geometrical parameters, are displayed in Figures 1 and 2.

It is clear that, for molecules involving several methyl groups each having a small rotational barrier, many secondary minima exist on the potential surfaces within a small energy range, so that it is difficult to claim that the geometries arising from our study are absolute minima. However, the energy shift relative to the absolute minimum, if any, is expected to be small and, more importantly, to carry over to the whole dissociation energy curve and therefore to lead to negligible errors in the calculated bonding energies.

For each compound, the bonding energy has been calculated as the difference between the energy of the molecule at equilibrium and the sum of the energies of the separate ionic and neutral fragments. This technique has proved to yield MP2 results in good agreement with sophisticated computational levels, unlike the alternative method that consists of computing the dissociation limit as a supersystem involving both fragments.[3,4,57,63,71b] The calculated bonding energies of the 18 radical cations are displayed in Table 1. The calculations performed in the smallest basis set, 6-31G(d), will be discussed first.

Let us first consider the second-row dimers (X = F, O, N) and begin with the $N\therefore N$ bond. Relative to the parent unsubstituted compound, $H_3N\therefore NH_3^+$, the dimethyl-substituted derivative undergoes a significant loss of bonding energy, which decreases by 6.5 kcal/mol. Further substitution of the molecule leads to a further decrease of the bonding energy, by 4.3 kcal/mol for the tetrasubstitued derivative. The bond weakening is somewhat damped from the tetra- to hexasubstitued compound but remains significant with a bonding energy decrease of 2.8 kcal/mol. All in all, the fully susbstituted $N\therefore N$ bond is weakened by some 14 kcal/mol, in sharp contrast with the $S\therefore S$ bond, which has been shown to be nearly insensitive to methyl substitution. Methyl substitution also weakens the $O\therefore O$ bond quite significantly, with a bond energy decrease of 8.5 kcal/mol for the first disubstitution and another 8.5 kcal/mol for the second one. Thus, the substituent weakening effect is not only stronger than in the $N\therefore N$ bond but displays no damping effect from the first to the second substitution. Now the most dramatic weakening substituent effect occurs for the $F\therefore F$ bond, whose disubstituted derivative is bonded by only 15 kcal/mol, to be compared with the very strong three-electron bond of 48 kcal/mol of the parent unsubstituted compound. This huge substituent effect points to a qualitative difference between the $F\therefore F$ bond and the $N\therefore N$ and $O\therefore O$ analogues. Be it as it may, the substituent effect of the methyl group weakens all three-electron bonds between heteroatoms of the second row of the periodic table, and the weakening effect increases with the electronegativity of the heteroatom or, perhaps more properly stated (see below), with the number of lone pairs that are born by the heteroatom.

To ascertain that the observed tendencies are not basis-set-dependent, all of the bonding energies have been recalculated in a basis set of much higher quality than before, the triple-ζ polarized 6-311G(2df,p) standard basis set (parenthesized values in Table 1). With a single exception ($MeF\therefore FMe^+$), the calculated bonding energies are about the same in both basis sets, slightly smaller in the large basis set for second-row compounds and on the contrary slightly larger for third-row compounds. All the tendencies that have been discussed above, even in their details, are identical as calculated in both basis sets. The exception, $MeF\therefore FMe^+$, further emphasizes the exceptional bond weakening effect of methyl substitution on the $F\therefore F$ bond, which has already been noted from 6-31G(d) results. In the larger basis set, the $F\therefore F$ bond is now weakened

