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Ab Initio Studies of $\pi\cdots\pi$ Interactions: The Effects of Quadruple Excitations[†]

Brian W. Hopkins and Gregory S. Tschumper*

Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677-1848

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To examine the effects of including quadruple excitations in the electron correlation treatment when computing the binding energy of van der Waals dimers, we have calculated MP2, CCSD, CCSD(T), and CCSD(TQ) interaction energies for several van der Waals complexes ranging from helium dimer to furan dimer. Through comparison of CCSD(TQ) and CCSD(T) binding energies the first direct assessment of the effects of quadruple excitations on $\pi\cdots\pi$ interactions is presented. The influence of triple excitations is assessed not only in the conventional manner that permeates the literature (comparison of CCSD(T) and MP2 interaction energies) but also via comparison of CCSD(T) and CCSD data. In systems exhibiting significant electron delocalization, it is well-known that triples contributions to binding energy are quite large (on the order of 1 kcal mol^{-1}). In these cases, quadruple excitations are nonnegligible and tend to be an order of magnitude smaller than the correction to the binding energy from triple excitations (on the order of 0.1 kcal mol^{-1}). The largest quadruples correction observed was +0.2 kcal mol^{-1} for the furan dimer.

I. Introduction

Much of chemistry is dominated not by covalent interactions but by weaker, more subtle intermolecular forces.[1] One important example is the van der Waals force that binds together nonpolar organic molecules. These forces are often strongest in systems that have interacting π-electron clouds. Such $\pi\cdots\pi$ interactions play a key role in determining the structure and function of proteins[2,3] and nucleic acids.[4] Furthermore, $\pi\cdots\pi$ dispersion interactions are among the primary forces driving ligand binding to biological macromolecules.[5]

Due in part to their importance in medicinal chemistry and biochemistry, van der Waals interactions (and in particular $\pi\cdots\pi$ interactions) have been subjected to a great deal of theoretical scrutiny. Recently, works published by several groups have analyzed $\pi\cdots\pi$ stacking interactions at very high levels of electronic structure theory. Hobza and co-workers have studied several aromatic dimers including benzene dimer[6] and dimers of pyrrole, pyrimidine, and triazine.[7,8] Sinnokrot, Valeev, and Sherrill examined the benzene dimer very closely.[9] Leininger et al. studied the uracil dimer in two different geometries.[10] Most recently, Tsuzuki, Honda, and Azumi computed interaction energies for 17 different orientations of the thiophene dimer, 10 of which can legitimately be called "stacked" complexes.[11] All of these studies involved CCSD(T) calculations with double-ζ basis sets augmented with at least polarization functions on all heavy atoms. As shown in Table 1, in many of these cyclic, conjugated systems the interaction energy determined with CCSD(T) differed substantially from the corresponding values determined using second-order Møller−Plesset perturbation theory. The CCSD(T) corrections to the MP2 binding energy range from 0.21 kcal mol^{-1} for one geometry of the thiophene dimer[11] up to 2.75 kcal mol^{-1} in the case of 1-aminopyrimidine dimer.[7]

The large differences between MP2 and CCSD(T) binding energies indicate that inclusion of triple excitations is very important in stacked aromatic dimers. In addition, the large triples contributions suggest a potentially important role for quadruple excitations. In short, the results bring up the question posed by Šponer and Hobza:[8] if triples corrections are in excess of 1 kcal mol^{-1} (as much as 50−100% of the binding energy), can we really neglect the effects of quadruple excitations on $\pi\cdots\pi$ interactions? The present work is the first attempt to address this important question for $\pi\cdots\pi$ van der Waals dimers.

TABLE 1: Results of Previous Calculations Showing a Large Difference between MP2 and CCSD(T) Interaction Energies[a]

	interaction energies	
system	MP2	CCSD(T)
benzene dimer [b]	−4.95	−2.78
pyrrole dimer [c]	−0.63	+0.45
pyrimidine dimer [c]	−3.87	−2.64
triazine dimer [c]	−3.77	−2.79

[a] All energies are in kcal mol^{-1}. [b] Benzene dimer in parallel-displaced geometry. See ref 9. [c] Dimers in antiparallel geometry. See ref 8.

Many small van der Waals dimers have already been examined with ab initio methods that include high-order excitations via Møller−Plesset perturbation theory. Thus, some insight into the contributions of high-order excitations to binding energy has already been attained. However, work by Olsen and co-workers[12,13] and Leininger et al.[14] has cast considerable doubt upon the reliability of the MP*n* expansion past the second order. In fact, both Olsen and Leininger went so far as to recommend restricting the use of the MP*n* series to MP2 and using alternative methods to include higher order excitations. van der Waals interaction energies reported by Woon[15,16] show a slow convergence in the cases of He_2 and Ne_2, while exhibiting an oscillatory behavior in the case of Ar_2. From the somewhat limited data series (only MP2, MP3, and MP4) it is not clear whether binding energy determined via the MP*n* series is convergent with respect to *n* in the case of the argon dimer. In all cases the coupled cluster results converged much more rapidly than those from the MP*n* series, with CCSD(T) results being more reliable than MP4 data. Thus, we have reexamined

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* Corresponding author. E-mail: tschumpr@olemiss.edu.

