Halogen Bond of Halonium Ions: Benchmarking DFT Methods for the Description of NMR Chemical Shifts

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ABSTRACT: Because of their anisotropic electron distribution and electron deficiency, halonium ions are unusually strong halogen-bond donors that form strong and directional three-center, four-electron halogen bonds. These halogen bonds have received considerable attention owing to their applicability in supramolecular and synthetic chemistry and have been intensely studied using spectroscopic and crystallographic techniques over the past decade. Their computational treatment faces different challenges to those of conventional weak and neutral halogen bonds. Literature studies have used a variety of wave functions and DFT functionals for prediction of their geometries and NMR chemical shifts, however, without any systematic evaluation of the accuracy of these methods being available. In order to provide guidance for future studies, we present the assessment of the accuracy of 12 common DFT functionals along with the Hartree–Fock (HF) and the second-order Møller–Plesset perturbation theory (MP2) methods, selected from an initial set of 36 prescreened functionals, for the prediction of $^1$H, $^{13}$C, and $^{15}$N NMR chemical shifts of $[N−X−N]^+$ halogen-bond complexes, where X = F, Cl, Br, and I. Using a benchmark set of 14 complexes, providing 170 high-quality experimental chemical shifts, we show that the choice of the DFT functional is more important than that of the basis set. The M06 functional in combination with the aug-cc-pVTZ basis set is demonstrated to provide the overall most accurate NMR chemical shifts, whereas LC-oPBE, oB97X-D, LC-TPSS, CAM-B3LYP, and B3LYP to show acceptable performance. Our results are expected to provide a guideline to facilitate future developments and applications of the $[N−X−N]^+$ halogen bond.

1. INTRODUCTION

Halogen bonding is the attractive interaction of the electron-depleted region of a halogen with a Lewis base.1 As it is highly directional and resembles hydrogen bonding to a great extent, halogen bonding is applicable as a complementary tool in the modulation of molecular recognition events in chemistry and in biology. The strongest halogen-bond complexes have so far been furnished using especially electron-poor and thereby vastly electrophilic halogen-bond donors, typically obtained by perfluorination,2 or even more efficiently using halonium ions as halogen-bond donors.3 The halogens of the former and more extensively studied classical halogen-bond complexes possess a distinct strong covalent bond and a distinct weak halogen bond,3 whereas those of the latter form three-center, four-electron bonds.4 The halonium ion of such three-center bonds simultaneously interacts with two Lewis bases with comparable bond strengths and lengths.5 Strong, three-center halogen bonds of halonium ions with nitrogen,6,14 oxygen,13 sulphur,16–18 selenium,19,20 tellurium,21 halogen,22 and mixed nitrogen and oxygen23,24 electron donors have lately received ample attention and also found applications in supramolecular chemistry, for example.3,18,23–29 Although the halogen bond of neutral organic halogen bond donors, such as of iodoperfluorocarbons, is weak (<10 kJ/mol),31 those of halonium ions are typically >50 kJ/mol and often even >100 kJ/mol.3,31 This strength is expected to originate from the vast electron deficiency of halonium ions, as compared to the slight electrophilicity of common neutral halogen-bond donors.2 Their positive charge makes halonium ions to exceptionally strong halogen-bond donors. Accordingly, the halogen bonds of halonium ions have been reported to possess remarkably short donor–acceptor distances ($R_{XB} = 0.65−0.69$, where $R_{XB} = d_{XB}/(X_{adv} + B_{adv})$),3 as compared to conventional neutral halogen bonds ($R_{XB} > 0.9$). The halogen bonds involving a charged species are expected to possess a larger electrostatic character and thereby act over longer distances. Thereto, induction is expected to play a more prominent role for charged as compared to neutral species.32 Overall, the strong, three-center halogen bond of halonium ions shows a number of features different from those of conventional, weak halogen

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halogen bonds. Its description may therefore need different computational treatment, for instance, for the accurate estimation of the chemical shift of atoms involved or nearby the interaction.

