Reliable structures and energetics for two new delocalized \(\pi\cdot\pi\) prototypes: cyanogen dimer and diacetylene dimer††

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Two new prototype delocalized \(\pi\cdot\pi\) complexes are introduced: the dimers of cyanogen, \((N\equiv C\equiv C\equiv N)\_2\), and diacetylene, \((HC\equiv C\equiv CH)\_2\). These dimers have properties similar to larger delocalized \(\pi\cdot\pi\) systems such as benzene dimer but are small enough that they can be probed in far greater detail with high accuracy electronic structure methods. Parallel-slipped and T-shaped structures of both cyanogen dimer and diacetylene dimer have been optimized with 15 different procedures. The effects of basis set size, theoretical method, counterpoise correction, and the rigid monomer approximation on the structure and energetics of each dimer have been examined. MP2 and CCSD(T) optimized geometries for all four dimer structures are reported, as well as estimates of the CCSD(T) complete basis set (CBS) interaction energy for every optimized geometry. The data reported here suggest that future optimizations of delocalized \(\pi\cdot\pi\) clusters should be carried out with basis sets of triple-\(\zeta\) quality. Larger basis sets and the expensive counterpoise correction to the molecular geometry are not necessary. The rigid monomer approximation has very little effect on structure and energetics of these dimers and may be used without consequence. Due to a consistent cancellation of errors, optimization with the MP2 method leads to CCSD(T)/CBS interaction energies that are within 0.2 kcal mol\(^{-1}\) of those for structures optimized with the CCSD(T) method. Future studies that aim to resolve structures separated by a few tenths of a kcal mol\(^{-1}\) should consider the effects of optimization with the CCSD(T) method.

1. Introduction

Complexes of molecules with delocalized (conjugated) \(\pi\) electron clouds are exceptionally difficult to study even in comparison with other van der Waals complexes.\(^1\)\(^-\)\(^10\) In fact, a recent invited article in this journal presented a benchmark database of weakly bound complexes and highlighted the need to move beyond the MP2 level of theory when the dispersion contribution to binding becomes significant.\(^9\) Consider, for example, the dimers listed in Table 1. MP2 and CCSD(T) interaction energies are quite similar for \((N_2)_2\) and \((C_2H_2)_2\) while MP2 tends to substantially overestimate the attractive forces of \(\pi\cdot\pi\) stacking in complexes with delocalized \(\pi\) electron clouds. Recent work has suggested that highly accurate studies of these complexes require correlated methods that include the effects of quadruple excitations.\(^11\) For instance, the inclusion of perturbative approximations to quadruple excitations increases the binding energy in the cyanogen dimer parallel-slipped and T-shaped configurations by 0.10 and 0.07 kcal mol\(^{-1}\), respectively.\(^11\) This represents a considerable obstacle since the classic prototype \(\pi\cdot\pi\) system, benzene dimer, is much too large to study at this level of detail. Hence, much work has been carried out to develop less demanding electronic structure techniques that can accurately describe this type of non-covalent interaction.\(^12\)\(^-\)\(^14\) If we are to gain an understanding of the detailed physics of conjugated \(\pi\cdot\pi\) systems, we will need a newer, smaller prototype system that can be examined in more detail than is possible for benzene dimer.

Cyanogen \((N\equiv C\equiv C\equiv N)\) is one of the smallest known closed-shell, neutral, conjugated molecules. As such, its dimer is an ideal prototype for conjugated \(\pi\cdot\pi\) interactions. Unfortunately, little is known about the \((N\equiv C\equiv C\equiv N)_2\) system. The first theoretical work on cyanogen dimer dates to 1984, when Hasanean and Evans studied nine dimer structures at the HF level of theory and with an empirical atom–atom potential method.\(^15\) Unfortunately, the HF level of theory was demonstrably inadequate for describing the system; five of the nine HF potential curves plotted by Hasanean and Evans were purely repulsive. Because dispersion forces are extremely important in the binding of \(\pi\)-type dimers, MP2 theory may be considered the lowest level of theory that can reasonably be expected to describe their structure and energetics. For this reason, neither Hartree Fock nor density functional methods have been employed in this study.

In 1991, molecular beam electric resonance spectroscopy performed by Klemperer and coworkers\(^16\) indicated a T-shaped \((N\equiv C\equiv C\equiv N)_2\) structure in \(C_2\nu\) symmetry. No
other structures were observed in the experiment. Subsequently the group of de Almeida examined T-shaped, linear, and parallel structures at the HF level of theory.\(^{17}\) Important nonplanar structures (including some of those studied by Hasanein and Evans) were neglected entirely by de Almeida et al., and the work went on to conclude that the T-shaped structure was the global minimum on the dimer potential energy surface.

