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Borazine and Benzene Homo- and Heterodimers

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The homodimers of benzene and borazine as well as a heterodimer consisting of one benzene (bz) and one borazine (bor) molecule are investigated using MP2, SCS−MP2, and CCSD(T) theories in conjunction with basis sets of up to quadruple-ζ quality. Dimer geometries were completely optimized using the resolution of the identity approximation of MP2 with a QZVPP basis set and characterized by computation of harmonic vibrational frequencies using triple-ζ basis sets. While significant higher order correlation effects beyond MP2 are important for the benzene dimer, these are very small for the borazine dimer and intermediate for the heterodimer. The spin-component scaling (SCS) correction of MP2 produces binding energies for the borazine dimer that are too low but yields very good agreement with CCSD(T) for the heterodimer. The decrease in the intermolecular distance in the sandwich (**S**) configurations from bz_2 via bz-bor to bor_2 is accompanied by an increased binding energy and a change from second-order stationary points to a minimum for bor_2. The **T** isomer is less stable than the **S** configuration for bor_2, but it is preferred over the **S** and a parallel-displaced (**PD**) arrangement in the heterodimer. The following order of stability is obtained for the minima at the extrapolated CCSD(T) level: **T**(bz-bor) > **S**(bor_2) > **PD**(bz-bor) > **PD**(bor_2) > **T**(bor_2) > **PD**(bz_2). The most stable isomer at all levels of theory, **T**(bz-bor), features a NH$\cdots\pi$ interaction.

Introduction

The isoelectronic substitution of CC by BN units links benzene to its “inorganic” analogue borazine.[1] This heterocyclic compound, first isolated in 1926 by Stock and Pohland,[2] shows some similarity with benzene in its physical properties,[1] and the benzene−borazine pair is thus a textbook example for demonstrating the similarity of isoelectronic compounds.[3] A large number of investigations and controversial discussions have attempted to delineate whether and to what degree the aromaticity of benzene is retained in the isoelectronic six-membered heterocyclic compound.[4−26] The reactivity of borazine with respect to polar reagents is higher than that observed for benzene due to the polarity of the B−N bonds arising from the difference in electronegativity between boron and nitrogen (Pauling[27] scale: 2.0 vs 3.0). However, the homodimerization yielding species with six new covalent C−C or B−N bonds is endothermic for benzene and as well as for borazine according to computations, and this result was interpreted as indicative of a sizable amount of aromaticity of borazine.[16] There appears now to be a consensus in the literature that the aromaticity of borazine is about half of that of benzene based on energetic, structural, and magnetic criteria.

The interest in borazine is not limited to developing an understanding of fundamental theoretical bonding concepts. Borazine and its derivatives currently enjoy attention in materials chemistry as precursors for nonoxidic BN-containing ceramics[28−41] and boron nitride nanotubes or other nanostructures.[42−45] Such materials are of interest for mechanical, optoelectronic, and optical applications like UV laser devices.[46]

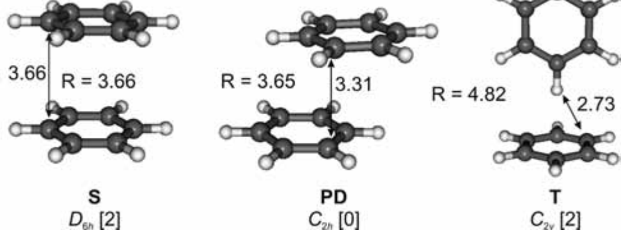

Figure 1. The benzene dimers considered in this study. Sandwich (**S**), parallel-displaced (**PD**), and **T** form. Selected MP2/QZVPP distances between atoms and between ring centers (R) are given in angstroms. The number of imaginary vibrational frequencies as computed at the MP2/TZVPP level of theory is given in brackets.

In view of the fundamental and technological importance of borazine, it is astonishing that its intermolecular interactions have received only limited attention, especially as a particularly rich body of theoretical literature is available for the benzene dimer as summarized in the recent paper by Lee and coworkers.[47] Among the three major isomers of the benzene dimer, sandwich (**S**), parallel-displaced (**PD**), and **T** form, the latter two appear to be almost isoenergetic (see Figure 1).[47−64] The structural details of the possible dimers, however, are still the subject of ongoing scrutiny.[47,57,63−65]

A different energetic order of isomers is expected for the borazine dimer based on electrostatic grounds. Because of the polar B−N bonds of the monomers, short intermolecular B$\cdots$N distances are expected, and these are indeed found in the most

