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Theoretical Investigations on How to Reproduce d–π Bonds: Transition-Metal Cation–Benzene Complex Calculations

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Reproducibilities of d–π bonds were investigated on calculating complexes of first-row transition-metal cation (M^+) and benzene (Bz). Calculations were carried out for half-sandwich MBz^+ and sandwich $MBz_2{}^+$ complexes with several types of density functional theories (DFTs) and single-configurational wave function theories (WFTs). As a result, it was concluded that electron correlations are required to give the binding energies of d–π bonds even qualitatively, and DFTs would reproduce d–π bonds with quantitative accuracies only if electron correlations and long-range exchange interactions were both taken into consideration in exchange-correlation functionals used. In MBz^+ calculations, WFTs fairly underestimated the binding energies for early transition metals (M = Sc–Cr) because of multiconfigurational effects. In contrast, DFTs overestimated them for late transition metals (M = Fe–Cu) due to insufficient long-range interactions in exchange functionals. For $MBz_2{}^+$, DFTs and WFTs gave similar binding energies for $MBz_2{}^+$, although WFTs slightly overestimated them for late transition metals. Furthermore, it was suggested that the experimental binding energies of $CrBz_2{}^+$ and $MnBz_2{}^+$ are probably misestimated.

Density functional theory (DFT)[1] is used in quantum chemistry calculations for a wide variety of systems including nanomaterials and biomolecular systems. In particular, it is widely accepted that DFT calculations are excellent at giving accurate chemical properties and reasonable reaction mechanisms of transition-metal complexes. However, some theoretical studies have suggested that DFT calculations give poor chemical bonds for some transition-metal complexes. It has been reported that DFT calculations have problems in reproducing d–π bonds. For example, Sakaki et al. suggested that DFT significantly underestimated binding energies for the d–π bonds of $[Pt(C_2H_4)(PH_3)_2]$ and $[X(CO)(PH_3)_2]\cdot C_{60}$ (X = IrH, RhH, and IrCl) complexes.[2,3] As far as we know, there are no studies elucidating why DFT poorly reproduces d–π bonds.

Recently, Wedderburn et al. calculated the geometries and binding energies of first-row transition-metal-cation complexes with benzene (Bz) for half-sandwich (MBz^+) and sandwich ($MBz_2{}^+$) structures by DFT calculations using a hybrid B3LYP functional.[4] For these systems, the binding energies have been experimentally estimated by measuring the cross-section of a Xe ionic collision dissociation.[5] By comparing calculated binding energies with the experimental ones, they suggested that B3LYP seriously underestimated the dissociation energies of $MBz_2{}^+$ complexes, although it gave accurate dissociation energies for MBz^+ complexes. What we should notice is that the M–Bz bonds of these complexes consist of only d–π bonds, for which DFT calculations would give poor binding energies as mentioned above. Therefore, it is expected that we would be able to make clear the reason why DFT calculations have underestimated d–π binding energies by calculating first-row transition-metal cation–benzene complexes with various types of exchange-correlation functionals.

To test DFT functionals for reproducing d–π bonds, we employ long-range correction (LC) scheme,[6] in which long-range exchange interactions are supplemented by combining with the Hartree–Fock (HF) exchange integral.[6,7] In this scheme, electron repulsion operator $1/r_{12}$ is divided into short- and long-range parts by using the standard error function as

$$\frac{1}{r_{12}} = \frac{1 - erf(\mu r_{12})}{r_{12}} + \frac{erf(\mu r_{12})}{r_{12}} \tag{1}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ for coordinate vectors of electrons, $\mathbf{r}_1$ and $\mathbf{r}_2$, and μ is the only parameter that determines the ratio of these parts. Based on eq 1, the short-range part of generalized-gradient-approximation exchange functionals are combined with the long-range part of the HF exchange integral.[6,8] The LC scheme has recently been found to solve significant DFT problems,[8–13] despite being conceptually simple with only one parameter. We would like to emphasize that this scheme is also useful for checking how long-range exchange interactions affect chemical properties, because we can easily control the rate of long-range exchange effects by varying the only parameter μ in eq 1.