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these and other dimers using coupled cluster theory to incorporate the effects of triple and quadruple excitations.

In addition to questions about the convergence of the MPn expansion, previous studies of van der Waals dimers have been limited to systems of small size. In small dimers, both triple and quadruple excitations have negligible effects on overall interaction energies. This result is not unexpected. Rare gas dimers (Rg$\cdots$Rg) and rare gas$\cdots\pi$ dimers (Rg$\cdots\pi$) are bound very weakly, with interaction energies on the order of 0.1 kcal mol^{-1} or smaller. The effect of triple excitations in these systems is very small. Both characteristics make small Rg$\cdots$Rg and Rg$\cdots\pi$ systems fundamentally different from larger systems such as the benzene dimer. Consequently, not only should these small dimers be revisited with the coupled cluster method, but larger systems that are more tightly bound and show large triples corrections should also be examined.

Larger van der Waals dimers, including cyanogen dimer and 1,3-butadiene dimer, have been studied previously. However, no work has examined the effects of quadruple excitations in these dimers. Calculations that explicitly include quadruple excitations are extremely expensive for systems of this size. An accurate assessment of quadruples is possible, however, with coupled cluster methods that include high-order excitations perturbatively. By using the CCSD(TQ) method to efficiently include connected quadruple substitutions,[17] we can examine the effects of quadruple excitations on larger systems. The thrust of this work is to identify and examine systems that are large enough to show appreciable triples corrections to binding energy but small enough to allow determination of the quadruples corrections.

II. Theoretical Methods

In the interest of thoroughness, and in order to illustrate trends with different basis sets and counterpoise corrections, several dimers involving rare gas atoms were studied. Rare gas dimers were studied in experimentally determined equilibrium geometries.[18] He$\cdots$N$_2$, Ar$\cdots$C$_2$H$_2$, and (N$_2$)$_2$ were studied using the high-level optimized geometries available in the literature.[19−21] For some systems, however, reliable structures were not readily available. These systems were optimized at the MP2 level with the aug-cc-pVDZ basis set specifically for this work. Details of monomer and dimer geometries are given with the data for the respective systems.

For all dimers, interaction energies (E_{INT}) were computed via the supermolecular approach from the energies of the dimer (E_{AB}) and monomers (E_{A} and E_{B}).

$$E_{\mathrm{INT}} = E_{\mathrm{AB}} - E_{\mathrm{A}} - E_{\mathrm{B}} \tag{1}$$

For all systems, E_{INT} was computed using the coupled cluster method including all single and double excitations as well as a perturbative, noniterative approximation of connected triple and quadruple excitations [CCSD(TQ)][17,22−26] as well as at the CCSD(T)[22−26] and MP2[27] levels. The central focus of this work is the importance of triple and quadruple excitations in determining reliable interaction energies. As a measure of the contribution to E_{INT} from triple excitations, we define the quantity $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ in the customary way.[8−11,28,29]

$$\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}} = E_{\mathrm{INT}}^{\mathrm{CCSD(T)}} - E_{\mathrm{INT}}^{\mathrm{MP2}} \tag{2}$$

The effects of triple excitations can also be assessed relative to CCSD interaction energies.

$$\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}} = E_{\mathrm{INT}}^{\mathrm{CCSD(T)}} - E_{\mathrm{INT}}^{\mathrm{CCSD}} \tag{3}$$

Equation 2 appears to have been adopted as the standard assessment of triple corrections. Even when MP2, CCSD, and CCSD(T) interaction energies are reported, the effect of triple excitations is measured with $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$, not $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$.[10] To the best of our knowledge, the present work represents the first assessment of triples corrections to $\pi\cdots\pi$ interaction energies using eq 3 rather than eq 2.

The contribution to E_{INT} from quadruple excitations, $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$, is defined in a similar manner.

$$\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}} = E_{\mathrm{INT}}^{\mathrm{CCSD(TQ)}} - E_{\mathrm{INT}}^{\mathrm{CCSD(T)}} \tag{4}$$

The CCSD(TQ) interaction energy is related to these quantities by

$$E_{\mathrm{INT}}^{\mathrm{CCSD(TQ)}} = E_{\mathrm{INT}}^{X} + \delta_{X}^{\mathrm{CCSD(T)}} + \delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}} \tag{5}$$

where X is either MP2 or CCSD. Where possible, CCSD(TQ) calculations were carried out using the aug-cc-pVDZ basis set.[30] However, for systems larger than (C$_2$H$_2$)$_2$ such calculations were cost prohibitive. In all of the larger systems CCSD(TQ) energies were computed using the 6-31G*(0.25) basis set.[31−33] This basis set is a modified 6-31G* basis set in which the polarization function exponents on all heavy atoms have been reduced to 0.25. The utility of such basis sets for describing van der Waals forces has been established.[32,33] Furthermore, the 6-31G*(0.25) basis set reproduces aug-cc-pVDZ trends in $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ very well. $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ computed with the 6-31G*(0.25) and aug-cc-pVDZ basis sets are tabulated in the Supporting Information. The 6-31G*(0.25) basis set provides a reliable means for assessing the effect of high-order excitations on the interaction energies in the complexes studied here.