Interestingly, despite the similarity of their methods, the HF results of the de Almeida and Evans studies disagree with respect to the nature of the end-to-end linear structure. Using the 6-31G basis, Evans’s HF calculations show a purely repulsive potential curve as the molecules approach end-to-end. By contrast, de Almeida’s HF/4-31G calculations do identify an end-to-end linear stationary point on the dimer surface. This disagreement may be due to the rigid monomer approximation, which was employed by Evans but not by de Almeida. Such a result is notable in that it highlights the sensitivity of the dimer surface to subtle geometrical effects; because the minima are very shallow, even slight changes in theoretical methods can qualitatively change the nature of the potential energy surface (PES).

The dimer of diacetylene (HC≡C–C≡CH) has been studied somewhat more thoroughly.\(^{18}\) Diacetylene is the smallest of the polyynes thought to be of value as molecular “rods” in the construction of nanoscale molecular machines.\(^{19}\) The interaction between diacetylene units has already been used in the construction of a “molecular zipper” by Shu et al.\(^{20}\) In addition to their importance in the construction of nanomaterials, both polycycloacetylenes and cyanopolyacetylenes are known to be present in extraterrestrial space.\(^{21–25}\) These molecules have been spectroscopically observed in the atmosphere of Saturn’s largest moon, Titan,\(^{21–24}\) where they are thought to be formed in the upper polar stratosphere and to play an important role in various photochemical processes.\(^{25}\) They are also thought to exist in the atmospheres of the giant planets that comprise most of our solar system,\(^{25}\) and have been observed in the envelope of gases that surrounds the solar system beyond the outermost planetary orbits.\(^{25,26}\)

Karpfen examined the surface of the diacetylene dimer at the MP2 level and identified six stationary points: a Y-shaped minimum in \(C_3\) symmetry; two distinct parallel-slipped minima in \(C_{2h}\) symmetry; a cross-shaped minimum in \(D_{2h}\) symmetry; a T-shaped transition state in \(C_N\) symmetry; and a stacked second-order saddle point in \(D_{2h}\) symmetry.\(^{27}\) In the same work, Karpfen examined the acetylene dimer in considerably more detail; this included performing optimizations with larger basis sets and computing single-point interaction energies at the MP4, CCSD, and CCSD(T) levels of theory. These calculations on acetylene dimer showed virtually no change in the dimer structure with increasing basis set size, and only minute changes in the interaction energy of \((\text{C}_2\text{H}_2)\) were observed as more sophisticated treatments of electron correlation were applied. Karpfen therefore concluded that the more rigorous theoretical treatment was not necessary for the study of the larger diacetylene complex. These results, however, are not really applicable to the dimer of diacetylene. As seen in Table 1, interactions between molecules with delocalized or conjugated \(\pi\) electron clouds are fundamentally different from those in small \(\pi\cdot\pi\) prototypes like acetylene dimer or the dimer of molecular nitrogen. MP2 calculations are known to give accurate results for simple \(\pi\cdot\pi\) systems.\(^{3,11}\) For conjugated systems, however, the results of MP2 calculations are erroneous, often overstating the binding energy of conjugated \(\pi\cdot\pi\) complexes by as much as 100%.\(^{3,9,28,29}\)

Despite its well known tendency to overestimate the stability of stacked, delocalized \(\pi\cdot\pi\) complexes, the MP2 method continues to be used for geometry optimizations of dimers bound by delocalized \(\pi\cdot\pi\) interactions. The effect of using MP2 optimized geometries on the energetics of these types of dimers is not well known, as most delocalized \(\pi\cdot\pi\) complexes are much too large to optimize with more accurate theoretical methods. Only recently has this effect been examined when Sherill and co-workers estimated CCSD(T) optimized structures of the benzene dimer by using MP2 potential energy curves that had been corrected for the difference between MP2 and CCSD(T) interaction energies and found that changes to their best estimates of the interaction energies were on the order of 0.2 kcal mol\(^{-1}\).\(^{3}\) The fact remains, however, that it is currently unknown exactly which theoretical methods are adequate to study the shape of such a surface. The thrust of this work aims to determine how the energetics of delocalized \(\pi\cdot\pi\) systems are affected by geometrical perturbations introduced when popular approximations are implemented during optimization procedures (e.g., smaller basis set, lower theoretical method, counterpoise correction, rigid monomer approximation). Having identified the most reliable procedures for the characterization of \(\pi\cdot\pi\) interactions, detailed characterizations of the PESs of these new prototypes will soon be presented. This work will greatly assist the development of less demanding computational methods for \(\pi\cdot\pi\) interactions (e.g., force fields, density functional methods, semi-empirical methods).

### 2. Theoretical methods

The stationary points selected for study here are the very low lying and high symmetry parallel-slipped and T-shaped structures (see Fig. 1). These structures are analogous to the parallel-slipped and T-shaped structures known to be important on the potential energy surfaces of benzene dimer and other aromatic complexes.\(^{3}\) These two points on each dimer

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**Table 1** Results of previous studies that demonstrate the difference between MP2 and CCSD(T) \(\pi\cdot\pi\) stacking interaction energies in parallel-slipped systems with and without delocalized \(\pi\) electron clouds. All energies are in kcal mol\(^{-1}\).

