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On the Interaction of Dihydrogen with Aromatic Systems[†]

Olaf Hübner,[‡] Andreas Glöss,[§] Maximilian Fichtner,[‡] and Wim Klopper*,[‡,§]

Institut für Nanotechnologie, Forschungszentrum Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany, and Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

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Second-order Møller−Plesset (MP2) calculations (using the approximate resolution of the identity, RI-MP2) in the TZVPP basis are performed to study the interaction of molecular hydrogen with the aromatic systems C_6H_5X (X = H, F, OH, NH_2, CH_3, and CN), $C_{10}H_8$ (naphthalene and azulene), $C_{14}H_{10}$ (anthracene), $C_{24}H_{12}$ (coronene), *p*-$C_6H_4(COOH)_2$ (terephthalic acid), and *p*-$C_6H_4(COOLi)_2$ (dilithium terephthalate). Various adsorption positions are studied for C_6H_5F. The most favorable configuration places H_2 above the aromatic plane with its axis pointing toward the middle of the ring. The electronic (van der Waals) interaction energy for the differently substituted benzenes correlates with the ability of the substituents to enrich the aromatic system electronically. The largest interaction energy (among the singly substituted benzenes) is found for aniline (4.5 kJ mol^{-1}). Enlarging the aromatic system increases the interaction energy; the value for coronene amounts to 5.4 kJ mol^{-1}. Extending the basis set and including terms linear in the interelectronic distances increases the interaction energy by about 1 kJ mol^{-1} relative to that of the TZVPP basis, whereas the inclusion of higher excitations by coupled-cluster calculations (including all single and double excitations with a perturbative estimate of triples, CCSD(T)) decreases the interaction energy by about the same amount.

1. Introduction

There is hope to use hydrogen extensively as fuel in the future, for example, in fuel cells, and in this way to achieve emissionless energy management. Currently, different ways to store hydrogen are investigated: high-pressure tanks, liquified hydrogen, and storage in solids.[1] Storage in solids is based on chemisorption, for example, in metal hydrides, or physisorption on large internal surfaces, for example, in microporous materials as charcoal or zeolites. Whereas until now materials based on physisorption have exhibited only relatively small storage capacities, the isoreticular metal organic frameworks (MOFs) synthesized by Yaghi and co-workers[2,3] seem to be promising candidates for achieving higher loadings. At room temperature and a pressure of 20 bars, loadings of 1 wt % H_2 have been observed.[3] The MOFs are built from Zn_4O tetrahedra that bind to six aromatic dicarboxylic acids, forming a cubic structure. Each of the two carboxy groups binds to a different Zn center.

The new perspectives in adsorptive hydrogen storage are our motivation to investigate the interaction between molecular hydrogen and aromatic systems. One way to increase the storage capacity of MOFs might be the modification of the aromatic systems that link the Zn_4O tetrahedra. The subject of the present study is to characterize the possible binding sites of H_2 at aromatic compounds and investigate how different substituents alter the weak intermolecular interaction. Because a high storage capacity with respect to the overall weight is an important requirement for an effective storage medium, our investigation is restricted to benzene derivatives of elements of the first row only (light substituents). In the first step, the interaction energies for a large number of different adsorption positions are determined, taking fluorobenzene as an example. Various substituted benzenes are studied in the second step. This study is performed for the most favorable configuration of dihydrogen at fluorobenzene found in the first step. The individual systems considered are C_6H_6, C_6H_5F, C_6H_5OH, $C_6H_5NH_2$, $C_6H_5CH_3$, and C_6H_5CN. Furthermore, to study the changes induced by extending the aromatic system, we perform calculations on naphthalene, azulene, anthracene, and coronene. Because the real MOFs incorporate aromatic dicarboxylates, an attempt is made to obtain a better estimate for the situation in real systems by investigating the interaction of H_2 with terephthalic acid and the corresponding dilithium salt. $C_6H_4(COOLi)_2$ is considered to be the simplest model system for a dicarboxylate bound to the metal centers.

