Effects of Heterogeneity in Small π-Type Dimers: Homogeneous and Mixed Dimers of Diacetylene and Cyanogen

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⑤ *Supporting Information*

ABSTRACT: The homo- and heterogeneous dimers of diacetylene (H−C≡C−C≡C−H) and cyanogen (N≡C−C≡N) were studied using ab initio electronic structure computations to probe the effects of heterogeneity on noncovalent interactions between systems with delocalized π electron networks. Full geometry optimizations and harmonic vibrational frequencies were performed using the robust coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) method with the triple-ζ plus 2 sets of polarization functions TZ2P(f,d)++ basis set. Seven basic configurations were examined for each dimer (cross, stacked, parallel-slipped, parallel-tipped, linear, T-shaped and Y-shaped), but only four stationary points were identified on the potential energy surfaces (PESs) of the homogeneous cyanogen dimer and the mixed diacetylene/cyanogen dimer. Six previously characterized stationary points on the diacetylene dimer PES were re-examined with the CCSD(T) method and the TZ2P(f,d)++ basis set for consistency. Second-order Møller−Plesset perturbation theory (MP2) and CCSD(T) complete basis set (CBS) limit interaction energies were estimated using the explicitly correlated MP2-F12 and CCSD(T)-F12 methods in conjunction with the VQZ-F12 basis set. On the cyanogen dimer PES, the C_{2v} T-shaped structure is the only minimum, with an average electronic interaction energy, E_{int}, of −1.96 kcal mol^{-1} at the CCSD(T) CBS limit. The C_s Y-shaped structure (in agreement with previous results) is the global minimum on the diacetylene dimer PES, having a mean CCSD(T) CBS limit E_{int} of −1.75 kcal mol^{-1}. Three low-lying minima have been identified on the diacetylene/cyanogen dimer PES, a $C_{\infty v}$ linear, a C_{2v} cross, and a C_s parallel-slipped structure with average CCSD(T) CBS limit interaction energies of −2.00, −2.16, and −2.45 kcal mol^{-1}, respectively.

1. INTRODUCTION

Noncovalent interactions play significant roles in the organization of many molecular and supra-molecular systems.[1−5] These forces impact the arrangement and function of large molecular clusters,[6] biomolecules,[7−12] organic crystals[13] and nanomaterials.[14,15] Additionally, certain drugs rely on noncovalent interactions to enhance specificity.[16,17]

The attractive forces between aromatic moieties, often collectively referred to as $\pi\cdots\pi$ or stacking interactions, have received considerable attention in recent years,[18] but it is now becoming recognized that aromaticity is not a requirement for those favorable interactions.[19] The linear molecules cyanogen (ethanedinitrile or simply Cy) and diacetylene (1,3-butadiyne or simply Di) are small but useful model systems for π-type interactions.[20] It is rather challenging to compute accurate interaction energies for the dispersion-bound dimers of these simple molecules,[21] a trait more commonly associated with larger aromatic molecules such as those found in benchmark databases of noncovalent interaction energies.[22−28] Because of their small size, it has been possible to study cooperative effects in trimers,[29] examine dynamical electron correlation effects beyond the coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) level,[30] probe the basis set dependence of CCSD(T) higher-order correlation corrections,[31] and even compute CCSD(T) harmonic vibrational frequencies analytically for six fully optimized stationary points on the potential energy surface (PES) of (Di)$_2$.[32]

The present study extends our characterization of these small noncovalent complexes to the mixed Di/Cy dimer and provides the first detailed exploration of the Di/Cy PES. Only the parallel-displaced configuration has been examined in earlier work reporting that the heterogeneous parallel-displaced dimers exhibited appreciably larger interaction energies than their homogeneous counterparts.[33] Although the PES of (Cy)$_2$ was explored with Hartree−Fock (HF) computations as early as 1984,[34] this investigation provides the first harmonic vibrational frequencies beyond the HF level of theory.[35] To provide a consistent description of all 3 dimer systems that can be formed from the Cy and Di monomers, this work optimizes various stationary points of (Di)$_2$, (Cy)$_2$, and Di/Cy and computes the corresponding harmonic vibrational frequencies at the CCSD(T) level of theory with a triple-ζ basis set augmented with two sets of polarization functions as well as diffuse s- and p-type functions. These high-level frequency computations will furnish benchmark values that may be of growing importance in light of the Hessian index discrepancies recently reported between MP2 and density function theory (DFT) computations for simple hydrocarbon/water dimers.[36] Comparison of the structures and energetics of these small homo- and heterodimers may also provide some insight into aromatic donor−acceptor interactions where alternating electron-rich and electron-deficient aromatic groups are used to create supramolecular assemblies.[3,37−42]