Conventional halogen bonds, D−X···D (where D acts as an electron donor, whereas X is a halogen that acts as an electron acceptor), have been extensively studied, computations greatly supporting the interpretation of experimental observations\(^3\),\(^5\),\(^33\) and the overall understanding of the halogen-bonding phenomenon.\(^34\) For such conventional bonds, extensive benchmarking studies have been carried out, surveying the accuracy of a wide set of DFT methods and wave functions\(^35\),\(^36\) and providing guidance for further investigations. The strong, three-center halogen bond of halonium ions has been repeatedly reviewed from an experimental perspective;\(^3\),\(^7\),\(^8\),\(^37\),\(^38\) however, in contrast, its computational treatment has so far received less attention. Apart from scarce examples of entirely theoretical studies,\(^39\),\(^40\) most investigations analyzing three-center halogen bonds used DFT predominantly to support the interpretation of experimental data, most often of NMR chemical shifts obtained in solutions.\(^3\),\(^5\),\(^11\),\(^13\),\(^15\),\(^41\) In the past decade, diverse computational methods (DFT functionals and basis sets) have been used, however, without giving any guidance on or evaluation of the applied methods’ accuracy regarding the computed spectroscopic parameters or the geometry and the energy of such complexes.\(^1\),\(^3\),\(^13\),\(^39\),\(^41\) The DFT description of three-center, four-electron halogen bonds is challenging because of the self-interaction error inherent to DFT\(^43\) and to the incomplete description of nondynamic electron correlations in these bonds.\(^44\) Unsurprisingly, discrepancies between experimental observations and computational results have been reported in some cases.\(^12\)

In earlier work, we assessed B3LYP against B3LYP-D3, MP2, and M06-2X\(^8\) and compared the outcome to independent CCSD(T) calculations.\(^42\) We have shown that the contribution of dispersion to the overall interaction energy of three-center halogen bonds, [D−X−D]\(^\bullet\), is minor, in contrast to its major impact for conventional neutral and weak halogen bonds, D−X···D.\(^8\) This is due to the partial ionic character, unusual strength, and shortness of the halogen bonds of halonium ions.\(^3\) Moreover, we proved the influence of basis-set superposition error (BSSE) to be negligible.\(^7\) Herein, we report the comprehensive assessment of the accuracy of DFT methods and two wave functions (HF and MP2) for the description of NMR chemical shifts of three-center, four-electron halogen-bond systems, that is, the exceptionally strong halogen-bond complexes of halonium ions. For this investigation, we used the three-center, four-electron halogen-bond model systems that have so far been experimentally most extensively studied (Figure 1)\(^1\),\(^3\),\(^13\),\(^37\) and have also been used as benchmark systems in various contexts,\(^3\),\(^45\),\(^46\) providing ample and reliable experimental data for comparison. As the counterion has previously been demonstrated to not influence [N−I−N]\(^\bullet\) halogen bonds significantly, it was omitted in the current calculations.\(^9\)

2. COMPUTATIONAL DETAILS

The geometries of [N−X−N]\(^\bullet\) complexes were optimized at the ωB97X-D/aug-cc-pVTZ level of theory. The ωB97X-D functional was chosen as it is known to adequately account for electron correlations for systems exhibiting noncovalent interactions\(^17\),\(^48\) including halogen bonding.\(^17\) Dichloromethane solvation effects were included using the polarizable continuum model (PCM) of Tomasi and co-workers.\(^39\) For geometry optimization, the substrate solvation cavities were modeled using the united-atom radii (UA0), while for chemical shielding calculations, the substrate solvation cavities were modeled using the Bondi atomic radii\(^51\) as suggested by Willoughby and co-workers.\(^52\) Vibrational frequency calculations were followed at the same level of theory to ensure the optimized geometry corresponding to geometry minima.

