Inorganic Chemistry

Nature of "Hydrogen Bond" in the Diborane–Benzene Complex: Covalent, Electrostatic, or Dispersive?

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Motivated by the recent discovery of unusual "hydrogen bonding"-like interaction between a borane system and benzene molecules in a molecular crystal, we carried out quantum mechanical calculations on a model complex, diborane–benzene cluster. The aim is to understand the nature of this unique interaction, which is expected to play an essential role in this novel class of molecular crystals. As analyzed in the present study, the interaction between diborane and benzene is special in the following aspects: (1) this interaction is mostly dispersive; (2) the observed pseudodirectionality with one of the diborane bridge hydrogen directed toward the benzene centroid minimizes the van der Waals contact; and (3) in the "hydrogen bond" map, this interaction is located in a unique region, which is presently populated by a few known molecular complexes with very different chemical characteristics. It is anticipated that the results from the present analysis will provide meaningful guidance for molecular engineering with diborane–benzene as a building block and for stabilization of this and possible other hydrogen bonds by dispersive contributions.

Introduction

The interaction involving X–H···A is often observed as structal scaffolds in molecular complexes such as molecular crystals or biopolymers.[1–3] Broadly defined, all of the interactions involving a hydrogen atom acting as a bridge to attract two atoms can be called "hydrogen bonds",[1] although there are some more narrowed definitions of hydrogen bonds based on various criteria including energetic, geometries, and interactive types, etc.[1,4] Based on the broad definition, there are quite a few nonclassical "hydrogen bond" types which especially include X–H···Ar (Ar stands for aromatic ring) interactions.[1,5–7] As shown in Figure 1,

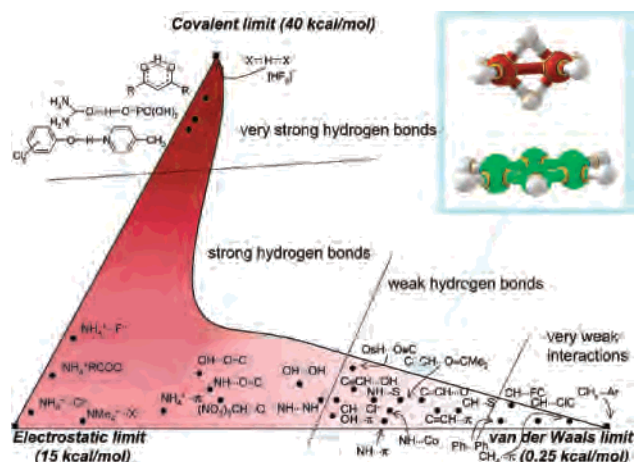**Figure 1.** The "hydrogen bonding" interactions by the broad definition involving X–H···A as the structural unit. Reprinted with permission from *Acc. Chem. Res.* **2002**, *35*, 565–573. Copyright 2002 American Chemical Society.

"hydrogen bonding" strength, which ranges from 0.25 kcal/mol to 40 kcal/mol,[1] can be contributed by various interac-

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tions, for instance, electrostatic (including polar/polar and polar/induced-polar interactions), van der Waals (dispersion/repulsion), and covalent (charge transfer) interactions.[8]

Recently, an unusual "hydrogen bonding" interaction between a borane system n-$B_{18}H_{22}$ and benzene molecules was discovered in a molecular crystal.[9] In this crystal structure, a bridging hydrogen atom in n-$B_{18}H_{22}$ directly interacts with benzene by facing the benzene centroid. So far, little has been known about this type of interaction. For instance, what is the strength of this interaction? Is this interaction covalent, electrostatic, or dispersive? Does this interaction have directionality? Understanding the nature of this unusual interaction by answering these questions is important, especially for crystal engineering and design and other possible generality. The present work is devoted to this aim by carrying out quantum mechanical calculation analysis on the model complex between diborane and benzene.

