# Benchmark calculations of the shielding constants in the water dimer

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## Abstract

The NMR shielding constants in $(H_2O)_2$ have been calculated using GIAO-SCF, MP2, MP4 and CCSD methods and for a range of basis sets. According to the obtained results the 6-311++G[**] or aug-cc-pVDZ basis sets are recommended for SCF calculations, and the aug-cc-pVXZ series is suggested for correlated calculations of the interaction-induced changes in the shielding constants. The counterpoise correction improves the results towards the basis set limit and is essential in the case of $^{17}O$ shielding. Correlation effects are substantial for the changes in $^{17}O$ shielding, less so for $^{1}H$ shielding. They are overestimated by the MP2 method. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

NMR shielding constants are among the most important spectroscopic parameters in chemistry. They are basic tools in the detection and characterisation of hydrogen bonds, in particular in biological systems [1–3]. The most widely used parameter in these studies is the isotropic shielding (or chemical shift) of the proton forming the hydrogen bond [1,4]. However, the $^{15}N$ and $^{17}O$ shielding parameters of the proton acceptor atom and the proton donor atom are also gaining in importance [3–6].

The usefulness of shielding constants in the experimental detection of hydrogen bonds gave rise to a considerable number of theoretical ab initio studies of the shielding constants in hydrogen-bonded systems [4,7–15]. The water dimer itself has been investigated several times in this respect [9,12,13]. Various wave function models have been applied in these papers. However, in none of these studies have some basic aspects of the calculations been systematically examined, namely the choice of the basis set, the advisability of using the counterpoise correction, and the significance of electron correlation effects.

The choice of basis set in calculations of complexation-induced changes in shielding constants is difficult, since the basis set should be appropriate for both the calculations of the shielding constants and the interaction energy. As far as we know, there is no systematic study of this problem in the literature. The problem of using the counterpoise correction method in calculations of the interaction energy was widely discussed [16–19]. However, there is little literature on the counterpoise correction method when applied to NMR properties [10,12,14,20]. From the practical point of

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view, there are two questions to be answered. First, is the value of the counterpoise correction for the shielding constant a measure of the basis set incompleteness? Second, does the application of the counterpoise correction bring the calculated changes in the shielding constant nearer the basis set limit?

The problem of the significance of electron correlation in the calculations of the shielding constants has been extensively investigated for isolated molecules [21–24]. However, little is known of these effects on the complexation-induced changes in the shielding constants, where two factors are interconnected: the role of electron correlation in the interaction energy and in the calculations of the shielding constants. Computational studies in this subject seldom go beyond the SCF level [12,14,15].

These issues are addressed in the present letter. We report the shielding constants in the water dimer calculated by means of the SCF and MP2 methods with a wide range of basis sets currently in use in ab initio calculations. The convergence of the results with the basis set size is discussed and some suggestions on the optimal choice of basis set are made. Afterwards, the NMR shielding constants of water and their hydrogen-bond-induced changes calculated at the SCF and MP2 levels are compared with the results obtained using CCSD and higher-order perturbation theory methods.

## 2. Computational details

The calculations of the NMR shielding constants have been carried out by means of the SCF, CCSD, MP2 and MP4 methods, using the gauge including atomic orbitals (GIAO) [25–27]. The employed basis sets range from small basis sets of the 3-21G, 6-21G and 6-311G variety [28] to the correlation-consistent Dunning basis sets (cc-pVXZ, X = D,T,Q,5), correlation-consistent Dunning basis sets augmented by diffuse orbitals (aug-cc-pVXZ), and by core–valence correlating orbitals (aug-cc-pCVXZ) [29–31]. The calculations of the shielding constants at the SCF and MP2 levels have been performed using the GAUSSIAN98 software [28]. The ACES II software [32] has been

used for the MP4 and CCSD calculations. The basis set superposition error (BSSE) for the complexation-induced changes of the shielding constants has been estimated using the counterpoise correction method [16].

The vibrationally averaged geometrical parameters suggested in [33] have been used for the water monomer. The experimental intermolecular geometrical parametres of the dimer are taken from Ref. [34].

## 3. Results

### 3.1. The choice of basis set

In this chapter the convergence of the calculated complexation-induced shielding constants in water with basis set size is discussed and the optimal medium-size basis sets for this type of calculation are suggested. The counterpoise correction is considered as a measure of the basis set incompleteness and as a method for improving the results of the calculations. Firstly these issues are discussed for the SCF calculations, then for the correlated MP2 calculations.

