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Counterpoise estimates of the BSSE in the evaluation of protonation energies

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Counterpoise estimates of the BSSE in the evaluation of protonation energies have been calculated for basis sets ranging from minimal to split-valence plus polarization quality. Three-, five- and six-membered-ring heterocycles have been chosen as suitable model compounds for this study. Counterpoise corrections are significant, at the minimal basis set and 3-21G levels, when considering both, absolute and relative protonation energies and depend on the nature of the centre which undergoes protonation. In general, second- and third-order counterpoise corrections to the protonation energies are comparable to the corresponding SCF values. BSSE depend not only on the size of the basis sets but also on their quality. The presence in the basis of quite diffuse functions (either *sp* or *d*) leads to lower protonation energies and greater BSSE. Relative protonation energies are not substantially affected by BSSE or correlation effects.

Key words: BSSE — Protonation energies

1. Introduction

The possibility of obtaining gas-phase proton-transfer equilibrium constants with high accuracy by means of ion-cyclotron resonance (ICR) techniques [1] or high-pressure mass spectroscopy [2] has stimulated a growing interest in the analysis of factors - such as substituent effects [3], charge distributions [4], geometrical distortions [5], lone-pair interactions [6], etc. - affecting the intrinsic basicity of organic and inorganic compounds. In this sense, *ab initio* molecular orbital calculations helped at providing some additional insight into those factors. In particular, they have been used with success in reproducing (and in many cases in explaining) the trends of relative gas-phase basicities within a homologous series of compounds [3]; in predicting gas-phase Proton Affinities (PA) prior to their experimental measurement [7] or in identifying the preferred protonation centre [3c, 3i, 8] (identification which can be seldom carried out experimentally [9]).

To obtain accurate proton affinities the employment of very extended basis and thereby adequately describe correlation effects seems to be unavoidable [10]. Unfortunately, basis sets of this size rarely can be applied to study organic bases of real chemical interest and one is compelled to evaluate only relative gas-phase proton affinities using small basis sets (usually minimal basis) in the confidence that most of the errors arising from the finite character of the basis cancel. Actually, quite often, minimal bases reproduce fairly well relative gas-phase basicities; but there are no few exceptions for either small (imine-type [11]) or large (azole- [12] or azine-type [13]) compounds.

In this paper we aim at analyzing one of the sources of errors which can contribute to these discrepancies. Protonation energies are usually evaluated as the energy differences between the protonated and the unprotonated species, but while both systems are isoelectronic, the protonated form presents an additional nuclear centre and, as a consequence, more basis functions are employed in its description. Therefore, it seems obvious that basis set superposition effects are of some relevance in this particular problem and that basis set superposition errors (BSSE) can be of some importance when calculating protonation energies.

The evaluation of BSSE, both at SCF and post-SCF levels, has been the subject of a number of theoretical studies [14]. Although it seems now clear that this error can be only made negligible by the use of very large basis sets, which are, as indicated above, practically prohibitive for most systems of chemical interest, the BSSE is not always smaller the larger is the basis. In fact it has been shown [15] that while some minimal basis sets yield remarkably small BSSE, basis sets of $DZ+P$ quality yield surprisingly large ones. In view of the partial success of *ab initio* calculations to provide relative protonation energies, at even using small basis sets, it seems appealing to know: (a) if this source of error in evaluating intrinsic basicities is quantitatively important for this kind of basis sets, (b) how this error changes when enlarging the basis, (c) whether it depends on the nature of the center which undergoes protonation, (d) what is the importance of this error in beyond Hartree–Fock calculations for different basis sets. Actually, in some specific cases it has been found [16] that BSSE at the post-SCF level is comparable to its SCF analog. It would be also interesting to investigate how it changes when the basis include very diffuse components, either on the basic center or on the incoming proton, which seem to play an important role in the description of the electric multipole moments and polarizability of the base [17], (e) whether its magnitude depends on the size of the molecule which undergoes protonation.

To answer this series of questions we have selected two different sets of model compounds. On one hand we have considered three-membered ring heterocycles, whose size allows a thoughtful analysis of the BSSE at high levels of accuracy and on the other, some medium-size organic compounds, as imidazole or pyrazole, which have aroused much interest precisely because of their properties as bases, and which will permit us to answer point (e).