In this study, we investigate how to reproduce d–π bonds theoretically by assessing DFTs including LC functionals and ab initio single-configurational wave function theories (WFTs) for calculations of first-row transition-metal cation–benzene complexes.

Computational Details

Geometry optimizations of MBz^+ and $MBz_2{}^+$ have been carried out using the Kohn–Sham method[1] with Becke 1988 exchange[14] +

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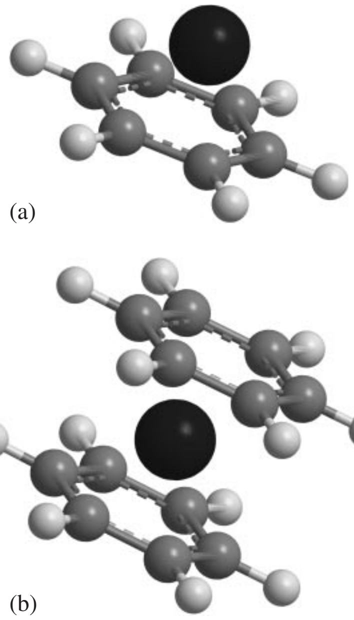

Figure 1. (a) Half-sandwich structure of MBz^+ and (b) sandwich structure of $MBz_2{}^+$.

OP correlation[15,16] (BOP), hybrid B3LYP[17] (B3LYP), and long-range corrected BOP (LC-BOP) functionals.[6,8] For the LC-BOP functionals, we have examined two values of the parameter μ: $\mu = 0.33$ (LC-BOP1),[6] which is the original value and is suitable for excited-state[9] calculations, and $\mu = 0.47$ (LC-BOP2),[8] which was recently re-optimized for ground-state calculations.[8] We have also optimized these geometries using ab initio Hartree–Fock (HF)[18] and second-order Møller–Plesset perturbation (MP2) methods,[18] for comparison. Besides, we have performed geometry optimizations on coupled-cluster singles and doubles (CCSD)[19] method for MBz^+ complexes. We have also executed single-point CCSD + perturbative triples (CCSD(T))[19] calculations with optimized MP2 geometries. As the basis set, we have used Ahlrichs' triple-zeta valence polarization (TZVP) functions[20] in order to compare our results with those of a previous study.[4] The dissociation energies have been evaluated for detaching one benzene molecule:

$$MBz^+ \rightarrow M^+ + Bz \tag{2}$$

$$MBz_2{}^+ \rightarrow MBz^+ + Bz \tag{3}$$

Following previous studies,[4] we have assumed half-sandwich and sandwich structures for MBz^+ and $MBz_2{}^+$ complexes (Figure 1), respectively. Zero-point vibrational corrections have been taken into account in binding energy calculations. All calculations have been carried out using the development version of Gaussian03 program.[21]

Results and Discussion

Geometries and Binding Energies of MBz^+. First, we optimized the geometries of MBz^+ complexes for half-sandwich structures and calculated the M-ring binding energies.

Figure 2 shows the optimized M-ring distances of MBz^+ for first-row transition metals. In this figure, it is shown that only the HF results are much different from those of other methods. This indicates that electron correlations play a crucial role to reproduce accurate d–π bond of MBz^+. Actually, similar M-ring distances have been given for other methods taking account of electron correlations. Except HF results, LC-BOP have provided the shortest distances and CCSD mostly the longest ones. All present methods gave very close results for the C–C and C–H distances and H bending angles (from C_6 plane) of Bz, which are not shown in this article, within the differences of 0.034 Å (C–C), 0.016 Å (C–H), and 0.057° (H bending). This indicates that the calculated M-ring distances may give information on the reproducibilities of d–π bonds.

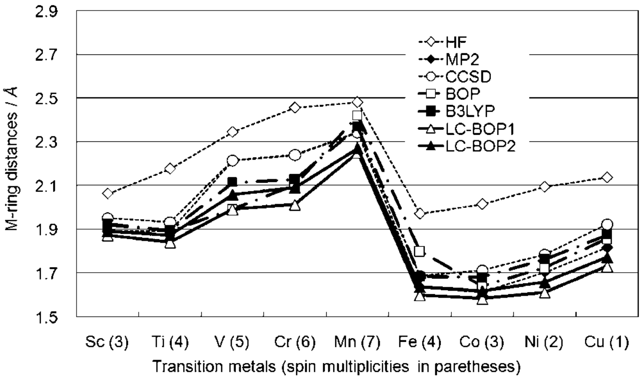

Figure 2. Plots of the optimized M-ring distances of MBz^+ for first-row transition metals. In parentheses, optimal spin multiplicities are given.