Chemical shielding constants (σ) were obtained at the GIAO-HF, GIAO-MP2, and GIAO-DFT levels.\(^3\),\(^5\) For the two former, two wave function methods were used including HF\(^56\) and MP2.\(^57\) For the latter, 12 commonly used functionals were used including an LSDA (SVWN5\(^58\),\(^59\)), a GGA (PBE\(^60\),\(^61\)), a meta GGA (TPSS\(^62\)), a hybrid (B3LYP),\(^63\),\(^64\) four long-range-corrected functionals (CAM-B3LYP,\(^65\) LC-ωPBE\(^66\),\(^67\) ωB97X-D\(^68\),\(^69\) and LC-TPSS\(^70\)) as well as four Truhlar’s functionals of the M06 family: M06-L\(^71\), M06,\(^72\) M06-2X\(^72\), and M06-HF.\(^73\)

Three different basis sets of triple-ζ-polarized quality augmented with diffuse functions were employed for describing the C, H, O, N, F, Cl, Br, and I atoms: the Pople’s 6-311++G(d,p),\(^74\),\(^75\) the Ahlrichs’ def2-TZVP,\(^76\),\(^77\) and the Dresden (SDD)\(^80\),\(^81\) and the Dunning’s aug-cc-pVTZ\(^78\),\(^79\) basis sets. For heavy atoms (e.g., I), scalar relativistic effects were assessed by two effective core potentials (ECPs): (i) the Stuttgart—Dresden (SDD)\(^80\),\(^81\) and (ii) the Los Alamos National Laboratory (LANL2)\(^82\) where the former is superior compared with the latter. The small-core relativistic pseudopotentials of SDD have been carefully designed to explicitly treat the Pauli repulsion of the core, their Coulombic and exchange effects on the valence space, and the scalar relativistic corrections as well as their two-component extensions describing outer-core and valence spin—orbit interactions.\(^81\) As we calculated the NMR shielding tensors at the chemical equilibrium geometries, we expect that the use of small-core relativistic pseudopotentials handle the heavy-atom light-atom (HALA) effects to some extent. The remaining HALA effects, which cannot be handled by relativistic ECP, may explain the discrepancy between the calculated and the experimental values to some extent. Although the \(^1\)H and \(^13\)C NMR chemical shifts are dominated by the diamagnetic term in the shielding constants,\(^13\)N NMR chemical shifts have been previously shown to be determined by the paramagnetic term. This has earlier been discussed by Pazderski,\(^58\) for example.

To evaluate the performance of different methods and basis sets, we used the root mean square deviation (rmsd) and the
normalized root mean square deviation (\(\text{rmsd}\)), which were computed as follows over \(N\) nuclei

\[
\text{rmsd} = \sqrt{\frac{\sum_N (\delta_{\text{calc}} - \delta_{\text{exp}})^2}{N}}
\]

\(1\)

\[
\text{lrmsd} = \left( \frac{\text{rmsd}}{\sum \text{rmsd}} \right)_H + \left( \frac{\text{rmsd}}{\sum \text{rmsd}} \right)_{13C} + \left( \frac{\text{rmsd}}{\sum \text{rmsd}} \right)_{15N}
\]

\(2\)

where \(\delta_{\text{calc}}\) and \(\delta_{\text{exp}}\) are the calculated and experimental chemical shifts, respectively.

All calculations were performed using the Gaussian 16 Rev. C.01 package. The geometry optimization and NMR chemical shift calculations were performed using ultraline grid integration and tight convergence criteria for the forces and displacement. For the NBO analysis of [bis-(pyridine)iodine(I)]-type complexes, we direct the reader to refs 8, 10.

3. RESULTS AND DISCUSSION

We assessed the performance of 12 commonly used DFT functionals as well as of two wave function methods with regard to their capability of reproducing experimental \(^1\text{H}\), \(^{13}\text{C}\), and \(^{15}\text{N}\) NMR chemical shifts of three-center, four-electron \([\text{N--X--N}]^+\) halogen-bond complexes. We also evaluated the performance of three different families of basis sets utilizing six selected functionals.

