

Theoretical investigation on the interaction between beryllium, magnesium and calcium with benzene, coronene, circumcoronene and graphene



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ABSTRACT

The interaction energies (IE) between benzene and beryllium, magnesium and calcium were calculated at the CCSD(T)/CBS level and including corrections for core-valence and relativistic effects. The IE are 1.8, 2.3 and 3.2 kcal/mol for Be, Mg and Ca, respectively. In contrast with our previous findings for the benzene–Li complex, we found that the non-ionic structure is more stable than the ionic configuration. Thus, charge-transfer from alkaline earths to benzene would not take place. The performance of MP2 and DFT functionals is poor. At the complete basis set limit, M06-2X, M06-L, B97D and MP2 exhibited similar MAD (~ 0.7 – 0.8 kcal/mol). When larger aromatic models were considered, the IE were similar to those computed for benzene. Finally, taking into account the drawbacks of the DFT functionals, the computed IE for the non-ionic adsorption of Be, Mg and Ca onto graphene, are tentatively estimated as 2.1, 2.7 and 2.9 kcal/mol, respectively.

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1. Introduction

There is current interest in the study of the interaction between carbon nanomaterials and alkaline/alkaline earth elements [1–10]. The main reason is that the adsorption of these elements can help improve the hydrogen storage capabilities of nanostructures [1–5]. In fact, this is one of the most important challenges for humanity in the 21st century, if fossil fuels are to be replaced. In a recent work, we investigated the interaction between lithium and carbon nanomaterials [11–13] and also between benzene and lithium [14]. For the latter complex, we observed that the ionic structure (C_{2v}) is more stable than the non ionic one (C_{6v}), and that both structures correspond to minima in the potential energy surface. Although the interaction between alkaline earth +2 cations and aromatic compounds has been studied in detail [15], the binding of the neutral elements and benzene has received less attention. Motivated by the interesting results that we obtained for the benzene–lithium complex, in this work we attempted to determine the most stable configuration for the benzene–X complex, X = Be, Mg and Ca. Because these systems are relatively small, the CCSD(T) method can be selected to obtain reference values and test the performance of several DFT functionals that can be used for larger systems which are intractable at the CCSD(T) level. Herein we present: (a) a detailed CCSD(T), DFT and MP2 investigations of

the benzene–X, X = Be, Mg and Ca complexes, (b) a DFT study of the interaction between coronene, circumcoronene and graphene with the alkaline earth elements Be, Mg and Ca. We expect that our work can help shed light into the interaction between alkaline earth elements and carbon nanomaterials.

2. Methods

The complexes formed by benzene and the alkaline earth elements Be, Mg and Ca, were studied employing DFT functionals and wavefunction methods. The reference values were obtained with the aid of the CCSD(T) [16–19] method and Dunning's correlation consistent basis sets, cc-pCVXZ (X = T, Q) [20–21]. Core correlation effects were estimated as the difference between the full and frozen core CCSD(T) calculations. The full CCSD(T) calculations are indicated as full-CCSD(T). Scalar relativistic effects were estimated by applying perturbative techniques at the MVD2 level as implemented in CFOUR [22–23]. The complete basis set limit was reached utilizing the two-parameter expression $E = B + Cl_{max}^3$, suggested by Halkier et. al. [24], where l_{max} is the maximum angular momentum quantum number l of the basis set, E is the total energy and B and C are parameters which are obtained through fitting. The CCSD(T) method cannot be applied for the rest of the systems that we investigated because they are too large. For this reason, we analysed the performance of several DFT functionals, MP2 and G4 theory [25]. The DFT functionals considered were: M06-2X, M06-L [26–27], B3LYP [28–29], B3LYP-gcP-D3 [30–31] and B97D

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[32]. For the DFT calculations we used the cc-pCVXZ basis sets to gauge the performance when much extended basis sets are considered. We also utilized Popl es 6-31G* basis set [33] given that for large systems, the cc-pCVXZ basis sets are too large. In all DFT calculations we used tight thresholds for optimizations and the ultra-fine grid was selected. The CCSD(T) calculations were performed with CFOUR [22–23] while the DFT and G4 ones were undertaken with Gaussian 09 [34]. Finally, the periodic calculations were carried out at the M06-L/6-31G* and B97D/6-31G* levels of theory. The size of the unit cell was 5×5 (50 carbon atoms). The number of k -points sampling was 500.

3. Results and discussion

3.1. Complexes between benzene and the alkaline earth elements Be, Mg and Ca

In our recent work about the benzene lithium complex, we found that the C_{6v} (non ionic) and C_{2v} (ionic) structures are minima at the M06-2X and MP2 levels of theory. The latter structure is more stable by 1.8 kcal/mol, at the CCSD(T)/CBS level, including corrections for core correlation and relativistic effects. Taking this result into consideration, we first investigated whether the C_{6v} and C_{2v} structures exist for the alkaline earth elements. In the case of beryllium, we optimized the C_{6v} and C_{2v} structures at the M06-2X/cc-pCVTZ and MP2/cc-pCVTZ levels of theory. The structures are presented in Fig. 1. Both methodologies indicated that the less symmetric structure is a first order transition state with imaginary wave numbers of 322i and 229i cm^{-1} , respectively. The C_{2v} structure is located 1.5 and 1.0 kcal/mol above the C_{6v} one, at the M06-2X/cc-pCVTZ and MP2/cc-pCVTZ levels of theory, respectively. For magnesium, all of our attempts to locate the ionic structure failed and converged to the non ionic one. Finally, for calcium, we were able to optimize the C_{6v} and C_{2v} structures at the MP2/cc-pCVTZ level of theory. The structures are presented in Fig. 1. However, the ionic structure is 10.8 kcal/mol above the more symmetric isomer. For the sake of completeness, we computed the relative energy of both structures at the CCSD(T)/cc-pCVTZ level of theory. For this calculation, the input was the MP2/cc-pCVTZ geometry. In good agreement with the MP2 result, the value for the relative energy is 10.9 kcal/mol at the CCSD(T)/cc-pVTZ level, favoring the C_{6v} structure.