<table>
<thead>
<tr>
<th>System</th>
<th>MP2</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen dimer(^a)</td>
<td>−0.58</td>
<td>−0.51</td>
</tr>
<tr>
<td>Acetylene dimer(^a)</td>
<td>−1.99</td>
<td>−1.72</td>
</tr>
<tr>
<td>Benzene dimer(^a)</td>
<td>−4.95</td>
<td>−2.78</td>
</tr>
<tr>
<td>Pyrrole dimer(^a)</td>
<td>−0.63</td>
<td>+0.45</td>
</tr>
<tr>
<td>Pyrimidine dimer(^a)</td>
<td>−3.87</td>
<td>−2.64</td>
</tr>
<tr>
<td>Triazine dimer(^a)</td>
<td>−3.77</td>
<td>−2.79</td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. 11. \(^{b}\) Ref. 4. \(^{c}\) Ref. 3.
surface have been subjected to substantial scrutiny in order to determine the precise theoretical treatment necessary to accurately describe the structure of each dimer. Broadly, we have considered the effects of theoretical method, basis set, counterpoise correction, and the rigid monomer approximation on the overall structure and energetics of both the parallel-slipped and T-shaped structures of the cyanogen and diacetylene dimers. In order to quantify the effects of all of these factors on the structure of each dimer, we report the intermolecular geometrical parameters of the dimers. For T-shaped structures (see Fig. 1), there is only one such parameter, $R_1$, that indicates the distance between the center of mass of the cross of the T and the proximal atom on the leg of the T. For the parallel-slipped structures, there are two relevant parameters: the distance $R_1$ between the two lines containing the C–C single bonds in the monomers and the parallel distance $R_2$ of slip between the midpoints of the C–C single bonds of the two monomers.

The parallel-slipped and T-shaped structures of both $(\text{N} \equiv \text{C} \equiv \text{C} \equiv \text{N})_2$ and $(\text{HC} \equiv \text{C} \equiv \text{C} \equiv \text{CH})_2$ have been optimized at the MP2 and CCSD(T) levels of theory in conjunction with a series of double-, triple-, and quadruple-$\xi$ basis sets. Three of the basis sets, denoted a$\alpha$X where $X = \text{D}$, T, Q, are taken from Dunning’s correlation consistent family of basis sets (cc-pVXZ for H and aug-cc-pVXZ for N and C). The a$5\alpha$Z basis set is also used in this work but only for single point energy computations. In addition to the a$\alpha$X basis sets, we have employed both the DZP++ and TZ2P(f,d)++ basis sets. These are the standard Huzinaga–Dunning DZ and TZ basis sets augmented with polarization functions as well as with one set of even-tempered diffuse functions on all atoms. For consistency, we use the terms a$\alpha$X, DZP++, and TZ2P(f,d)++ to describe the basis sets used for both cyanogen and diacetylene dimer. It is important to note, however, that cyanogen contains no hydrogen atoms, and in such cases the a$\alpha$X, DZP++, and TZ2P(f,d)++ basis sets are simply the aug-cc-pVXZ, the DZP+, and the TZ2P(f)+ basis sets, respectively.

Basis set superposition error is well known to be a concern in weakly bound clusters such as those studied here. The counterpoise correction of Boys and Bernardi is a popular method for correcting this error and has been incorporated into energy derivatives. It is therefore possible to compute a CP-corrected optimized geometry in addition to a CP-corrected energy. The differences between the CP-corrected and uncorrected geometries can be used to quantify the importance of BSSE in the geometry of the dimer. For this reason, we have computed CP-corrected geometries at the MP2 level with the

Fig. 1 The intermolecular geometrical parameters reported for the parallel-slipped (left) and T-shaped (right) structures of $(\text{HC} \equiv \text{C} \equiv \text{C} \equiv \text{CH})_2$ (top) and $(\text{N} \equiv \text{C} \equiv \text{C} \equiv \text{N})_2$ (bottom). See text for precise definitions of $R_1$ and $R_2$. 

aDZ, aTZ, DZP++, and TZ2P(f,d)++ basis sets for both the parallel-slipped and T-shaped structures.

Due to the small magnitude of $\pi \cdots \pi$ interactions, it is commonly assumed that the these intermolecular forces have negligible effects on the intramolecular geometries of monomers in $\pi \cdots \pi$ complexes, and many theoretical studies of such systems very frequently employ the rigid monomer approximation. In order to assess the quality of this approximation, we have optimized the T-shaped and parallel-slipped cyanogen and diacetylene dimer structures within the rigid monomer (RM) approximation in addition to performing full geometry optimizations.