#### 3.1.1. SCF calculations

Table 1 contains the $^{17}$O and $^{1}$H isotropic shielding constants and their complexation-induced changes calculated at the SCF level using small to medium size basis sets and the large aug-cc-pV5Z basis set. The latter results should approach the basis set limit.

The hydrogen-bond-induced change in the $^{1}$H shielding depends little on the basis set size. The calculated value is in good agreement with the assumed basis set limit already for the basis sets containing 50–60 functions for the water dimer. It is worth noting that even the $\Delta\sigma(^{1}H)$ values obtained by means of the smallest basis sets are in qualitative agreement with the assumed basis set limit, in contrast to the absolute shielding $\sigma(^{1}H)$ in the $H_2O$ monomer.

The calculations of the hydrogen-bond-induced changes in the $^{17}$O shielding constants require the use of larger basis sets than those needed for the calculations of the changes in the $^{1}$H shielding.

Table 1
The NMR shielding constants for $H_2O$ and their changes upon dimer formation calculated at the SCF level; counterpoise corrected (cc) and uncorrected (n-cc) results

| Basis set | n of $f$[a] | $\sigma(^{17}O)$ | $\sigma(^1H)$ | $\Delta\sigma(^{17}O)^{acc}$[b] | | $\Delta\sigma(^{17}O)^{don}$[c] | | $\Delta\sigma(^1H)$[d] | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | n-cc | cc | n-cc | cc | n-cc | cc |
| 3-21G | 26 | 333.38 | 32.32 | 6.49 | 1.51 | 10.52 | 11.40 | −2.03 | −2.00 |
| 6-31G | 26 | 319.02 | 32.11 | 0.23 | −0.91 | 8.44 | 9.02 | −2.36 | −2.29 |
| 6-31G* | 38 | 321.36 | 31.25 | −1.23 | −2.19 | 6.91 | 7.39 | −2.21 | −2.15 |
| 6-31G** | 50 | 331.56 | 30.57 | −1.46 | −2.77 | 6.52 | 6.84 | −2.45 | −2.45 |
| 6-311G** | 60 | 335.61 | 30.88 | 0.20 | −5.02 | 6.96 | 6.79 | −2.43 | −2.44 |
| 6-31++G** | 62 | 331.51 | 30.29 | −3.95 | −5.30 | 1.55 | 1.04 | −2.66 | −2.67 |
| 6-311++G** | 72 | 318.49 | 30.69 | −3.32 | −5.20 | 2.36 | 1.46 | −2.64 | −2.62 |
| 6-311++G(2d,2p) | 94 | 319.92 | 30.28 | −4.58 | −4.84 | 1.19 | 1.08 | −2.61 | −2.59 |
| cc-pVDZ | 48 | 339.86 | 30.81 | −2.00 | −4.53 | 5.90 | 6.35 | −2.41 | −2.41 |
| aug-cc-pVDZ | 82 | 329.66 | 30.61 | −4.37 | −4.74 | 0.88 | 0.75 | −2.53 | −2.58 |
| aug-cc-pCVDZ | 90 | 328.03 | 30.13 | −4.46 | −4.76 | 0.89 | 0.79 | −2.54 | −2.58 |
| aug-cc-pV5Z | 574 | 320.15 | 29.92 | −4.96 | −4.96 | 1.09 | 1.09 | −2.62 | −2.62 |

[a] Number of contracted basis functions for the dimer.
[b] The hydrogen-bond induced change in the $^{17}O$ shielding of proton acceptor.
[c] The hydrogen-bond induced change in the $^{17}O$ shielding of proton donor.
[d] The hydrogen-bond induced change in the shielding of the proton forming the hydrogen bond.

The results obtained with basis sets without diffuse functions are practically meaningless for the proton donor. For the proton acceptor the counterpoise corrected results obtained with the 6-311G** and cc-pVDZ basis sets are in approximate agreement with the aug-cc-pV5Z results, but this consistency may be accidental, since BSSE is very large. The most reliable results are obtained with basis sets containing more than 80 functions. Also the 6-311++G** counterpoise corrected results are in agreement with the aug-cc-pV5Z ones, although BSSE is large. It reveals that the addition of the diffuse functions does not obviate, as was suggested in [12], the need for the counterpoise correction if the basis set is not balanced.