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stable gas-phase homodimer of borazine according to an ab initio investigation by Kawahara et al.[66] Experimental studies are unavailable for the borazine dimer to the best of our knowledge at this time. The ab initio study by Kawahara et al.[66] reported potential energy curves obtained at the MP2 level for a number of **S**, **T**, and **PD** geometries by incrementally varying intermolecular distances using fixed MP2/6-311G** monomer geometries. Higher order correlation effects, considered at the coupled cluster CCSD(T) level, were found to be small. This approach gives the eclipsed parallel sandwich structure with B above N stacking as the most stable configuration. The **T** and **PD** configuration are slightly higher in energy, but only for the most stable sandwich isomer has the geometry been fully optimized and its nature as a minimum been confirmed.[66] More recently, Koskilinna et al.[67] investigated the sandwich dimer with the B3LYP hybrid functional in the context of the mechanical properties of hexagonal boron nitride.

Although the arrangement of molecules in solid-state structures does not necessarily relate to the preferred relative orientation of molecules in gas-phase dimers, it is instructive to briefly consider the crystal structure of borazine that was reported by Boese et al.[68] Interestingly, the molecule has C_2 symmetry with slight deviations from the expected D_{3h} symmetry.[68] This is in agreement with the electron diffraction study of Harshbarger et al.[69] who could not unambiguously chose between either the C_2 or the D_{3h} molecular point group with very large vibrational motion. The crystal packing of borazine does not indicate any distortion of the molecules, and it furthermore does not resemble that of benzene. Most interestingly, the expected stacking of molecules with boron directly above nitrogen is also not observed. Rather, the shortest intermolecular distances between rings are B···B and N···N contacts.[68]

This contribution focuses at improving the understanding of the noncovalent interaction involving borazine by accurately evaluating the geometry and the binding energy. In addition to reconsidering the borazine dimer employing full geometry optimization and large basis sets, we wish to delineate the geometric and energetic consequences of substitution of one borazine by a benzene molecule, resulting in a heterodimer composed of borazine and benzene. Such aggregates have not been investigated previously but are expected to be of relevance in the materials chemistry of BN-doped and $B_xC_yN_z$ nanoscale structures, such BCN, BC_2N, and BC_4N hybrid nanomaterials.[70-72]

The computational investigation of weakly bound molecules is a challenge for computational chemistry, as an accurate description of the dispersion energy is essential. This requires an inclusion of electron correlation effects at least at the second-order Møller−Plesset (MP2) perturbation theory level. The resolution of the identity (RI) approximation allows the economical use of the required large basis sets of quadruple-ζ quality in both the energy evaluation and the geometry optimizations without introducing significant errors. Higher order correlation effects are most accurately considered using coupled cluster theory with inclusion of single, double, and a perturbative estimate of triple excitations, CCSD(T). Because of its high formal scaling of $O(N^7)$, CCSD(T) can hardly be employed for systems of the size considered here with one-electron basis sets approaching completeness. We thus follow the common strategy and extrapolate from MP2 energies obtained with large basis sets of quadruple-ζ quality and CCSD(T) corrections from a smaller basis set to a complete basis set (CBS) CCSD(T) value. We also employ Grimme's spin-component-scaled MP2 method (SCS−MP2),[73] that was shown recently to yield improved interaction energies compared to conventional MP2.[55,58,61,74]

Computational Methods

The following basis sets of double-ζ, triple-ζ, and quadruple-ζ quality developed by the Ahlrichs group were used in the present investigation: SV(P) [B/C/N: 3s2p1d; H: 2s],[75] TVZP [B/C/N: 5s3p1d; H: 3s1p],[76] TZVPP [B/C/N: 5s3p2d1f; H: 3s2p1d],[77] and QZVPP [B/C/N: 7s4p3d2f1g; H: 4s3p2d1f][78] in conjunction with the corresponding fitting bases.[77,79] Furthermore, Dunning's[80] augmented correlation consistent aug-cc-pVDZ basis set was employed.

The geometries were fully optimized within the respective point group constraints using the resolution-of-identity (RI) approximation for fast computations of two-electron integrals within the second-order Møller−Plesset perturbation theory (MP2).[77,81] The recent study of benzene dimers by Lee et al.[47] confirms that the errors due to the RI approximation are negligible for both relative energies and geometry parameters. We thus only use the acronym MP2 throughout this paper. The SV(P), TZVP, TZVPP, and QZVPP basis sets were used for geometry optimization; for the QZVPP basis a total of 1044 contracted Gaussian basis functions resulted for the dimers considered here. For the sake of conciseness only the QZVPP geometries of the dimers are discussed. Harmonic vibrational frequencies were determined using the TZVPP basis set by finite differences of analytic gradients and were scaled by a factor of 0.953 when determining zero-point vibrational energies (ZVPE).[82]