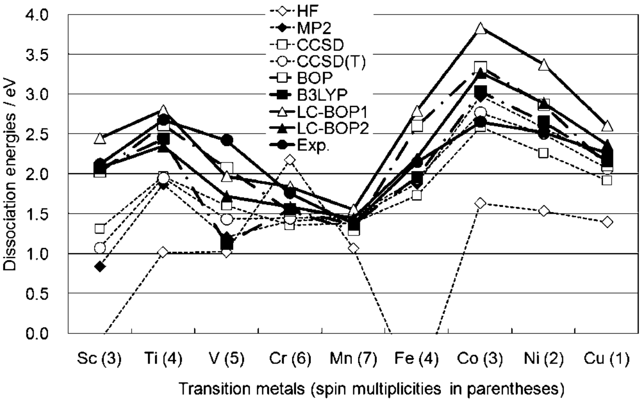

Figure 3. Plots of the calculated binding energies of MBz^+ for first-row transition metals. The experimental values are also shown for comparison.

In Figure 3, the calculated binding energies are illustrated with experimental results. HF method gave very poor binding energies as expected from the optimized M-ring distances. As mentioned above, this result indicates that electron correlations are required to discuss the d–π bond even from a qualitative point of view. Except for HF results, calculated binding energies showed a similar tendency to the experimental values. LC-BOP2 gave accurate binding energies of MBz^+ for early transition metals (M = Sc–Cr), but comparatively overestimated them for late transition metals (M = Fe–Cu). In contrast, WFTs (CCSD, CCSD(T), and MP2) underestimated binding energies for early transition metals, but gave accurate results for late transition metals. No present methods provided good results for both early and late transition metals. Therefore, it is presumed that highly balanced electron correlations including multiconfigurational effects are required to reproduce accurate binding energies of MBz^+ for all Ms.

It was also found in Figure 3 that LC-BOP gave higher binding energies for $\mu = 0.33$ than it did for $\mu = 0.47$ on the

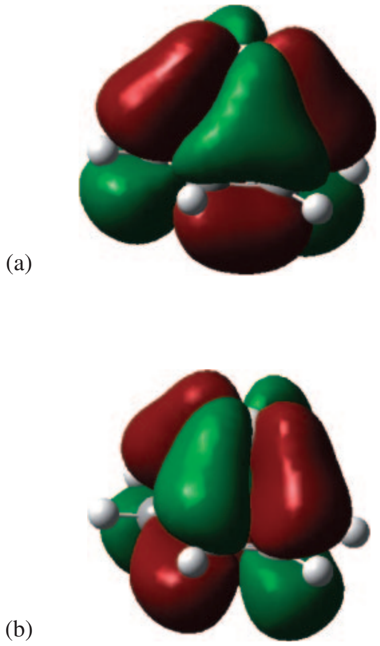

Figure 4. SOMOs of $ScBz^+$ given by LC-BOP1. Approximate orbitals were also obtained by other methods used.

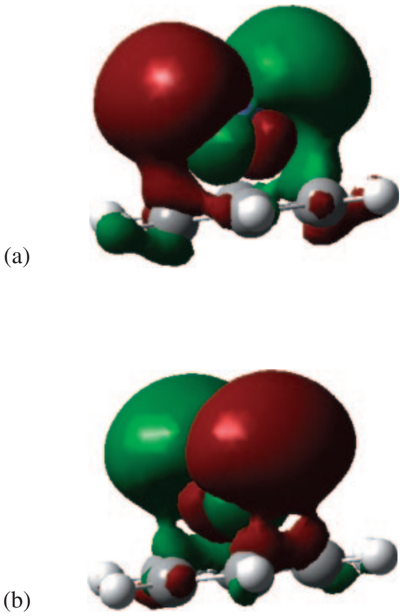

Figure 5. SOMO (a) and LUMO (b) of $NiBz^+$ given by LC-BOP1. Approximate orbitals were also obtained by other methods used.