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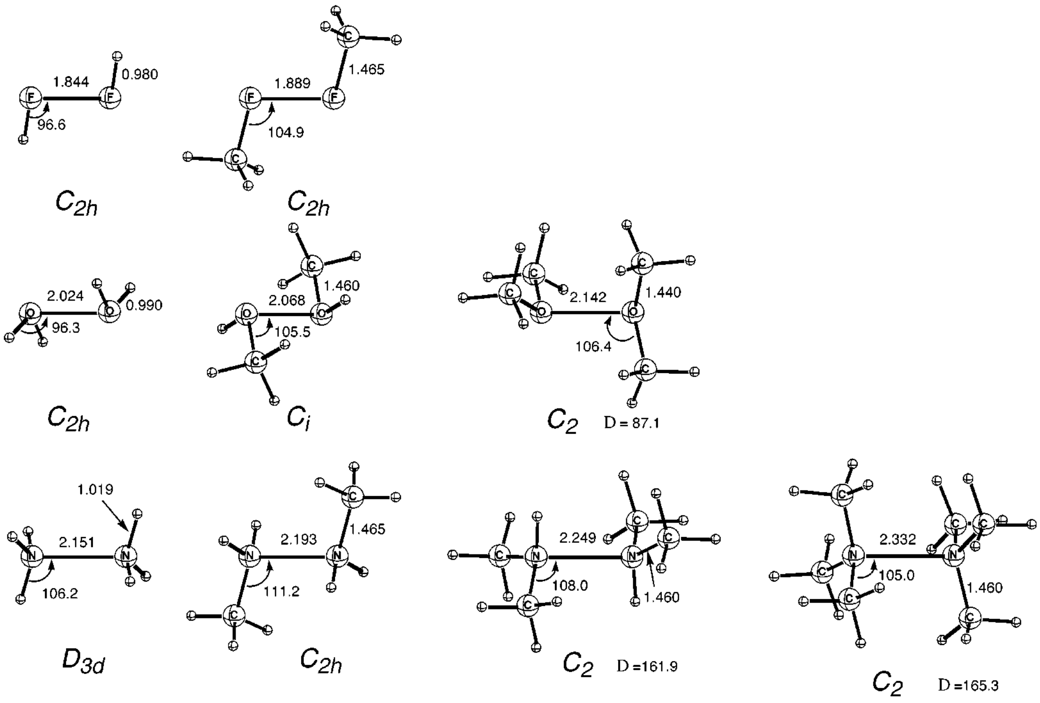

Figure 1. MP2-optimized geometries for the second-row three-electron-bonded cations. Bond lengths are in angstroms, and angles are in degrees.