To estimate the influence of the basis set superposition error (BSSE) on structures, the geometries of the three most stable configurations of the bz_2 (**PD**), bor_2 (**S**), and bz-bor (**T-NH-1**) dimers were optimized at the MP2/QZVPP level taking into account the BSSE by using the counterpoise (CP) method of Boys and Bernardi[83] during the optimization procedure. The intermolecular distance does not change for bz_2-**PD** and increases only by 0.05 and 0.04 Å for bor_2-**S** and bz-bor-**T-NH-1**, respectively (vide infra for descriptions of these configurations). As the changes in intramolecular distances are rather small when taking BSSE into account at the MP2/QZVPP level, we have chosen to focus on the uncorrected structures in view of the computational expense associated with obtaining BSSE corrected geometries.

The MP2/QZVPP geometries were used in subsequent single point computations. These employed the spin component scaled MP2 method within the RI approximation (SCS−MP2) in conjunction with the QZVPP basis set.[73] Higher order correlation effects were accounted for in single energy computations by using coupled-cluster theory involving single, double, and a perturbative estimate of triple excitations [CCSD(T)][84,85] in conjunction with the aug-cc-pVDZ basis set. The binding energies of dimers were corrected for BSSE a posteriori by using the CP method.[83] The difference between CP corrected MP2 (non-RI, as obtained from the CCSD(T) run) and CCSD(T) energies computed with the aug-cc-pVDZ basis set is considered the CCSD(T) correction, ΔCCSD(T). This is used for extrapolation to complete basis set (CBS) CCSD(T) data by adding ΔCCSD(T) to the MP2/QZVPP interaction energy.

Besides these supermolecular calculations, we also employed symmetry adapted perturbation theory (SAPT)[86] to study the interaction between benzene and borazine molecules. This was motivated by the ability of SAPT to dissect the total interaction energy into physically meaningful quantities, i.e., electrostatic, induction, and dispersion interactions and Pauli repulsion. Terms of order higher than second, which could be obtained from supermolecular Hartree−Fock computations, were not considered because it is not recommended for nearly nonpolar monomers such as benzene.[57] The geometries used in the SAPT computations were those obtained from full optimization (without CP correction) at the MP2/QZVPP level of theory. Hartree−Fock wave functions used for the SAPT analysis were computed for the monomers at their geometries in the dimers using the aug-cc-pVDZ basis set.

All electron correlated methods employed the frozen core approximation. All calculations employing the RI approximation (i.e., MP2 and SCS−MP2) were performed with the Turbomole[87] program suite, while CCSD(T) and SAPT data were obtained with Molpro.[88]

Results and Discussion

1. Benzene Homodimer. The benzene dimer has been the subject of numerous computational investigations,[47−55,58−64] and an overview of the pertinent literature up to 2007 can be found in the detailed investigation reported by Lee et al.[47] The sandwich dimer **S** was established to be less stable than either the **T** from or the **PD** dimer. The latter two are almost isoenergetic. We here do not strive to improve upon the accuracy already achieved for the benzene dimer. Rather, we wish to obtain geometry and energy data for comparison with previous computations and with the borazine homo and the borazine-benzene hetero dimer. We have thus picked the most stable configurations among the **S** and **PD** dimers identified by Lee et al.[47] (named S_{aa} and D_{aa}, respectively, by these authors). Among the **T** dimers, we considered the conventional C_{2v} conformer (called T_{ba} by Lee et al.[47]).

The benzene monomer geometry obtained at the MP2/QZVPP level of theory (r_{CC} = 1.3915 Å, r_{CH} = 1.0808 Å) is in very good agreement with the reference values of Gauss and Stanton (r_{CC} = 1.3915 Å, r_{CH} = 1.0800 Å).[89] The intermonomer distances in the **S** (3.66 Å), **PD** (3.65 Å), and **T** (4.82 Å) dimers displayed in Figure 1 are found to be in good agreement with literature data obtained at similar levels of theory, 3.68 Å, 3.67 Å, and 4.86 Å, respectively.[47] These distances, however, are shorter than the available CCSD(T) estimates by 0.1−0.2 Å.[47,54,59] As mentioned in Computational Methods, the intermolecular distance does not increase for the **PD** isomer when BSSE is corrected for during the geometry optimization by the counterpoise method. The deformation energy upon dimer formation with respect to the monomer amounts to only 0.01 mH for all benzene dimers.

The sandwich conformer has two imaginary vibrational frequencies of 49*i* cm^{-1} (E_{1g}) at the RIMP2/TZVPP level of theory. The **PD** isomer, on the other hand, is a minimum on the PES, while the **T** aggregate corresponds to a second-order saddle point (25*i* cm^{-1}, B_1 and 14*i* cm^{-1}, B_2).

