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Problematic Energy Differences between Cumulenes and Poly-ynes: Does This Point to a Systematic Improvement of Density Functional Theory?

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Relative energetics of the C_3H_4 (allene (**1**) and propyne (**2**)), C_5H_4 (penta-1,2,3,4-tetraene (**3**) and penta-1,3-diyne (**4**)), and C_7H_4 (hepta-1,2,3,4,5,6-hexaene (**5**) and hepta-1,3,5-triyne (**6**)) cumulene and poly-yne structures were systematically examined using DFT (B3LYP, BLYP, and BP86), MP2, and CCSD(T) theories. The isomer energy separations, ΔE, were studied with three schemes: standard optimizations and energy determinations (CCSD(T)/cc-pVXZ//MP2/cc-pVTZ), heats of formation predictions via isodesmic and homodesmotic reactions (CCSD(T)/cc-pVTZ//MP2/cc-pVTZ), and BHLYP functional analysis fitted to experimental data. For the C_3H_4 isomers, ΔE was determined to be −1.4 and −1.4 kcal/mol for the first two schemes, with the BHLYP functional analysis being fit to the experimental ΔE of −1.4 ± 0.5 kcal/mol. The three schemes yield ΔE values of −8.8, −10.1, and −11.7 kcal/mol, respectively, for the C_5H_4 isomers **3** and **4**. The C_7H_4 isomers **5** and **6** are separated by −14.3, −16.3, and −19.7 kcal/mol when the three schemes are applied. The theoretical heats of formations, ΔH_f, for **1** and **2** are 45.5 (47.4 ± 0.3) and 44.1 kcal/mol (46.0 ± 0.2) at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level, respectively (experimental values in parentheses). At the same level of theory, **3**−**6** give ΔH_f's of 111.1, 101.1, 171.6, and 155.4 kcal/mol, respectively. Results from BXLYP (X being a variable to describe the amount of HF exchange included) and energy decomposition analyses in conjunction with previous studies lead to the conclusions that gradient-corrected functionals are not properly constructed to handle delocalized cumulenes and that they tend to overstabilize them.

I. Introduction

Chemical computations have become an indispensable tool in the study and understanding of molecular structures and concepts such as resonance,[1−3] strain,[1,4−7] aromaticity,[8−15] as well as many others. This is in large part because of the fact that theoretical approaches can now rival experimental measurements, something shown to be true for small systems (1−4 heavy atoms) some time ago.[16] There are many elaborate schemes to evaluate the absolute and, more importantly, the relative energies of small molecules. Examples are G2,[17] G3,[18] and CBS[19] theories, as well as focal point analysis[20−22] energy extrapolations that have proven to be extremely accurate. However, when studies of larger systems are undertaken, these highly accurate methods may become prohibitively time-consuming. Very often, density functional theory (DFT)[23−25] then becomes the method of choice. Fortunately, DFT works well for quite a number of systems (some notable exceptions are known),[26−28] but the transferability of the quality of the results of smaller to larger molecules has yet to be examined in detail. A particular case in point, and the focus of the present work, is the poor performance of DFT for the relative energy separation of allene (**1**) and propyne (**2**). Knowing related energy differences is crucial in the prediction of relative energies and properties of, for instance, carbon-rich materials.[29−31] A typical example is monocyclic C_{20}, which may be a cumulene or a poly-yne (Figure 1).[32−35]

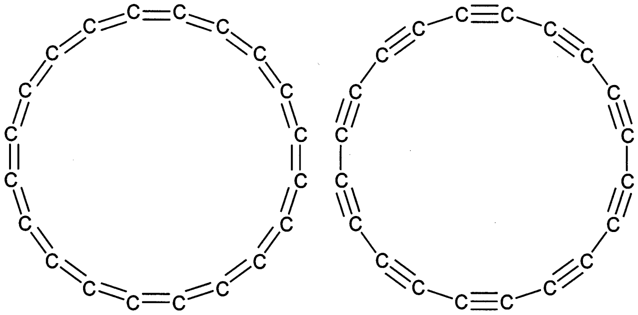

Figure 1. Monocyclic cumulene and poly-yne isomers of C_{20}.

Insight into this and related problems involving DFT can thus be gained through the systematic study of allene and propyne as well as their higher analogues at the highest level of theory possible. The results are important to many fields but will be of particular interest to the combustion and atmospheric chemistry communities, in part because of the discovery of the carbon- and hydrogen-rich atmosphere of Saturn's largest moon, Titan.[36−39] Large efforts are ongoing to determine and understand the chemical nature of medium to large organic molecules that compose much of the extraterrestrial atmospheres and may be indicative of the prebiotic earth environment.[40−42] Our effort is in part fueled by this, in addition to the fact that larger organic molecules existing in various states of unsaturation have been detected in numerous interstellar media.[43,44] Therefore, the pursuit of accuracy in treating medium to large systems by DFT is essential until new breakthroughs in computer technology and/or parallelization are made that allow the scaling problems[45] of more highly accurate methods (e.g., coupled cluster theory) to