There is a considerable amount of theoretical work in the literature dealing with the interaction of H_2 with carbonaceous compounds. For example, the interaction energy of H_2 with polycyclic aromatic hydrocarbons has been calculated using the second-order Møller−Plesset (MP2) method and various density functionals[4−6] as well as using a bifunctional density functional approach.[5] Furthermore, the interaction energy has been determined for a graphite surface by density functional calculations.[7,8] In addition, the interaction of dihydrogen with graphite and carbon nanotubes has been the subject of numerous theoretical investigations using various model potentials: adsorption isotherms have been calculated by grand canonical Monte Carlo simulations,[9−18] and the arrangement of H_2 molecules inside single-walled carbon nanotubes has been studied on the basis of molecular dynamics simulations.[19] Other investigations have been concerned with the recombination of hydrogen atoms on graphite surfaces[20−23] and the motion of chemisorbed hydrogen atoms through carbon nanotube walls.[24] The calculation of the interaction energy by density functional methods is questionable because of the inherent difficulties of current functionals in

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* To whom correspondence should be addressed. E-mail: klopper@chem-bio.uni-karlsruhe.de.

[‡] Forschungszentrum Karlsruhe.

[§] Universität Karlsruhe.

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correctly accounting for the dispersion interaction. Although experiments indicate an interaction potential of about 5 kJ mol^{-1} for the interaction of H_2 with a graphite surface,[25,26] the corresponding local density approximation (LDA) values[7,8] amount to about 8 kJ mol^{-1}, and a value of only 2.4 kJ mol^{-1} has been obtained with a gradient-corrected functional.[8]

Our study relies primarily on MP2 calculations.[27] To determine the quality of the calculated MP2 interaction energies and possibly to obtain improved estimates for the interaction energies, we have investigated both the effect of higher excitations and basis-set extension. The effect of including higher excitations is investigated by coupled-cluster calculations including all single and double excitations (CCSD)[28] as well as a noniterative, perturbative estimate for the triple excitations [CCSD(T)].[29]

Effects of basis-set extension are studied by means of computing the MP2 interaction energies in a basis set larger than TZVPP. Clearly, the molecular systems studied here are too large to use basis sets with up to *k*-type functions, as can be done for small molecules.[30] Therefore, rather than using extremely large basis sets, we use the MP2-R12 method[31] to approach the limit of a complete one-particle basis. This method includes terms that are linear in the interelectronic distances into the wave function and has proved successful on various occasions for the computation of both energy barriers (e.g., cf. ref 32) and intermolecular interaction energies (e.g., the water dimer,[33,34] the benzene dimer,[35] and the benzene−neon and −argon van der Waals interactions[36]).

2. Methods

All structures were optimized by MP2 calculations using the approximate resolution of the identity (RI-MP2). The calculations were carried out with the program TURBOMOLE.[37,38] Within the RI-MP2 calculations, the 1s orbitals of C, N, O, and F were not correlated (frozen-core approximation). For all atoms, the calculations were performed in the triple-ζ valence (TZV) basis[39] supplemented with the polarization functions of the cc-pVTZ basis.[40] This basis is denoted TZVPP. The appropriate auxiliary-TZVPP basis set was used for the resolution-of-the-identity approximation.[41]

The CCSD(T) calculations were performed with the program package MOLPRO[42−44] using the same basis set (TZVPP) as for the MP2 calculations, again in the frozen-core approximation. The MP2-R12 calculations were carried out with the program SORE.[31] The basis set denoted aug-cc-pVQZ′ was derived from the aug-cc-pVTZ and aug-cc-pVQZ basis sets.[40] On the C and N atoms and on the H_2 molecule, the aug-cc-pVQZ basis set was used, with the two g shells removed on C and N (the SORE program is limited to f-type functions) and the two f shells removed on H_2. On all other H atoms, the aug-cc-pVTZ basis set was used, with the two d shells deleted.