2. COMPUTATIONAL METHODS

The CCSD(T) method,[43−47] commonly referred to as the "Gold Standard" of single-reference, ground state quantum chemistry, was used to fully optimize all dimer and monomer structures within their respective molecular point groups. Residual Cartesian gradients were less than 1.0×10^{-7} $E_h\, a_0^{-1}$ for all optimized structures. The nature of each stationary point was characterized as a minimum or a higher-order saddle point based on CCSD(T) harmonic vibrational frequency calculations. The Huzinaga−Dunning triple-ζ basis set with two sets of polarization functions, one set of even-tempered diffuse functions and one set of higher angular momentum functions (f and d) on all atoms, denoted TZ2P(f,d)++, was employed.[48−50] This basis set contains the same types and numbers of polarization and higher angular momentum functions as the more popular correlation consistent triple-ζ basis set augmented with diffuse functions (aug-cc-pVTZ).[51,52] The most significant difference stems from the diffuse functions. The TZ2P(f,d)++ only adds a single diffuse s-type function to H and a set of diffuse s- and p-type functions to C and N. In contrast, the aug-cc-pVTZ basis set adds diffuse functions for each value of the angular momentum (s, p, and d for H and s, p, d, and f for C and N). Although the TZ2P(f,d)++ basis set is appreciably smaller, second-order Møller−Plesset perturbation theory (MP2) optimizations of the T-shaped and parallel-displaced configurations of $(Cy)_2$ and $(Di)_2$ reveal that structures obtained with the two basis sets yield nearly identical MP2 complete basis set (CBS) limit interaction energies (within 0.03 kcal mol^{-1}).[20] The number of basis functions associated with each type of atom are summarized in Table 1 of Reference 31.

Interaction energies (E_{int}) were computed for all optimized dimer stationary points by taking the difference between the electronic energy of the complex and that of separated, fully optimized fragments.

$$E_{int} = E(\text{complex}) - \sum E(\text{fragments}) \qquad (1)$$

Note that the dissociation energy (D_e) of a minima on the PES dissociation energy is simply $-E_{int}$. For each stationary point, the CCSD(T) complete basis set (CBS) limit electronic energy, $E_{int}^{CCSD(T)/CBS}$, was determined using three computational procedures. First, explicitly correlated MP2-F12 computations employing the 3C(FIX) ansatz provided MP2 CBS electronic interaction energies, $E_{int}^{MP2/CBS}$.[53−56] The associated cc-pVQZ-F12 basis set (denoted VQZ-F12)[57,58] was used. The corresponding default density fitting and resolution of the identity basis sets in the Molpro 2010 software package[59] were used. A correction for higher-order correlation effects, $\delta_{MP2}^{CCSD(T)}$, was then calculated by considering the difference between CCSD(T) and MP2 interaction energies computed with a correlation consistent triple-ζ basis set that augments the heavy (i.e., non-hydrogen) atoms with diffuse functions (i.e., cc-pVTZ for H and aug-cc-pVTZ for C and N).

$$\delta_{MP2}^{CCSD(T)} = \Delta E_{int}^{CCSD(T)/haTZ} - \Delta E_{int}^{MP2/haTZ} \qquad (2)$$

The CCSD(T) CBS limit was calculated by applying this correction for high order correlation effects to MP2 CBS electronic interaction energies.

$$E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)} \qquad (3)$$

Additionally, for each stationary point, $E_{int}^{CCSD(T)/CBS}$ was estimated with explicitly correlated CCSD(T)-F12 computations with the VQZ-F12 basis set. The perturbative triples contribution to the CCSD(T)-F12b energy was not scaled. Explicitly correlated methods provide interaction energies close to the CBS limit, where basis set superposition error (BSSE)[60,61] vanishes. Also, in a recent report by our group, CP corrections did not uniformly improve the description of higher-order correlation correction to the CCSD(T) CBS limit for these systems.[31] Nevertheless, counterpoise (CP) corrected[62,63] CCSD(T)-F12b interaction energies have also been computed to provide another means of assessing the quality of the estimated CBS limits.