The convergence of the calculated $H_2O$ shielding constants and their hydrogen-bond-induced changes in the series of the correlation consistent basis sets is depicted in Fig. 1 (the shieldings in $H_2O$ monomer) and Fig. 2 (dimerisation-induced changes of the shieldings). The cardinal number $X$ is equal to 2 for the aug-cc-pVDZ basis set of double-zeta quality, 3 for aug-cc-pVTZ, etc.

Analysis of Fig. 1 leads to the conclusion that in the cc-pVXZ series the increase of the cardinal number $X$ by one caused reduction in error approximately by a factor of 3. The addition of diffuse functions (in aug-cc-pVXZ sets) speeds up

considerably the convergence of the shielding constants with the extension of the basis set, in particular for the $^{17}O$ shielding, for which the aug-cc-pVTZ result is very near the basis set limit. For the $^1H$ shielding the convergence of the aug-cc-pVXZ results towards the basis set limit is similar as for the cc-pVXZ series and slower than for the $^{17}O$ shielding.

Fig. 1 clearly indicates that there is little gain in using the Dunning basis sets with core–valence correlating functions (of the aug-cc-pCVXZ variety) in the calculations of the NMR shielding constants. For the $^{17}O$ shielding in the water monomer (Fig. 1) some improvement over the original basis set can be observed only for the smallest aug-cc-pCVDZ set. Not suprisingly, the calculated $^1H$ shielding is practically unaffected by this extension of the basis sets, since the added functions are centered on the oxygen nucleus.

The convergence of the hydrogen-bond-induced changes in the NMR shielding constants with the systematic increase in the basis set (Fig. 2) is less smooth than that of the absolute shielding constants of the $H_2O$ monomer (Fig. 1). However, certain trends are clearly visible. The basis set limit is probably approached, since the calculated results change little when the cardinal number $X$ is increased from 4 to 5. Fig. 2 also shows that the
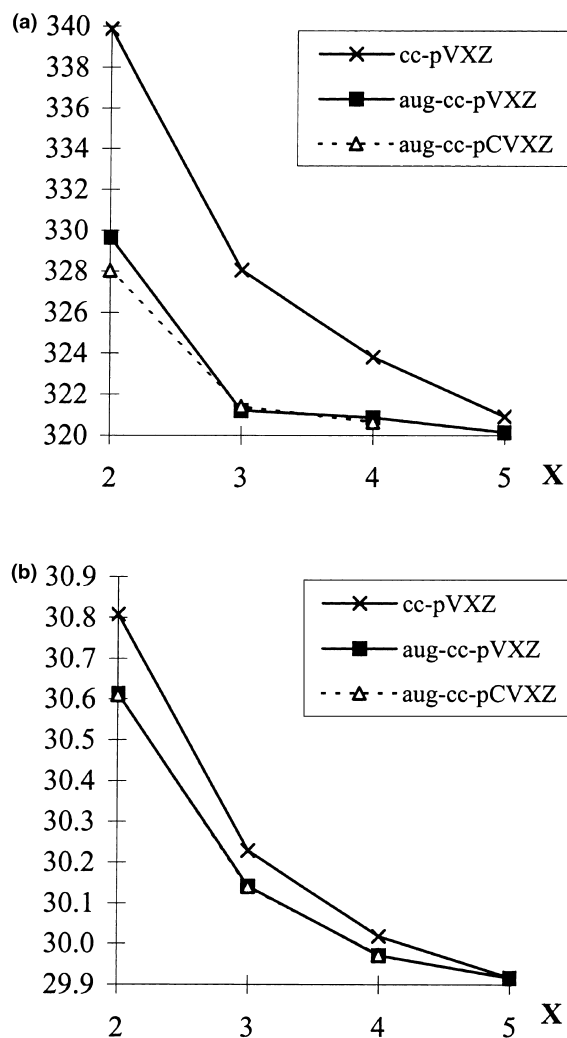
Fig. 1. The convergence of the calculated NMR shielding constants (in ppm) for $H_2O$ monomer with the size of the correlation consistent basis set: (a) $^{17}O$ isotropic shielding; (b) $^1H$ isotropic shielding.