All interaction energies were corrected for the basis-set superposition error (BSSE) by the full counterpoise procedure.[45]

For some of the optimized structures, the order of the stationary points was determined by computing the harmonic vibrational frequencies, which were obtained by numerical differentiation of analytical gradients.

3. Results and Discussion

3.1. Adsorption Position. Figure 1 shows the stationary points for a series of adsorption positions of H_2 on the C_6H_5F molecule. The energetically most favorable structures are characterized by a dihydrogen pointing toward the plane of the fluorobenzene. Structure **A**, the lowest-energy structure of all, has the axis of the hydrogen molecule pointing approximately toward the middle of the ring. According to the frequency calculations, this structure is a minimum of the potential energy surface. Structure **B** at 1.43 kJ mol^{-1} above **A**, the next structure in energetic order, aligns the axis of the dihydrogen parallel to the molecular plane and is a transition structure. The following structures with increasing energy, structures **C** (minimum) and **D** (transition structure) at 1.97 and 2.48 kJ mol^{-1}, respectively, have the hydrogen molecule pointing toward the F atom, namely, above the molecular plane and within the molecular plane, respectively. Therefore, the first structure in energetic order that places the hydrogen within the aromatic plane already lies more than 2 kJ mol^{-1} above the most favorable structure. More than about 3 kJ mol^{-1} higher in energy, one finds additional structures that have the dihydrogen lying within the plane or intersecting the plane. (Structures **E** and **G** have the H_2 coordinated to the C−C bond that is parallel to the C−F bond; structures **F**, **K**, and **L** have the H_2 at the F atom; and structures **H**, **I**, and **J** have the H_2 at the H atom that is in the para position with respect to the F atom.) Hence, by far the most favorable site for the H_2 molecule is a position where the axis is perpendicular to the aromatic plane and points to about the middle of the ring. Therefore, such a configuration is used in the subsequent study of various substituted benzenes. The lowest stationary point that places the hydrogen in the vicinity of the F atom lies almost 2 kJ mol^{-1} higher in energy. This is more than half of the calculated interaction energy between H_2 and C_6H_5F in the most stable configuration. In fact, other substituents such as amino groups still might be able to exhibit an increased interaction with H_2 compared to that with the hard fluorine atom, but they would most likely not be able to outperform the delocalized aromatic electron distribution.

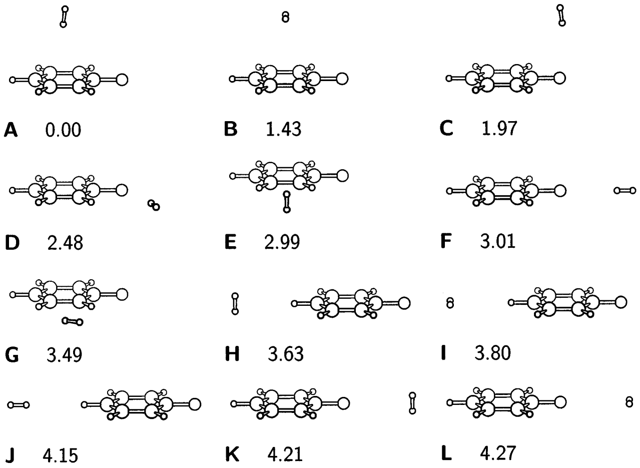

Figure 1. Structures of stationary points of $H_2 \cdots C_6H_5F$ and relative MP2/TZVPP interaction energies (kJ mol^{-1}).