For each optimized structure, an estimate of the CCSD(T) complete basis set interaction energy ($E_{\text{int}}^{\text{bestest}}$) was determined to gauge the impact of the various optimization procedures on $\pi \cdots \pi$ stacking energies. This best estimate was constructed by combining the MP2 interaction energy at the CBS limit ($E_{\text{int}}^{\text{MP2}}$) with the difference between MP2 and CCSD(T) interaction energies computed with the aTZ basis set ($\Delta E_{\text{int}}^{\text{MP2}}$). The MP2 CBS limit was generated via the two point (aQZ/a5Z) extrapolation of Helgaker et al. $E_{\text{int}}^{\text{bestest}}$ is used to judge the reliability of each optimization procedure and to generate guidelines for the optimization methods needed to obtain quantitatively accurate structures and energetics for similar complexes in the future. Note, however, that CP corrections have not been applied to the interaction energies because the $\Delta E_{\text{int}}^{\text{MP2}}$ term converges very rapidly with respect to the AO basis set and BSSE tends to be negligible for the expansive aQZ and a5Z basis sets.

Calculations for this work were carried out with a variety of quantum chemistry software packages. MP2 optimizations were performed using the analytic gradients available in the Gaussian 03 suite of programs. CCSD(T) optimizations were carried out with the analytic gradients in the ACES II package. Geometries were considered converged when Cartesian gradients fell below $1 \times 10^{-5} E_h a_0^{-1}$. MPQC45 and PSI346 were used for most MP2 and CCSD(T) single point energy calculations, and all energies were converged to $1 \times 10^{-7} E_h$. All calculations (optimizations and single point energies) incorporated the frozen-core approximation.

### Table 2: Important intermolecular geometrical parameters for all optimized structures. Definitions of $R_1$ and $R_2$ for the parallel-slipped and T-shaped dimer structures are shown in Fig. 1. All distances are in Å.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_{1p}$</th>
<th>$R_{2p}$</th>
<th>$R_{1m}$</th>
<th>$R_{2m}$</th>
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<td>Parallel-slipped (N == C==C == N)$_2$</td>
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<td>2.899</td>
<td>3.208</td>
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<td>3.597</td>
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<td>CCSD(T)</td>
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<td></td>
<td></td>
<td></td>
<td>2.700</td>
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</tr>
</tbody>
</table>

3. Results and discussion

3.1 Dimer structures

The T-shaped and parallel-slipped dimer structures have been optimized at the MP2 level of theory with five different basis sets (aDZ, aTZ, aQZ, DZP++, and TZ2P(f,d)++). Despite the fact that the dimers of cyanogen and diacetylene are substantially smaller than benzene dimer, optimizations with the CCSD(T) method were not feasible with the large aTZ and aQZ basis sets. Additionally, CCSD(T) optimizations were not performed with the aDZ basis set due to peculiar discrepancies with the diacetylene monomer (vide infra).

Although the intermonomer geometrical parameters depicted in Fig. 1 and listed in Table 2 can change by a few tenths of an Å with the various optimization procedures, the optimized structures are energetically quite similar given the extremely flat nature of the potential energy surfaces. The T-shaped dimers appear to be somewhat less sensitive to the optimization procedures than the parallel-slipped structures. Interestingly, most of the monomers in the fully optimized dimers shown in Fig. 1 are distorted even more slightly from linearity (by $\approx 1^\circ$). Nevertheless, all of the T-shaped structures belong to the $C_{2v}$ point group. The monomer forming the top of the T bows slightly away from the monomer forming the leg of the T in the cyanogen dimer, while it bows toward the leg of the T in the diacetylene dimer. Likewise, all of the parallel-slipped structures identified still belong to the $C_{2h}$ point group despite the fact that the “free” terminal atoms of the monomers bow slightly away from each other while the other terminal atoms of the monomers bow toward each other. Cartesian coordinates for all optimized structures can be found in the ESL.‡

Optimizations of the diacetylene monomer warrant special attention. Both the aDZ basis used here and the parent fully augmented aug-cc-pVDZ basis set have difficulty describing the nature of the diacetylene monomer. MP2 and CCSD(T) calculations using these basis sets erroneously indicate that the linear structure of the diacetylene molecule has a doubly degenerate imaginary vibrational frequency of 105i cm$^{-1}$. 

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and 186i cm\(^{-1}\), respectively, that corresponds to the two degenerate bending modes that move the H atoms into a trans configuration. This result is reminiscent of the spurious imaginary frequencies recently reported for MP2 optimized structures of benzene and other arenes.\(^{47}\) The diacetylene situation is unique, however, insofar as the spurious frequencies arise here with a correlation consistent basis set. Previous examples of this phenomenon were explained by “an insidious basis set incompleteness error that varies strongly with [out-of-plane] geometric distortions” specific to the split valence basis sets \((e.g.,\ 6-311G)\). The correlation-consistent basis sets were described by Moran et al. as a remedy to this problem; that the problem seems to be occurring in these basis sets is thus a matter demanding further investigation.

3.1.1 Effect of basis set on structure. It is clear from the MP2/aTZ data in Table 2 that the intermolecular parameters \(R_1\) and \(R_2\) converge very quickly with respect to the cardinal number of the basis set \((X = D, T, Q)\). While the aDZ and aTZ geometrical parameters may differ by as much as 0.093 Å, results obtained with aTZ basis set are nearly identical to those from the large aQZ basis set. The aTZ and aQZ results differ by only a few thousandths of an Å which is quite remarkable given the extraordinarily flat nature of the PES along \(R_1\) and \(R_2\).