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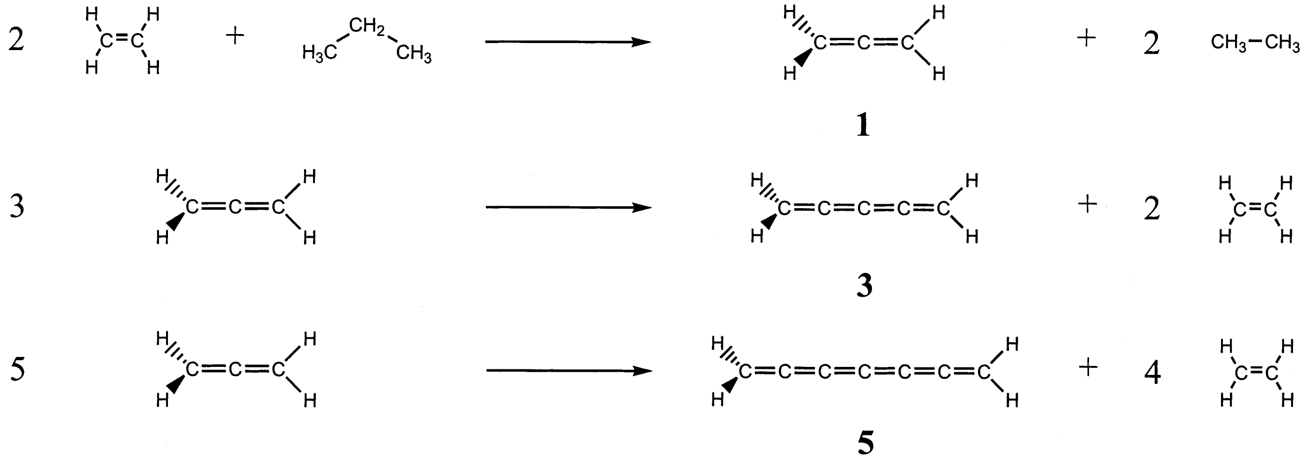

Figure 2. Isodesmic and homodesmotic equations employed in the prediction of heats of formation for allene (**1**), penta-1,2,3,4-tetraene (**3**), and hepta-1,2,3,4,5,6-hexaene (**5**). All structures were optimized at the MP2/cc-pVTZ level of theory.

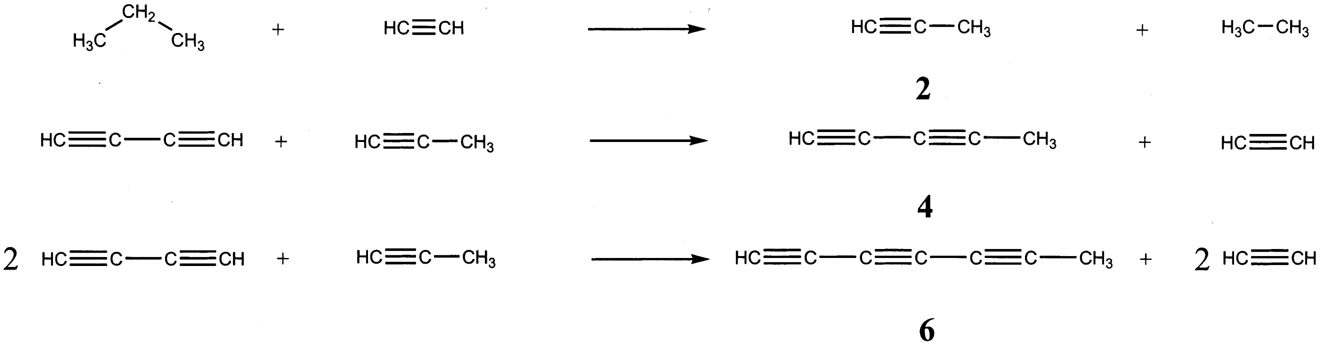

Figure 3. Isodesmic and homodesmotic equations employed in the prediction of heats of formation for propyne (**2**), penta-1,3-diyne (**4**), and hepta-1,3,5-triyne (**6**). All structures were optimized at the MP2/cc-pVTZ level of theory.

be overcome. Our analysis may also point to deficiencies in current DFT methodologies, aiding the attempt to systematically improve these highly useful methods.

A 2000 paper by Feller and Dixon[46] computed the atomization energies of allene and propyne at the CCSD(T)/aug-cc-pVQZ level of theory and extrapolated to values of 48.1 ± 0.5 and 46.5 ± 1.5 kcal/mol, respectively. This corresponds to an energy difference of −1.6 ± 2.0 kcal/mol, which is very close to the reported experimental energy difference of −1.4 ± 0.5 (47.4 ± 0.3−46.0 ± 0.2) kcal/mol.[47] We have generated appropriate isodesmic and homodesmotic equations to determine and predict the heats of formation (ΔH_f) of the C_3H_4, C_5H_4, and C_7H_4 cumulene and poly-yne isomers (Figures 2 and 3). These equations evaluated at the CCSD(T) level of theory may be compared to the results obtained via atomization energies as well as allow conclusions to be drawn about the accuracy of previously reported experimental results.

In addition, Kafafi, in 1998, investigated DFT methodologies and proposed a new functional (K2−BVWN) to accurately describe long-range molecular interactions and improve electronic and thermodynamic computations.[48] Kafafi concludes that the K2−BVWN functional is comparable to G2 theory when computing heats of formation and other energy-dependent properties. However, in this improved DFT scheme the relative energetics of allene and propyne are still miscalculated [ΔH_f(allene) = 43.1 kcal/mol and ΔH_f(propyne) = 44.3 kcal/mol] to yield an energy difference of 1.2 kcal/mol with the wrong sign.

It has been previously theorized that higher cumulenes will tend to break linearity as the length of the carbon chain increases.[49,50] Originally, such systems were thought to behave in the opposite manner with longer cumulated carbon chains tending to stay linear.[51] In an initial investigation of this phenomenon, Liang and Allen performed constrained optimizations at the RHF/4-31G level with energies computed through MP4(SDQ)/6-31G. From these optimizations and energetic analyses, the authors predicted bending frequencies that are extremely low and in many cases negative. As these results were inconclusive and left many unanswered questions, Liang, Xie, Schaefer, Kim, and Kim undertook a subsequent study.[50] The follow-up study explicitly examined CCC bending frequencies at the SCF, MP2, and CISD levels with moderately sized basis sets (6-31G, DZ, and TZ). The latter investigation revealed that the structural determination of higher cumulenes is largely basis set and method dependent with CISD/6-31G and MP2/6-31G yielding imaginary CCC bending frequencies (in cm^{-1}) of 560*i* and 754*i*, whereas CISD/TZ and MP2/TZ gave 382 and 177*i*.