Fig. 2. The convergence of the calculated complexation-induced changes in the NMR shielding constants (in ppm) for $H_2O$ with the size of the correlation consistent basis set; the counterpoise corrected and uncorrected results: (a) the change in $^1H$ isotropic shielding; (b) the change in $^{17}O$ isotropic shielding of the proton acceptor; (c) the change in $^{17}O$ isotropic shielding of the proton donor.

addition of the diffuse functions is essential for this type of calculation. A striking example of this is the change in the proton donor shielding, for which the cc-pV5Z result (402 basis functions) is equally near to the aug-cc-pV5Z result (an assumed basis set limit) as the aug-cc-pVDZ result (82 basis functions) is. In contrast, the addition of the core–valence correlating functions does not have any significant effect on the results, as for the absolute shielding constants of the monomer.
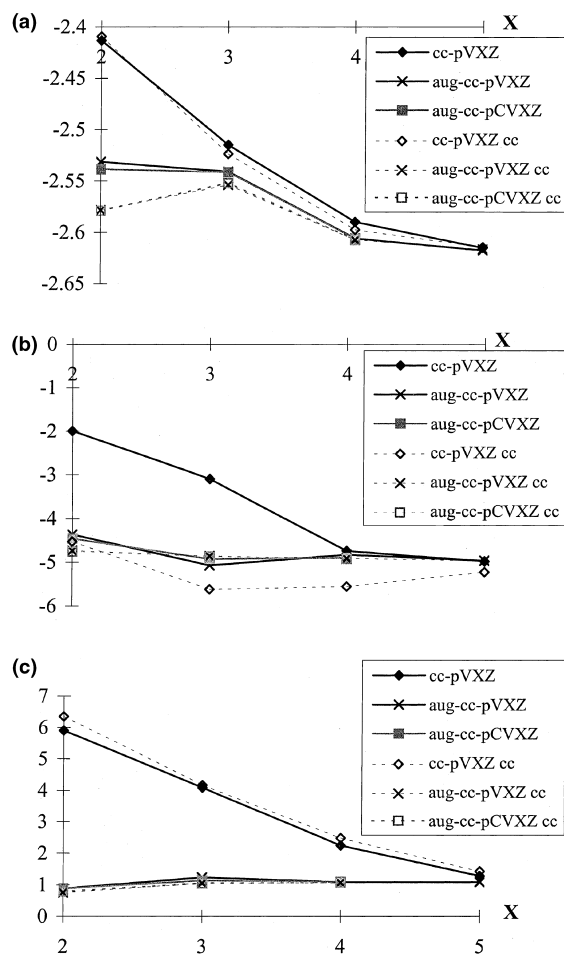
The application of the counterpoise correction improves very considerably the result of the calculations of the shielding change in the proton acceptor, especially when the cc-pVXZ basis sets are used. It improves also, although to a lesser extent, the calculated changes in the other shieldings.

To sum up, we suggest the following for calculations of the hydrogen-bond induced changes in the shielding constants of large systems, where

only small basis sets can be used. The 6-31++G** basis set can be recommended for SCF calculations of the changes in the proton shieldings and the application of the counterpoise correction is then not necessary. For the SCF calculations of the hydrogen-bond-induced changes in the shielding constants of the heavier nuclei (here: [17]O) the use of the larger 6-311++G** basis set would be advisable, if possible enriched by additional polarisation functions. The other good choice is the aug-cc-pVDZ basis set. The application of the counterpoise correction is essential in that case, especially if the basis sets of the 6-31G or 6-311G variety are used. When the use of larger basis sets is possible and the estimation of the basis set limit is attempted, the series of the augmented correlation-consistent basis sets aug-cc-pVXZ is recommended. The addition of the tight core–valence correlating functions does not seem necessary.