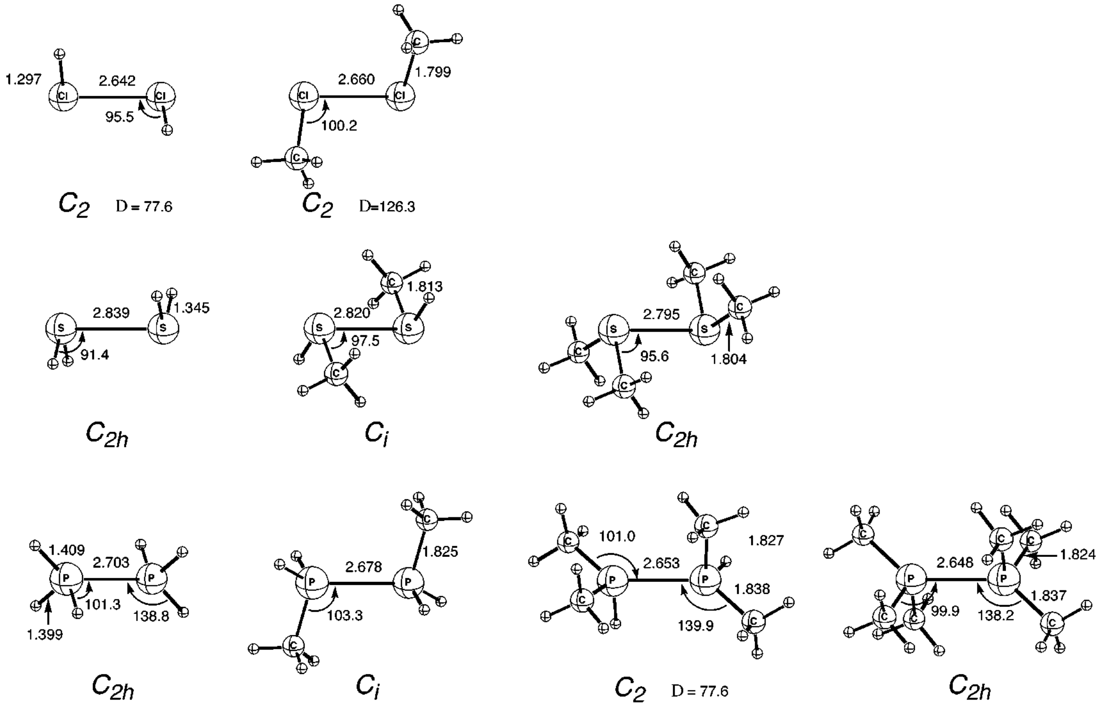

Figure 2. MP2-optimized geometries for the third-row three-electron-bonded cations. Bond lengths are in angstroms, and angles are in degrees.

from 45 to 7 kcal/mol upon methyl substitution, a reduction by a factor of 6, pointing to a peculiarity of the F∴F bond that deserves some explanation (vide infra).

It is interesting to examine the substituent effect on the geometries and more specifically on the essential geometrical parameter in this study, the X−X bond length. Still restricting our attention to second-row compounds, the optimized geometries are displayed in Figure 1. It is seen that in all cases, the decrease in bonding energy due to methyl substitution is accompanied by a bond lengthening, as intuitively expected. The lengthening is rather significant, about 0.04−0.07 Å for each disubstitution of the F∴F and O∴O bonds. For the N∴N bond, the bond lengthenings are also significant, between 0.04 and 0.08 Å at each step of the substitutions. The remarkable fact is that, while the bond energy weakening effect was found to be damped after each substitution in these second-row systems (vide supra), the bond lengthenings are on the contrary stronger and stronger at each step.

Let us now consider the third row dimers (X = Cl, S, P) and their bonding energies (Table 1). In agreement with former computational studies,[43−45] the S∴S bond appears to be little affected by substitution as far as bonding energies are concerned.

The weakening effect is reduced to 0.5 kcal/mol for the first disubstitution, and practically nothing for the second. Similar results are found for the Cl∴Cl bond which is practically unaffected by methyl substitution, in sharp contrast to the isoelectronic F∴F bond (vide supra). Last, the P∴P bond undergoes a weak but regular *strengthening* after each disubstitution.

Quite interesting are the geometrical variations that accompany methyl susbtitution in third row dimers. Although bonding energies are unaffected in the Cl∴Cl and S∴S bonds, the latter species undergo a small but non-negligible *decrease* of their bond lengths, by 0.02−0.03 Å, following each step of substitution, whereas simple considerations based on steric effects would lead to the prediction of the opposite tendency. As for the P∴P bond, which is stronger and stronger after each substitution, it also undergoes some gradual and significant bond length shortenings from the parent compound to the fully substituted one.

To summarize, methyl susbtitution weakens the bonding energies of all second-row dimers and increases their bond lengths. On the other hand, it leaves the bonding energies of the third-row dimers nearly unchanged or makes them slightly increase, while the three-electron bond lengths become shorter. These computational findings, which display some internal consistency within a given row of the periodic table but some apparent contradiction when different rows are considered, are intriguing enough to deserve a qualitative analysis to elucidate the root causes for the observed facts.