Although the experimental heats of formation of allene (**1**) and propyne (**2**) are published, these data for larger cumulenes and poly-ynes are unknown. This work will be the first to report high quality heats of formation for C_5H_4 [penta-1,2,3,4-tetraene (**3**) and penta-1,3-diyne (**4**)] and C_7H_4 [hepta-1,2,3,4,5,6-hexaene (**5**) and hepta-1,3,5-triyne (**6**)], in addition to addressing the question of their linearity (the numbering scheme refers to Figures 2 and 3 and will be used througout).

In the current work, we will focus on comparing results of various DFT computations with those obtained using higher levels of theory, i.e., explicitly correlated methods (MP2 and CCSD(T)). This will be done throughout the current study in an attempt to ascertain the origin of the energetic errors which result when DFT is applied to the study of cumulenes and poly-ynes. Finally, our results should allow researchers to better formulate strategies to attack interesting computational problems as well as yield useful information about larger cumulenes and poly-ynes to assist future thermodynamic, kinetic, and atmospheric studies.

II. Theoretical Methods

Computations were performed with the Q-Chem[52] (DFT and MP2) or ACESII[53] (MP2 and CCSD(T)) quantum chemistry software packages. We employed three functionals (B3LYP,[54,55] BLYP,[56,55] and BP86[56,57]) at the DFT[23,24] level and ten Pople-type basis sets that ranged from 6-31G(d) to 6-311++G(2df,2pd)[1] (refer to figures). At the MP2[58] and CCSD(T)[59,60,61] levels of theory, Dunning's correlation-consistent basis sets were used (cc-pVXZ, X = D, T, and Q).[62]

Stationary points were obtained via standard analytic gradient methods,[63−65] with Cartesian gradients converged to 10^{-5} hartree/bohr, at all levels of theory. Structures and energetics were compared between the explicitly correlated methods, DFT, and experimental results (when available). It was found for allene and propyne that MP2/cc-pVTZ structures were quite close to the CCSD(T)/cc-pVTZ as well as to the experimental structures.

The allene and propyne geometries were optimized at both MP2 and CCSD(T) levels of theory using the cc-pVXZ (X = D and T) basis sets. The highest level energetics obtained for these were CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ. Penta-1,2,3,4-tetrane (**3**) and penta-1,3-diyne (**4**) also were optimized at both the MP2/cc-pVXZ (X = D and T) and CCSD(T)/cc-pVDZ levels of theory with energies reported (CCSD(T)/cc-pVTZ//MP2/cc-pVTZ). Finally, we obtained the hepta-1,2,3,4,5,6-hexaene (**5**) and hepta-1,3,5-triyne (**6**) structures at the MP2/cc-pVXZ (X = D and T) and CCSD(T)/cc-pVDZ levels of theory and higher order energetics with CCSD(T)/cc-pVTZ//MP2/cc-pVTZ.

III. Results

A. C_3H_4 Isomers: Allene and Propyne. Energy separations (ΔE) for the C_3H_4 isomers (allene and propyne) computed at various DFT levels of theory (B3LYP, BLYP, and BP86) are displayed in Figure 4. To facilitate the analysis of these data, results are reported as ΔE(computed) − ΔE(experimental) (i.e., the error) where propyne is experimentally 1.4 kcal/mol lower in energy then allene. This helps to highlight trends in functional and basis set performance for these systems. It is clear that at all levels of theory examined DFT performed poorly for the C_3H_4 isomers, as the relative energetics were reversed. B3LYP/6-311G exhibits the smallest deviation from experiment, with a still unacceptable error of 2.9 kcal/mol. This may be considered a "Pauling point", where fortuitous error cancellation leads to an apparently reasonable result.

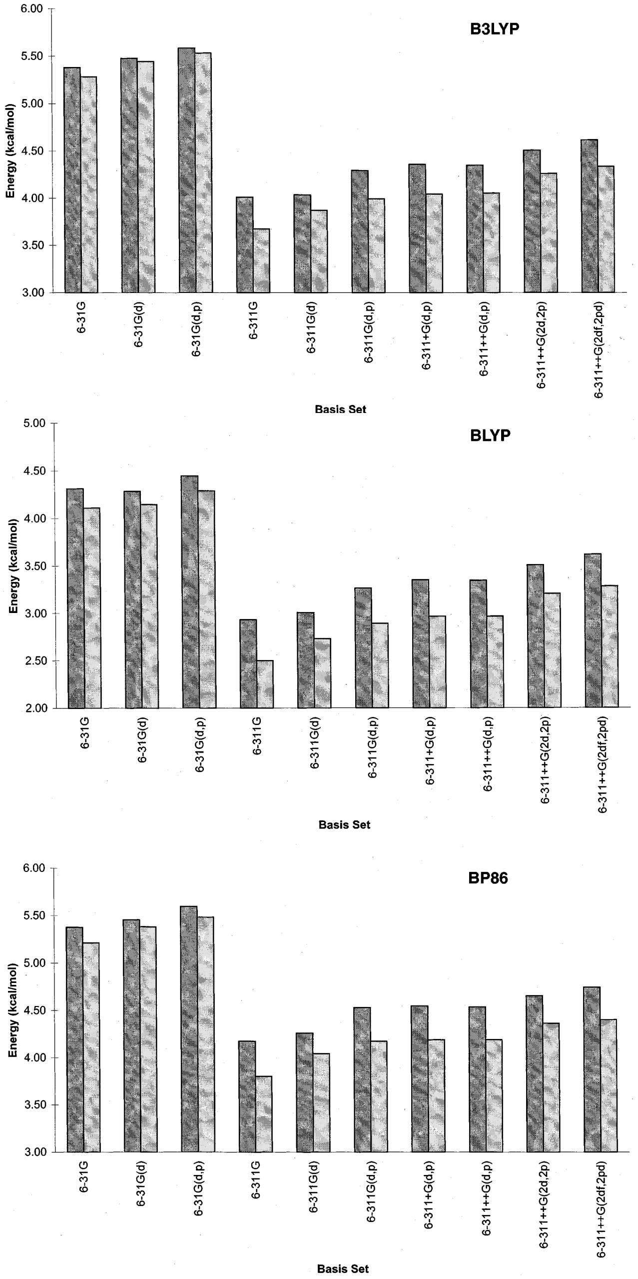

Figure 4. Deviations between theory and experiment [ΔE(theory) − ΔE(exp)] for the energy separation between allene (**1**) and propyne (**2**). A total of 10 Pople-type basis sets were employed at the B3LYP-(a), BLYP(b), and BP86(c) levels of theory. Dark gray bars correspond to ZPVE uncorrected results, with the light gray bars being ZPVE corrected.