Basis set superposition error (BSSE) is a concern in weakly bound dimers. BSSE can be effectively eliminated via the counterpoise (CP) correction of Boys and Bernardi.[34−36] For small dimers we have computed CP-corrected interaction energies. In the larger systems the CP correction was cost prohibitive. However, we observe that in all of the systems for which the CP correction was computed, the trends in $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ are unaffected by the CP correction. These trends can be seen in the Supporting Information to this work. Consequently, the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ trends reported for the large, non-CP-corrected systems should be representative.

All calculations were carried out with the ACESII,[37] PSI3,[38] and Gaussian 98[39] quantum chemistry software packages. All calculations used spherical harmonic (5d) Gaussian basis functions. Energies were converged to 10^{-8} E_{h}. Cartesian gradients were converged to 10^{-4} E_{h} bohr^{-1}. All frequency calculations were carried out using analytic second derivatives.

III. Results and Discussion

III.A. Rare Gas Dimers. As the smallest systems bound by dispersion interactions, the three smallest homonuclear rare gas dimers (He$_2$, Ne$_2$, and Ar$_2$) were studied. Because of their small size, the CP correction was affordable in these systems. CCSD(TQ)/aug-cc-pVTZ calculations were also possible for these dimers. Consequently, these systems were used to evaluate the performance of both the non-CP-corrected calculations and the 6-31G*(0.25) basis set.

The interatomic distances for He$_2$, Ne$_2$, and Ar$_2$ were 2.967, 3.087, and 3.759 Å, respectively. The interaction energy E_{INT}

TABLE 2: Binding Energies (E_{INT}^{X}) and Corrections to the Binding Energies from Triple ($\delta_{X}^{\mathrm{CCSD(T)}}$) and Quadruple ($\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$) Excitations Where X = MP2 or CCSD[a]

system	$E_{\mathrm{INT}}^{\mathrm{MP2}}$	$E_{\mathrm{INT}}^{\mathrm{CCSD}}$	$\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$	$\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$	$\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$
			Rg⋯Rg		
He_2	−0.022	−0.025	−0.004	−0.002	+0.004
Ne_2	−0.071	−0.085	−0.035	−0.021	+0.005
Ar_2	−0.233	−0.148	+0.047	−0.039	+0.002
			Rg⋯π		
He⋯N_2	−0.12	−0.11	−0.00	−0.01	+0.00
Ar⋯C_2H_2	−0.45	−0.42	+0.06	+0.03	+0.01
			$\pi\cdots\pi$		
$(N_2)_2$	−0.58	−0.32	+0.07	−0.19	+0.01
$(C_2H_2)_2$[b]	−1.99	−1.58	+0.17	−0.24	+0.03
$(C_2H_2)_2$[c]	−2.45	−2.02	+0.13	−0.30	+0.04
$(C_2H_2)_2$[d]	−0.08	+0.17	+0.14	−0.11	+0.01

[a] All values are in kcal mol^{-1} and were computed with the aug-cc-pVDZ basis set. [b] Acetylene dimer in parallel-slipped geometry. [c] Acetylene dimer in T-shaped geometry. [d] Acetylene dimer in rectangular geometry.

of each dimer was computed with the MP2, CCSD(T), and CCSD(TQ) theoretical methods in conjunction with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. E_{INT} for Ne_2 was computed with the 1s orbitals frozen. The aug-cc-pVDZ data are summarized in Table 2; the aug-cc-pVTZ data show the same trends and are available in the Supporting Information for this work.

Two different frozen core approximations were explored for the argon dimer. The data shown in Table 2 were computed with the 1s, 2s, and 2p orbitals frozen. In addition, E_{INT} for the system was computed with only the 1s orbitals frozen; these data are available in the Supporting Information. Correlating the 2s and 2p electrons led to a more reliable value for E_{INT}; however, the trends in $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ were unaffected.

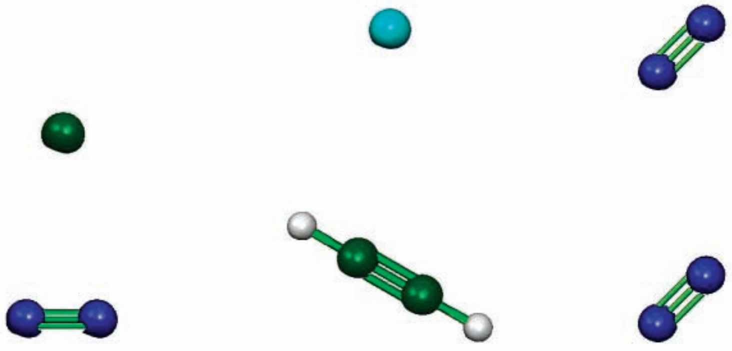
As is evident in Table 2, these dimers are very weakly bound. Binding energies are on the order of 0.1 kcal mol^{-1}. Furthermore, both $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ values are very small, being on the order of 0.01 kcal mol^{-1}. $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ values are an order of magnitude smaller, being in general on the order of 0.001 kcal mol^{-1}. Although both interaction energies and contributions from triple excitations increased as the size of the dimers increased from He_2 through Ar_2, the increase was not dramatic enough to make the Rg⋯Rg systems useful models for aromatic dimers.