The interaction energies (Table 1) for **S**, **PD**, and **T** configurations obtained here at the MP2/QZVPP level agree to within 0.1−0.2 kcal mol^{-1} with the MP2 data of Lee et al. using the aug-cc-pVQZ basis set.[47] The CCSD(T) correction [ΔCCSD(T)], based in the present paper on the difference between MP2 and CCSD(T) using the aug-cc-pVDZ basis, appears to be too large in comparison with the corrections derived by Sinnokrot and Sherrill.[54] These authors noted a pronounced dependence of the size of ΔCCSD(T) on the intermolecular distances, with larger corrections at shorter distances. The MP2/QZVPP structures used in the present investigation are more compact than those obtained with MP2/AVQZ and in particular the estimated CBS-CCSD(T) geometries.[47] This effects larger ΔCCSD(T) values and thus accounts for smaller CCSD(T)/CBS interaction energies (by 0.4−0.6 kcal mol^{-1}) than that determined by Lee et al.[47] using a more sophisticated extrapolation scheme and CBS-CCSD(T) geometries. The SCS−MP2 interaction energies with and without CP correction bracket our extrapolated CCSD(T) values. Compared to the benchmark data of Lee et al.[47] the SCS−MP2 energies without CP correction appear to provide better agreement.

TABLE 1: Interaction Energies (in kcal mol^{-1}) of the Sandwich (S), Parallel-Displaced (PD), and T Configurations of the Benzene Dimer[a]

method	basis set	S	PD	T
MP2	QZVPP	−3.2	−4.6	−3.4
ΔCCSD(T)	aVDZ	+1.9	+2.5	+1.0
CCSD(T)	est-CBS	−1.2	−2.1	−2.4
CCSD(T)[b]	est-CBS	−1.66	−2.73	−2.77
SCS−MP2	QZVPP (no CP)[c]	−1.8	−2.9	−2.6
SCS−MP2	QZVPP (CP)[c]	−1.4	−2.3	−2.1

[a] Based on structures fully optimized at the MP2/QZVPP level of theory. [b] Data taken from Lee et al.[47] These are based on estimated CCSD(T) CBS geometries. [c] CP: counterpoise correction.

TABLE 2: Geometrical Parameters of Borazine As Computed at the MP2 Level of Theory with Different Basis Sets

basis set	r(BN)/Å	r(NH)/Å	r(BH)/Å	$\angle_{NBN}$/deg	$\angle_{BNB}$/deg
SV(P)	1.433	1.016	1.217	117.4	122.6
TZVP	1.433	1.008	1.191	117.1	122.9
TZVPP	1.431	1.006	1.191	116.9	123.1
QZVPP	1.428	1.005	1.190	116.9	123.1
exp.[a]	1.4355 ± 0.0021	1.050 ± 0.012	1.258 ± 0.014	117.7 ± 1.2	121.1 ± 1.2
exp.[b]	1.429(1)	not determ.	not determ.	117.1(1)	122.9(1)

[a] Electron diffraction.[69] [b] Mean values from X-ray single crystal diffraction.[68]

2. Borazine Homodimer. The geometry of the borazine monomer is of D_{3h} symmetry in agreement with numerous computational investigations. Typically, bond lengths decrease with increasing basis set size, and this is also observed here (Table 2). While the MP2/SV(P) calculations reproduce the electron diffraction data well, the BN distance and the bond angles obtained with the much larger QZVPP basis set are in better agreement with the X-ray data of Boese et al.[68]

The borazine dimer configurations considered here are based on the investigation by Kawahara et al.[66] We could identify a total of four stationary points (see Figure 2): sandwich **S** (P_{gauche}), parallel-displaced **PD** (S_{syn}), and two T forms named $\mathbf{T}_{1N}$ and $\mathbf{T}_{1Nrot}$ (abbreviations in parentheses are those of Kawahara et al.[66] that will not be used here for the sake of consistency with the commonly used benzene dimer nomenclature). Both **S** and **PD** configurations correspond to minima on the potential energy surface. The two $\mathbf{T}_1$ isomers only differ in the relative orientation of borazine rings. The $\mathbf{T}_{1Nrot}$ isomer, that has not been studied previously, appears to lie in a very shallow area of the potential energy surface: at the MP2/TZVPP level it has one very small imaginary vibrational frequency of 4*i* cm^{-1} (A″). For $\mathbf{T}_{1N}$, on the other hand, the Hessian index is zero with the smallest vibrational frequency being 18 cm^{-1} (A″). Kawahara et al.[66] also considered relative monomer orientations of other T forms, labeled $\mathbf{T}_2$ and $\mathbf{T}_{1B}$, not depicted in Figure 2. These isomers are characterized either by an interaction of a borazine edge with the borazine π-system of the second monomer ($\mathbf{T}_2$) or by a BH⋯π interaction ($\mathbf{T}_{1B}$). Both isomers do not correspond to