The CCSD(T) geometry optimizations and harmonic vibrational frequencies were carried out with the analytical gradients and Hessians available in the CFOUR software package.[64] The MP2-F12 and CCSD(T)-F12 computations were performed using the Molpro 2010 software package.[59] The frozen core approximation was employed for all MP2 and CCSD(T) computations.

3. RESULTS AND DISCUSSION

3.1. Cyanogen Dimer. Four stationary points on the $(Cy)_2$ potential energy surface have been characterized: a stacked configuration in D_{2h} symmetry, a cross configuration in D_{2d} symmetry, a parallel-slipped configuration in C_{2h} symmetry, and a T-shaped configuration in C_{2v} symmetry. These structures are shown in Figure 1, along with key intermolecular geometrical
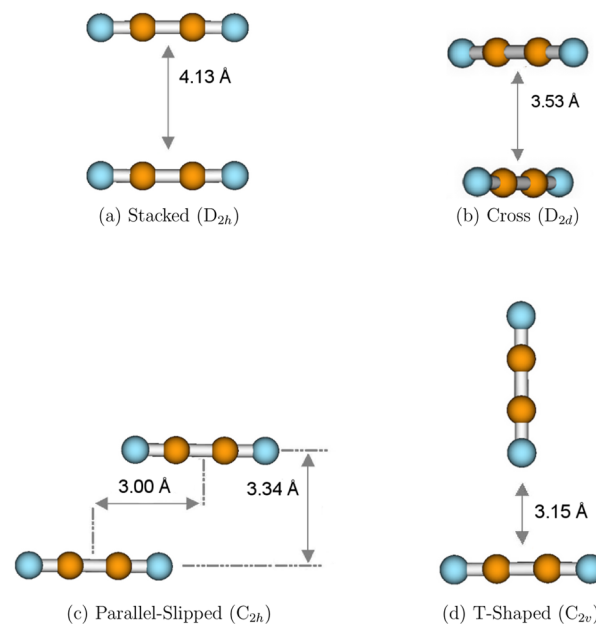
Figure 1. Configurations, intermolecular geometrical parameters (in Å) and point group symmetries of $(Cy)_2$. Arrows in parallel-slipped structure denote "horizontal" and "vertical" separations between midpoints of the C−C bonds.
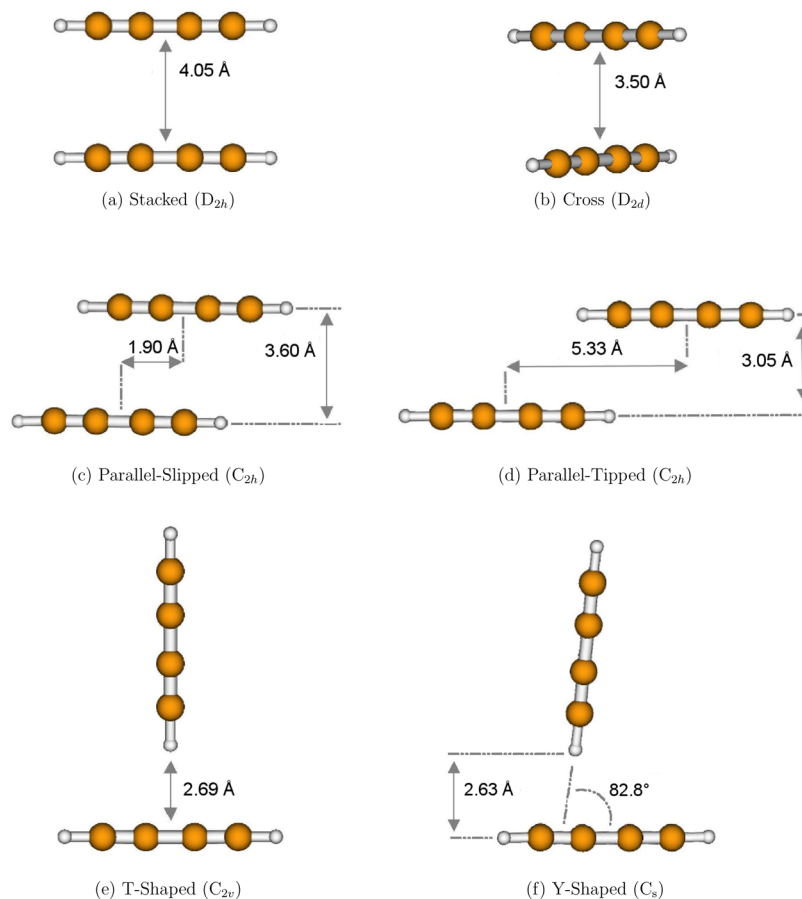
parameters that are typically defined relative to the midpoint of one or both central C−C bonds. It should be noted that although the cyanogen and diacetylene appear to be linear in all of the figures, they are often slightly bowed, as described in detail elsewhere.[20,32]

For each configuration, estimates of the MP2 and CCSD(T) complete basis set (CBS) limits of E_{int} are reported in Table 1.