3.2. Substituted Benzenes. Figure 2 shows the optimized structures of the adducts of H_2 with different substituted benzenes. The given interaction energies are corrected for BSSE. The MP2/TZVPP interaction energy between H_2 and benzene amounts to 3.91 kJ mol^{-1}. That for fluorobenzene is somewhat smaller, 3.58 kJ mol^{-1}. Going from fluorobenzene to phenol and then to aniline increases the interaction energy in each case by about 0.5 to 4.00 and 4.52 kJ mol^{-1}, respectively. The value for toluene, 4.40 kJ mol^{-1}, is somewhat smaller than that for aniline. The lowest interaction energy of the six systems is obtained for benzonitrile. The differences in the interaction energies do not come as a surprise. They correlate with the ability of the substituents to enrich the aromatic system electronically. With one lone pair and only a slightly larger

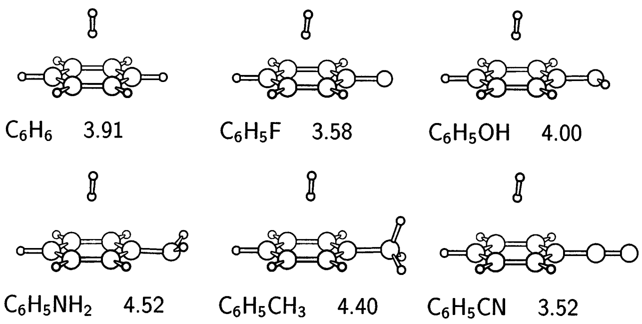

Figure 2. Structures of adsorption complexes between dihydrogen and differently substituted benzenes ($H_2\cdots C_6H_5X$) and MP2/TZVPP interaction energies (kJ mol^{-1}) corrected for BSSE. All structures are confirmed to be minima of the potential energy surface.

TABLE 1: Distance between the Aromatic Plane[a] and the Closer H of H_2 and Inclination of the H_2 Axis with Respect to the Normal of the Aromatic Plane for the Various Aromatic Systems (MP2/TZVPP)

system	distance (pm)	angle (deg)
$H_2\cdots C_6H_6$	269.8	0.0
$H_2\cdots C_6H_5F$	270.3	6.6
$H_2\cdots C_6H_5OH$	268.1	4.8
$H_2\cdots C_6H_5NH_2$	265.9	4.3
$H_2\cdots C_6H_5CH_3$	266.6	2.9
$H_2\cdots C_6H_5CN$	270.6	7.0
$H_2\cdots C_{10}H_8$[b]	266.6	5.7
$H_2\cdots i\text{-}C_{10}H_8$[c]	266.6	18.2
$H_2\cdots C_{14}H_{10}$	262.7	0.0
$H_2\cdots C_{24}H_{12}$	259.5	0.0
$H_2\cdots C_6H_4(COOH)_2$	268.6	0.0
$H_2\cdots C_6H_4(COOLi)_2$	266.5	0.0

[a] Because the six ring carbon atoms do not unambiguously define the aromatic plane, the aromatic plane is defined by three next but one carbon atoms. Using the plane defined by the second set of next but one carbon atoms yields the same distances within the given digits. [b] Naphthalene. [c] Azulene.

electronegativity than carbon, nitrogen seems to have the optimum properties. The increasing electronegativity of oxygen and fluorine then decreases the capability to push electrons into the aromatic system. The methyl group lacks the lone pairs. The electron-withdrawing CN functionality leads of course to a more electron-poor aromatic system.

The differences in the interaction energies are accompanied by changes in the distance between the aromatic plane and the H_2 molecule (Table 1). Ordering the six systems by increasing interaction energy or by decreasing distance yields the same sequence. The longest distance for the system with the smallest interaction energy, benzonitrile, amounts to 271 pm, whereas for aniline the smallest distance of 266 pm is found.