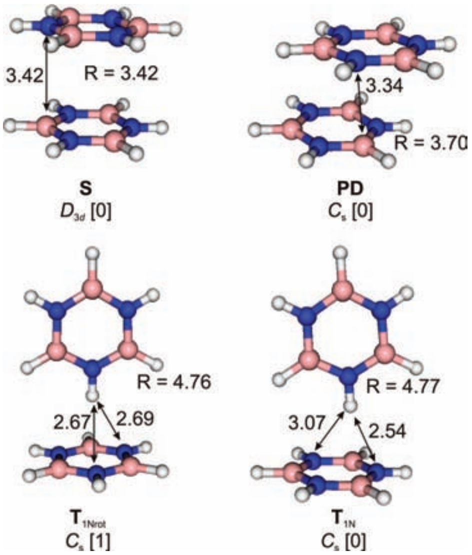

Figure 2. Minima of borazine dimers considered in this work (blue: N atoms). Selected MP2/QZVPP distances between atoms and between ring centers (R) are given in angstroms. The number of imaginary vibrational frequencies as computed at the MP2/TZVPP level of theory is given in brackets.

TABLE 3: Interaction Energies (in kcal mol^{-1}) of the Sandwich (S), Parallel-Displaced (PD), and T Configurations of the Borazine Dimer[a]

method	basis set	S	PD	T_{1N}	T_{1Nrot}
MP2	QZVPP	−3.4	−3.0	−2.7	−2.6
ΔCCSD(T)	aVDZ	+0.1	+0.1	+0.1	+0.0
CCSD(T)	est.-CBS	−3.3	−2.9	−2.6	−2.6
SCS−MP2	QZVPP (no CP)[b]	−2.7	−2.3	−2.1	−2.1
SCS−MP2	QZVPP (with CP)[b]	−2.0	−1.6	−1.7	−1.7

[a] Based on structures fully optimized at the MP2/QZVPP level of theory. [b] CP: counterpoise correction.

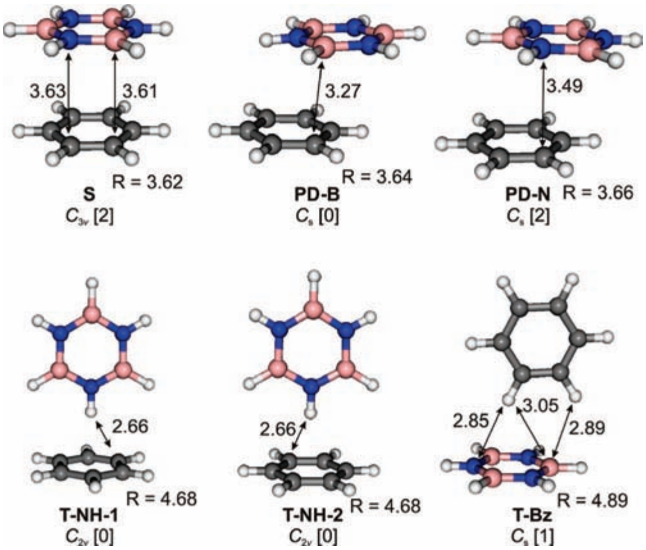

Figure 3. Stationary points located for the benzene−borazine heterodimer (blue: N atoms) using the MP2/QZVPP level of theory. Selected MP2/QZVPP distances between atoms and between ring centers (R) are given in angstroms. The number of imaginary vibrational frequencies at the MP2/TZVPP level are given in brackets.

stationary points when computed in C_s symmetry and collapse to $\mathbf{T}_{1N}$ upon geometry optimization.

As expected, the geometries of the individual borazine molecules do change only very slightly upon dimerization. The N−H bonds in the two $\mathbf{T}_1$ isomers pointing toward the π face of the other borazine ring are only slightly elongated (≤0.002 Å). The corresponding borazine rings have the largest deformation energy with respect to the monomer, but it is still only 0.08 mH. These minor changes do not warrant any further discussion here.

The interaction energies (Table 3) determined at the MP2 level are of similar magnitude as those of the benzene dimer. However, the influence of higher order correlation effects at the CCSD(T) level is found to be small, in agreement with the observations of Kawahara et al.[66] The correction ΔCCSD(T) amounts to only 0.1 kcal mol^{-1} for all isomers considered. The inclusion of higher order correlation thus does not change the energetic ordering of isomers obtained at MP2, **S** > **PD** > $\mathbf{T}_{1N}$ > $\mathbf{T}_{1Nrot}$, but rather confirms that the dimer featuring B···N intermolecular interactions is most favorable. As the CCSD(T) correction is smaller, the borazine dimers are generally more strongly bound than the benzene dimers at the extrapolated CCSD(T) level.