3.1. Test Set. For the evaluation of computational methods’ ability to accurately describe the NMR chemical shifts of three-center, four-electron \([\text{N--I--N}]^+\) halogen-bond complexes, a set of 14 systems (Figure 1) providing 170 reliable experimental NMR chemical shift values was selected. The calculated \(^1\text{H}\), \(^{13}\text{C}\), and \(^{15}\text{N}\) chemical shielding tensors (\(\sigma\)) were converted into \(^1\text{H}\), \(^{13}\text{C}\), and \(^{15}\text{N}\) chemical shifts (\(\delta\) in ppm, where \(\delta = \sigma_{\text{ref}} - \sigma\)) utilizing the proton and carbon atoms of tetramethylsilane (TMS) as a reference for \(^1\text{H}\) and \(^{15}\text{N}\) NMR chemical shifts and the nitrogen of nitromethane as a reference for \(^{13}\text{N}\) NMR chemical shifts. As the experimental chemical shifts were obtained in dichloromethane-\(d_2\) solution, the corresponding implicit solvent model was used. Calculated and experimental \(^1\text{H}\), \(^{13}\text{C}\), and \(^{15}\text{N}\) NMR chemical shifts are given for all discussed halogen-bond complexes in the Supporting Information.

3.2. Exchange–Correlation Functionals. DFT is widely known as an inexpensive method for calculating NMR chemical shifts. As previously shown by Stouchev and co-workers, the choice of the method is the main source of error and the accuracy varies depending mainly on the choice of functionals. Following a prescreening of 36 functionals utilizing \(1\text{I--H}\) as well as two wave function (HF and MP2) methods, we selected 12 commonly used functionals for further evaluation. To avoid any bias arising from molecular conformational changes, that is, molecular vibrations, the shielding constants were calculated with equilibrium geometries obtained at the \(6-31G(d)\) level of theory. This geometry is in excellent agreement with the experimentally obtained X-ray structure, especially as indicated by the rmsd of 0.1036 for complex \(1\text{I--H}\) (Figure 2). The rmsd of \(^1\text{H}\), \(^{13}\text{C}\), and \(^{15}\text{N}\) NMR chemical shifts with respect to the experimental values is shown in Figure 3. Explicit NMR chemical shifts for all considered nuclei on all levels of theory discussed here are given in the Supporting Information.

All methods perform reasonably well in reproducing experimental \(^1\text{H}\) chemical shifts as indicated by the rmsd values ranging from 0.25 to 1.47 ppm (Figure 3a), with the M06-HF functional providing the least accurate prediction, yielding an rmsd of 1.47 ppm. It is worth noting that HF shows comparable accuracy to DFT and MP2, which is in agreement with the previous work of Flag and co-workers. The best match to the experimental \(^1\text{H}\) NMR chemical shifts is obtained when using the TPSS, M06-L, PBE, or B3LYP functionals. For \(^{13}\text{C}\) NMR chemical shifts, a larger variance in accuracy is observed, as reflected by the rmsd values ranging from 2.74 to 51.48 ppm (Figure 3b). The good performance of PBE and TPSS functionals has been pointed out by previous studies and is in agreement with our observation of the PBE, TPSS, and M06 functionals achieving the lowest rmsd values. The inclusion of HF exchange improves the calculated NMR shifts for the M06 family (M06-L: 0% HF exchange, M06: 27% HF exchange, M06-2X: 54% HF exchange, and M06-HF: 100% HF exchange), with the optimum of 27% HF exchange obtained with the M06 functional. However, the inclusion of 100% of HF exchange in M06-HF lowers the quality of the chemical shift prediction. This observation agrees with the recent finding by Truhlar and co-workers that an excessive inclusion of HF exchange amplifies the static correlation error. This is due to the HF exchange deteriorating the ability of local exchange in DFT functionals to account for the localization effects associated with static correlation. MP2 shows good performance, with an rmsd of 4.56 ppm over the entire set of studied complexes.