whole, while the former contains smaller long-range exchange interactions than the latter does. This may indicate that long-range exchange interactions decrease the overall level of binding energies. We should notice that present single-configurational WFTs gave accurate binding energies for late transition metals as mentioned above, while these theories are based on HF wave function which gives sufficient long-range exchange interactions. Therefore, it is supposed that multiconfigurational effects fairly contribute to the binding energies for early transition metals, in which d orbitals are vacant or half-filled by electrons, because these WFTs are single-configurational. These results may indicate that sufficient long-range exchange and multiconfigurational effects are required, at least partly, to reproduce accurate binding energies of MBz^+ for both early and late metals.

So, why are multiconfigurational effects important in the d–π bonds of early transition metal–benzene complexes? Figure 4 displays the singly-occupied molecular orbitals (SOMOs) of $ScBz^+$, which were calculated by LC-BOP1. This figure shows that SOMOs correspond to two E_2 (Sc $d_{x^2-y^2}$ + Bz E_{2u}) orbitals which are degenerate with the same orbital energies, while $ScBz^+$ has C_{6v} point group symmetry. Similar orbitals are also found in the SOMOs of other early transition-metal complexes. In contrast, these orbitals are contained in doubly-occupied orbitals for late transition-metal complexes. We therefore suppose that the multiconfigurational character of the early transition-metal complexes may be related to these SOMOs. Instead, late transition-metal complexes contain two other E_1 orbitals which are mainly composed of degenerate d_{xz} and d_{yz} orbitals of M^+ in SOMO (or HOMO) and LUMO. The SOMO and LUMO of $NiBz^+$ calculated by LC-BOP1 are shown in Figure 5. Therefore, multiconfigurational effects attributed to the degeneracy of these orbitals may cause CCSD to slightly underestimate the binding energies for late transition-metal complexes. It is supposed that accurate CCSD(T) binding energies for late metal complexes may be explained by the picture that CCSD(T) implicitly contains a part of near-degeneracy effects. However, these near-degeneracies are attributed to the high symmetry of benzene, we would not find these multiconfigurational effects for d–π bonds of low symmetry.

Geometries and Binding Energies of MBz_2^+. Next, we carried out the geometry optimizations of MBz_2^+ complexes for sandwich structures and the calculations of their M-ring binding energies.

The optimized M-ring distances of MBz_2^+ are shown in Figure 6. Similarly to the results of MBz^+, close M-ring distances were given by all present methods but HF. The difference is that BOP and B3LYP gave longer distances than others except for HF on the whole. It is presumed that this may be attributed to long-range exchange interactions, because only BOP and B3LYP insufficiently contain long-range interactions. In addition, the present methods gave very close results for other parameters such as C–C and C–H bond distances and H bending angles with the maximum differences of 0.027 Å (C–C), 0.007 Å (C–H), and 0.017° (H bending).

Figure 7 displays the calculated binding energies of MBz_2^+ with the experimental results. From this figure, it is easily found that all the calculated results are much different from the experimental ones for $CrBz_2^+$ and $MnBz_2^+$. As suggested in conventional studies,[4] we also conclude that this significant difference may be due to the misestimations of the experiment. To reveal the cause of the discrepancy, we plotted the remaining energies after subtracting the binding energies of MBz^+ from those of MBz_2^+ for M = Cr and Mn[5] in this figure. As a result, we found that the remaining energy is very close to CCSD(T) and MP2 results for $MnBz_2^+$ (See cross marks (Ref.) in Figure 7). Therefore, we suspect that the binding energy of $MnBz^+$ was misestimated for the dissociation of two Bz molecules in the experiment. It is actually supposed that in the