Table 1. Number of Imaginary Vibrational Frequencies (n_i), CBS Limit Interaction Energies (E_{int} in kcal mol^{-1}) and Higher-Order Correlation Effects ($\delta_{MP2}^{CCSD(T)}$ in kcal mol^{-1}) for Stationary Points of Cyanogen Dimer

structure	n_i [a]	E_{int} [a]	$E_{int}^{MP2/CBS}$ [b]	$\delta_{MP2}^{CCSD(T)}$ [c]	$E_{int}^{CCSD(T)/CBS}$ [d]	$E_{int}^{CCSD(T)/CBS}$ [e]	$E_{int}^{CCSD(T)/CBS}$ [e,f]	Average $E_{int}^{CCSD(T)/CBS}$
stacked	2	+0.02	−0.21	+0.28	+0.07	+0.08	+0.10	+0.08
cross	1	−0.64	−1.09	+0.51	−0.58	−0.57	−0.55	−0.57
parallel-slipped	1	−1.72	−2.37	+0.60	−1.77	−1.76	−1.73	−1.75
T-shaped	0	−2.02	−2.42	+0.45	−1.97	−1.97	−1.95	−1.96

[a]CCSD(T)/TZ2P(f,d)++. [b]MP2-F12/VQZ-F12. [c]$\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$. [d]$E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$. [e]CCSD(T)-F12/VQZ-F12. [f]Counterpoise Corrected.

(a) Stacked (D$_{2h}$)

(b) Cross (D$_{2d}$)

(c) Parallel-Slipped (C$_{2h}$)

(d) Parallel-Tipped (C$_{2h}$)

(e) T-Shaped (C$_{2v}$)

(f) Y-Shaped (C$_s$)

Figure 2. Configurations, intermolecular geometrical parameters (in Å) and point group symmetries of (Di)$_2$. Arrows in parallel structures denote "horizontal" and "vertical" separations between midpoints of the C−C bonds.

The last column reports the average of the three CCSD(T) CBS values. There is little difference between the three procedures used to generate the CCSD(T) CBS limit, the maximum deviation from the mean is ±0.02 kcal mol^{-1}.

The T-shaped structure is a minimum on the surface, having an average electronic interaction energy (E_{int}) at the CCSD(T) CBS limit of −1.96 kcal mol^{-1}. The parallel-slipped structure is a transition state (i.e., one imaginary frequency) that lies only 0.21 kcal mol^{-1} above the minimum at the same level of theory. The other two configurations (cross and stacked) are more than 1 kcal mol^{-1} higher in energy at all levels of theory. The cross configuration has one doubly degenerate imaginary frequency while the stacked structure has two imaginary frequencies.

MP2 overbinds the dimers of Cy relative to CCSD(T) by as much as 0.60 kcal mol^{-1} as shown by the column of $\delta_{MP2}^{CCSD(T)}$ values in Table 1. Their magnitudes are appreciable relative to E_{int} for every configuration of Cy dimer, and these higher-order

correlation corrections produce some significant differences between the MP2 and CCSD(T) PESs. At the MP2 CBS limit, the parallel-slipped structure is essentially isoenergetic with the T-shaped minimum, whereas the two structures are separated by at least −0.20 kcal mol^{-1} on the CCSD(T) PESs. It is also interesting to note that the stacked structure is bound by 0.21 kcal mol^{-1} at the MP2 CBS limit. With the CCSD(T) method, however, the structure actually lies above the dissociation limit (i.e., a positive interaction energy), a situation reminiscent of anion/π interactions between halide anions and the face of benzene.[65,66]