An even larger quality variation of prediction is observed for \(^{15}\text{N}\) NMR chemical shifts, in line with previous reports. The rmsd values range from 7.04 to 79.48 ppm, with the M06 and LC-TPSS functionals performing the best (rmsd of M06 7.94 and of LC-TPSS 7.04 ppm), comparable to that of the previously suggested KT3/pS-3 method. HF and MP2 are among the methods least reliably describing the \(^{15}\text{N}\) NMR chemical shifts of these systems. Similar to that observed for \(^{13}\text{C}\) NMR chemical shift predictions mentioned above, the inclusion of HF exchange leads to an improvement of the calculated \(^{15}\text{N}\) NMR chemical shifts, with the optimum being seen for 27% HF exchange included in the M06 functional.

The quality of prediction of \(^{15}\text{N}\) NMR chemical shifts is strikingly lower than those of \(^1\text{H}\) and \(^{13}\text{C}\) NMR shifts (Figure 3) that is explained by the widely acknowledged shortcoming of DFT at describing charge-transfer interactions. Thus, the energy of charge-transfer states is typically strongly underestimated because of the incomplete compensation of electron self-repulsion by the approximate exchange–correlation functional, while HF typically strongly overestimates it. As the nitrogen atoms are directly involved in the charge-transfer
interaction, here termed halogen bonding, their chemical shift calculations are affected the most. A substantial electron transfer in the charge-transfer complexes of pyridines has previously been demonstrated.107,108 Moreover, the discrepancy of the predicted $^{15}$N NMR chemical shifts can also be attributed to (i) the remaining HALA effects which cannot be handled by relativistic ECP, (ii) zero-point vibrations for temperature corrections, and (iii) the incomplete description of nondynamical electron correlations in these bonds. The good performance of the M06 functional is thus not unexpected, as this method has been specifically designed to deal with the self-interaction error, thereby compensating this weakness.109 The observation of improved accuracy of $^{15}$N NMR chemical shift prediction upon adjustment of HF exchange further corroborates this explanation.

The maximum deviations in the prediction of the chemical shifts of all three nuclei, given in Table 1, support the abovementioned conclusions. Hence, M06-HF provides by far the poorest performance for $^1$H NMR chemical shifts, whereas TPSS, M06-L, PBE, and B3LYP give the most accurate predictions. For $^{13}$C NMR chemical shifts, TPSS, PBE, M06, MP2, and B3LYP are the most accurate, whereas M06-HF remains giving the largest deviations from reality. In our hands, the most accurate $^{15}$N NMR chemical shifts were predicted by LC-TPSS, M06, M06-2X, CAM-B3LYP, and LC-αPBE, whereas a large number of functions appear to not be applicable for the prediction of $^{15}$N NMR data for halonium ions' halogen-bond complexes.

Table 1. Maximum Absolute Deviations from the Experimental Values of 14 [N−I−N]$^+$ Halogen-Bond Complexes of the Predicted $^1$H, $^{13}$C, and $^{15}$N NMR Chemical Shifts for 12 DFT Functionals as Well as HF and MP2 (in ppm)

| functional | $^1$H | $^{13}$C | $^{15}$N |
|------------|-------|---------|---------|
| HF         | 0.66  | 15.96   | 73.90   |
| SVWN       | 0.58  | 13.48   | 50.70   |
| PBE        | 0.46  | 7.79    | 50.25   |
| TPSS       | 0.38  | 5.36    | 42.98   |
| B3LYP      | 0.46  | 8.59    | 21.77   |
| M06-L      | 0.38  | 12.19   | 41.34   |
| M06        | 0.57  | 8.27    | 6.44    |
| M06-2X     | 0.98  | 24.65   | 9.95    |
| M06-HF     | 1.85  | 67.01   | 80.83   |
| CAM-B3LYP  | 0.56  | 12.33   | 9.70    |
| LC-αPBE    | 0.71  | 15.65   | 10.40   |
| α-B97X-D   | 0.59  | 10.07   | 13.10   |
| LC-TPSS    | 0.78  | 17.79   | 4.98    |
| MP2        | 0.69  | 8.37    | 81.65   |