Experimental Section

All of the calculations were carried out using the Gaussion03 program.[10] The structures were obtained by energy minimization with the constraint of various distances d between the bridging diborane hydrogen and the benzene centroid at the level of B3LYP/6-311++G**. To correctly obtain the interaction energy, the BSSE is estimated using the counterpoise analysis method for various levels of calculations. The energetic analysis was carried out in various levels of treatments including HF/6-311++G**, B3LYP/6-311++G**, the perturbation methods[11,12] (MP2/6-311++G** and MP3/6-311++G**), and the coupled cluster method[13] (CCSD-(T)/6-31+G**). Molecular orbitals were generated in the CACHe program linked with Gaussion03. To analyze the contributions from orbital overlaps, natural bonding orbital analysis was carried out based on the energy minimum at the level of HF/6-311++G**, from which two of the dominant overlaps were identified.

Results and Discussion

To decompose these effects (covalent, electrostatic, dispersive), initially, the interaction between diborane and

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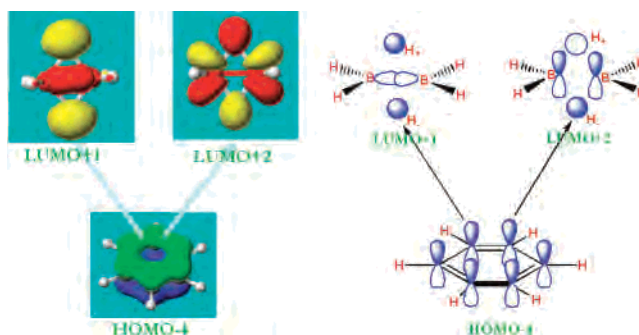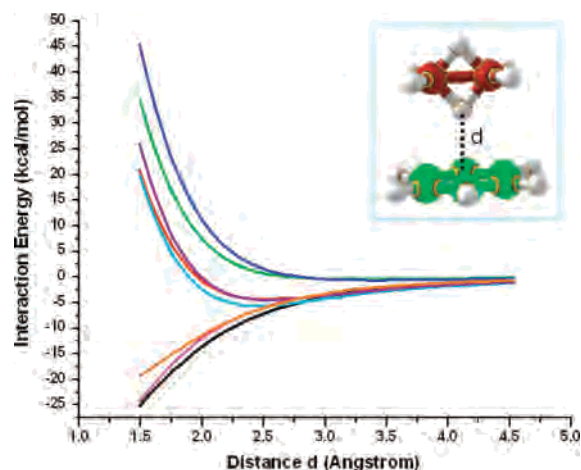(13) Lindgren, I.; Morrison, J. *Atomic many body theory*; Springer: Berlin, 1982.

Figure 2. Major molecular orbital overlaps responsible for the covalent effects of diborane–benzene interactions. On the right: schematic pictures showing orbital overlaps; on the left: orbital overlaps shown by density illustration of molecular frontier orbitals, which were obtained from the calculation at the HF/6-311++G** level.

benzene is analyzed from the covalent point of view, using the Hartree–Fock (HF) method, in which the dispersion interaction is not treated. As shown in Figure 2, the charge-transfer effect of diborane–benzene can be described as the interaction contributed by $\pi\rightarrow\pi^*$ orbital overlaps (detailed orbital analysis is included in the Supporting Information). Specifically, the overlaps between the HOMO-4 orbital (the fourth highest occupied orbital after the HOMO) of benzene and the LUMO+1 and LUMO+2 orbitals (the first and second lowest unoccupied orbitals after the LUMO) of diborane contribute dominantly to covalent interactions in this complex, as indicated by Natural Bonding Orbital (NBO) analysis. However, these orbital overlaps are unusual, because they are not traditional face-to-face but face-to-head (benzene π orbital to diborane π^* orbitals) overlaps. Here, the diborane molecule π^* orbital is an in-plane antiorbital, accompanying the three-center two-electron bond (Figure 2). Interestingly, in this case, the head portion of the nearest diborane π^* orbital approaches benzene in a direction where the center of the benzene π orbital is located. In this direction, the benzene π orbital has only a small density distribution, and its shape appears to be hollow in the middle (Figure 2). Consequently, as shown by the results of electronic structural calculations at the level of HF/6-311++G** (blue line in Figure 3), the diborane–benzene complex has a very shallow energy minimum such that the favorable interaction energy is only −0.59 kcal/mol. In this energy minimum, the nearest diborane bridge hydrogen is 3.41 Å away from the benzene center. The minimized structure is illustrated in the embedded box of Figure 3.