The zero-point vibrational energy (ZPVE) does not qualitatively alter the energetics of (Cy)$_2$. For example, the CCSD(T)/TZ2P(f,d)++ unscaled harmonic vibrational frequencies decrease the magnitude of E_{int} by 0.24 kcal mol^{-1}, yielding a ZPVE-corrected interaction energy (E_{int}°) of −1.72 kcal mol^{-1}. Vibrational frequencies are reported in the Supporting Information so that scaling factors and other

Table 2. Number of Imaginary Vibrational Frequencies (n_i), CBS Limit Interaction Energies (E_{int} in kcal mol^{-1}), and Higher-Order Correlation Effects ($\delta_{MP2}^{CCSD(T)}$ in kcal mol^{-1}) for Stationary Points of Diacetylene Dimer

structure	n_i [a]	E_{int} [a]	$E_{int}^{MP2/CBS}$ [b]	$\delta_{MP2}^{CCSD(T)}$ [c]	$E_{int}^{CCSD(T)/CBS}$ [d]	$E_{int}^{CCSD(T)/CBS}$ [e]	$E_{int}^{CCSD(T)/CBS}$ [e,f]	Average $E_{int}^{CCSD(T)/CBS}$
stacked	2	−0.52	−1.05	+0.60	−0.45	−0.44	−0.40	−0.43
cross	0	−1.36	−2.05	+0.87	−1.18	−1.17	−1.12	−1.16
parallel-slipped	1	−1.42	−2.27	+0.81	−1.46	−1.44	−1.40	−1.43
parallel-tipped	1	−1.61	−1.92	+0.26	−1.66	−1.65	−1.62	−1.64
T-shaped	1	−1.84	−1.95	+0.27	−1.68	−1.68	−1.65	−1.67
Y-shaped	0	−1.94	−2.04	+0.28	−1.76	−1.76	−1.73	−1.75

[a]CCSD(T)/TZ2P(f,d)++. [b]MP2-F12/VQZ-F12. [c]$\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$. [d]$E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$. [e]CCSD(T)-F12/VQZ-F12. [f]Counterpoise Corrected.

schemes can be employed to compute ZPVE-corrected interaction energies for all dimer structures reported in this study.

3.2. Diacetylene Dimer. The six stationary points of (Di)$_2$ that have been characterized at the CCSD(T)/TZ2P(f,d)++ level of theory are shown in Figure 2. Four configurations are analogous to those of the Cy dimer. For (Di)$_2$, the Y-shaped (C_s symmetry) and parallel-slipped (C_{2h} symmetry) stationary points have also been located. Estimates of the MP2 and CCSD(T) CBS limits of E_{int} are reported in Table 2. Again, the three estimates of the CCSD(T) CBS limit interaction energies are virtually identical, always lying within ±0.04 kcal mol^{-1} of their average.

The Y-shaped structure appears to be the global minimum on the PES, with an electronic interaction energy of −1.75 kcal mol^{-1} at the average CCSD(T) CBS limit. The cross configuration is also a mimimum, but it lies 0.59 kcal mol^{-1} higher in energy. Three other stationary points, T-shaped, parallel-tipped, and parallel-slipped, are transition states that actually lie below the cross local minimum and within a few tenths of a kcal mol^{-1} of the global minimum. Lastly, the stacked structure is a higher-order saddle point with two imaginary frequencies that lies more than 1 kcal mol^{-1} above the global minimum. In contrast to (Cy)$_2$, however, E_{int} remains negative at the CCSD(T) level of theory for the stacked structure of (Di)$_2$ despite the sizable $\delta_{MP2}^{CCSD(T)}$ correction. Higher-order correlation effects approach 0.9 kcal mol^{-1} in (Di)$_2$ leading to rather different descriptions of the surface between the MP2 and CCSD(T) methods. For example, MP2 CBS E_{int} values indicate that the cross minimum is nearly isoenergetic with the Y-shaped global minimum. At the CCSD(T) CBS limit, however, the cross minimum lies nearly 0.6 kcal mol^{-1} above the Y-shaped structure.