The data in Table 2 also show slightly larger MP2 intermonomer parameters for the fairly compact DZP++ and TZ2P\((f,d)++\) basis sets relative to results obtained with the much larger aTZ and aQZ correlation consistent basis sets. For example, \(R_1\) for the MP2/TZ2P\((f,d)++\) optimized structures is, on average, only 0.053 Å longer than in the MP2/aTZ optimized structures.

3.1.2 Effect of electron correlation on structure. Electron correlation generally has a larger effect on the structure of these \(\pi\cdots\pi\) dimers than does the basis set. CCSD(T) intermonomer parameters \((R_1\) and \(R_2\) in Table 2) obtained with the DZP++ and TZ2P\((f,d)++\) basis sets are on the order of 0.1 Å longer than the corresponding MP2 values. Interestingly, the differences between the MP2 and CCSD(T) intermonomer parameters tend to be more significant with the TZ2P\((f,d)++\) basis set than with the DZP++ basis set.

3.1.3 Effect of counterpoise correction on structure. Examining the CP corrected intermonomer parameters \((R_1^\text{CP}\) and \(R_2^\text{CP}\)) in Table 2, one sees rather large changes when a small double-\(\zeta\) quality basis set is employed. With the DZP++ basis set, the CP correction increases the monomer separation and the slip by well over 0.1 Å in every case and by as much as 0.3 Å in two cases. However, the effect of the CP correction quickly decreases when a larger basis set is used. CP corrections with the TZ2P\((f,d)++\) and aTZ basis sets increase the intermonomer parameters by only 0.062 and 0.041 Å on average, respectively. Interestingly, the MP2/TZ2P\((f,d)++\) optimized parameters are quite similar to the MP2/aTZ data. For example, the \(R_1\) values differ by only 0.018 Å on average. This similarity between optimized geometrical parameters obtained with the TZ2P\((f,d)++\) basis set and those from counterpoise corrected optimizations with large correlation consistent basis sets has been observed elsewhere for other weakly bound systems.\(^{48-51}\)

3.1.4 Effect of the rigid monomer approximation on structure. Despite the fact that the monomers are not perfectly linear in the fully optimized dimers, the rigid monomer approximation has almost no effect on the intermonomer geometrical parameters. Comparing the rigid monomer parameters \((R_1^\text{RM}\) and \(R_2^\text{RM}\)) in Table 2 to the fully optimized values \((R_1\) and \(R_2\)), one sees that the parameters typically change by less than 0.01 Å.

3.2 Dimer energetics

Having discussed the effects of the various optimization procedures on the structures of the dimers, we can now examine how the \(\pi\cdots\pi\) interaction energies are affected by these geometrical changes. Such effects must be carefully dissected because the typical procedure for computing high-accuracy \(\pi\cdots\pi\) interaction energies \((E_{\text{INT}}^{\text{BestEst}}}) involves combining large basis set MP2 computations \((\delta_{\text{INT}}^{\text{MP2}}}) with corrections from a small basis set CCSD(T) computation \((\delta_{\text{CCSD(T)}})\).\(^{9,52}\) Consequently, the three energetic parameters associated with