Interpretation of the Results

Since the three-electron bonds have a rather peculiar but clear relationship to S, the overlap between the highest occupied orbitals of each constituting fragment $H_{n-p}Me_pX$, this latter parameter will be at the center of our endeavor to interpret the above computational results. The overlaps could of course be calculated ab initio. However, we have deemed it useful to interpret the tendencies observed for the S parameter as a function of substitution in terms of the perturbative interactions between the methyl group(s) and the axial atomic orbital of the X atom. Such an analysis requires knowledge of the atomic orbital energies, which are not unambiguously defined at the ab initio level. On the other hand, the extended Hückel molecular orbital (EHMO) theory is free from such ambiguities and is the ideal framework for analyzing orbital interactions, having amply proved its usefulness as a complement to ab initio calculations for interpretative purposes. Therefore, and since we are interested in qualitative tendencies rather than accurate values of the overlap S, this parameter will be calculated by means of EHMO theory, using the ab initio optimized geometries.

Overlaps in the Model Unsubstituted Systems at Equilibrium Distances. Recall that the bonding energy in three-electron-bonded systems is a quadratic function of the overlap S between the highest occupied orbitals of each fragment $H_{n-p}Me_pX$ and that the optimal value of S is 0.17 according to a simple MO model. Let us consider the unsubstituted systems first ($n = 0$, first column of Table 2).

It is striking that none of the second-row unsubstituted dimers can reach the optimal value for the overlap, which turns out to be smaller than 0.17 in all cases. Moreover, there is a break between $H_3N∴NH_3^+$, which displays an overlap of 0.14, and the other second-row dimers, which display significantly smaller values, ca. 0.09−0.10. This situation is reminiscent of the "lone pair bond weakening effect" (LPBWE), which has been found to be responsible for a similar break in the series of homonuclear X−X two-electron bonds (X = C, N, O, F), as regards bonding energies as well as bond lengths.[78] This effect, which is associated with the presence of lone pairs on the X atom, has been interpreted as arising from the mutual Pauli repulsion that takes place between the lone pairs of each atom or between the lone pairs and the bonding electrons. There is no reason this effect should not be at work in three-electron bonds as well, all the more as these bonds are rather weak and oppose a weak resistance to the repulsive effect. In accord, the Pauli repulsion between the NH_3 fragments, which bear no lone pair, is much weaker, being reduced to a simple steric effect between N−H bonds, and the $H_3N∴NH_3^+$ system approaches the optimal S value of 0.17.

As has been noted for the two-electron bonds, the LPBWE is much less important in third-row than in second-row compounds, owing to larger bond lengths. Thus, $HCl∴ClH^+$ reaches an overlap of 0.14, despite its large number of lone pairs, and the LPBWE vanishes in $H_2S∴SH_2^+$, which displays the optimal overlap predicted by the model. As for the $H_3P∴PH_3^+$ system, which bears no lone pairs, it is obviously free from the LPBWE with a rather large value of S, which largely passes the theoretical optimal value. However, we will see below that this system is different from the others and cannot be considered as a pure three-electron bond.

Overlaps in Substituted Systems. The tendencies that have been noted above in the bonding energies of substituted compounds can now be related to the corresponding overlaps. A close correlation between the two quantities is found in the second-row dimers. As the bonding energies were found above to gradually decrease at each substitution step, the corresponding overlaps decrease in the same way. We will see in the next section that this overlap decrease is a consequence of the conjugation that takes place between the methyl group(s) and the atomic orbital of the X atom. This conjugation leads to a delocalization of the fragment orbital, which becomes less concentrated on the X atom and has less overlap capability with the neighboring fragment orbital. If it were not for the LPBWE, the system could retrieve the optimal overlap by shortening its bond length. However the repulsive effect of the LPBWE precludes any bond shortening, so that any weakening of the bond ends up to a bond lengthening. In accord, all substitutions in second-row dimers have the concomitant effects of decreasing the bonding energy and lengthening the bond. The same effect is seen in the $HCl∴ClH^+$ case, in which the LPBWE is still at work as can be seen by its overlap which is smaller than 0.17: substitution induces an overlap weakening which is associated with a bond lengthening.