3.3. MP2-R12 and CCSD(T). To assess the quality of the obtained MP2/TZVPP results, the MP2, MP2-R12, and CCSD(T) interaction energies for selected systems calculated with the TZVPP and aug-cc-pVQZ′ basis sets are shown in Table 2. The size of the individual contributions due to the enlargement of the basis set, the inclusion of terms that are linear in interelectronic distances, and the inclusion of higher excitations are very similar for the different systems. The enlargement of the basis set from TZVPP to aug-cc-pVQZ′ increases the MP2 interaction energy between dihydrogen and benzene by 0.89 kJ mol^{-1}. Including the terms that are linear in the interelectronic distance adds another 0.11 kJ mol^{-1} to this value. For the whole set of systems given in Table 2, the corresponding contributions lie between 0.89 and 0.95 kJ mol^{-1} and between 0.08 and 0.12 kJ mol^{-1}, respectively. However, in comparing the MP2 and CCSD(T) values for the TZVPP basis set, one finds that taking into account higher excitations beyond MP2 decreases the interaction energy for benzene by 0.85 kJ mol^{-1}. The values for aniline and toluene are only slightly larger, 0.94 and 0.95 kJ mol^{-1}, respectively. For aniline, subtracting the difference between the MP2 and CCSD(T) values with the TZVPP basis set from the MP2-R12 result yields an estimate for the interaction energy of 4.64 kJ mol^{-1}, a value that differs by only 0.12 kJ mol^{-1} from the MP2/TZVPP result of 4.52 kJ mol^{-1}. The same holds for the other systems.

TABLE 2: Interaction Energies (kJ mol^{-1}) between Dihydrogen and Various Aromatic Systems Corrected for BSSE[a]

system	CCSD(T)/ TZVPP	MP2/ TZVPP	MP2/ aug-cc-pVQZ′	MP2-R12/ aug-cc-pVQZ′
$H_2\cdots C_6H_6$	3.06 (4.01)	3.91 (4.87)	4.80 (5.81)	4.91 (5.20)
$H_2\cdots C_6H_5NH_2$	3.58 (4.65)	4.52 (5.59)	5.46 (6.55)	5.58 (5.89)
$H_2\cdots C_6H_5CH_3$	3.45 (4.48)	4.40 (5.43)	5.32 (6.41)	5.43 (5.72)
$H_2\cdots C_{10}H_8$[b]		4.28 (5.40)	5.21 (6.36)	5.30 (5.62)
$H_2\cdots i\text{-}C_{10}H_8$[c]		4.77 (5.91)	5.72 (6.78)	5.80 (6.07)
$H_2\cdots C_{14}H_{10}$		4.70 (5.98)		
$H_2\cdots C_{24}H_{12}$		5.42 (6.97)		

[a] Uncorrected values are in parentheses. [b] Naphthalene. [c] Azulene.

Hence, although the near-basis-set-limit MP2 interaction energies exceed the TZVPP values by about 1 kJ mol^{-1} (1.00−1.06 kJ mol^{-1} for the systems investigated), taking into account higher excitations by means of CCSD(T) calculations reduces the interaction energies by about the same amount. Therefore, the MP2/TZVPP calculations are considered to yield appropriate estimates for this kind of weak van der Waals interaction energy. There is no deep underlying reason for this apparent compensation of errors. The MP2/TZVPP results are not at the limit, neither with respect to the one-particle basis nor with respect to the many-particle basis, but the two contributions do have opposite signs. Because both contributions behave uniformly, at least for the three different systems studied by CCSD(T), it is concluded that the MP2/TZVPP results provide useful estimates.

Of course, the true adsorption energy contains a contribution from the zero-point vibrational energies. For the smaller systems, values for the zero-point vibrational energies have been obtained from harmonic vibrational frequencies. But because, especially for the weak interactions, the potential energy surfaces are strongly anharmonic, a correction based on the harmonic force constants would be meaningless and is therefore not attempted.

Our MP2 value for benzene (4.91 kJ mol^{-1}) is close to the values of 4.96 and 5.06 kJ mol^{-1} from Heine et al.[6] and Tran et al.,[5] respectively. The discrepancy of the latter might be attributed to the fact that these authors did not optimize the benzene structure but froze the distances (e.g., the C−C distance at the graphite value).