III.B. Rare Gas⋯π Systems. Because of the very small E_{INT}, $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$, and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ observed in the rare gas dimers, small van der Waals dimers involving one rare gas atom interacting with a π-electron cloud were examined. As with the Rg⋯Rg dimers, calculations on Rg⋯π dimers were needed to test the performance of non-CP-corrected and 6-31G*(0.25) calculations. Two of the most extensively studied systems of this type have been He⋯N_2[19,40] and Ar⋯C_2H_2.[20,41−43] As a result, high-quality theoretical structures were available for these two systems. The He⋯N_2 system was studied at the MP4 geometry of Hu and Thakkar;[19] the Ar⋯C_2H_2 system was studied at the MP4 geometry of Tao, Drucker, and Klemperer.[20] The structures of these dimers are shown in Figure 1. The interaction energies E_{INT} for He⋯N_2 and Ar⋯C_2H_2 were determined using the MP2, CCSD(T), and CCSD(TQ) methods in conjunction with the aug-cc-pVDZ basis set. CCSD(TQ)/aug-cc-pVTZ calculations were not feasible for the Ar⋯C_2H_2 system. However E_{INT} was computed with the aug-cc-pVTZ basis set at the MP2, CCSD(T), and CCSD(TQ) levels for He⋯N_2 and at the MP2 and CCSD(T) levels for Ar⋯C_2H_2. In all calculations the 1s orbitals of C, N, and Ar atoms were frozen along with the 2s and 2p orbitals of Ar, since correlating the 2s and 2p electrons of Ar had little impact on $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ in Ar_2. The MP2 E_{INT} and values of $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$, $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$, and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ for both dimers calculated with the aug-cc-pVDZ basis set are reported in Table 2. As observed in the Rg⋯Rg dimers, the trends in $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ are the same when computed with the aug-cc-pVTZ basis set.

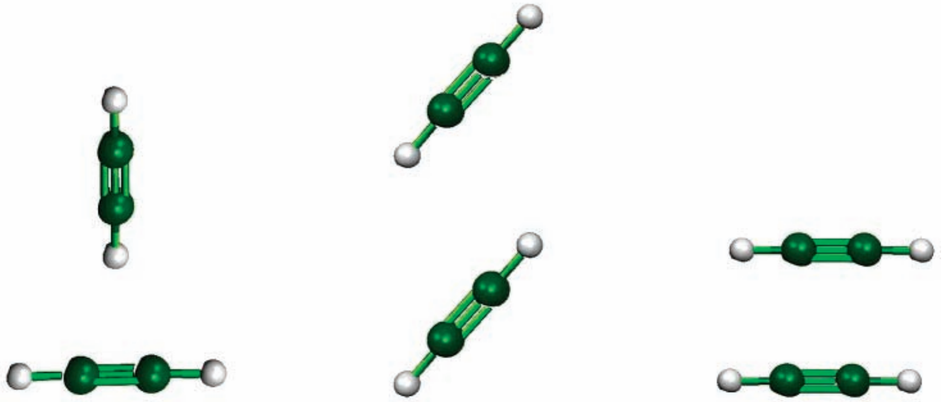
These Rg⋯π dimers are more tightly bound than the Rg⋯Rg dimers. E_{INT} in the larger Ar⋯C_2H_2 dimer approaches 0.5 kcal mol^{-1}. However, $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ for the Rg⋯π dimers are no greater than those seen in the Rg⋯Rg systems. These values are still on the order of 0.01 kcal mol^{-1}. Given the very small triples contributions, it is not surprising that the quadruple excitations have essentially no effect on the binding of these dimers. Quadruples contributions in these two dimers remain on the order of 0.001 kcal mol^{-1}. As with the Rg⋯Rg dimers, increasing the basis set size from aug-cc-pVDZ to aug-cc-pVTZ has very little effect on the magnitude of $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$, $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$, and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$. These quantities appear to be relatively insensitive to basis set size.

III.C. Small $\pi\cdots\pi$ Systems. The next logical step after rare gas⋯π systems is the examination of simple $\pi\cdots\pi$ dimers, such as $(N_2)_2$ and $(C_2H_2)_2$. MP2, CCSD, CCSD(T), and CCSD(TQ) interaction energies were computed for $(N_2)_2$ and three configurations of $(C_2H_2)_2$ using the aug-cc-pVDZ basis set. For $(N_2)_2$, MP2, CCSD, and CCSD(T) interaction energies were computed with the aug-cc-pVTZ basis set. CCSD(TQ)/aug-cc-pVTZ calculations on the dimer were not possible. Results for these two $\pi\cdots\pi$ systems are reported in Table 2. All results were obtained with the 1s orbitals of C and N frozen. The results obtained with the aug-cc-pVTZ basis set are tabulated in the Supporting Information.