In order to better discuss point (c) we have included, in the first set, heterocycles containing nitrogen, oxygen and sulfur as heteroatom (azirane, oxirane and thiirane and their unsaturated counterparts, azirene, oxirene and thiirene). For the same reason, the second set includes, together with imidazole, pyrazole and pyridine, oxazole and isoxazole, as suitable model systems where two different basic centers are present on the same molecule.

2. Computational details

For three-membered-ring heterocycles, we have examined a reasonably large set of different atomic bases including the standard sets which are commonly used in the evaluation of protonation energies: STO-3G, 3-21G, 6-31G, 6-31G* and 6-31G**. Moreover, since the characteristics of the polarization functions seem to play an important role in the magnitude of the BSSE, at least when evaluating some particular complexes [18], we have considered also interesting to specifically analyze this point for protonation processes, by using "*d*" functions more diffuse than those included in the standard (6-31G* and 6-31G**) sets. In this sense, the 6-31G*/1 basis set differs from the 6-31G* in the exponent of the "*d*" functions centered on the heavy atoms, which is now one half ($\alpha = 0.4$) the standard value. In the 6-31G*/2 only the exponent of the "*d*" functions located on the basic center is changed, keeping the exponents of the remaining ones equal to the standard ($\alpha = 0.8$) value. In a similar way we have defined 6-31G**/1 and 6-31G**/2 basis sets. The 6-31G**/3 basis differs from the standard set in the exponent of the polarization functions centered on the incoming proton, which is also taken equal to one half ($\alpha = 0.55$) the standard value.

Since in protonation processes the electrostatic interactions between the bare proton and the base are likely some of the most important contributors to the stability of the protonated species, it seems important to have a reliable description of the electric multipole moments and polarizability of the base. To achieve this we have supplemented the standard 6-31G* basis with an additional diffuse set of "*d*" functions centered on the basic atom (6-31G* + *d* basis). The value adopted for the exponent of this additional set of polarization functions ($\alpha = 0.25$) was that proposed by van Duijneveldt et al. [17] as the optimum one to obtain reliable multipole moments and polarizabilities. For the particular case of sulfur containing compounds (thiirane and thiirene) where an adequate description of the polarization of the valence shell of the heteroatom can be crucial, two different sets of the 6-31G* + *d* quality were studied: the one already described, where the exponents of the *d* functions on sulfur are equal to 0.8 and 0.25 and another one, where we have adopted the values proposed by Siegbahn et al. [19] (1.18 and 0.39).

We have also considered the possibility of increasing the flexibility of the basis by supplementing the 6-31G* basis set by adding a very diffuse ($\alpha = 0.1$) *sp* shell on the basic center (6-31G* + p basis set) or on the incoming proton (6-31G* + p_H basis set).

The geometries of the different neutral and protonated species were fully optimized at the different levels of accuracy indicated above by using a suitable gradient optimization procedure [20].

Electron correlation effects were included by using the Møller–Plesset perturbation theory to second (MP2) and third (MP3) order [21–23]. Correlation energies were only evaluated for basis sets suitable for beyond-Hartree–Fock calculations (6-31G, 6-31G* or larger). In all cases the corresponding SCF structures were employed.

The BSSE was evaluated using the counterpoise procedure of Boys and Bernardi [24]. In this approach, we evaluate the energy of the unprotonated species within the basis set of the protonated form, with the "ghost orbitals" centered at the same point in space as the proton in the cation.

For medium-size bases (pyrazole, imidazole, pyridine, oxazole and isoxazole) the geometry optimization of neutral and protonated forms was restricted to the STO-3G, 3-21G and 6-31G levels for economic reasons. Nevertheless, in order to have an estimation of the effects of including polarization functions on both, heavy- and hydrogen-atoms, single point calculations using 6-31G*, 6-31G**, 6-31G* + d and 6-31G* + p basis sets at 6-31G optimized structures (to be referred hereafter as 6-31G*//6-31G, 6-31G**//6-31G, 6-31G* + d//6-31G and 6-31G* + p//6-31G, respectively) were performed for all of them.