The SCS−MP2 interaction energies are in qualitative agreement with the CBS-CCSD(T) values with respect to the energetic ordering of isomers. However, the SCS correction lowers the binding energies by the substantial amount of 0.9−1.3 kcal mol^{-1} compared to standard MP2 for all borazine dimers. As the CCSD(T) correction is only 0.1 kcal mol^{-1}, SCS−MP2 underestimates the binding compared to the extrapolated CCSD(T) data, and this discrepancy is increased further if CP correction is taken into account. Note that Antony and Grimme found non-CP corrected SCS−MP2 with basis sets of triple-ζ quality to produce results in good agreement with CCSD(T) due to a good error compensation. Our results with a quadruple-ζ basis appear to parallel these observations.

3. The Benzene−Borazine Heterodimer. We have considered a number of isomers for the benzene−borazine heterodimer (see Figure 3). The deformation energies of benzene and borazine in the dimers is less than 0.09 mH with respect to the free molecules. This shows that the geometries of the six-membered ring molecules are hardly changed upon interaction.

The sandwich structure in C_{3v} symmetry is a second-order stationary point with the TZVPP basis set (39i cm^{-1}, E), as found for the benzene dimer above. Among the parallel-displaced conformers, the one with boron and carbon atoms lying on top of each other (**PD-B**) is a minimum while the one with close contact between nitrogen and carbon atoms (**PD-N**) is a second-order stationary point (47i cm^{-1}, A″ and 8i cm^{-1}, A″).

We found three T isomers, but only two of them, **T-NH-1** and **T-NH-2**, correspond to minima. The **T-NH-1** and **T-NH-2** isomers are closely related: the two rings are rotated with respect to each other around the H−N−B−H axis by 30°. Both **T-NH** conformations are featuring NH−π interactions as evidenced by the elongation of the N−H bond (by 0.003 Å) that is pointing toward the aromatic π system. On the other hand, a conformer with a benzene CH bond interacting with the heteroaromatic π system of a borazine molecule converges to the structure **T-Bz** displayed in Figure 3. The **T-Bz** isomer is a saddle point (4i cm^{-1}, A″). It should be noted that the nature of the stationary points obtained needs to be taken with some caution in view of the very small size of the imaginary vibrational frequencies and the limited numerical accuracy in the evaluation of the Hessian by finite differences of analytic gradients.

The binding energies (Table 4) computed at MP2/QZVPP are in the same range as those for the benzene and the borazine dimers. The **PD-B** and the **T-NH-1** isomers have very similar

TABLE 4: Interaction Energies (in kcal mol^{-1}) of the Sandwich (S), Parallel-Displaced (PD), and T Configurations of the Benzene−Borazine Heterodimer[a]

method	basis	S	PD-B	PD-N	T-NH-1	T-NH-2	T-Bz
MP2	QZVPP	−2.9	−4.2	−3.2	−4.2	−4.2	−2.3
ΔCCSD(T)	aVDZ	+0.8	+1.2	–	+0.7	–	–
CCSD(T)	est-CBS	−2.1	−3.0	–	−3.5	–	–
SCS−MP2	QZVPP (no CP)[b]	−2.0	−3.0	−2.2	−3.4	−3.4	−1.7
SCS−MP2	QZVPP (with CP)[b]	−1.5	−2.2	−1.6	−2.9	−2.9	−1.4

[a] Based on structures fully optimized at the MP2/QZVPP level of theory. [b] CP: counterpoise correction.

TABLE 5: Binding Energies D_e and D_0 (in kcal mol^{-1}) for the Minima of the Benzene and Borazine Homo- and Heterodimers (bz$_2$, bor$_2$, and bz-bor) As Determined at the Extrapolated CCSD(T) Level of Theory[a]

	bz-bor-**T-NH-1**	bor$_2$-**S**	bz-bor-**PD**	bor$_2$-**PD-B**	bor$_2$-**T$_{1N}$**	bz$_2$-**PD**
D_e	−3.5	−3.3	−3.0	−2.9	−2.6	−2.1
D_0	−3.1	−3.0	−2.6	−2.6	−2.4	−1.8

[a] The zero-point vibrational energy corrections were determined at the MP2/TZVPP level of theory.

binding energies at the MP2/QZVPP level. The CCSD(T) correction differs by 0.5 kcal mol^{-1} and thus the hydrogen bonded isomer prevails at the CBS-CCSD(T) level by about 0.5 kcal mol^{-1}. The SCS−MP2/QZVPP method similarly favors the **T-NH-1** over the **PD-B** form by 0.4 kcal mol^{-1}.