Previous work[21,44−47] has characterized several points on the $(N_2)_2$ potential energy surface (PES), showing a clear minimum energy structure in the parallel-slipped[21] configuration shown in Figure 1. This geometry was adopted in the work presented here. E_{INT}, $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$, $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$, and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ of $(N_2)_2$ are comparable to those seen in the Rg⋯π systems. The triples and quadruples corrections, while the largest seen so far, are still too small to model the behavior of $(C_6H_6)_2$. Nevertheless, a pattern is emerging. In all cases, $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ seems to be approximately one-tenth the magnitude of $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$. In addition, $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ is roughly the same magnitude as $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ but has opposite sign. That is, CCSD tends to underbind the dimers by approximately the same amount as MP2 overbinds them.



(a) He$\cdots N_2$ $[C_{2v}]$ (b) Ar$\cdots C_2H_2$ $[C_s]$ (c) $(N_2)_2$ $[C_{2h}]$



(d) T-shaped $(C_2H_2)_2$ $[C_{2v}]$ (e) Parallel slipped $(C_2H_2)_2$ $[C_{2h}]$ (f) Rectangular $(C_2H_2)_2$ $[D_{2h}]$

Figure 1. The nonconjugated Rg$\cdots\pi$ and $\pi\cdots\pi$ dimers studied. The point group of each structure is given in square brackets.

$(C_2H_2)_2$ has also been studied widely. Two different structures are known to be of importance on the $(C_2H_2)_2$ PES. Some experiments[48,49] and computations[50] have suggested a structure in C_{2h} symmetry, analogous to the parallel-slipped form of $(N_2)_2$. Other experiments[51,52] and higher level ab initio calculations[53−63] point to a T-shaped structure (in or near C_{2v} symmetry) as the global minimum energy structure. Both geometries were studied here. A rectangular arrangement (D_{2h}) was also examined.

These geometries, shown in Figure 1, were optimized at the MP2/aug-cc-pVTZ level for this work. The interaction energies of these three structures are reported in Table 2. The binding energies, $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$, vary widely across the three geometries. $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$, however, remains one-tenth the magnitude of $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ for all three structures. While the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ values seen for $(C_2H_2)_2$ are larger than those seen for any of the smaller systems, they remain an order of magnitude smaller than the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ observed in $(C_6H_6)_2$. Consequently, even these systems are not adequate models for the behavior of $(C_6H_6)_2$ or other aromatic dimers.

In an attempt to increase the effect of triple excitations on this small model system, $(C_2H_2)_2$ was also studied as the C≡C triple bond was stretched. As this happens, the multireference character of the molecule increases, making triple excitations more important. The E_{INT} of the C_{2h} acetylene dimer was thus determined with C≡C bond lengths ranging from 1.23 to 1.43 Å in 0.01 Å increments. At each bond length, all geometrical parameters were optimized in C_{2h} symmetry with MP2 theory and the aug-cc-pVDZ basis set except the C≡C bond lengths. The E_{INT} of the stretched dimers were then computed using MP2 and CCSD(T) with the aug-cc-pVDZ basis set.

As the length of the C≡C bonds was increased, the interaction energy E_{INT} grew steadily more negative. This effect was more pronounced in the MP2 data than in the CCSD(T) data. In other words, $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ did increase as the C≡C bond length was stretched. Similarly, $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ grew more negative as the bond length increased. The MP2, CCSD, and CCSD(T) interaction energies for all 20 points are available as Supporting Information for with this work. Unfortunately, $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ increase in magnitude slowly as the bond is stretched. Even the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ at a bond length of 1.43 Å remains considerably smaller (+0.39 kcal mol^{-1}) than the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ in $(C_6H_6)_2$. The single-reference coupled cluster methods will fail to describe the multireference nature of the stretched C≡C bond long before $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ increases to a magnitude comparable to that in $(C_6H_6)_2$.

III.D. Conjugated $\pi\cdots\pi$ Systems. The failure of simple $\pi\cdots\pi$ systems to model the behavior of $(C_6H_6)_2$ suggests that the large $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ observed in aromatic dimers may be closely related to delocalization in the π-electron system. Therefore, several of the smallest neutral, conjugated, $\pi\cdots\pi$ complexes were examined as well. Some obvious choices, such as allyl

TABLE 3: Binding Energies (E_{INT}^{X}) and Corrections to the Binding Energies from Triple ($\delta_{X}^{\mathrm{CCSD(T)}}$) and Quadruple ($\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$) Excitations Where X = MP2 or CCSD[a]

system	$E_{\mathrm{INT}}^{\mathrm{MP2}}$	$E_{\mathrm{INT}}^{\mathrm{CCSD}}$	$\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$	$\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$	$\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$
$(\mathrm{NCCN})_2$[b]	−3.92	−2.67	+0.84	−0.41	+0.10
$(\mathrm{NCCN})_2$[c]	−3.90	−3.08	+g0.56	−0.26	+0.07
$(\mathrm{C_4H_6})_2$[d]	−4.09	−2.75	+0.79	−0.55	+0.07
$(\mathrm{C_4H_6})_2$[e]	−4.42	−2.96	+0.90	−0.56	+0.08
$(\mathrm{C_4H_6})_2$[f]	−2.39	−1.09	+0.80	−0.50	+0.06
$(\mathrm{C_4H_6})_2$[g]	−5.29	−2.85	+1.45	−0.89	+0.13
(furan)$_2$	−3.78	−1.76	+1.20	−0.82	+0.20