3. Results and discussion

The computed counterpoise corrections (CC) to the protonation energies of three membered ring heterocycles, at both SCF and post-SCF levels, are listed in Table 1, for each standard basis set. Table 1 also shows the correlation corrections, at both MP2 and MP3 levels, evaluated using the larger bases.

Perusal of this table indicates that BSSE are quite important at the minimal basis set level, being some CC as high as 13 kcal/mol. Counterpoise corrections decrease by a factor of 2 to 4 when a split-valence 3-21G basis set is used. At these two levels of accuracy BSSE's on absolute protonation energies depend on the nature of the center which undergoes protonation, being greater (about twice) upon oxygen- or sulfur- than upon nitrogen-protonation. Moreover, the difference in the corresponding relative errors is still more significant since in general, nitrogen bases are stronger than oxygen or sulfur bases.

It is surprising to find that CC on the protonation of thiirane or thiirene at 3-21G (or 6-31G) level are quite small. This seems to be a direct consequence of the inadequacy of split-valence basis [25] to describe the protonated forms of this kind of sulfur-containing cycles, which are predicted to be very loosely bound species.

In general, the counterpoise corrections at the 3-21G level are twice those obtained at the 6-31G level, revealing that a poorer description of the innermost shells has

Table 1. Counterpoise and correlation (within parenthesis) corrections to the protonation energies of three-membered-ring heterocycles (all values in kcal/mol)

	Azirane	Azirene	Oxirane	Oxirene	Thiirane	Thiirene
STO-3G	5.0	5.2	11.6	13.0	11.2	12.4
3-21G	2.0	2.6	3.3	5.8	1.7	0.5
6-31G						
SCF	1.3	1.5	1.0	1.1	0.3	0.3
MP2	4.0 (3.7)	4.3 (5.2)	3.4 (7.1)	3.5 (5.4)	2.3 (1.5)	2.3 (0.0)
MP3	3.9 (2.3)	4.0 (3.4)	3.0 (5.6)	3.1 (3.4)	2.4 (0.7)	2.3 (1.2)
6-31G*						
SCF	0.3	0.4	0.5	0.8	0.2	0.2
MP2	1.7 (5.1)	1.9 (6.6)	1.9 (5.6)	1.0 (7.3)	2.0 (0.0)	2.1 (2.9)
MP3	1.7 (3.1)	1.8 (4.4)	1.7 (3.4)	1.2 (4.4)	2.1 (2.2)	2.2 (0.3)
6-31G**						
SCF	0.4	0.5	0.7	0.9	0.3	0.2
MP2	3.1 (4.9)	3.2 (5.0)	3.7 (4.5)	4.0 (4.4)	3.2 (0.6)	3.4 (0.5)
MP3		3.1 (2.6)	3.5 (2.2)	3.8 (1.6)		

a noticeable influence in the BSSE. A similar finding was reported by Hobza et al. [15] in a study of $(HF)_2$ and $(H_2O)_2$ complexes.

A further decrease by a factor of 2 to 4 in the counterpoise corrections is found when including polarization functions in the basis. These results seem to indicate that, at lower levels of accuracy, the counterpoise model plays the role of a polarization. In other words, when one calculates, at minimal or split-valence levels, the energy of the unprotonated species using the basis set of the protonated form, the "ghost orbitals" behave as polarization functions, describing the charge density far from the nucleus of the corresponding basic center and in the region physically occupied by its lone-pair orbitals. Of course this effect is greater the lower is the flexibility of the basis set and becomes maximum at the minimal basis set level. It seems also reasonable to find that this effect is quantitatively different for nitrogen- than for oxygen- or sulfur-protonation, because in the latter cases the existence of two lone-pair orbitals in the region described by the "ghost orbitals" makes the counterpoise correction greater.