In Table 1, we present the binding energies (BE) and the most important bond distances determined for the C_{6v} benzene–X complexes, X = Be, Mg, Ca. The basis set dependence of the BE is quite weak as evidenced by the change of the BE upon increase of the basis set from cc-pCVTZ to cc-pCVQZ. When extrapolation to the complete basis set limit is accomplished, core correlation is included and relativistic effects are evaluated, the BE are 1.8, 2.3 and 3.2 kcal/mol, at the CCSD(T) level. These values are considerably smaller than the BE determined at the same level of theory for the C_{6v} and C_{2v} structures of the benzene–lithium complex, which are 4.9 and 6.7 kcal/mol, respectively. Therefore, the interaction between benzene and the three alkaline earth elements Be, Mg, Ca is very weak. The distance between the alkaline earth atom and benzene increases as we move down in the periodic table. It is 3.325   for beryllium, 3.597   for magnesium and 3.699   for calcium, at the CCSD(T)/cc-pCVTZ level of theory.

Regarding the performance of M06-2X and MP2 with respect to CCSD(T), as regards BE, it is verified a marginally better performance of M06-2X, and for both methods the agreement with CCSD(T) is improved as we move from Be to Ca. The worst scenario is observed for beryllium since MP2 overestimates the BE by 1.4 kcal/mol and M06-2X does so by 1.1 kcal/mol. For magnesium, M06-2X and MP2 yielded BE which are 0.5 and 0.8 kcal/mol larger.

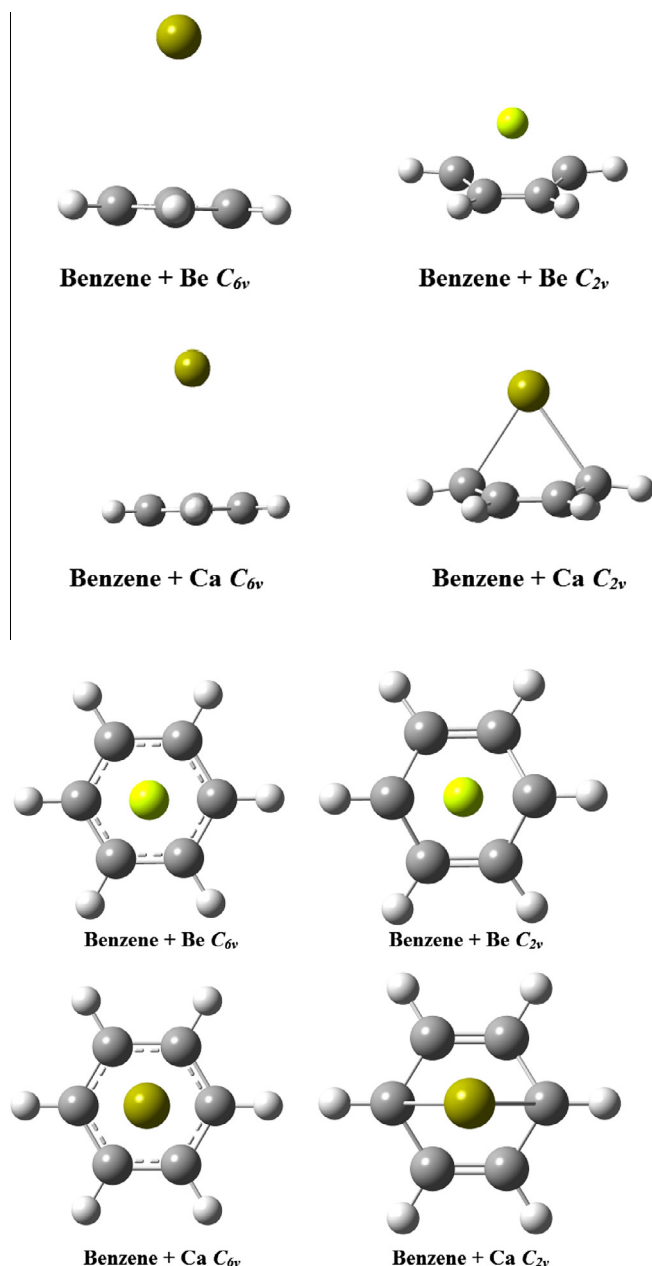


Fig. 1. Optimized structures for the benzene + Be and benzene + Ca complexes, at the MP2/cc-pCVTZ level of theory, top shows the side view and bottom shows the top view.

However, for calcium, the overestimation is only 10 and 22 % at the MP2 and M06-2X/cc-pVQZ levels, respectively. This overestimation of the BE predicted by M06-2X and MP2 is translated into an underestimation of the distance between the alkaline earth atom and benzene. Since M06-L and D97D are fast methods for periodic calculations, it is interesting to test their performance. In the case of M06-L, when the cc-pCVQZ basis set is utilized, the BE determined for Be is only 0.2 kcal/mol larger than the CCSD(T) result whereas for Mg, the BE predicted is 0.3 kcal/mol lower than the CCSD(T) result. However, M06-L strongly underestimates the BE between Ca and benzene by 1.1 kcal/mol. The mean absolute deviation (MAD) of M06-L M06-2X, B97D and MP2, with respect to the CCSD(T) values are: 0.7, 0.8, 0.7 and 0.8 kcal/mol, respectively when the cc-pCVQZ basis set is employed. From a qualitative stand point, it is very important to stress that B97D is the only DFT

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