[a] All values are in kcal mol^{-1} and were computed with the 6-31G*(0.25) basis set. [b] $(\mathrm{NCCN})_2$ in parallel-slipped geometry. [c] $(\mathrm{NCCN})_2$ in T-shaped geometry. [d] Eclipsed 1,3-butadiene in parallel geometry. [e] Eclipsed 1,3-butadiene in antiparallel geometry. [f] Anti 1,3-butadiene in parallel geometry. [g] Anti 1,3-butadiene in antiparallel geometry.

radical and cyclobutadiene, were abandoned because of technical obstacles. All conjugated monomers and dimers were optimized with MP2 theory and the aug-cc-pVDZ basis set. Interaction energies for dimers were computed with MP2, CCSD, and CCSD(T) techniques with the aug-cc-pVDZ basis set. All energies were computed with the frozen core approximation.

CCSD(TQ)/aug-cc-pVDZ calculations are not feasible for systems of this size. As discussed in section 2, for these large systems interaction energies have been determined with MP2, CCSD, CCSD(T), and CCSD(TQ) in conjunction with the 6-31G*(0.25) basis set. The results are summarized in Table 3.

III.D.1. Cyanogen Dimer. Cyanogen (NCCN) is perhaps the smallest closed-shell, neutral, conjugated molecule. With MP2 theory and the aug-cc-pVDZ basis set, the NCCN monomer is a linear molecule in which both the C≡N triple bonds are longer than ordinarily observed and the C−C single bond is shorter than usual, indicating noticeable delocalization of the π-electron system. The dimer system was optimized with MP2/aug-cc-pVDZ to a parallel-slipped structure analogous to the $(\mathrm{N_2})_2$ global minimum, as shown in Figure 2. Computation of analytic frequencies confirmed that this geometry is a minimum at this level of theory.

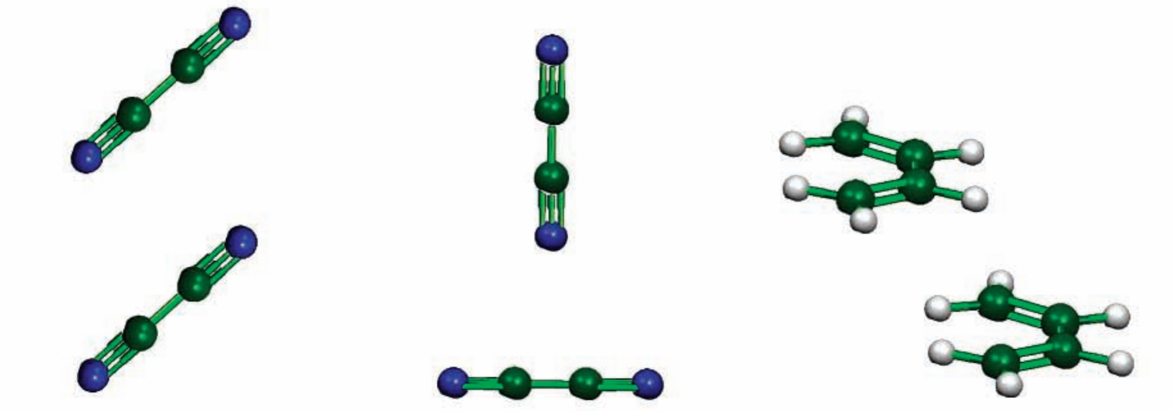
RHF calculations[64,65] have indicated that the global minimum energy structure of cyanogen dimer is T-shaped (C_{2v} symmetry.) An experiment[66] has also suggested a T-shaped cyanogen dimer. Consequently, a T-shaped structure of cyanogen dimer was also optimized at the MP2 level with the aug-cc-pVDZ basis set. Analytic frequencies show this structure to be a transition state at this level of theory. The discrepancy between MP2 and RHF computations is not surprising since RHF calculations do not (by definition) incorporate dispersion interactions and may not adequately describe this system.

In the parallel-slipped configuration, the MP2/aug-cc-pVDZ E_{INT} for $(\mathrm{NCCN})_2$ is −2.90 kcal mol^{-1}. $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ for this structure of cyanogen dimer is much larger than that seen in nonconjugated π systems and is comparable to the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ values seen in the benzene dimer. In this system, $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ is +0.10 kcal mol^{-1}. Thus, we again observe a $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ correction on the order of one-tenth of the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ correction.