Overall for $^1$H, $^{13}$C, and $^{15}$N NMR chemical shifts, the M06 functional performs best among the 12 functionals studied here, offering a reasonable balance between cost and accuracy. Although it does not offer the lowest error in prediction of $^1$H chemical shifts, the outcome is acceptable and simultaneously it is clearly among the best for prediction of $^{13}$C and by far the very best for $^{15}$N NMR chemical shift prediction. B3LYP and the four long-range-corrected functionals CAM-B3LYP, LC-
ωPBE, ωB97X-D, and LC-TPSS perform reasonably well and hence may be used without taking larger risks.

3.3. Basis Sets. Pople’s 6-311++G(d,p), Ahlrichs’ def2-TZVP, and Dunning’s aug-cc-pVTZ, three of the most commonly used basis sets of triple-ζ quality augmented with diffuse functions, were evaluated for their performance using the six best performing functionals B3LYP, CAM-B3LYP, LC-TPSS, LC-ωPBE, ωB97X-D, and M06. We chose triple-ζ-quality basis sets as these are known to provide a good compromise between accuracy and cost, whereas those beyond triple-ζ do not significantly improve the accuracy. Those of lower quality were expected to not yield reliable enough predictions and were therefore omitted.

In our hands, all three basis sets showed comparable performance in describing 1H and 15N NMR chemical shifts (Figure 4) with 6-311++G(d,p) typically providing slightly better results than def2-TZVP and aug-cc-pVTZ. However, at the prediction of 13C NMR chemical shifts, the Dunning’s aug-cc-pVTZ basis set is superior for this purpose, even over Jensen’s pcS-n112 and pcSseg-n113 basis sets that have been designed specifically for prediction of NMR chemical shifts. The comparison of the predicted chemical shifts obtained with Dunning’s aug-cc-pVTZ basis set with those obtained using mixed basis sets of Pople’s 6-311+G(d,p) for I and Jensen’s aug-pc-2 for H and N demonstrates the Dunning’s basis set to be superior (Supporting Information Table S30). Further tests on complex 1-F−H and 1-Cl−H utilizing aug-pcSseg-3 indicated severe self-consistent field (SCF) convergence problems, whereas the influence of improved core−valence (aug-cc-CVTZ) was found to be negligible.

Altogether, when predicting both 1H, 13C, and 15N NMR chemical shifts, the Dunning’s aug-cc-pVTZ, which possesses high-quality polarization and diffuse functions, performs the best among the three families of basis sets studied here. This is clearly the first choice for 13C NMR prediction, whereas 6-311++G(d,p) is for 1H NMR. For the prediction of 15N NMR chemical shifts, the choice of the basis set appears to not play a significant role.

3.4. Halogen. The relative contribution of charge transfer to the three-center, four-electron halogen-bond interaction has been shown to depend on the type of halogen involved.3,8 We, therefore, compared the quality of chemical shift prediction as a function of the identity of the central halogen(I) for the abovementioned 12 DFT functionals as well as for HF and MP2 (Figure 5). For 1H NMR chemical shifts, the highest quality of prediction was observed for the chlorine(I)-centered complexes, independent of the functional, followed by bromine(I) and iodine(I), for which the variance in accuracy is comparable. The lowest accuracy is seen for prediction of fluorine-centered halogen bonds, which in turn are vastly different in character from the halogen bonds of the other three halogens.4,8 The accuracy of 13C NMR chemical shift prediction for [N−X−N]+ halogen bonds appears virtually independent of the type of halogen involved (Figure 5b). Apart
from the strikingly low-quality predictions by HF and M06-HF, the error of $^{15}$N NMR chemical shift prediction is typically the largest for the iodine(I)-centered bonds; however, the trends are less uniform, with LC-TPSS showing the opposite order of accuracy for the different halogens than M06-L, for example. Altogether, the optimal choice of the functional is here demonstrated to be more halogen-dependent for the $^{15}$N NMR chemical shift prediction than for the $^1$H NMR and especially for the $^{13}$C NMR chemical shift predictions.