\begin{table}[h]
\centering
\caption{Effects of basis set and correlation treatment used for optimization on the MP2 and CCSD(T) interaction energies of the dimers of cyanogen and diacetylene. All energies are in kcal mol\(^{-1}\).}
\begin{tabular}{|c|c|c|c|}
\hline
Method & Basis & \(E_{\text{INT}}^{\text{MP2}}\) & \(\delta_{\text{CCSD(T)}}\) & \(E_{\text{INT}}^{\text{BestEst}}\) \\
\hline
Parallel-slipped \((\text{N}\equiv\text{C}\equiv\text{N})_2\) & MP2 & aDZ & -2.55 & +1.02 & -1.53 \\
 & MP2 & aTZ & -2.51 & +0.99 & -1.52 \\
 & MP2 & aQZ & -2.51 & +0.96 & -1.55 \\
 & MP2 & DZP++ & -2.52 & +0.92 & -1.60 \\
 & MP2 & TZ2P\((f,d)++\) & -2.50 & +0.87 & -1.63 \\
 & CCSD(T) & DZP++ & -2.41 & +0.68 & -1.73 \\
 & CCSD(T) & TZ2P\((f,d)++\) & -2.33 & +0.62 & -1.72 \\
T-shaped \((\text{N}\equiv\text{C}\equiv\text{N})_2\) & MP2 & aDZ & -2.47 & +0.66 & -1.81 \\
 & MP2 & aTZ & -2.44 & +0.62 & -1.81 \\
 & MP2 & aQZ & -2.44 & +0.62 & -1.81 \\
 & MP2 & DZP++ & -2.47 & +0.62 & -1.85 \\
 & MP2 & TZ2P\((f,d)++\) & -2.43 & +0.58 & -1.86 \\
 & CCSD(T) & DZP++ & -2.42 & +0.50 & -1.92 \\
 & CCSD(T) & TZ2P\((f,d)++\) & -2.36 & +0.46 & -1.91 \\
\hline
Parallel-slipped \((\text{H}\equiv\text{C}\equiv\text{C})_2\) & MP2 & aDZ & -2.41 & +1.45 & -0.97 \\
 & MP2 & aTZ & -2.49 & +1.28 & -1.21 \\
 & MP2 & aQZ & -2.48 & +1.26 & -1.22 \\
 & MP2 & DZP++ & -2.52 & +1.25 & -1.27 \\
 & MP2 & TZ2P\((f,d)++\) & -2.46 & +1.14 & -1.32 \\
 & CCSD(T) & DZP++ & -2.39 & +0.96 & -1.43 \\
 & CCSD(T) & TZ2P\((f,d)++\) & -2.21 & +0.82 & -1.39 \\
\hline
T-shaped \((\text{H}\equiv\text{C}\equiv\text{C})_2\) & MP2 & aDZ & -1.98 & +0.36 & -1.61 \\
 & MP2 & aTZ & -1.94 & +0.34 & -1.59 \\
 & MP2 & aQZ & -1.94 & +0.34 & -1.60 \\
 & MP2 & DZP++ & -1.97 & +0.33 & -1.65 \\
 & MP2 & TZ2P\((f,d)++\) & -1.94 & +0.32 & -1.61 \\
 & CCSD(T) & DZP++ & -2.01 & +0.30 & -1.71 \\
 & CCSD(T) & TZ2P\((f,d)++\) & -1.91 & +0.27 & -1.64 \\
\hline
\end{tabular}
\end{table}
this additive scheme ($E_{\text{INT}}^{\text{MP2}}, \delta_{\text{MP2}}^{\text{CCSD(T)}},$ and $E_{\text{INT}}^{\text{BestEst.}}$) are reported for the various optimized structures.

The interaction energies in Table 3 that correspond to MP2/aTZ optimized structures also exhibit rapid convergence with respect to the cardinal number of the basis set (X = D, T, Q). While the energetic parameters for the aDZ and aTZ optimized structures differ by more than 0.1 kcal mol$^{-1}$, the values never deviate by more than 0.03 kcal mol$^{-1}$ for the MP2/aTZ and MP2/aQZ optimized structures (which, as noted earlier, are virtually identical). Even the energetic data associated with the MP2/DZP++ and MP2/TZ2P(f,d)++ optimized structures are still within 0.12 kcal mol$^{-1}$ of the $E_{\text{INT}}^{\text{MP2}}, \delta_{\text{MP2}}^{\text{CCSD(T)}},$ and $E_{\text{INT}}^{\text{BestEst.}}$ values for the MP2/aQZ structures.

### 3.2.1 Effect of electron correlation on energetics.

By simply comparing the $E_{\text{INT}}^{\text{BestEst.}}$ values in Table 3 for CCSD(T) optimized structures to those optimized at the MP2 level with the same basis set, it would appear that there is no need to optimize structures with the “Gold Standard” of quantum chemistry (i.e., the CCSD(T) method). For example, the best estimates of the interaction energies for CCSD(T)/TZ2P(f,d)++ fully optimized structures differ by no more than 0.09 kcal mol$^{-1}$ from the values for the MP2/TZ2P(f,d)++ structures. However, changes to $E_{\text{INT}}^{\text{MP2}}$ and $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ can be much larger, especially for the parallel-slipped structures. In the case of the parallel-slipped diacetylene dimer, the MP2 CBS limit of the interaction energy changes by +0.25 kcal mol$^{-1}$ when the MP2/TZ2P(f,d)++ structure is reoptimized with the CCSD(T) method. At the same time, the $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ correction changes by −0.32 kcal mol$^{-1}$. Due to error cancellation, the best estimate of the interaction energy changes by only −0.07 kcal mol$^{-1}$. These observations are remarkably consistent with the predictions of Sinnokrot and Sherrill for the parallel-slipped benzene dimer where estimated CCSD(T)/aug-cc-pVQZ* potential energy curves suggest that the interaction energy will decrease by 0.15 kcal mol$^{-1}$ (from −2.78 to −2.63 kcal mol$^{-1}$) when the CCSD(T) optimized structure is used rather than the MP2 one.7

### 3.2.2 Effect of counterpoise correction on energetics.

Similarly, the CP correction does not appear to have any effect on the energetics when looking at $E_{\text{INT}}^{\text{BestEst.}}$ in Table 4. However, with the DZP++ basis set the $E_{\text{INT}}^{\text{MP2}}$ and $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ change by −0.44 and +0.48 kcal mol$^{-1}$, respectively, for parallel-slipped diacetylene dimer when the CP procedure is applied during the geometry optimization. Again, error cancellation produces best estimates of the interaction energy that differ by only 0.04 kcal mol$^{-1}$. When one progresses to the larger TZ2P(f,d)++ basis set, the magnitude of these deviations are substantially reduced. With this basis set, the energetic parameters change by no more than 0.12 kcal mol$^{-1}$ when structures are reoptimized with CP-corrected gradients.