Another important point is that second- and third-order counterpoise corrections to the protonation energies are comparable, and in some cases larger, than the SCF values.. This implies that absolute protonation energies become about 8.0 (or more) kcal/mol lower upon inclusion of both, counterpoise and correlation corrections. It is also interesting to emphasize that the inclusion of extra components in the basis does not lead necessarily to a decrease of the BSSE and that the change observed in its magnitude may be markedly different if electron correlation is taken into account. For instance, and illustrating the first point, we have found that the corrections when polarization functions are included only on the heavy atoms (6-31G* basis), are about the same as those obtained when polarization functions are also centered on hydrogens (6-31G** basis). It should be noticed however (illustrating the second point) that this is true only at the SCF level, since at the MP2 or MP3 levels the CC when employing the larger basis set are about twice those obtained when using the former. In fact, it is quite significant that at the 6-31G** level the second and third order counterpoise corrections are quite similar to those obtained with the unpolarized 6-31G basis. This seems to indicate that the inclusion of polarization functions on the hydrogens, which implies that the protonated species are relatively better described than the unprotonated ones, amelliorates however the description of electron correlation in the lone-pair region of the basic center.

We shall discuss now the sensitivity of the BSSE to the characteristics of the polarization functions. Since these characteristics may affect also the value of absolute and relative protonation energies, we have restricted our analysis to azirane, oxirane and thiirane whose experimental gas-phase proton affinities are known [26].

In Table 2 we have summarized our absolute protonation energies together with the corresponding counterpoise corrections calculated at the SCF as well as correlated levels of theory for each non-standard basis set. Several facts of this table should be singled out for comment: Our results at the 6-31G*/1 level show that not only the size but also the quality of the basis set have a certain influence in the magnitude of the BSSE. Actually, when the polarization functions centered on the heavy atoms are more diffuse the BSSE increases, being about twice that obtained when a 6-31G* basis is employed in SCF calculations (see Table 1); this increase is more moderate when taking into account correlation effects.

The CC obtained at the 6-31G*/2 level clearly show that the polarization functions which contribute the most to this increase in the BSSE are those centered on the heavy atom. Actually the BSSE's obtained with this basis set are almost identical to those found when a 6-31G*/1 basis is used. However, the corresponding absolute protonation energies obtained at the 6-31G*/2 level, i.e. when only the "*d*" functions on the basic centre become more diffuse, are closer to the experimental values [26].

Similar effects, although much more moderate, are observed when considering the results obtained at the 6-31G**/1 and 6-31G**/2 levels i.e. when the basis set includes also polarization functions on the hydrogen atoms, the increase in the BSSE when more diffuse "*d*" functions are used is not very significant (see Table 1).

The use of more diffuse polarization functions on the incoming proton (6-31G**/3 basis set) does not affect significantly to the BSSE either at the SCF or correlated levels of theory.

When the basis set is augmented either by a set of "*d*" functions or a single *sp* shell centered on the basic atom, one observes a small decrease of the absolute protonation energies, probably as a consequence of a better description of the multipole moments of the bases; actually, their calculated dipole moments become 0.1 D to 0.2 D smaller and closer to the experimental outcomes. However, the values obtained either for these absolute protonation energies or for the corresponding CC do not differ markedly from those obtained with the smaller,

Table 2. Absolute protonation energies and counterpoise corrections (within parenthesis) for some three-membered-ring heterocycles using different polarized basis sets (all values in kcal/mol)

	Azirane	Oxirane	Thiirane	
6-31G*/1				
SCF	230.8 (0.6)	197.2 (1.0)	200.0 (0.2)	
MP2	224.7 (2.0)	191.1 (2.4)	196.4 (1.2)	
MP3	226.7 (1.9)	193.3 (2.2)	199.0 (1.2)	
6-31G*/2				
SCF	231.0 (0.4)	195.7 (0.7)	199.8 (0.2)	
MP2	225.4 (1.8)	189.9 (2.2)	197.2 (1.3)	
MP3	227.5 (1.7)	192.1 (2.0)	199.7 (1.2)	
6-31G**/1				
SCF	235.2 (0.7)	203.1 (1.1)	201.1 (0.2)	
MP2		197.9 (4.2)		
6-31G**/2				
SCF	235.1 (0.5)	201.5 (1.0)	201.0 (0.3)	
MP2		196.5 (4.0)		
6-31G**/3				
SCF	236.1 (0.6)	202.3 (1.0)	201.8 (0.3)	
MP2		197.5 (3.7)		
6-31G* + *d*				
SCF	230.6 (0.9)	196.2 (1.1)	200.0 (0.1)[a]	201.4 (0.2)[b]
MP2	224.4 (2.1)	190.1 (2.5)	193.4 (1.3)[a]	199.6 (1.1)[b]
MP3	226.7 (1.9)	192.5 (2.3)		200.7 (1.1)[b]
6-31G* + *p*				
SCF	231.0 (1.0)	193.2 (0.4)	199.7 (0.3)	
MP2	224.8 (2.5)	186.1 (1.2)	199.4 (1.9)	
MP3	227.1 (2.3)	188.9 (1.3)	201.7 (2.0)	
6-31G* + p_H				
SCF	232.3 (2.2)	195.6 (1.9)	199.7 (0.5)	
MP2	228.2 (5.2)	191.3 (4.9)	197.6 (4.8)	
MP3	230.2 (4.9)	193.3 (4.3)	199.5 (4.5)	