It was noted earlier by Bachorz et al.[61] that the SCS−MP2 method reduces the binding energy of hydrogen bonded systems that are usually better described by MP2 than dispersive $\pi-\pi$ interactions. This behavior thus might not allow a balanced description of systems where hydrogen bonding and $\pi-\pi$ interactions are competitive. We observe here for the benzene−borazine dimer good agreement for the interaction energies between non-CP corrected SCS−MP2 and CBS-CCSD(T), but this observation might not be transferable to other systems in light of the observations by Bachorz et al.[61] As above, the CP correction reduces the SCS−MP2 interaction energies and results in larger deviations from our CBS-CCSD(T) values.

4. Comparison of the Various Configurations of Benzene and Borazine Homodimers and the Benzene−Borazine Heterodimer. Among all minima considered in this study, the T isomer **T-NH-1** of the benzene−borazine heterodimer (bz-bor) is the most stable isomer (Table 5). The bor$_2$ sandwich is slightly less stable, but both complexes have similar dissociation energies after taking into account zero-point vibrational energies.

Considering the sandwich isomers only, the interaction energy increases from bz$_2$ via bz-bor to bor$_2$. This change in stability goes along with a shortening of the intermolecular distance and the transition from a second-order stationary point to a minimum. At the SCS−MP2 level, bor$_2$ is roughly 1 kcal mol^{-1} more stable than bz$_2$, but this difference is increased to 2 kcal mol^{-1} at our CBS-CCSD(T) level. The trends observed for the parallel-displaced configurations are closely related to those for the sandwich dimers: **PD** is more favorable for bz$_2$ and bz-bor, where **S** corresponds to a higher-order saddle point, but it is less favorable for bor$_2$. The intermolecular distances in all **PD** isomers are shorter than in the corresponding **S** isomers.

The T-forms are most favorable in the heterodimeric system, and they have comparable binding energies in both benzene and borazine homodimers. Taking the borazine NH···π homodimer (**T$_{1N}$**) as a reference point, substitution of the hydrogen bond acceptor from borazine to benzene increases the interaction energy in the heterodimer **T-NH-1**. On the other hand, if the hydrogen bond donor is changed from borazine to benzene, the interaction energy decreases in **T-Bz**.

5. Interaction Energy Contributions from SAPT. The individual contributions to the interaction energy of representative stationary points on the bz$_2$, bor$_2$, and bz-bor potential energy surface are determined using symmetry adapted perturbation theory (SAPT) based on Hartree−Fock wave functions for the monomers (Table 6). These contributions are the electrostatic, induction, and dispersion energies to first and second-order ($E_{\mathrm{el}}^{(10)}$, $E_{\mathrm{ind}}^{(20)}$, $E_{\mathrm{disp}}^{(20)}$) and their respective exchange counterparts ($E_{\mathrm{exch}}^{(10)}$, $E_{\mathrm{exch-ind}}^{(20)}$, $E_{\mathrm{exch-disp}}^{(20)}$), where the superscript zero indicates that intramonomer correlation is not accounted for. The latter three terms are also known as Pauli repulsion.

The SAPT interaction energies (Table 6) are in good agreement with our extrapolated CCSD(T) values (Table 5) for the bor$_2$ isomers where the energies are underestimated by up to 0.4 kcal mol^{-1}. For the benzene containing isomers, on the other hand, the underestimation of the interaction energies is more pronounced: 0.7−0.9 kcal mol^{-1} for bz-bor isomers and as much as 1.2 kcal mol^{-1} for bz$_2$-**PD**. The differences are likely due to the limited size of the basis set and the inadequate description of intramolecular correlation effects of the individual SAPT terms at the Hartree−Fock level. This assumption is based on the good agreement between high level ab initio data and

TABLE 6: Symmetry-Adapted Perturbation Theory (SAPT) Interaction Energy (E_{int}) and Contributions to It (in kcal mol^{-1}) at Selected Geometries Optimized at the MP2/QZVPP Levels[a]