Clearly, in the computational model based on the HF calculations, the diborane–benzene interaction is unique in the following two aspects. (a) As d (defined as the distance between the center of benzene and its nearest bridging diborane hydrogen as shown in the embedded box of Figure 3) is decreased, diborane and benzene reach their interaction energy minimum long before they display van der Waals contact, which occurs at 2.70 Å for the distance d. This value is estimated based upon van der Waals radii of aromatic carbons and nonpolar hydrogens). (b) The interaction energy is zero until d is decreased at least down to 2.90 Å. In the Hartree-Fock (HF) calculation, no dispersion effect is included. Therefore, covalent (charge transfer) and electro-

Figure 3. Interaction energies calculated with various relative distances between the bridging hydrogen of diborane and the benzene centroid. Blue line: computed at the level of HF/6-311++G**; green line: computed at the level of B3LYP/6-311++G**; red line: computed at the level of MP2/6-311++G**; cyan line: computed at the level of MP3/6-311++G**; purple line: computed at the level of CCSD(T)/6-31+G**; black line: estimated dispersion effect by taking the difference between the values obtained at the levels of MP2 and HF; magenta line: estimated dispersion effect by taking the difference between the values obtained at the levels of MP3 and HF; orange line: estimated dispersion effect by taking the difference between the values obtained at the levels of CCSD(T) and HF. In the embedded box, the minimized structure of the diborane–benzene complex is shown.

static interactions should be responsible for the results discussed above. The classical estimation of electrostatic interactions, based on calculated Mulliken charges, shows that polar interactions have a very modest contribution to the diborane–benzene complex formation when they are approaching each other (0.05 kcal/mol at the energy minimum); this is also true when the higher level quantum mechanical treatments were applied as discussed later. Therefore the unique observations as discussed above should mostly be attributed to the covalent effect, which reaches a maximum at a relatively long distance d due to the special $\pi \rightarrow \pi^*$ orbital overlaps. Consequently, after reaching this energy minimum, as the distance d shortened, these orbital overlaps decay very slowly, causing the moderate increase of interaction energy as indicated by the observation (b).

In order to understand the contribution of the dispersion effect to the diborane–benzene complex formation, the perturbation methods[11,12] MP2/6-311++G**, MP3/6-311++G**, and the coupled-cluster method[13] CCSD(T)/6-31+G** are employed. At these levels, with the explicit inclusion of the electron-correlation effects, the energy minimum moves from the distance d of 3.41 Å to that of 2.47 Å computed at the MP2 level (shown by the cyan line in Figure 3) and of 2.53 Å computed at both the MP3 level (shown by the red line in Figure 3) and the CCSD(T) level (shown by the purple level). And in these models, 5.53 kcal/mol (MP2) and 4.30 kcal/mol (MP3 and CCSD(T)) of the binding affinities are obtained for the diborane–benzene interaction. The modest difference among the results obtained at these these levels may be due to the overestimation of electron correlation effect in the MP2 calculations. Therefore, the data obtained from the CCSD(T) calculations will be utilized for the following discussions. It should be noted that