3.5. Electron Density. The electron density of the halogen-bond acceptor Lewis base is known to influence halogen-bond strength,2,10 and therefore, we evaluated whether the electron density of the studied systems may modulate the accuracy of the chemical shift prediction. Whereas the prediction of $^1$H and $^{13}$C NMR chemical shifts showed little dependence on the electron density of the pyridines (typically <0.2 ppm variation of error for $^1$H NMR and <2 ppm for $^{13}$C NMR, Figure 6), that of the $^{15}$N NMR chemical shift showed
>5 ppm variation. Different functionals exhibit somewhat dissimilar behavior; however, overall, the accuracy of $^{15}$N NMR chemical shift prediction appears to be to some extent better for the most electron-rich NMe$_2$-substituted [N$^-$$I^-$$N$]$^+$ complex, which possesses the strongest halogen bond, for most of the studied functions. All in all, the choice of the DFT functional has a larger influence on the quality of the outcome than the electron density of the halogen-bond complex. In our hands, the choice of the basis set does not have a significant impact on the quality of NMR chemical shift predictions, neither upon variation of nuclei (Figures S29 and S45) nor upon altering the electron density (Figures S30 and S46). An NBO analysis of the 1-I$^–$R complexes (Figure 1) corroborates our earlier findings that the halogen bonds of halonium ions have a strong charge-transfer character. The iodine(I) of the [N$^-$$X^-$$N$]$^+$ complexes transfers 0.55–0.59 positive charge to the pyridine rings (Table 2). Our data suggest that the delocalization from the N lone-pair orbitals into the N$^-$$X^*$ bond orbital is the dominant contribution to the stabilization of the three-center, four-electron halogen bond. The extent of charge transfer depends on the electronic

Figure 6. Rmsd of the predicted NMR chemical shifts with respect to experimental values for 6 [N$^-$$I^-$$N$]$^+$ halogen-bond complexes (Figure 1), evaluating the performance of 12 DFT functionals as well as HF and MP2. (a) $^1$H NMR chemical shifts. (b) $^{13}$C NMR chemical shifts. (c) $^{15}$N NMR chemical shifts.
character of the para-substituent of the 1–I complexes and hence on the electron density of the Lewis basic nitrogen.10,11 Most extensive charge transfer is observed for the most electron-rich 1–I–NMe2 whereas the least for the most electron-poor 1–I–CF3 complex. An increase in charge-transfer character of 1–I complexes is seen to be associated with the shortening of the N–I bond (R_{N–I}) and hence with an increase in bond strength. This is in agreement with previous experimental observations.10,11 Simultaneously, the Coulombic character of the bond decreases. It is worth noting that a gradual increase in charge delocalization (1.059, Br 0.72, and CI 0.84) and simultaneous decrease in electrostatic character of the halogen bond have previously been reported upon the decrease in halogen size,35 which was associated with the weakening of the interaction (1 > Br > CI).