TABLE 1: Energy Separations for the C_3H_4 Isomers Allene (1) and Propyne (2)[a]

level of theory	ΔE (kcal/mol)
MP2/cc-pVDZ	−4.6 (−4.4)
MP2/cc-pVTZ	−4.5 (−4.3)
MP2/cc-pVQZ//MP2/cc-pVTZ	−4.8
CCSD(T)/cc-pVDZ	−0.5 (−0.3)
CCSD(T)/cc-pVTZ	−1.0 (−0.7)
CCSD(T)/cc-pVQZ//MP2/cc-pVTZ	−1.4
experimental[47]	−1.4

[a] ΔE values are in kcal/mol and are computed from $E(\mathbf{2}) - E(\mathbf{1})$. T_0 values are in parentheses, when computed.

MP2 and CCSD(T) theories were also employed with results presented in Table 1. From these data, there is little doubt that MP2 overestimates the stability of **2** compared to **1** with the MP2/cc-pVQZ//MP2/cc-pVTZ result yielding an energy separation of −4.8 kcal/mol. This appears not to be a geometrical problem but is instead due to the inaccurate treatment of dynamical electron correlation. When the level of theory is increased to CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ, which has only minor effects on the structure (Tables 2 and 3), the energy separation comes to within 0.02 kcal/mol of the experiment. The latter difference, of course, is less than the uncertainty in the experiments. The assumption that MP2/cc-pVTZ structures, for covalently bonded molecules, are in good agreement with both CCSD(T)/cc-pVTZ and experimental structures is vital to the examination of higher cumulene and poly-yne analogues (Figure 5).[66] However, DFT optimized geometries (Figures 6

TABLE 2: Optimized Bond Lengths (in Å) for Allene 1[a]

level of theory	R_{CC} double bond	R_{CH} bond
MP2/cc-pVDZ	1.320	1.094
MP2/cc-pVTZ	1.301	1.076
CCSD(T)/cc-pVDZ	1.329	1.097
CCSD(T)/cc-pVTZ	1.308	1.079
experimental[67]	1.313	1.102

[a] Vibrationally averaged experimental results.

TABLE 3: Optimized Bond Lengths (in Å) for Propyne 2[a]

level of theory	R_{CC} triple bond	R_{CC} single bond	R_{CH} bond
MP2/cc-pVDZ	1.230	1.468	1.074
MP2/cc-pVTZ	1.209	1.452	1.056
CCSD(T)/cc-pVDZ	1.229	1.477	1.078
CCSD(T)/cc-pVTZ	1.207	1.460	1.057
experimental[67]	1.206	1.459	

[a] Vibrationally averaged experimental results.

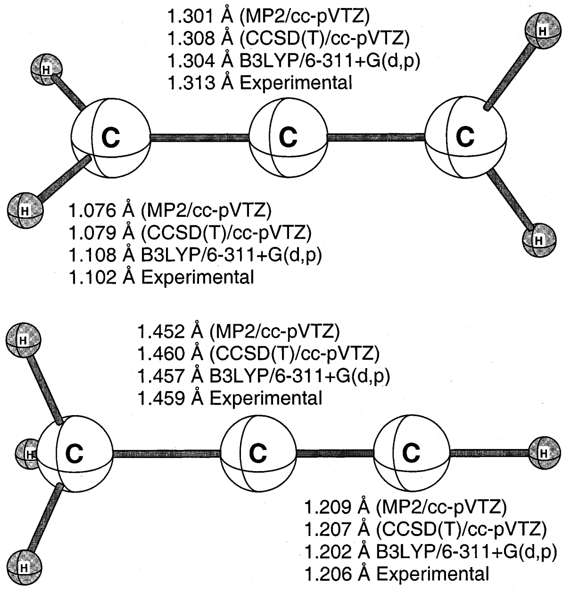

Figure 5. MP2/cc-pVTZ, CCSDT(T)/cc-pVTZ, B3LYP/6-311+G(d,p), and vibrationally averaged experimental carbon−carbon single, double, and triple bond lengths for allene (**1**) and propyne (**2**).[67]

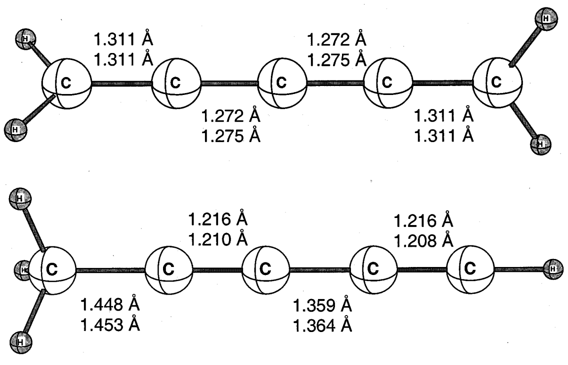

Figure 6. MP2/cc-pVTZ (top) and B3LYP/6-311+G(d,p) (bottom) optimized carbon−carbon single, double, and triple bond lengths for penta-1,2,3,4-tetraene (**3**) and penta-1,3-diyne (**4**).

and 7) also are good approximations to both CCSD(T) and experimental structures,[67] and this will be important when considering the study of much larger carbon-rich systems.