To further confirm the above reasoning, let us now consider the cases where the LPBWE is negligible. In this case one may expect that any overlap weakening due to fragment orbital delocalization is immediately compensated for by a shortening of the bond, which retrieves the optimal overlap. In such a case, substitution is expected to have no significant effect on the overlap and to lead to bond *shortening*. This is exactly what is

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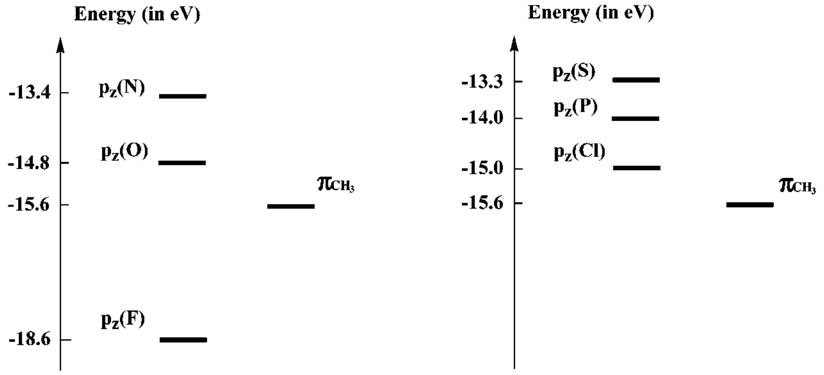

Figure 3. EHMO energy levels of the p_z orbital of the X atom and of the π_{CH_3} orbital of the methyl substituent.

Table 3. Coefficients of the p_z Orbitals in the σ^* Orbitals of the Dimers

	number of substitutions			
	0	1	2	3
p_z(F)	0.965	0.487		
p_z(O)	0.983	0.842	0.781	
p_z(N)	0.979	0.926	0.913	0.911
p_z(Cl)	0.995	0.827		
p_z(S)	1.000	0.901	0.938	
p_z(P)	0.823	0.711	0.735	0.736

found in the S∴S case: the overlaps vary by only 0.003 or less, while the bond length decreases by ca. 0.02 Å at each substitution step, thus leaving the bonding energy nearly unchanged. Similar tendencies are found in the P∴P case.

Now that a relationship between overlaps, bonding energies, and bonding distances have been established, let us try to relate the overlaps to the conjugation of the methyl group(s) with the X atoms.

MO Analysis of the Delocalization Effect. As a result of conjugation between a methyl group and the X atom, the highest occupied orbital of a $H_{n-p}Me_pX$ fragment can be more or less delocalized. This has some obvious consequences on the overlap between the fragment orbitals in the molecule: the more localized the orbital, the better the overlap. The conjugation involves the highest occupied orbital of the methyl group, referred to as π_{CH_3}, and that of the X atom, referred to as p_z. The interaction is all the more important as the two interacting orbitals lie close in energy. Figure 3 shows the energy levels of the p_z orbitals of the X atoms relative to π_{CH_3}, as obtained with the EHMO level computation.

According to this figure, the conjugation of the methyl group is expected to be more important with oxygen than with nitrogen and to be less and less important in the series Cl, P, S. These qualitative predictions, which strictly apply only to the first methyl substitution, are fully confirmed by the data reported in Table 3, the coefficients of the p_z orbital in the σ^* orbital of the dimers. These coefficients decrease upon methyl substitution by 14% and 5%, respectively, for the H_2O and H_3N fragments, and by 17%, 14%, and 10%, respectively, for the HCl, H_2S, and H_3P fragments.

The correlation between overlaps and p_z coefficients is very clear in second-row dimers, as these two quantities vary together in all cases. However, it is not so for third-row dimers. As an example, for the Cl∴Cl dimer, the p_z coefficients decreases by 17% upon substitution while the overlap S decreases by only 6%. This might be due to the greater diffuseness of third-row atoms orbitals, as compared to those of second-row elements.