### 3.1.2. MP2 calculations

Usually, calculations including electron correlation effects have higher basis set requirements than SCF ones. This is true also in the case of shielding constants and their hydrogen-bond induced changes, as is clear when Table 2, reporting the MP2 results, is compared with Table 1, reporting the SCF results. This tendency is more noticeable for the [17]O shielding constant than for the ^{1}H shielding constant, since electron correlation effects on the latter are small. For the change of the shielding constant of the proton donor oxygen the results obtained with the smallest basis sets (up to 60 functions) are of the wrong sign, even after the counterpoise correction. Otherwise, the conclusions concerning the role of the diffuse and core–valence correlating functions drawn from the SCF results are valid also for the MP2 results. Predictably, the basis sets of the 6-31G or 6-311G variety, suitable for the calculations on the SCF level (see Table 1) perform less well in the MP2 calculations. The 6-311++G(2d,2p) results are rather inferior to the aug-cc-pVDZ ones, although the latter basis set is smaller: BSSE is larger for 6-311++G(2d,2p) and the calculated change of the shielding constant of the proton donor oxygen is different from that obtained with the aug-cc-pVQZ basis set, the largest we have managed to use for the MP2 calculations.

Table 2 shows that the counterpoise correction for the shielding constants at the MP2 level is of similar magnitude as on the SCF level for all tested basis sets. It confirms previous observations [14,15] that the interaction-induced shielding

Table 2

The NMR shielding constants for $H_2O$ and their changes upon dimer formation calculated at the MP2 level; counterpoise corrected (cc) and uncorrected (n-cc) results

| Basis set | $n$ of $f$[a] | $\sigma(^{17}O)$ | $\sigma(^1H)$ | $\Delta\sigma(^{17}O)^{acc}$[b] | | $\Delta\sigma(^{17}O)^{don}$[c] | | $\Delta\sigma(^1H)^d$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | n-cc | cc | n-cc | cc | n-cc | cc |
| 3-21G | 26 | 344.20 | 32.30 | 6.51 | 0.42 | 9.24 | 10.59 | −1.85 | −1.83 |
| 6-31G | 26 | 338.57 | 32.00 | 0.04 | −2.06 | 6.24 | 7.11 | −2.19 | −2.11 |
| 6-31G* | 38 | 343.47 | 31.07 | −0.67 | −2.95 | 4.76 | 5.40 | −2.05 | −1.98 |
| 6-31G** | 50 | 346.80 | 30.89 | −0.94 | −3.42 | 4.65 | 5.16 | −2.34 | −2.35 |
| 6-311G** | 60 | 354.60 | 31.11 | 0.48 | −6.12 | 5.15 | 5.11 | −2.28 | −2.31 |
| 6-31++G** | 62 | 351.33 | 30.48 | −4.26 | −6.27 | −1.25 | −1.85 | −2.59 | −2.62 |
| 6-311++G** | 72 | 338.37 | 30.85 | −3.09 | −6.48 | −0.20 | −1.76 | −2.57 | −2.56 |
| 6-311++G(2d,2p) | 94 | 339.09 | 30.41 | −5.45 | −6.14 | −2.04 | −2.63 | −2.48 | −2.46 |
| cc-pVDZ | 48 | 356.23 | 31.04 | −2.01 | −5.40 | 4.00 | 4.69 | −2.28 | −2.29 |
| aug-cc-pVDZ | 82 | 348.07 | 30.69 | −6.10 | −6.01 | −3.26 | −3.07 | −2.38 | −2.43 |
| aug-cc-pCVDZ | 90 | 346.45 | 30.68 | −6.11 | −6.03 | −3.22 | −3.05 | −2.38 | −2.43 |
| aug-cc-pVTZ | 184 | 340.45 | 30.14 | −6.18 | −6.15 | −3.00 | −3.17 | −2.37 | −2.38 |
| aug-cc-pVQZ | 344 | 340.37 | 29.91 | −6.12 | −6.20 | −3.23 | −3.25 | −2.42 | −2.43 |

[a] Number of contracted basis functions for the dimer.
[b] The hydrogen-bond induced change in the [17]O shielding of proton acceptor.
[c] The hydrogen-bond induced change in the [17]O shielding of proton donor.
[d] The hydrogen-bond induced change in the shielding of the proton forming the hydrogen bond.

constants differ in this respect from the interaction energy [18,19]. As for the SCF results, the application of the counterpoise correction improves most significantly the hydrogen-bond induced changes in the proton acceptor oxygen calculated with the basis sets which do not contain diffuse functions.