without including the appropriate dispersion effect treatment, the density functional theory (DFT) calculations at the level of B3LYP/6-311++G** (green line in Figure 3) obtain similar results to those at the HF level calculations. By taking the difference between the values obtained at the levels of CCSD(T) and HF, the dispersion interaction contribution can be estimated, as described by the orange line in Figure 3. At the energy minimum obtained in the CCSD(T) calculations, the dispersion interaction contributes a favorable energy of −5.64 kcal/mol to binding affinity, and the other interaction contributes an unfavorable energy of 1.34 kcal/mol, which is calculated at the HF level based on the CCSD(T) energy minimum structure. It should be noted that this energy decomposition may not be accurate because all of the energy contributions are based upon the minimum-energy structure obtained at the CCSD(T) level calculations. As discussed above, treated at the HF level without dispersion energy included, this system has a different energy minimum; this system can be stabilized by other effects (mostly covalent interaction) with a −0.59 kcal/mol interaction energy. When the CCSD(T) calculations are carried out, 1.93 kcal/mol binding affinity loss from other interactions (including repulsion interaction) has to be paid by the dispersion effect in order to relocate the energy minimum. So from this aspect, the energy contribution decomposition for the diborane–benzene interaction should be as follows: 0.59 kcal/mol from the covalent effect, ~0 kcal/mol from the electrostatic effect, and 3.71 kcal/mol from the dispersion interaction. In summary, it is obvious that the diborane–benzene interaction is mostly the dispersive effect, with a favorable energy of −3.71 kcal/mol (−5.64 kcal/mol + 1.34 kcal/mol + 0.59 kcal/mol).

Because of the small covalent interaction component and the lack of strong directionality due to the unusual $\pi \rightarrow \pi^*$ orbital overlaps, together with the fact that the dispersion effect is directionally insensitive, it is expected that in more complex systems, the relative distance and the relative tilting angle between the borane system and benzene molecule can be flexible in certain ranges, depending on the local molecular environments such as polarity or stacking effects. As observed in the crystal structure of the n-$B_{18}H_{22}$–benzene system, the distance between the benzene ring centroid and the nearest bridging hydrogen of the borane system is 2.80 Å; at this distance, only a 0.2 kcal/mol of energy increase is required as indicated by the CCSD(T) level calculations. This amount can be easily paid by other environmental factors such as crystal packing and thermal effects. Beside the relative distance, the plane with B−H−B atoms in the n-$B_{18}H_{22}$–benzene system is also not perpendicular to the benzene ring as it is in the diborane–benzene complex. However, less than a 0.1 kcal/mol energy increase is predicated from the CCSD calculation. As more borane–benzene crystal structures are identified in the future, various distances and tilting angles in the range from the approaches of 2.5−2.9 Å can be discovered due to the specific molecular electronic properties and crystal packing patterns. The seeming directional effect with the bridging hydrogen from

borane aligned toward the benzene centroid occurs because in this direction maximal van der Waals contact can be obtained.

After the analysis in the present work, let us turn back to Figure 1 and locate the diborane−benzene interaction in the "hydrogen bond" map. Interestingly, this interaction should be assigned in a unique region as a weak hydrogen bond with mostly van der Waals character.

Conclusion

Traditionally, the hydrogen bond is considered as a strong interaction with mostly electrostatic and covalent contributions.[4] Based on the analysis in the present work, diborane−benzene should not be considered as a hydrogen bond, at least within the traditionally narrow-defined framework. In particular, describing this interaction by directly connecting a bridging hydrogen of diborane and the benzene centroid as done in Figure 3 can be misleading, because of dominant van der Waals interaction plus smaller effects that may occur in more extended molecular and crystalline aspects. In summary, the interaction between diborane and benzene is special in the following aspects: (1) this interaction is mostly dispersive; (2) the observed pseudodirectionality with one of the diborane bridge hydrogens directed toward the benzene centroid is to maximize the van der Waals contact; and (3) in the "hydrogen bond" map, this interaction is located in a unique region, presently populated by a few known molecular complexes with very different chemical characteristics.

Supporting Information Available: Molecular orbital analysis of the covalent interaction between diborane and benzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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