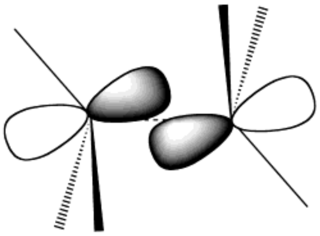

Figure 4. Schematic representation of the P−P bonding orbital of $H_3P\therefore PH_3^+$, in its most stable configuration.

A last case remains to be examined, that of the F∴F bond. At variance with all other heteroatoms, fluorine possesses a p_z orbital that lies *lower* in energy than the π_{CH_3} of methyl. As the final HOMO of the fragment is the antibonding combination of p_z and π_{CH_3}, it turns out to be more concentrated on the methyl group than on the X atom in the MeF substituted fragment. As a consequence of this extreme delocalization, the overlap between the two MeF fragment is dramatically decreased, and so is the bonding energy. This explains the break that has been noted in the substituent effects between the F∴F and other three-electron-bonded systems.

P∴P Case. With respect to the other cases, the P∴P bond displays two apparent anomalies. First, the overlap parameter S is very large, about 0.3, and much larger than the optimal parameter of 0.17. Second, the P−P bonding distances look abnormally short. Indeed, the bonding distances of the second-row dimers increase in the series F∴F, O∴O and N∴N, in accord with the increasing diffuse character of the orbitals. The distances also increase from Cl∴Cl to S∴S but fall off from S∴S to P∴P (Figure 2). The two anomalies are consistent with each other and are easily explained if one considers the geometry of $H_3P\therefore PH_3^+$ in details (Figure 4).

It appears that the two axes of the PH_3 pyramids do not point toward each other. Thus, the P−P bond in this radical cation is not a pure three-electron bond, but the three-electron interaction is combined with an interaction of another kind, presumably electrostatic, of dipole−dipole and/or hydrogen-bond type. Hence the short distance and the large overlap.

Conclusion

Methyl substitution has an important effect on bonding energies and bonding distances of three-electron-bonded radical cations of the second row, of the general type $[H_mX\therefore YH_n]^+$ (X, Y = N, O, F; n, m = 1−3). The demonstration has been made above for symmetrical systems, for technical reasons and for the sake of simplicity, but the property obviously extends to unsymmetrical systems ($X \neq Y$) and to all alkyl substituents, of which methyl is a faithful model. The substituent effect results, in all these cases, in a weakening of the bonding energy that is concomitant with a bond lengthening. The effect of a single substitution is stronger and stronger in the series $N\therefore N$, $O\therefore O$, $F\therefore F$, and the overall effect grows with the number of substitutions. It is due to the conjugation of the methyl group with the axial atomic orbital of the X atom, which results in a delocalization of the highest occupied orbital of the $H_{n-p}Me_pX$ fragment, which makes the overlap with the other fragment difficult.

In sharp contrast with second-row compounds, third-row three-electron bonds turn out to be practically insensitive to methyl substitution, although the methyl group conjugates in a non-negligible way with the X atoms. The reason for this insensitivity is 2-fold: (i) owing to the diffuseness of third-row orbitals, the delocalization of the HOMO of the $H_{n-p}Me_pX$ fragment does not much hinder its overlap capability with the other fragment, and (ii) the substituted molecule may adjust (in this case, shorten) its bond length to restore an optimal overlap between both fragment orbitals. This possibility is precluded in second-row compounds by the presence of side repulsive interactions between the fragments.

The three-electron bond is a rather peculiar type of bonding, being quadratic in a fragment overlap term that has an optimal value in the region of weak overlaps. Even if the optimal value of 0.17, which is given by the EHMO model, must not be considered as accurate, it is rewarding to see that several intriguing paradoxes, such as the contrasted sensitivities of third-row versus second-row compounds to substituent effects or the break between the $F\therefore F$ bond and the other ones, can be accounted for by simple considerations in terms of perturbative MO theory. Owing to these qualitative considerations, it is possible to generalize the predictions for third-row compounds to lower rows of the periodic table, in which three-electron bonds should be found to be insensitive to alkyl substituent effects as a general rule.

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