[a] Exponents of the "*d*" functions centered on sulfur equal to 1.18 and 0.39

[b] Exponents of the "*d*" functions centered on sulfur equal to 0.8 and 0.25

6-31G*/2 or 6-31G*/1, basis sets. This means that only the more diffuse of the two sets of "*d*" functions centered on the basic atom contributes to the decrease in the calculated protonation energies and the parallel increase in the BSSE. Consequently, the same quantitative effects are obtained when this set is replaced by a diffuse *sp* shell or by making more diffuse the "*d*" functions of a 6-31G* basis. These results also show that the inclusion in the basis of a set of diffuse functions (*sp* or *d*) located on the basic center leads to protonation energies, which after including the counterpoise correction, are in better agreement with the corresponding experimental values.

A completely different behavior is found when the basis is augmented by including a single diffuse *sp* shell on the incoming proton. The results obtained with the 6-31G* + p_H basis set show that, at the SCF or post-SCF levels of accuracy, the absolute protonation energies are greater and the corresponding BSSE much greater than those obtained with the unsupplemented basis. The first finding is a direct consequence of the improvement in the description of the protonated species, but the important point is that the relative increase in the corresponding BSSE is quantitatively more important. The final consequence is that protonation energies at the 6-31G*+p_H level, after counterpoise corrections, although much higher than those discussed above, when diffuse functions are centered on the atom which undergoes protonation, are lower than those obtained with a 6-31G* basis.

In general CC for thiirane and thiirene are one half those obtained for oxygen and nitrogen bases. This may be a consequence of the fact that, being sulfur a second row atom, there are more orbitals centered in that region of space and the relative influence of the "ghost" orbitals becomes smaller. It is worth also noting that, for sulfur containing compounds, the additional diffuse component of supplemented 6-31G*+*d* or 6-31G*+*p* basis sets, participates significantly in the description of electron correlation effects. In fact, while for 6-31G*-type of basis the second order correlation corrections are quite small (about 1.5 kcal/mol or less), for 6-31G*+*d* or 6-31G*+*p* basis sets, they become considerably greater (about 6.6 kcal/mol). We can therefore conclude that whereas for systems where the basic center is a first-row atom, singly polarized basis sets, as 6-31G*, provide a reasonably good description of electron correlation effects in protonation processes, for sulfur containing compounds this requires the inclusion of an additional set of diffuse (either *sp* or "*d*") functions.

Finally, it must be remarked that for basis of a 6-31G or better quality, relative protonation energies are not significantly affected by either correlation or counterpoise corrections since both are practically independent on the nature of the basic center and depend only on the size and quality of the basis set.

We present in Table 3 the absolute protonation energies and the corresponding CC obtained for medium-size compounds. These results show that the conclusions reached when dealing with smaller systems are applicable to the present cases, but the most significant fact is that the magnitude of the BSSE is practically the same for three-, five- or six-membered rings in protonation process. As a

Table 3. Absolute protonation energies and counterpoise corrections (within parenthesis) for some five- and six-membered-ring heterocycles using different basis sets (all values in kcal/mol)