Note that CCSD(T)/TZ2P(f,d)++ vibrational frequencies indicate the parallel-slipped structure as a transition state even though it was a minimum on the CCSD(T)/DZP++ PES.[32] This mode corresponds to an A$_u$ out-of-plane twisting motion of monomers relative to each other that converts the parallel-slipped stationary point to a cross-like structure. Such a discrepancy is not too surprising given the extremely flat nature of the PES in this region. In each case, the magnitude of the frequency associated with the mode in question was less than 20 cm^{-1} (18 cm^{-1} with the DZP++ basis set versus 5i cm^{-1} with the TZ2P(f,d)++ basis set). This small difference could potentially be resolved by using tighter convergence criteria for the geometry optimizations, but the quality of the basis set is the more likely culprit. BSSE can also induce qualitative changes in intermolecular PESs.[67] Unfortunately we do not currently have the means to analytically evaluate CP corrected gradients and Hessians at the CCSD(T) level of theory. The

vibrational frequencies are reported in the Supporting Information so that interested readers can directly compare the DZP++ and TZ2P(f,d)++ vibrational frequencies for the parallel-slipped structure of (Di)$_2$.

As with (Cy)$_2$, ZPVE does not qualitatively change the energetics for (Di)$_2$. The magnitude of E_{int} for the cross and Y-shaped minima decrease by 0.14 and 0.28 kcal mol^{-1}, respectively. E_{int}° is −1.02 kcal mol^{-1} for the former and −1.46 kcal mol^{-1} for the latter. The unscaled harmonic vibrational frequencies are reported in the Supporting Information for each stationary point.

3.3. Diacetylene/Cyanogen Dimer. Three low-lying minima have been located on the Di/Cy dimer PES (shown in Figure 3). Estimates of the MP2 and CCSD(T) CBS limit of E_{int} are reported in Table 3. Once again, the three methods for obtaining the CCSD(T) CBS limit interaction energy are nearly identical, with deviations from the mean not exceeding ±0.03 kcal mol^{-1}. The parallel-slipped structure (C_s symmetry) appears to be the global minimum with an average CCSD(T) CBS limit interaction energy of −2.45 kcal mol^{-1}. The cross
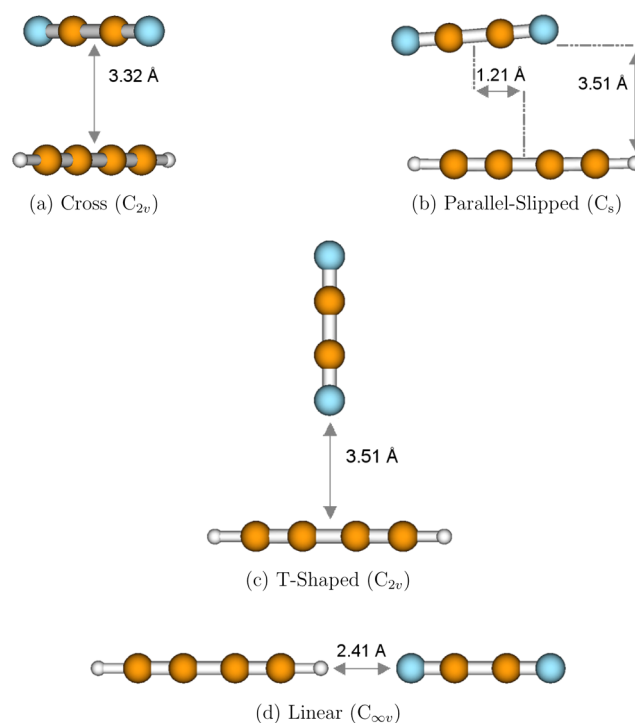
Figure 3. Configurations, intermolecular geometrical parameters (in Å), and point group symmetries of the mixed Di/Cy dimer. Arrows in parallel-slipped structure denote "horizontal" and "vertical" separations between midpoints of the C−C bonds.

Table 3. Number of Imaginary Vibrational Frequencies (n_i), CBS Limit Interaction Energies (E_{int} in kcal mol^{-1}), and Higher-Order Correlation Effects ($\delta_{MP2}^{CCSD(T)}$ in kcal mol^{-1}) for Stationary Points of Diacetylene/Cyanogen Dimer

structure	n_i [a]	E_{int} [a]	$E_{int}^{MP2/CBS}$ [b]	$\delta_{MP2}^{CCSD(T)}$ [c]	$E_{int}^{CCSD(T)/CBS}$ [d]	$E_{int}^{CCSD(T)/CBS}$ [e]	$E_{int}^{CCSD(T)/CBS}$ [e,f]	Average $E_{int}^{CCSD(T)/CBS}$
T-shaped	2	−0.43	−0.51	+0.29	−0.22	−0.22	−0.20	−0.21
linear	0	−2.07	−2.18	+0.18	−2.00	−2.00	−2.00	−2.00
cross	0	−2.24	−3.08	+0.89	−2.19	−2.17	−2.13	−2.16
parallel-slipped	0	−2.32	−3.30	+0.82	−2.48	−2.45	−2.42	−2.45

[a]CCSD(T)/TZ2P(f,d)++. [b]MP2-F12/VQZ-F12. [c]$\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$. [d]$E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$. [e]CCSD(T)-F12/VQZ-F12. [f]Counterpoise Corrected.