B. C_7H_4 Isomers: Hepta-1,2,3,4,5,6-hexaene and Hepta-1,3,5-triyne. The DFT energy separations for the C_5H_4 isomers penta-1,2,3,4-tetraene (**3**) and penta-1,3-diyne (**4**) are illustrated in Figure 8 (Supporting Information) for B3LYP, BLYP, and BP86, respectively. These results demonstrate that B3LYP again gives much larger ΔE values as compared to those of BLYP and BP86. The C_3H_4 "Pauling point" at B3LYP/6-311G arises also and gives a ΔE of −4.3 kcal/mol with penta-1,3-diyne lower in energy. Both BLYP and BP86 clearly underestimate energy separation between **3** and **4** (Figure 8 parts b and c, Supporting Information).

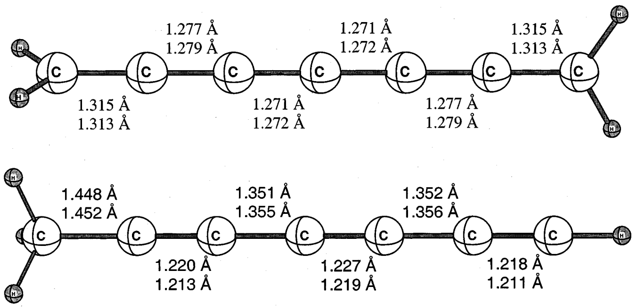

Figure 7. MP2/cc-pVTZ (top) and B3LYP/6-311+G(d,p) (bottom) optimized carbon−carbon single, double, and triple bond lengths for hepta-1,2,3,4,5,6-hexaene (**5**) and hepta-1,3,5-triyne (**6**).

TABLE 4: Energy Separations for the C5H4 Isomers Penta-1,2,3,4-tetraene (3) and Penta-1,3-diyne (4)[a]

level of theory	ΔE (kcal/mol)
MP2/cc-pVDZ	−15.6 (−15.2)
MP2/cc-pVTZ	−15.8 (−14.8)
MP2/cc-pVQZ//MP2/cc-pVTZ	−15.6
CCSD(T)/cc-pVDZ	−8.0 (−7.3)
CCSD(T)/cc-pVTZ//MP2/cc-pVTZ	−8.8

[a] ΔE values are in kcal/mol and are computed from E(**4**) − E(**3**). T_0 values are in parentheses, when computed.

TABLE 5: Optimized Geometrical Parameters for Penta-1,2,3,4-tetraene (3)[a]

level of theory	R_{CC} double bond	R_{CC} double bond
MP2/cc-pVDZ	1.330	1.294
MP2/cc-pVTZ	1.311	1.272
CCSD(T)/cc-pVDZ	1.337	1.299

[a] Bond distances are listed from left to right as depicted in Figure 6.

These DFT data were then compared to the MP2 and CCSD(T) results reported in Table 4. Assuming a similar trend is followed for C_5H_4 as was the case for C_3H_4, it is clear that the MP2/cc-pVQZ//MP2/cc-pVTZ result of −15.6 kcal/mol overestimates the stability of penta-1,3-diyne and artificially increases the energy separation. When only the method of obtaining energy is improved, to CCSD(T)/cc-pVTZ//MP2/cc-pVTZ, the ΔE is decreased to −8.8 kcal/mol. This result validates the observed "Pauling point" and shows that all DFT levels of theory underestimate the energy separation for the C_5H_4 isomers in question.

Because no experimental geometrical parameters exist for **3** or **4**, DFT optimized structures were compared to MP2/cc-pVTZ structures to gauge the reliability (Figure 9, Supporting Information). Once again, if we accept that MP2/cc-pVTZ optimized geometries are good approximations to the experiment, as is the case for C_3H_4, we see that on average B3LYP performs best in reproducing these structures. Unlike energy separations, no glaring "Pauling point" exists for the structural parameters of **4**. However, the B3LYP/6-311+G(d,p) structure displays double bond values of 1.311 and 1.275 Å that are in excellent agreement with the MP2 bond distances for **3** (Table 5). The structural parameters of **4** at the same DFT level of theory yield triple bond lengths of 1.210 and 1.208 Å and single bond lengths

TABLE 6: Optimized Bond Lengths (in Å) for Penta-1,3-diyne (4)[a]

level of theory	R_{CC} single bond	R_{CC} triple bond	R_{CC} single bond	R_{CC} triple bond
MP2/cc-pVDZ	1.468	1.238	1.381	1.237
MP2/cc-pVTZ	1.448	1.216	1.359	1.216
CCSD(T)/cc-pVDZ	1.475	1.233	1.393	1.233

[a] Bond distances are listed from left to right as depicted in Figure 6.

TABLE 7: Energy Separations for the C_7H_4 Isomers Hepta-1,2,3,4,5,6-hexaene (5) and Hepta-1,3,5-triyne (6)[a]

level of theory	ΔE (kcal/mol)
MP2/cc-pVDZ	−22.9 (−22.2)
MP2/cc-pVTZ	−23.7 (−22.6)
MP2/cc-pVQZ//MP2/cc-pVTZ	−23.7
CCSD(T)/cc-pVDZ	−13.5 (−12.2)
CCSD(T)/cc-pVTZ//MP2/cc-pVTZ	−14.3

[a] ΔE values are in kcal/mol and are computed from E(**6**) − E(**5**). T_0 values are in parentheses, when computed.

of 1.364 and 1.453 Å, which are also in good agreement with the MP2 structure (Table 6).

At the MP2/cc-pVTZ level of theory, structure **3** is very close to D_{2d} symmetry, with the lowest vibrational mode being degenerate (154 cm^{-1}). Upon animation,[68] these frequencies were observed to correspond to carbon-chain bending, thus confirming the floppy character of this molecule. Similarly, the di-yne **4** experienced a small positive carbon-chain bending frequency of 154 cm^{-1}, which (in analogy to **3**) demonstrates its floppy nature.