### 3.2.3 Effect of rigid monomer approximation on energetics.

Interaction energies computed at the CCSD(T) and MP2 levels for fully optimized and rigid monomer structures are reported in Table 5. The two sets of values are virtually indistinguishable from each other; both the MP2 and CCSD(T) interaction energies for the dimers change by less than 0.08 kcal mol$^{-1}$ when the rigid monomer approximation is applied. The deviations tend to be slightly smaller for the TZ2P(f,d)++ basis set than for the DZP++ basis set.
Table 5  Effects of the rigid monomer approximation on the MP2 and CCSD(T) interaction energies of the dimers of cyanogen and diacetylene. All energies are in kcal mol$^{-1}$

| Optimization level | Fully optimized | Rigid monomer |
|--------------------|----------------|---------------|---------------|
|                     | $E_{\text{MP2}}$ | $\delta_{\text{MP2}}$ | $E_{\text{BestEst.}}$ | $E_{\text{MP2}}$ | $\delta_{\text{MP2}}$ | $E_{\text{BestEst.}}$ | $\Delta E_{\text{RM}}$ |
| Parallel-slipped (N=\text{C}-\text{C}≡\text{N})$_2$ | | | | | | | |
| MP2(DZP++) | -2.52 | +0.92 | -1.60 | -2.55 | +0.88 | -1.66 | -0.06 |
| CCSD(T)(DZP++) | -2.41 | +0.68 | -1.73 | -2.40 | +0.70 | -1.70 | +0.04 |
| MP2(TZ2P(f,d)++) | -2.50 | +0.87 | -1.63 | -2.50 | +0.83 | -1.67 | -0.04 |
| CCSD(T)(TZ2P(f,d)++) | -2.33 | +0.62 | -1.72 | -2.30 | +0.59 | -1.70 | +0.01 |
| T-shaped (N=\text{C}-\text{C}≡\text{N})$_2$ | | | | | | | |
| MP2(DZP++) | -2.47 | +0.62 | -1.85 | -2.41 | +0.63 | -1.78 | +0.07 |
| CCSD(T)(DZP++) | -2.42 | +0.50 | -1.92 | -2.38 | +0.54 | -1.84 | +0.08 |
| MP2(TZ2P(f,d)++) | -2.43 | +0.58 | -1.86 | -2.42 | +0.57 | -1.84 | +0.02 |
| CCSD(T)(TZ2P(f,d)++) | -2.36 | +0.46 | -1.91 | -2.36 | +0.48 | -1.88 | +0.02 |
| Parallel-slipped (HC=\text{C}-\text{C}≡\text{CH})$_2$ | | | | | | | |
| MP2(DZP++) | -2.52 | +1.25 | -1.27 | -2.54 | +1.20 | -1.34 | -0.07 |
| CCSD(T)(DZP++) | -2.39 | +0.96 | -1.43 | -2.36 | +0.95 | -1.40 | +0.05 |
| MP2(TZ2P(f,d)++) | -2.46 | +1.14 | -1.32 | -2.46 | +1.09 | -1.36 | -0.04 |
| CCSD(T)(TZ2P(f,d)++) | -2.21 | +0.82 | -1.39 | -2.18 | +0.80 | -1.38 | +0.01 |
| T-shaped (HC=\text{C}-\text{C}≡\text{CH})$_2$ | | | | | | | |
| MP2(DZP++) | -1.97 | +0.33 | -1.65 | -1.99 | +0.33 | -1.66 | -0.02 |
| CCSD(T)(DZP++) | -2.01 | +0.30 | -1.71 | -1.97 | +0.29 | -1.67 | +0.04 |
| MP2(TZ2P(f,d)++) | -1.94 | +0.32 | -1.61 | -1.92 | +0.30 | -1.62 | -0.00 |
| CCSD(T)(TZ2P(f,d)++) | -1.91 | +0.27 | -1.64 | -1.88 | +0.26 | -1.63 | +0.01 |

4. Conclusions

4.1 Structures

Fifteen different optimization procedures have been applied to the parallel-slipped and T-shaped structures of the cyanogen and diacetylene dimers. Use of the correlation consistent aDZ basis set (cc-pVDZ for H and cc-pVDZ for N and C) is not recommended for these systems because of anomalous imaginary frequencies associated with the diacetylene monomer. In contrast, the fairly compact TZ2P(f,d)++ basis set gives optimized intermonomer geometrical parameters that are very similar to those obtained from counterpoise corrected optimizations with the much larger aTZ basis set. As long as appropriate polarization and diffuse functions are included, the choice of basis set has only a modest effect on the intermonomer geometrical parameters (on the order 0.05 Å). The structures of the dimers are more sensitive to electron correlation than basis set. CCSD(T) intermonomer parameters are usually ≈0.1 Å longer than the MP2 values. With double-$\xi$ basis sets, counterpoise corrected optimized structures are significantly different (by 0.1–0.3 Å) from their uncorrected counterparts. However, the effect of the CP correction rapidly diminishes when a larger basis set is used. Differences are on the order of 0.05 Å when the TZ2P(f,d)++ basis set is used. The rigid monomer approximation has a negligible effect on the dimer structures.