isomer	$E_{\mathrm{el}}^{(10)}$	$E_{\mathrm{exch}}^{(10)}$	$E_{\mathrm{ind}}^{(20)}$	$E_{\mathrm{exch-ind}}^{(20)}$	$E_{\mathrm{disp}}^{(20)}$	$E_{\mathrm{exch-disp}}^{(20)}$	E_{int}
bz$_2$-**S**	−0.8 (7.3)	7.1	−2.6 (23.6)	2.4	−7.6 (69.2)	1.2	−0.3
bz$_2$-**PD**	−3.8 (19.3)	11.7	−5.2 (27.0)	4.9	−10.4 (53.7)	1.9	−0.9
bz$_2$-**T**	−2.5 (26.6)	5.5	−1.4 (15.2)	1.1	−5.6 (58.2)	0.7	−2.1
bor$_2$-**S**	−4.1 (28.8)	7.6	−2.6 (18.0)	2.4	−7.6 (53.3)	1.0	−3.3
bor$_2$-**PD**	−2.9 (24.2)	6.5	−2.1 (18.1)	2.0	−6.9 (57.7)	0.9	−2.5
bor$_2$-**T$_{1N}$**	−2.0 (26.7)	4.1	−1.2 (15.5)	0.8	−4.4 (57.9)	0.5	−2.2
bor$_2$-**T$_{1Nrot}$**	−1.7 (23.9)	3.8	−1.1 (15.2)	0.7	−4.2 (60.9)	0.4	−2.0
bz-bor-**S**	−1.6 (15.4)	5.9	−2.0 (19.5)	1.8	−6.7 (65.1)	0.9	−1.6
bz-bor-**PD**	−4.0 (23.4)	9.7	−3.9 (23.2)	3.6	−9.0 (53.4)	1.4	−2.2
bz-bor-**T**	−3.1 (29.2)	6.0	−1.7 (16.2)	1.2	−5.8 (54.6)	0.7	−2.8

[a] The contributions (in percent) of the attractive terms to the total attractive interaction are given in parentheses.

DFT-based SAPT approaches and SAPT2 observed earlier for the benzene dimer.[53,56,57]

For all ten isomers investigated, we find the first-order electrostatic ($E_{\mathrm{el}}^{(10)}$), the second-order induction ($E_{\mathrm{ind}}^{(20)}$), and the second-order dispersion ($E_{\mathrm{disp}}^{(20)}$) energies to be attractive while the exchange corrections are all repulsive throughout. The leading attractive interaction for all isomers and orientations is dispersion but its contribution varies significantly. For example, in the **S** isomers the overall attraction varies between 53−69%, where it is largest for bz_2 and lowest for bor_2. In the benzene-containing **PD** isomers (i.e., of bz_2 and bz-bor), the contribution of dispersion is smaller while the weight of the induction and in particular the electrostatic interaction is increasing when going from **S** to **PD**.

The bor_2 isomers, on the other hand, behave the opposite way: the contribution of dispersion is *increasing* for bor_2-**PD** compared to bor_2-**S**, while that of induction is decreasing. The bor_2-**S** isomer is outstanding insofar as it is one with the largest electrostatic contribution to the attractive interaction among all **S** and **PD** isomers. The importance of the electrostatic attraction in bor_2-**S** as revealed by the SAPT analysis is in agreement with the general expectation based on the polarity of B−N bonds. It is, however, noteworthy that even for this isomer the largest contribution to the attraction arises from dispersion.

The **T** isomers of bz_2, bz-bor, and bor_2 have rather similar weights of electrostatic, induction, and dispersion contributions. In agreement with the hydrogen bonding nature, the electrostatic interaction is rather large, ranging from 27−29%, while the induction amounts to only 15−16% of the attraction.

Conclusions

The present study of the benzene and borazine homo- and heterodimers using MP2, spin-component scaling (SCS) MP2, and CCSD(T) theories in conjunction with basis sets of up to quadruple-ζ quality confirms previous investigations insofar as the interaction energy is strongly overestimated for the benzene sandwich at the MP2 level compared to CCSD(T), while electron correlation effects beyond the MP2 approximation have only marginal effects on the borazine homodimers. Interestingly, the borazine−benzene heterodimers appear to behave intermediate in this respect. The SCS−MP2 approach is correcting for the deficiencies of MP2 in the case of the benzene sandwich: the SCS−MP2 binding energy is somewhat too large compared to our CBS-CCSD(T) data but in good agreement with results obtained with more sophisticated extrapolation schemes than that employed in the present paper. For the borazine dimer, it appears to be overcorrecting and thus produces interactions energies that are too low. On the other hand, the SCS−MP2 binding energies are in very good agreement with CBS-CCSD(T) for the heterodimers. In agreement with Antony and Grimme[74] we find that non-CP corrected SCS−MP2 yields better agreement with our CCSD(T) data for all the systems considered here. It is further encouraging to observe that the relative stabilities of dimer configurations is given qualitatively correctly at the MP2 and SCS−MP2 levels. In particular SCS−MP2 thus appears to be a reasonable alternative for the investigation of larger borazine-doped nanographene systems.

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