C. C_7H_4 Isomers: Hepta-1,2,3,4,5,6-hexaene and Hepta-1,3,5-triyne. Our results for the C_7H_4 isomers hepta-1,2,3,4,5,6-hexaene (**5**) and hepta-1,3,5-triyne (**6**) at the BLYP/6-311G and BP86/6-311G theory resulted in small energy separations of −1.7 and −1.2 kcal/mol, respectively (Figure 10 parts b and 10c, Supporting Information). As observed previously, B3LYP/6-311G performed substantially better yielding a ΔE of −7.5 kcal/mol. It is likely that this result underestimates the actual energy separation as the true ΔE value is expected to increase from the CCSD(T) computed ΔE of C_5H_4 −8.8 kcal/mol. Given the fact that once again DFT appears to perform poorly for ΔE, the coupled cluster method was utilized to help clarify the situation. As the computed energy separation at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory agrees well with the experiment for the C_3H_4 isomers, the corresponding ΔE of −14.3 kcal/mol for the C_7H_4 isomers should be a good approximation (Table 7) to the unknown experimental value.

Although the relative energies still present problems for DFT, the geometries are reproduced quite well, as noted for the C_3H_4 and C_5H_4 systems. DFT, at all levels investigated, was again successful in reproducing the MP2/cc-pVTZ structures (Figure 11, Supporting Information) for both C_7H_4 isomers studied (Tables 8 and 9). The computed double bond lengths for **5** are 1.277, 1.271, and 1.315 Å, with the structure possessing D_{2d} symmetry and a small degenerate positive carbon chain bending frequency of 76 cm^{-1} at the MP2/cc-pVTZ level of theory. The optimized structure of **6** at the MP2/cc-pVTZ level, which had very close to C_{3v} symmetry, also exhibited a small degenerate frequency (77 cm^{-1}) corresponding to carbon chain bending. The MP2 optimized bond distances were found to be 1.220, 1.277, and 1.218 Å for the CC triple bonds and 1.448, 1.352, and 1.351 Å for the CC single bonds.

TABLE 8: Optimized Bond Lengths (in Å) for Hepta-1,2,3,4,5,6-hexaene (5)[a]

level of theory	R_{CC} double bond	R_{CC} double bond	R_{CC} double bond
MP2/cc-pVDZ	1.335	1.298	1.294
MP2/cc-pVTZ	1.315	1.277	1.271
CCSD(T)/cc-pVDZ	1.339	1.304	1.299

[a] Bond distances are listed from left to right as depicted in Figure 7.

TABLE 9: Optimized Bond Lengths (in Å) for Hepta-1,3,5-triyne (6)[a]

level of theory	R_{CC} single bond	R_{CC} triple bond	R_{CC} single bond	R_{CC} triple bond	R_{CC} single bond	R_{CC} triple bond
MP2/cc-pVDZ	1.467	1.241	1.371	1.247	1.373	1.240
MP2/cc-pVTZ	1.448	1.220	1.351	1.227	1.352	1.218
CCSD(T)/cc-pVDZ	1.477	1.235	1.387	1.239	1.386	1.235

[a] Bond distances are listed from left to right as depicted in Figure 7.

D. Isodesmic and Homodesmotic Reactions. Appropriate isodesmic and homodesmotic reactions were devised to aid in the evaluation of the energy separations of the C_3H_4, C_5H_4, and C_7H_4 isomers (Figures 2 and 3). Structures in all reactions were optimized at the MP2/cc-pVTZ level of theory and single-point energies obtained at the CCSD(T)/cc-pVTZ level. In addition, CCSD(T)/cc-pVQZ heat of formation (ΔH_f) data were obtained for **1** and **2** in order to gain more insight into the accuracy of experimental results. The heats of formation of **1** and **2** at CCSD(T)/cc-pVTZ are 45.5 and 44.1 kcal/mol as well as 45.4 and 43.6 kcal/mol at CCSD(T)/cc-pVQZ, respectively. These yielded energy separations of −1.4 and −1.8 kcal/mol. Experimental heats of formation of allene and propyne are reported to be 47.4 ± 0.3 and 46.0 ± 0.2 kcal/mol, respectively, with a resulting ΔE of −1.4 ± 0.5 kcal/mol.[47] Hence, the computed heats of formation at both CCSD(T) levels are well within the experimental error bars reported.

In contrast to C_3H_4, there are no experimental heat of formation data for the C_5H_4 isomers. Therefore, the generally more accurate homodesmotic reactions were constructed and employed to compute ΔH_f values at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level. This resulted in ΔH_f values of 111.1 and 101.0 kcal/mol for **3** and **4**, respectively, and yielding a −10.1 kcal/mol energy separation.

Similarly, the C_7H_4 isomers have no reported experimental heat of formation data, and we employed homodesmotic equations again as a means of prediction of the ΔH_f. At the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory, the heats of formation of **5** and **6** were predicted to be 171.6 and 155.4 kcal/mol, respectively. This gives an energy separation of −16.2 kcal/mol.

IV. Discussion

A. C_3H_4 Isomers: Allene and Propyne. All three DFT levels reverse the relative energy of the C_3H_4 isomers allene and propyne. Given that both MP2 and CCSD(T) yield the correct relative energy separation for the isomers in question, we investigated how DFT ΔE values change with respect to the Becke and Hartree−Fock exchange contributions.

BXLYP (X describes the amount of HF exchange included) single-point energy computations were performed at the B3LYP/6-311+G(d,p) geometries while varying the contribution of the Becke DFT and HF exchange term (Table 11). The results of these computations show a smooth decline in the error in ΔE

TABLE 10: Theoretical Heats of Formation (in kcal/mol), ΔH_f, Obtained via Isodesmic (Allene (1) and Propyne (2)), and Homodesmotic (Penta-1,2,3,4-tetraene (3), Penta-1,3-diyne (4), Hepta-1,2,3,4,5,6-hexaene (5), and Hepta-1,3,5-triyne (6)) Reactions (Figures 2 and 3)[a]

molecule	level of theory	ΔH_f	expt
allene	CCSD(T)/cc-pVTZ	45.5	47.4 ± 0.3
	CCSD(T)/cc-pVQZ	45.4	
propyne	CCSD(T)/cc-pVTZ	44.1	46.0 ± 0.2
	CCSD(T)/cc-pVQZ	43.6	
penta-1,2,3,4-tetraene	CCSD(T)/cc-pVTZ	111.1	
penta-1,3-diyne	CCSD(T)/cc-pVTZ	101.0	
hepta-1,2,3,4,5,6-hexaene	CCSD(T)/cc-pVTZ	171.6	
hepta-1,3,5-triyne	CCSD(T)/cc-pVTZ	155.4	

[a] **1** and **2** are compared with experimental ΔH_f values.[47] All structures were optimized at the MP2/cc-pVTZ level of theory.