4.2 Energies

Overall, the interaction energies of (N=\text{C}-\text{C}≡\text{N})$_2$ and (HC=\text{C}-\text{C}≡\text{CH})$_2$ are relatively insensitive to the optimization procedure. Some statistics associated with the 15 different optimization procedures are reported in Table 6 for each structure. The largest, smallest, and average interaction energies ($E_{\text{MP2}}$ and $E_{\text{BestEst.}}$) along with the maximum deviation from the mean provide some insight into how widely the interaction energies vary with the optimization procedures.

As can be seen from Table 6, the 15 $E_{\text{BestEst.}}$ values tend to lie within 0.12 kcal mol$^{-1}$ of the average (−1.64 ± 0.12 kcal mol$^{-1}$) for parallel-slipped (N=\text{C}-\text{C}≡\text{N})$_2$, −1.85 ±

| Optimization level | Fully optimized | Rigid monomer |
|--------------------|----------------|---------------|---------------|
|                     | $E_{\text{MP2}}$ | $\Delta E_{\text{RM}}$ | $E_{\text{BestEst.}}$ | $\Delta E_{\text{RM}}$ |
| Parallel-slipped (N=\text{C}-\text{C}≡\text{N})$_2$ | | | | |
| Largest | -2.55 | -1.73 |
| Smallest | -2.30 | -1.52 |
| Average | -2.45 | -1.64 |
| Max. dev. | 0.15 | 0.12 |
| T-shaped (N=\text{C}-\text{C}≡\text{N})$_2$ | | | | |
| Largest | -2.47 | -1.92 |
| Smallest | -2.31 | -1.78 |
| Average | -2.41 | -1.85 |
| Max. dev. | 0.10 | 0.07 |
| Parallel-slipped (HC=\text{C}-\text{C}≡\text{CH})$_2$ | | | | |
| Largest | -2.54 | -1.43 |
| Smallest | -2.08 | -0.97$^a$ |
| Average | -2.38 | -1.31$^b$ |
| Max. dev. | 0.30 | 0.34$^c$ |
| T-shaped (HC=\text{C}-\text{C}≡\text{CH})$_2$ | | | | |
| Largest | -2.01 | -1.71 |
| Smallest | -1.82 | -1.59 |
| Average | -1.94 | -1.63 |
| Max. dev. | 0.12 | 0.08 |

$^a$ Changes to −1.21 when aDZ data omitted. $^b$ Changes to −1.33 when aDZ data omitted. $^c$ Changes to −0.12 when aDZ data omitted.
energies of these dimers (on the order of 0.05 kcal mol$^{-1}$). The parallel-slipped structure of (HC\textsubscript{2}C=C=CH\textsubscript{2}) is the only exception where the maximum deviation from the mean $E_{\text{best}}$\textsuperscript{EST} value jumps to more than 0.3 kcal mol$^{-1}$ ($-1.31 \pm 0.34$ kcal mol$^{-1}$). However, if data from the problematic aDZ basis (vide supra) is omitted, this distribution is narrowed to $-1.33 \pm 0.12$ kcal mol$^{-1}$. Consequently, the optimization procedure has little bearing on most applications.

The situation is rather different when the target accuracy of a study is on the order of a few tenths of a kcal mol$^{-1}$. Then, the geometry optimization procedure must be carefully considered along with core correlation, relativistic, and other subtle effects. Fortunately, the detailed examination of the energetics of these new $\pi \cdots \pi$ prototypes presented here provides some guidelines for high-accuracy studies of conjugated $\pi \cdots \pi$ complexes. Both the structures and energetics of these systems converge very rapidly with size of the basis set. Results obtained with the aTZ basis set are essentially identical to those computed with the much larger aQZ basis set. The rigid monomer approximation has very little impact on interaction energies of these dimers (on the order of 0.05 kcal mol$^{-1}$). It is also tempting to conclude that CP corrected optimizations and CCSD(T) optimizations have a negligible impact on energetics. However, the small changes to $E_{\text{best}}$(\textsuperscript{EST}) that occur when these procedures are applied are often due to the cancellation of more substantial errors in $E_{\text{MP2}}$ and $E_{\text{MP2}}$(\textsuperscript{CCSD(T)}). One should note that this cancellation will always occur at a point that is either a minimum or a transition state on both potential energy surfaces being compared. There is no guarantee that the errors will cancel at other points on the surface or if the PESs are qualitatively different.

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**References**