(C_{2v} symmetry) and linear ($C_{\infty v}$ symmetry) structures are also minima with slightly smaller average CCSD(T) CBS limit interaction energies of −2.16 kcal mol^{-1} and −2.00 kcal mol^{-1}, respectively. Although two unique C_{2v} T-shaped structures are possible for the mixed dimer, a stationary point was located only for the configuration where the cyanogen monomer lies on the 2-fold rotational axis of symmetry (as shown in Figure 3). That T-shaped structure is a second-order saddle point with an interaction energy of only −0.21 kcal mol^{-1} at the CCSD(T) CBS limit. No stationary point was found for the other T-shaped configuration that has the diacetylene monomer on the C_2 axis.

Again, MP2 tends to overbind relative to CCSD(T). Interestingly, the $\delta_{MP2}^{CCSD(T)}$ values of the mixed Di/Cy dimer are nearly identical to those of the corresponding $(Di)_2$ structures (within 0.02 kcal mol^{-1}). The C−H···N interaction associated with the linear Di/Cy appears to be much easier to describe than other configurations. It exhibits the smallest $\delta_{MP2}^{CCSD(T)}$ value (+0.18 kcal mol^{-1}) of any structure characterized on all three dimer PESs, and all three estimates of the CCSD(T) CBS limit E_{int} are identical (−2.00 kcal mol^{-1}).

ZPVE consistently decreases the magnitude of E_{int} for the three minima on the Di/Cy PES (by 0.21 to 0.34 kcal mol^{-1}). E_{int}° is −1.66 kcal mol^{-1} for the linear minimum, −1.95 kcal mol^{-1} for the cross structure, and −2.23 kcal mol^{-1} for the parallel-slipped global minimum. The unscaled harmonic vibrational frequencies for each stationary point can be found in the Supporting Information.

4. CONCLUSION

Four stationary points on the $(Cy)_2$ PES, six on the $(Di)_2$ PES, and four on the Di/Cy PES have been characterized via full geometry optimizations and harmonic vibrational frequencies computed with the CCSD(T) method and the TZ2P(f,d)++ basis set. CCSD(T) CBS limit interaction energies were estimated by combining explicitly correlated MP2-F12 computations with a higher-order correlation correction term. CCSD(T) CBS interaction energies were also estimated with CCSD(T)-F12 computations. Counterpoise corrections were also applied to CCSD(T)-F12 interaction energies. This work represents the first exploration of the Di/Cy PES and is also the first study to characterize stationary points of $(Cy)_2$ with correlated electronic structure methods.

Three minima were identified for the mixed Di/Cy dimer with interaction energies ranging from −2.00 to −2.45 kcal mol^{-1} at the average CCSD(T) CBS limit. In contrast, the homogeneous Cy dimer has only a single minimum on the PES, the T-shaped structure with an interaction energy approaching 2 kcal mol^{-1} at the same level of theory (−1.96 kcal mol^{-1}). The Y-shaped global minimum on the $(Di)_2$ PES has an even smaller interaction energy at the mean CCSD(T) CBS limit (−1.75 kcal mol^{-1}). There is second minimum on

the $(Di)_2$ PES (the cross structure), but it is appreciably higher in energy (E_{int} = −1.16 kcal mol^{-1}).

Comparison of E_{int} for the same configurations across the three dimer systems reveals some interesting trends. The cross and parallel-type configurations of these linear monomers, which are comparable to face-to-face (or "stacking") arrangements of aromatic systems, exhibit significantly larger interaction energies in the mixed dimer than in the homogeneous dimers. The situation is reversed for the T-shaped configurations, which are comparable edge-to-face arrangements of aromatic systems. These results are consistent with the preference for face-to-face stacking of alternating electron-rich and electron-deficient aromatic groups that has been used successfully as a design principle by several groups.[3,37−42]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Cartesian coordinates and harmonic vibrational frequencies for CCSD(T)/TZ2P(f,d)++ optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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