TABLE 11: Changes in C_3H_4 Isomer Energy Separation ΔE [$E(2) - E(1)$] while Varying the Amount of Becke and Hartree−Fock Exchange Included with the LYP Correlation Functional[a]

Becke exchange coefficient	ΔE (kcal/mol)
0.00	−1.91
0.10	−1.53
0.20	−1.14
0.30	−0.72
0.40	−0.29
0.50	0.15
0.60	0.62
0.70	1.11
0.80	1.62
0.90	2.15
1.00	2.71
experimental[47]	−1.4

[a] All computations were performed at the BXLYP/6-311+G(d,p)// B3LYP/6-311+G(d,p) level of theory and are not ZPVE corrected. The Hartree−Fock exchange coefficient is 1.00 − Becke exchange coefficient.

TABLE 12: Changes in the SCF Energy Decomposition as DFT and HF Exchange Coefficients are Varied for Propyne and Allene[a]

Becke coefficient	Δ one lectron	Δ total coulomb	Δ HF exchange	Δ DFT exchange	Δ DFT correlation
1.0	559.36594	−242.16743	0.00000	−1.70467	0.23006
0.9	555.87698	−238.38202	−0.37464	−1.79904	0.21797
0.8	552.49845	−234.73772	−0.75330	−1.82986	0.20636
0.7	549.21472	−231.21472	−1.13765	−1.79955	0.19516
0.6	546.02567	−227.81001	−1.52914	−1.70960	0.18440
0.5	542.92541	−224.51517	−1.92900	−1.56147	0.17404
0.4	539.90657	−221.32007	−2.33842	−1.35683	0.16408
0.3	536.96636	−218.21973	−2.75840	−1.09706	0.15451
0.2	534.10112	−215.20858	−3.18980	−0.78348	0.14530
0.1	531.30874	−212.28272	−3.63342	−0.41738	0.13648
0.0	528.58523	−209.43664	−4.08988	0.00000	0.12800
CCSD(T)	528.36970	−209.19717	−4.10729	0.00000	0.00000

[a] All computations were carried out at the B3LYP/6-311+G(d,p) optimized geometry using the 6-311+G(d,p) basis set. Energies are in kcal/mol and are defined as E(propyne) − E(allene). The Hartree-Fock exchange coefficient is 1.00 − Becke exchange coefficient.

(propyne−allene) as the percentage of HF exchange is increased. We thus see that for the allene and propyne isomers an optimal amount of Becke exchange to include in BXLYP computations is 13.4%. This value was obtained via a polynomial fit of the data and subsequent interpolation to the experimental ΔE of −1.4 kcal/mol. The polynomial fit yielded a formula of

$$y = 0.98x^2 + 3.6x - 1.9 \tag{1}$$

with an R^2 value of exactly 1.0. This is in sharp contrast to the current implementation of B3LYP which includes 72% Becke exchange energy.

In another attempt to understand these incorrect DFT relative energy orderings, an energy decomposition analysis was performed in which the total DFT energy was examined in terms of one-electron, total coulomb, HF exchange, DFT exchange, and DFT correlation contributions (Table 12, Supporting Information). The results of this analysis show erroneous DFT exchange behavior as the Becke exchange term is decreased from 90% to 60% of the total exchange term. The lower end of this scale, where the HF exchange contribution begins to dominate, shows a smooth decline in the DFT exchange included in the total energy. This is also the region that most accurately reproduces experimental energy separations. The DFT exchange term exhibits an abnormal peak at the 80% Becke contribution point rather than the steady decline in DFT exchange that is expected when the percent of Becke exchange is lowered from 100% to 0% (Table 11, Supporting Information). This is a quite disturbing result as the current implementation of the hybrid B3LYP functional has 72% of the exchange coming from the Becke term, whereas only 20% comes from the HF contribution and the remaining 8% from the Slater term. We therefore conclude that the errors observed with the C_3H_4 isomers are associated with the DFT exchange term and that by minimizing the contribution to the appropriate level experimental and high level theoretical results may be more accurately reproduced.

One feasible explanation for this conclusion was proposed by Gritsenko and co-workers.[69] The authors determined that for certain bonding schemes, i.e., transition states, DFT gradient corrected functionals can substantially underestimate the repulsive exchange contribution. The authors concluded that this is due to the delocalization of the DFT exchange hole over symmetric molecules such as allene. Thus, the overstabilization of delocalized systems, such as cumulenes, would lead directly to the results observed where the energetic ordering of the C_3H_4 isomers is actually reversed. More specifically, the aforementioned authors[69] point to an overestimation of the exchange self-interaction correction (SIC) term

$$E_x^{\mathrm{SIC}} = -\frac{1}{2}\sum_{i=1}\int \mathrm{d}r_1\,\mathrm{d}r_2 \frac{|\Psi_i(r_1)|^2|\Psi_i(r_2)|^2}{r_1 - r_2} \tag{2}$$

as a possible cause of this overstabilization. Gradient corrected functionals, which localize exchange holes, typically overestimate the exchange energy where the true Kohn−Sham exchange hole would be delocalized. From this, it is easy to see why a cumulene displays this overstabilization problem, whereas a more localized poly-yne is more accurately described by gradient corrected functionals.