4. SUMMARY

Evaluation of the capability of functionals and basis sets to predict NMR chemical shifts of three-center, four-electron halogen-bond complexes revealed the M06 exchange–correlation functional to give the overall best performance. Most functionals except M06-HF and M06-2X reproduce 1H and 13C NMR chemical shifts for this type of halogen-bond complexes reasonably well. It is worth noting that HF and MP2 provide comparably accurate predictions to DFT for 1H and 13C but not for 15N NMR chemical shifts. We found that only six of the DFT functionals (M06, B3LYP, CAM-B3LYP, LC-oPBE, ωB97X-D, and LC-TPSS) gave reasonably good accuracy at the prediction of 15N NMR chemical shifts for [N–I–N]+ halogen-bond complexes. B3LYP’s prediction accuracy is overall poorer, even if it by far outperforms a number of other functionals. In addition, the four long-range-corrected functionals LC-oPBE, ωB97X-D, LC-TPSS, and CAM-B3LYP as well as B3LYP (1H and 13C) show acceptable performance for strong three-center halogen-bond complexes. According to the commonly accepted “Jacobi’s ladder” specification of functionals, accurate prediction of NMR chemical shifts for [N–I–N]+ complexes is achieved when functionals of rung-4 and above are applied.114 Even if a certain functional may provide the best result for a certain nucleus, altogether, we recommend the use of the M06 method because of its ability to provide reliable chemical shift predictions for 1H, 13C, and 15N with consistent accuracy. As the 1H and 13C NMR chemical shifts are much better reproduced by most methods than the 15N NMR shifts, the computation of the latter data directs the selection of the functional.

The choice of the basis set has a lower influence on the quality of the prediction than that of the functional. According to our findings, the combination of the M06 functional with the aug-cc-pVTZ basis set provided the overall most accurate data for 1H, 13C, and 15N NMR chemical shift prediction. The prediction of 15N NMR chemical shifts is much less accurate than those of 1H and 13C NMR chemical shifts. The type of halogen and the electron density of the complex do not have a significant influence on the accuracy of the predictions. In contrast to conventional halogen bonds,35 the use of M06-L and M06-2X functionals is not advisable, whereas ωB97X-D appears to provide a reasonably good prediction for both conventional, weak, and for strong three-center halogen-bond complexes. It should be kept in mind that in contrast to the computation of conventional halogen bonds,36 dispersion and basis set superposition error are of insignificant importance at the description of the strong, charged three-center, four-electron halogen bonds of halonium ions. Double hybrid functionals were recently shown to provide promising accuracy at chemical shift prediction when compared to CCSD(T) benchmark data,115 however, are not yet implemented in the Gaussian 16 Rev. C.01 package for calculations of NMR shielding tensors, which was used in this investigation.

We expect that the practical guideline provided here will serve as a useful tool for the continued structural investigations and applications of three-center, four-electron [N–X–N]+ halogen-bond complexes. This motif has recently evolved into a useful supramolecular synthons, a mild synthetic agent for halonium transfer reactions, and an instructive model system for gaining further understanding of the chemical bonding phenomenon.3,4

### Table 2. Bond Distances (in Å), Natural Charge Analysis (in e), and Second-Order Perturbation of the Fock Matrix between the Nitrogen Lone Pair and the Accepting Central Atom (in kcal/mol) Calculated at the ωB97X-D/aug-cc-pVTZ-level of Theory

| Complex   | R_{N–I} (Å) | q_N | q_I | N_{N} → I_{N} |
|-----------|-------------|-----|-----|---------------|
| 1–I–NMe2 | 2.259       | −0.536 | +0.411 |               |
| 1–I–OMe  | 2.264       | −0.506 | +0.423 | 151.00        |
| 1–I–Me   | 2.267       | −0.482 | +0.426 | 149.53        |
| 1–I–H    | 2.269       | −0.476 | +0.434 | 146.94        |
| 1–I–CF3  | 2.272       | −0.459 | +0.446 | 144.04        |

# ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.jctc.0c00860.

Performance of 11 DFT functionals, HF, and MP2; performance of the 6-311++G(d,p) basis set; performance of the def2-TZVP basis set; and optimized geometries obtained at the ωB97X-D/aug-cc-pVTZ level of theory (PDF)

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**Notes**

The authors declare no competing financial interest.

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