3.4. Larger Aromatic Systems. The interaction energies for naphthalene, anthracene, and coronene are compiled in Table 2. The adsorption at anthracene and coronene has been calculated for complexes with dihydrogen pointing toward the central ring. Figure 3 shows the adsorption complexes between H_2 and naphthalene, azulene, terephthalic acid, and dilithium terephthalate. The interaction energies for naphthalene and anthracene amount to 4.28 and 4.70 kJ mol^{-1}, about 0.4 and 0.8 kJ mol^{-1} larger than for benzene, respectively. Thus, the annelation of two additional aromatic rings on opposite sides of benzene increases the interaction energy in each step by 0.4 kJ mol^{-1}. Surrounding the central ring by the total number of six rings (coronene) yields a value of 5.4 kJ mol^{-1} for the interaction energy. Hence, an extended aromatic system is

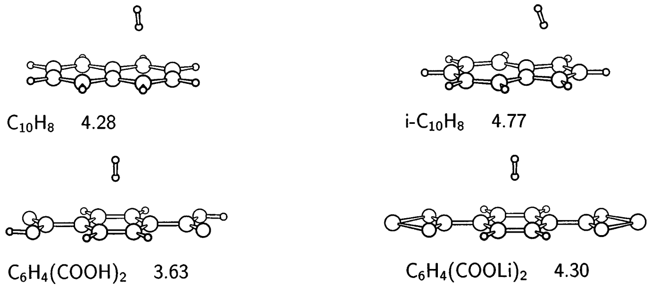

Figure 3. Structures of adsorption complexes between dihydrogen and selected aromatic systems and MP2/TZVPP interaction energies (kJ mol^{-1}) corrected for BSSE.

characterized by an increased interaction. The interaction energy for azulene, 4.77 kJ mol^{-1}, is 0.5 kJ mol^{-1} larger than for the isomeric naphthalene. The dihydrogen is bound to the five-membered ring. Apparently, the larger electron density at the five-membered ring increases the interaction, and the dipole moment also possibly contributes because the H_2 is somewhat inclined. Despite the pronounced difference between the interaction energies of naphthalene and azulene, the same distance of 267 pm from H_2 to the aromatic plane is obtained for both systems. Nevertheless, because in azulene H_2 is coordinated to the five-membered ring, the mean H_2−C distance is 9 pm smaller for azulene than for naphthalene (2.93 vs 3.02 pm). It is questionable if the enhanced interaction for a single hydrogen molecule with azulene might be an advantage compared to the interaction with naphthalene because naphthalene has two binding sites of the same kind but the calculations indicate that the coordination of H_2 at the seven-membered ring of azulene is 0.76 kJ mol^{-1} *weaker* than at the five-membered ring (obtained without correction for BSSE). Therefore, the overall interaction of dihydrogen with azulene is probably not superior to that of naphthalene.

Our finding of an increasing interaction with the extent of the aromatic system is in agreement with the results of Heine et al.[6] In general, the interaction energies calculated by these authors are larger than ours because they did not correct for BSSE. In this way, they claim to obtain near-basis-set-limit MP2 values, and this is probably right. But in all likelihood, the inclusion of higher excitations within the correlation treatment would lower the interaction energy; therefore, we do not agree with these authors' statement that their final physisorption energy would be too low.

Although our findings agree with those of Heine et al.,[6] they conflict with the results of Tran et al.,[5] who find only a very minor increase in the interaction energy with the size of the aromatic system. Tran et al. find that the anthracene value of 5.15 kJ mol^{-1} is larger by only 0.21 kJ mol^{-1} than the benzene value, and the increase in size from anthracene to coronene adds only 0.12 kJ mol^{-1}. Moreover, the dihydrogen on anthracene and coronene is oriented parallel to the aromatic plane. For a perpendicular orientation, the interaction energy decreases to 4.18 kJ mol^{-1} for anthracene and to 3.85 kJ mol^{-1} for coronene. This is a failure of the bifunctional approach, which predicts almost equal interaction energies for both orientations of H_2 on benzene (4.94 and 4.90 kJ mol^{-1}, respectively), whereas the MP2 results predict the perpendicular orientation to be 1.46 kJ mol^{-1} more favorable, similar to our results for fluorobenzene, where the perpendicular orientation is favored by 1.43 kJ mol^{-1}. Furthermore, our MP2 value for naphthalene (4.28 kJ mol^{-1}) is larger than the result of 3.56 kJ mol^{-1} obtained by Tran et al.[5] due to their poorer basis set.