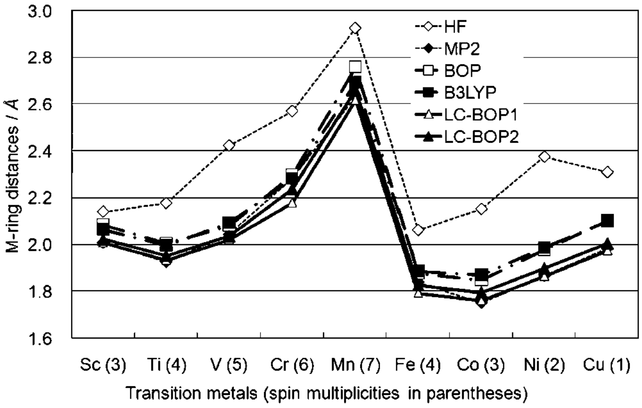

Figure 6. Plots of the optimized M-ring distances of MBz_2^+ for first-row transition metals. In parentheses, optimal spin multiplicities are given.

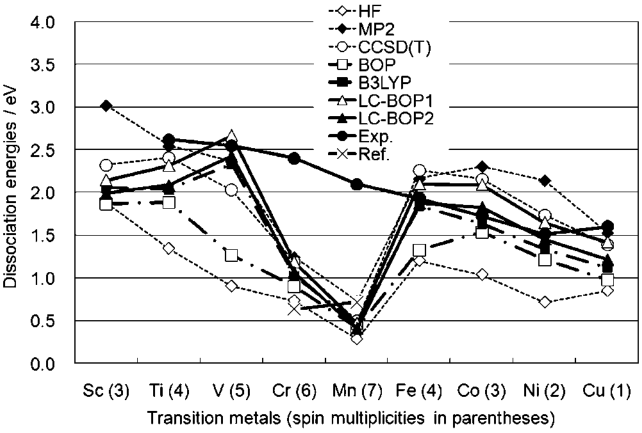

Figure 7. Plots of the calculated binding energies of MBz_2^+ for first-row transition metals. The experimental values are also shown for comparison.

referred collision cross-section experiment,[5] it may be hard to distinguish between the dissociations of one and two Bz.

For MBz_2^+, similar binding energies were given for sophisticated DFTs (B3LYP, LC-BOP1, and LC-BOP2) and WFTs (MP2 and CCSD(T)). We found minor differences in those of late transition-metal complexes: WFTs slightly overestimated binding energies, while sophisticated DFTs gave binding energies close to the experimental values. All these methods except for MP2 also underestimated the binding energies of $TiBz_2^+$. However, the calculated binding energies were not so poor totally. In contrast, pure BOP functional fairly underestimated the binding energies for VBz_2^+ and $FeBz_2^+$. This serious difference indicates that BOP lacks some interactions from the addition of another benzene, because BOP gave appropriate binding energies of MBz^+ for $M = V$ and Fe. Calculated accurate binding energies of LC-BOP1 and LC-BOP2 indicate that this obviously comes from the deficiency of long-range exchange interactions in pure BOP functional. Therefore, it is supposed that long-range exchange effects are required in part to give d–π bonds quantitatively in DFT calculations.

Finally, let us explain the calculated results by analyzing molecular orbitals of MBz_2^+ complexes. Figure 8 illustrates the SOMOs of $ScBz_2^+$ given by LC-BOP1 calculations. These

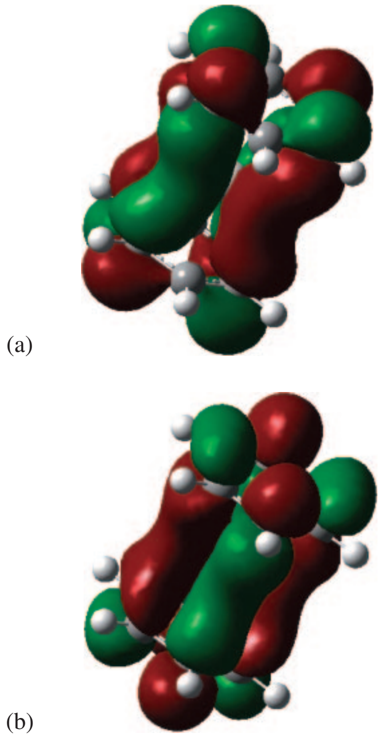

Figure 8. SOMOs of $ScBz_2^+$ given by LC-BOP1. Approximate orbitals were also obtained by other methods used.