### 3.2. Electron correlation effects

The NMR shielding constants in $H_2O$ monomer and their hydrogen-bond-induced changes calculated at different correlation levels with the aug-cc-pVTZ basis set are given in Table 3. In agreement with previous studies [14,15], the hydrogen-bond-induced change in ^{1}H shielding does not exhibit significant correlation effects, although for the absolute ^{1}H shielding in $H_2O$ monomer the MP4 and CCSD results differ significantly from the SCF ones. The most sensitive parameter to electron correlation effects is the change in the [17]O shielding of the proton donor, where the CCSD and MP4 calculations lead to results of opposite sign to the SCF one. The hydrogen-bond induced change in the [17]O shielding of the proton acceptor obtained at the SCF level is slightly lower than the results of more sophisticated calculations, but qualitatively correct.

From Table 3 we note that the MP2 method overestimates the electron correlation effects on the hydrogen-bond-induced changes of the shielding constants, as it does for the shielding constants in isolated molecules [21]. It seems that the scaling formula

$$\sigma^{corr} = \frac{1}{3}\sigma^{SCF} + \frac{2}{3}\sigma^{MP2} \qquad (1)$$

proposed by Chesnut [35] for the nuclear shieldings in isolated molecules may work also for their interaction-induced changes, in particular in the case of heavy atom shieldings.

It is worth noting that the CCSD, MP4(SDQ) and MP4 results are practically identical for the ^{1}H shielding and its interaction-induced change, and close in the case of [17]O shielding. This suggests that the less-time consuming CCSD method should be used when the inclusion of higher-order correlation effects in the calculations of the complexation-induced changes of NMR shielding constants is called for.

## 4. Summary and conclusions

The calculations of the shielding constants in the water dimer have been performed using a wide variety of basis sets and several computational methods ranging from SCF to MP4. The resulting conclusions and recommendations for the calculations of the shielding constants in hydrogen-bonded complexes can be summarised as follows.

The medium-size basis set to be recommended for SCF calculations of the hydrogen-bond-induced changes in the shielding constants is the 6-311++G** basis set, if possible enriched by additional polarisation functions. The smaller 6-31++G** set can be used for ^{1}H shieldings. The other good choice is the aug-cc-pVDZ basis set. The application of the counterpoise correction is essential for the heavy atom shieldings, especially if 6-31G or 6-311G basis sets are used, but not for the ^{1}H shieldings. When the use of larger basis sets is possible, we recommend the aug-cc-pVXZ basis sets. The addition of the tight core–valence corre-

Table 3
The NMR shielding constants for $H_2O$ and their changes upon the dimer formation calculated in aug-cc-pVTZ basis set

| | $\sigma(^{17}O)$ | $\sigma(^{1}H)$ | $\Delta\sigma(^{17}O)^{acc}$ [a] | $\Delta\sigma(^{17}O)^{don}$ [b] | $\Delta\sigma(^{1}H)$ [c] |
|---|---|---|---|---|---|
| SCF | 321.21 | 30.14 | −5.07 | 1.24 | −2.54 |
| MP2 | 340.45 | 30.18 | −6.18 | −3.00 | −2.37 |
| MP4(SDQ) | 331.75 | 30.43 | −5.73 | −1.60 | −2.44 |
| MP4 | 333.91 | 30.43 | −5.92 | −2.21 | −2.42 |
| CCSD | 330.97 | 30.44 | −5.61 | −1.32 | −2.45 |

[a] The hydrogen-bond induced change in the proton acceptor shielding.
[b] The hydrogen-bond induced change in the proton donor shielding.
[c] The hydrogen-bond induced change in the shielding of the proton forming the hydrogen bond.

lating functions does not noticeably improve the results.

The use of correlation-consistent basis sets from the aug-cc-pVXZ series, rather than the augmented 6-31G or 6-311G basis sets, is recommended for the MP2 calculations of the hydrogen-bond-induced changes in shielding constants. The counterpoise correction for the shielding constants at the MP2 level is of similar magnitude as at the SCF level, and also larger for the heavy atom shieldings.

The SCF results are reliable for the change in shielding of the proton engaged in the hydrogen bond formation. The use of more advanced methods is advisable for the changes in the heavy atom shieldings, especially for the change in the proton donor shielding, where SCF gives the wrong sign. The MP2 method tends to overestimate correlation effects on the hydrogen-bond-induced changes in the shielding constants. Therefore, if more accurate calculations cannot be performed, a better approximation of the actual values of these parameters can be obtained from the SCF and MP2 results by the Chesnut scaling formula.

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