Finally, Okamoto and Miyamoto[4] report an MP2 interaction energy of 8.4 kJ mol^{-1} for the interaction of H_2 with $C_{24}H_{12}$, which is more than 50% larger than our value of 5.4 kJ mol^{-1}. It is not clear whether the authors corrected their results for BSSE, and the neglect of the correction could be the reason for the discrepancy, especially given the small split-valence-type basis set used for $C_{24}H_{12}$.

In MOFs, the Zn_4O tetrahedra are linked by compounds with two carboxylate groups. The prototypical MOF contains only terephthalate;[2] therefore, in a first approach, the free terephthalic acid and dilithium terephthalate (as simple neutral dicarboxylate) are studied. For terephthalic acid, the calculations yield a BSSE-corrected interaction energy of 3.63 kJ mol^{-1}, a value that is 0.3 kJ mol^{-1} below the value for benzene, as expected for the electron-withdrawing carboxyl groups. The replacement of the acidic protons by lithium ions (D_{2h} structure instead of C_{2h}) increases the interaction energy to 4.30 kJ mol^{-1}, which is 0.4 kJ mol^{-1} larger than for benzene. Therefore, even if the influence of the Zn centers in MOFs is not as large as that of the Li ion, we also expect that in MOFs the interaction of H_2 with dicarboxylates is not decreased with respect to the corresponding aromatic systems without carboxy functionalities.

To investigate whether the interaction energy for the adsorption of one hydrogen molecule on both sides of an aromatic system is additive, calculations were performed on a system of benzene with two hydrogen molecules on each side. The dissociation energy for removing one H_2 from a system of two hydrogen molecules bound to benzene amounts to 3.87 kJ mol^{-1} (corrected for BSSE). This is smaller by only 0.04 kJ mol^{-1} than the energy for the detachment of a single H_2 bound to C_6H_6. As expected, the interaction energy for two hydrogen molecules bound from opposite sides to an aromatic system is almost additive.

4. Summary and Conclusions

The most favorable adsorption position of H_2 on C_6H_5F places the H_2 molecule above the aromatic plane with the axis pointing toward the middle of the ring. For the corresponding position on various substituted benzenes, the interaction energy increases with the ability of the substituent to enrich the aromatic system electronically. Among the singly substituted benzenes, the largest interaction energy is found for aniline. Enlarging the aromatic system increases the interaction energy. The values for anthracene and coronene exceed that for benzene by about 0.8 and 1.5 kJ mol^{-1}, respectively.

The interaction energy for the free dicarboxylic acid is smaller than for benzene (as expected for the electron-withdrawing group), but the replacement of hydrogen by lithium increases the interaction energy, indicating that in real MOFs the connection to metal centers probably does not decrease the interaction.

The enlargement of the basis set from TZVPP to aug-cc-pVQZ′ increases the interaction energy by something less than 1 kJ mol^{-1}, and the inclusion of terms that are linear in the interelectronic distance additionally increases the MP2 interaction energy by about 0.1 kJ mol^{-1}. Taking into account higher excitations by CCSD(T) calculations yields interaction energies that are about 1 kJ mol^{-1} smaller than the MP2 results (with the TZVPP basis set). Therefore, the MP2/TZVPP calculations accidentially yield appropriate values for the weak interaction between dihydrogen and the aromatic systems.

We conclude that larger aromatic systems should be favored over single benzene rings in order to increase the interaction of dihydrogen with aromatic systems. The systems should be supplemented with electron-pushing groups, preferably amino side groups. However, the overall magnitude of the increase in interaction is very moderate, and it is not likely to induce a substantially enhanced adsorption in this way. On the basis of the present investigation alone, it is not yet possible to predict the storage capacity of MOFs with various aromatic systems. This might be achieved by grand canonical Monte Carlo simulations using model potentials derived from calculations of the type described in the present work.

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