In the T-shaped configuration, the MP2/aug-cc-pVDZ E_{INT} for $(\mathrm{NCCN})_2$ is −3.00 kcal mol^{-1}. It should be noted that this transition state is lower in energy than the parallel-slipped minimum; this indicates the existence of an additional minimum energy structure. Such a structure would have lower symmetry and thus is not considered here. The contributions from triple and quadruple excitations in the T-shaped structure are smaller than those in the parallel-slipped structure. This is consistent with the trend seen in acetylene dimer, in which $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$, $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$, and $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ were smaller fractions of the total binding energy in the T-shaped structure than in the parallel-slipped structure. Nevertheless, $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ remains 1 order of magnitude lower than $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ in the T-shaped structure of the cyanogen dimer. As in the smaller $\pi\cdots\pi$ systems, $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ are of similar magnitude but opposite sign. In these larger systems, however, the discrepancy in the magnitudes of $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ is slightly larger when computed with the 6-31G*(0.25) basis set. With this smaller basis set the MP2 and CCSD interaction energies become more negative relative to the CCSD(T) interaction energy. As a result, the magnitude of $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$ is slightly reduced and the magnitude of $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ is slightly increased. This effect, however, does not impact $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$, which is the primary focus of this study.

III.D.2. 1,3-Butadiene Dimer. Another small, prototypical conjugated molecule is 1,3-butadiene. Four geometries of the 1,3-butadiene dimer were studied; they are shown in Figure 2c−f. In this molecule, rotation about the central C−C bond gives rise to several possible rotamers defined by the C=C−C=C torsional angle τ. These rotamers include a U-shaped eclipsed arrangement ($\tau = 0°$), a lightning-bolt-shaped anti arrangement ($\tau = 180°$), and several nonplanar gauche rotamers. Of these possibilities, two minima on the MP2/aug-cc-pVDZ surface were identified: the anti configuration and a gauche rotamer with $\tau \approx \pm 39°$. The anti rotamer is more stable than the gauche by approximately 3 kcal mol^{-1}. The eclipsed conformer is a transition state at this level of theory, 0.8 kcal mol^{-1} higher in energy than the gauche rotamer. Unfortunately, the nonplanarity of the molecule in the gauche conformation reduces the symmetry of the molecule. Because of the excessive computational demands of the CCSD(TQ) method, only the higher symmetry eclipsed···eclipsed and anti···anti dimer configurations can be considered. Both parallel and antiparallel alignments were studied (shown in Figure 2.) While all four structures are stationary points on the MP2/aug-cc-pVDZ PES, analytic frequency calculations showed that not all four stationary points are minima at this level of theory. The antiparallel arrangement of the anti···anti structure is a minimum; the parallel anti···anti and eclipsed···eclipsed structures are fourth-order saddle points. The antiparallel arrangement of the eclipsed···eclipsed structure is a third-order saddle point.

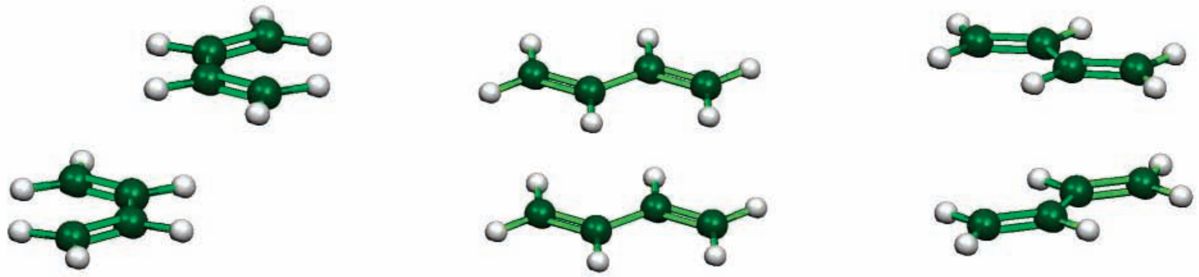
Interaction energies for the 1,3-butadiene dimer are reported in Table 3. The four stationary points of 1,3-butadiene show considerable variation in interaction energy, ranging from −2.3 kcal mol^{-1} to −5.3 kcal mol^{-1}. Triples corrections also exhibit a large variation across the potential energy surface, with dimers that are bound more tightly generally showing larger repulsive contributions from triple excitations. $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ ranges from 20% to 33% of the MP2 binding energy. $\delta_{\mathrm{CCSD(T)}}^{\mathrm{CCSD(TQ)}}$ is generally on the order of 0.1 kcal mol^{-1}, which is approximately one-tenth



(a) Parallel slipped $(NCCN)_2$ $[C_{2h}]$

(b) T-shaped $(NCCN)_2$ $[C_{2v}]$

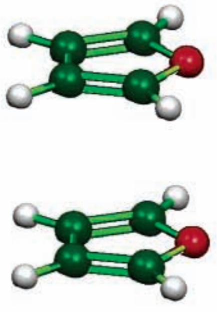
(c) Parallel eclipsed$\cdots$eclipsed dimer $[C_s]$



(d) Antiparallel eclipsed$\cdots$eclipsed dimer $[C_{2h}]$

(e) Parallel anti$\cdots$anti dimer $[C_{2h}]$

(f) Antiparallel anti$\cdots$anti dimer $[D_2]$



(g) Furan Dimer $[C_{2h}]$

Figure 2. The conjugated $\pi\cdots\pi$ dimers studied. The point group of each structure is given in square brackets.

of $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$. As with cyanogen dimer, calculations using the 6-31G*(0.25) basis set show a slight discrepancy between the magnitudes $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ and $\delta_{\mathrm{CCSD}}^{\mathrm{CCSD(T)}}$.