	STO-3G	3-21G	6-31G	6-31G*// 6-31G	6-31G**// 6-31G	6-31G* +*d*// 6-31G	6-31G* +*p*// 6-31G
Imidazole	283.4 (4.6)	249.9 (0.6)	247.1 (0.9)	240.1 (0.5)	242.8 (0.4)	239.8 (0.9)	238.9 (0.2)
Pyrazole	265.0 (4.0)	233.4 (0.4)	232.6 (0.7)	227.0 (0.2)	230.0 (0.4)	227.2 (0.6)	226.2 (0.2)
Pyridine	227.1 (4.7)	241.3 (0.3)	241.0 (0.7)	235.7 (0.3)	238.6 (0.4)	235.6 (0.8)	234.7 (0.3)
Oxazole							
N-prot.	263.0 (4.1)	228.1 (2.2)	226.2 (1.1)	222.3 (0.3)	225.0 (0.3)	222.0 (0.7)	221.4 (0.2)
O-prot.	209.7 (8.5)	176.5 (2.6)	172.4 (1.0)	161.7 (0.3)	166.4 (0.6)	162.8 (0.8)	161.5 (0.3)
Isoxazole							
N-prot.	250.9 (3.6)	216.7 (1.4)	217.3 (1.0)	215.2 (0.3)	218.1 (0.4)	215.5 (0.5)	214.6 (0.2)
O-prot.	216.6 (7.8)	186.6 (2.5)	183.9 (1.3)	170.2 (0.3)	174.8 (0.6)	170.8 (0.8)	169.7 (0.4)

consequence, the same BSSE dependence on the nature of the basic center is observed here for minimal and split-valence 3-21G basis sets. This permits us to conclude that for protonation process the BSSE would be about 10 kcal/mol for molecules which protonate on oxygen atoms and about 5 kcal/mol for molecules which protonate on nitrogen atoms if the basis sets used are of a minimal quality. In this respect, it should be taken into account that for many systems this error is of the same order as the difference between their absolute basicities, (for instance, imidazole is only 5 kcal/mol more basic than pyridine), and therefore it can affect the validity of the basicity ordering predicted at this level of accuracy.

Similarly to what has been found for three-membered ring heterocycles: (a) the inclusion of a diffuse set of functions (*sp* or *d*) on a split-valence basis set leads to lower corrected protonation energies which are, accordingly, in better agreement with experimental values. (b) relative protonation energies are not significantly affected by BSSE, if exception is made of the STO-3G minimal basis.

4. Conclusions

Our results show that calculated protonation energies, after counterpoise corrections, are still in error with respect to experimental values [3i, 26]. Even at the highest level of accuracy considered here, calculated values are about 10 to 15 kcal/mol higher than experimental ones. For small basis, as STO-3G, BSSE may be of the same order as the difference between absolute basicities of different species. This implies that, although STO-3G basis set usually yields the correct ordering, this result may be not meaningful.

At this level of accuracy counterpoise corrections to protonation energies depend strongly on the nature of the atomic center which undergoes protonation, since, for small basis sets, the "*ghost*" orbitals play the role of polarization functions.

In general BSSE at the 3-21G level are twice those observed at the 6-31G level, indicating that a proper description of the innermost shells may be of importance.

For many basis sets second- and third-order counterpoise corrections to the protonation energies are comparable, and in some cases larger, than the corresponding SCF values. We have also showed that enlarging the basis does not necessarily yield a smaller BSSE, because its magnitude depends not only on the size of the basis, but also on its quality and on the inclusion of correlation effects.

When a basis of a 6-31G* quality is augmented by diffuse functions, either *sp* or "*d*", on the basic center an appreciable increase in the BSSE is obtained. Simultaneously, and probably due to a better description of the electric multipole moments of the base, the absolute protonation energies so evaluated are lower, in better agreement with experimental evidence. These diffuse functions seem to be crucial to achieve an appropriate description of correlation effects in the protonation of sulfur-containing bases. It should be also emphasized that 6-31G*+*d* or 6-31G*+*p* basis sets, which are of a 6-311G* quality on the basic center, yield protonation energies and BSSE almost identical to those obtained at the 6-31G* level, if the exponent of the "*d*" functions centered on the basic position is made smaller. This would indicate that a further decrease of the calculated protonation energies would require basis sets even larger than a 6-311G* and likely the inclusion of correlation corrections to higher order.

Finally, we have also shown that relative protonation energies are not substantially affected by counterpoise or correlation corrections. The former do not change appreciably with the size of the molecule which undergoes protonation.

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