SOMOs have E_{2g} representation (Sc $d_{x^2-y^2} + 2 \times \text{Bz}\ E_{2u}$) of D_{6h} point group symmetry and obviously contain the SOMOs of $ScBz^+$ (E_2 orbitals) in Figure 4. Similar E_{2g} orbitals are contained in the SOMOs of MBz_2^+ for other early transition metals. It is therefore supposed that multiconfigurational effects are significant in the binding energy of these early transition-metal complexes. Actually, these binding energies were mostly underestimated by all present methods as mentioned above. SOMO and LUMO of $NiBz_2^+$ are also illustrated in Figure 9. This figure shows that these orbitals have much different characteristics from each other in contrast to the above-mentioned relationship between the SOMO and LUMO of $NiBz^+$ in Figure 5. Therefore, we suppose that multiconfigurational effects may be negligible for this complex and these effects may not cause the slight overestimations of the binding energies for late transition-metal complexes in WFT calculations. There is room for further investigation of these overestimations.

Conclusion

In this article we investigated the reproducibilities of d–π bonds by calculating first-row transition-metal cation–benzene complexes, MBz^+ and MBz_2^+, with several types of DFTs and WFTs. As a result, we found that highly balanced electron correlations and long-range exchange interactions are required at least partly to reproduce d–π bonds quantitatively regardless of DFTs or WFTs.

First, we carried out the geometry optimizations of half-sandwich MBz^+ complexes and calculated the M-ring binding energies. We found that all present methods but HF gave close M-ring distances and binding energies. However, WFTs underestimated the binding energies for the complexes of early transition metals (Sc–Cr), while DFTs gave accurate or slightly

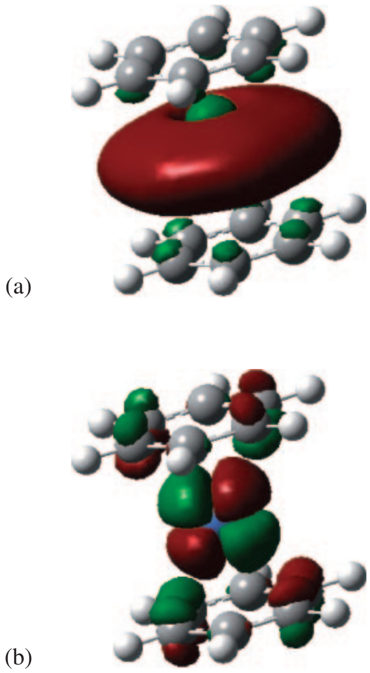

Figure 9. SOMO (a) and LUMO (b) of $NiBz_2^+$ given by LC-BOP1. Approximate orbitals were also obtained by other methods used.

low energies. From MO analyses, we suggested that this underestimation is due to the multiconfigurational effects from near-degenerate SOMOs. We supposed that this underestimation may not be found for d–π bonds of low symmetry, because this near-degeneracy is attributed to the high symmetry of benzene. We also found that long-range exchange interactions significantly affected the binding energies for the complexes of late transition metals (Fe–Cu) in DFT calculations, while WFTs gave accurate energies for these complexes. Therefore, we concluded that DFT calculations require long-range exchange effects in the calculations of d–π bonds.

Next, we calculated the geometries and binding energies of sandwich MBz_2^+ complexes. As a result, we suspected that the binding energies of $CrBz_2^+$ and $MnBz_2^+$ may be misestimated in the experimental study. For MBz_2^+, we found that pure BOP functional gives poor binding energies due to the lack of long-range exchange interactions. We also found that the binding energies of MBz_2^+ were underestimated for early transition metals. By MO analyses, we supposed that this is also due to multiconfigurational effects from near-degenerate SOMOs. Furthermore, WFTs overestimated the binding energy for late transition-metal complexes. However, we were not able to identify the cause of this overestimation from the MO analyses.

In summary, we concluded that highly balanced electron correlations and long-range exchange interactions should be included to reproduce d–π bonds quantitatively in DFT calculations. We suggest that these methods may give more accurate binding energies for other d–π bonds in low symmetry such as metal–alkene bonds.

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