III.E. Aromatic $\pi\cdots\pi$ Systems. Tsuzuki and co-workers have observed very large triples corrections to the interaction energy of several geometries of the thiophene dimer. Thiophene, however, is cumbersome because of the additional electrons from the sulfur atom. The oxygen analogue, furan, should exhibit similar behavior and be less expensive to study. In fact, furan is among the smallest neutral, closed-shell, aromatic systems. The furan dimer was studied in a parallel, sandwich-shaped structure shown in Figure 2.

The results of the calculations with the 6-31G*(0.25) basis set are summarized in Table 3. Results of calculations with the aug-cc-pVDZ basis set are available as Supporting Information. In this geometry, furan dimer is bound tightly and exhibits a very large, repulsive contribution from triple excitations. $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ in this system is the largest observed in this study ($+0.20$ kcal mol^{-1}).

We have examined the benzene dimer in the same parallel-displaced geometry used by the Sherrill group. Motivated by the notion that the large $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ in benzene dimer may be a property purely of the π-electron system, we examined the dimer with the MP2 and CCSD(T) methods and aug-cc-pVDZ basis set with all but the π-electrons frozen. Freezing the additional 48 electrons and 24 orbitals dramatically reduced the cost of the calculations. Unfortunately $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ was also dramatically reduced, to just $+0.36$ kcal mol^{-1}. The accuracy of the calculation also suffered, with the system unbound at the MP2 level ($E_{\text{INT}} = +0.47$ kcal mol^{-1}). Clearly, correlation of only the π-electrons does not provide an adequate description of these systems.

IV. Conclusions

In light of the data collected, the following statements can be made about the computed interaction energies of the conjugated $\pi\cdots\pi$ complexes.

(i) MP2 theory overbinds the dimers substantially relative to CCSD(T) and CCSD(TQ).

(ii) CCSD theory underbinds the dimers substantially relative to CCSD(T) and CCSD(TQ).

(iii) Contributions from triple excitations are large (on the order of 1 kcal mol^{-1}) and not uniform across the PES.

(iv) Contributions from quadruple excitations are small but not negligible (on the order of 0.1 kcal mol^{-1}), generally one-tenth of the contributions from triple excitations.

(v) Electronic structure techniques that include triple excitations are required to determine E_{INT} to chemical accuracy.

(vi) Electronic structure techniques that include quadruple excitations are required to determine E_{INT} to subchemical accuracy.

The geometrical preference of $(C_6H_6)_2$ is an example of a situation in which quadruple excitations are likely to be important. Sherrill and co-workers reported two different geometries of $(C_6H_6)_2$ with nearly identical binding energies. The T-shaped dimer they reported to have an estimated CCSD(T)/CBS E_{INT} of -2.74 kcal mol^{-1}; the parallel-displaced conformer showed a CCSD(T)/CBS E_{INT} of -2.78 kcal mol^{-1}. Recall that the value of $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ is not constant across the PES; for instance, in the anti···anti 1,3-butadiene dimer $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ was $+0.13$ kcal mol^{-1} at one geometry and $+0.06$ kcal mol^{-1} at another. Thus, in the benzene dimer the contributions of quadruple excitations could conceivably alter the energetic order of these two dimers. Experience suggests that $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ is greater in systems with larger $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ values. In $(C_6H_6)_2$, $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ in the parallel-displaced geometry is more than twice $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ in the T-shaped geometry. Thus, it is likely that $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ is considerably larger in the parallel-displaced geometry than in the T-shaped dimer. Since $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ destabilizes every dimer studied, the T-shaped dimer would become the global minimum structure. Reliable characterization of the $(C_6H_6)_2$ PES will thus require theoretical methods that include quadruple excitations. Work on this problem is now underway in our research group.

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Supporting Information Available: Tables of comparisons of $\delta_{\text{MP2}}^{\text{CCSD(T)}}$, $\delta_{\text{CCSD}}^{\text{CCSD(T)}}$, and $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ values computed with the aug-cc-pVDZ and 6-31G*(0.25) basis sets; $\delta_{\text{MP2}}^{\text{CCSD(T)}}$, $\delta_{\text{CCSD}}^{\text{CCSD(T)}}$, and $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ values computed with the 6-31G*(0.25) basis set obtained with and without CP correction; $E_{\text{INT}}^{\text{MP2}}$, $E_{\text{INT}}^{\text{CCSD}}$, $\delta_{\text{MP2}}^{\text{CCSD(T)}}$, $\delta_{\text{CCSD}}^{\text{CCSD(T)}}$, and $\delta_{\text{CCSD(T)}}^{\text{CCSD(TQ)}}$ values computed with the aug-cc-pVTZ basis set; $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ and $\delta_{\text{CCSD}}^{\text{CCSD(T)}}$ values computed with the aug-cc-pVDZ basis set for the stretched acetylene dimer. This material is available free of charge via the Internet at http://pubs.acs.org.

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