B. C_5H_4 Isomers: Penta-1,2,3,4-tetraene and Penta-1,3-diyne. Just as was the case for the C_3H_4 isomers, the energetic relationship between penta-1,2,3,4-tetraene (**3**) and penta-1,3-diyne (**4**) energies was reproduced incorrectly (relative to higher levels of theory) by the DFT functionals employed in the current study. Again, the hybrid B3LYP functional is the least sensitive to this DFT error, and thus, the same analysis tools used for the C_3H_4 isomers will be employed.

BXLYP computations were performed varying the contribution of Becke and HF exchange included (Table 13). Unlike the C_3H_4 isomers, there are no experimental data to consider. Thus, the results obtained will be equated to the highest level theoretical results (CCSD(T)/cc-pVTZ//MP2/cc-pVTZ) in the current study. It is expected that the optimal choice of Becke

TABLE 13: Changes in C_5H_4 Isomer Energy Separation Δ*E* [*E*(4) − *E*(3)] while Varying the Amount of Becke and Hartree−Fock Exchange Included with the LYP Correlation Functional[a]

Becke exchange coefficient	Δ*E* (kcal/mol)
0.00	−13.18
0.10	−12.08
0.20	−10.94
0.30	−9.76
0.40	−8.55
0.50	−7.29
0.60	−5.99
0.70	−4.64
0.80	−3.24
0.90	−1.79
1.00	−0.28

[a] All computations were performed at the BXLYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory and are not ZPVE corrected. The Hartree−Fock exchange coefficient is 1.00 − Becke exchange coefficient.

TABLE 14: Changes in C7H4 Isomer Energy Separation Δ*E* [*E*(6) − *E*(5)] while Varying the Amount of Becke and Hartree−Fock Exchange Included with the LYP Correlation Functional[a]

Becke exchange coefficient	Δ*E* (kcal/mol)
0.00	−22.11
0.10	−20.35
0.20	−18.53
0.30	−16.65
0.40	−14.71
0.50	−12.71
0.60	−10.64
0.70	−8.50
0.80	−6.30
0.90	−4.03
1.00	−1.69

[a] All computations were performed at the BXLYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory and are not ZPVE corrected. The Hartree−Fock exchange coefficient is 1.00 − Becke exchange coefficient.

exchange being 13.4%, obtained from the C_3H_4 case, will yield Δ*E* values that are larger than those obtained through CCSD(T)/cc-pVTZ computations. This is clearly the case, because the C_3H_4 results were fitted to an experimental value. For the C_5H_4 isomers, we only have the CCSD(T)/cc-pVTZ result, which if analogous to the C_3H_4 case, is an underestimate compared to the actual, still unknown, energy difference.

Using the 13.4% Becke exchange contribution as the model and the data obtained from the BHLYP computations, we can again fit the data to a polynomial function and predict the energy separation between the C_5H_4 isomers:

$$y = 2.25x^2 + 10.6x - 13.2 \qquad (3)$$

With these results at hand, we suggest that the actual relative energy separation should be between the CCSD(T)/cc-pVTZ result of −8.8 kcal/mol and the empirically fitted DFT result of −11.7 kcal/mol. This prediction seems feasible because the Δ*E* obtained from the C_5H_4 isodesmic reactions was −10.1 kcal/mol.

The previously performed energy decomposition of C_3H_4 was repeated for the C_5H_4 isomers. The results show an abnormal peak at the 80/20 Becke/HF exchange ratio. For this case, exchange energy problems seem to be more severe than for the C_3H_4 case. This is evident from the observation that the absolute error between the B3LYP/6-311G Δ*E* (a "Pauling point") and the Δ*E* obtained from isodesmic reactions is larger for the C_5H_4 isomers (6.9 kcal/mol) than for the C_3H_4 isomers (2.9 kcal/mol).

Results from the optimizations and vibrational frequency analyses yield insight into the linearity of the C_5H_4 isomers. Structures **3** and **4** were stated to have close to D_{2d} and C_{3v} symmetry when minima were confirmed. To evaluate this in greater depth, **3** and **4** were not allowed to break their respective point group symmetries. Optimizations and frequency analyses were then repeated with **3** in D_{2d} symmetry displaying a small imaginary frequency (79*i* cm^{-1}, MP2/cc-pVTZ) that corresponds to CCC bending. On the other hand, when **4** was coerced into C_{3v} symmetry, it showed a positive frequency of 154 cm^{-1} for the carbon-chain bending mode which is the same result obtained for slightly bent **4**.

Generally, these frequency differences are small and lead to the conclusion that both **3** and **4** are extremely floppy and, when allowed to bend, are minima on their MP2/cc-pVTZ potential energy hyper-surfaces. However, the energy differences between the approximate D_{2d} and C_{3v} minima and the explicit, nonbent, D_{2d} and C_{3v} structures are both less than 0.01 kcal/mol. It is clear that the CCC bending mode is easily energetically accessible.

C. C_7H_4 Isomers: Hepta-1,2,3,4,5,6-hexaene and Hepta-1,3,5-triyne. DFT computations on the C_7H_4 isomers **5** and **6** encountered the same problems indicated for the smaller analogues. The DFT computed energy separation at the B3LYP/6-311G level, −7.5 kcal/mol, is approximately half that of the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ computed Δ*E* of −14.3 kcal/mol. This difference between the DFT and CCSD(T) result, 6.8 kcal/mol, is approximately the same as the C_5H_4 error and thus as the system size gets larger it appears as if the DFT exchange problem tends to level off. However, this requires more evidence before strong conclusions should be drawn.

The BXLYP series of calculations performed on C_3H_4 and C_5H_4 were repeated on the C_7H_4 isomers (Table 14) and fitted to a polynomial function:

$$y = 3.2x^2 + 17.2x - 22.1 \qquad (4)$$

Using this function and the empirically determined ideal Becke exchange contribution of 13.4%, the DFT energy separation was predicted to be −19.7 kcal/mol. This DFT value is larger than the CCSD(T)/cc-pVTZ value of −14.3 kcal/mol but comes closer to the Δ*E* obtained from the C_7H_4 isodesmic equations, namely, −16.3 kcal/mol. From these results, it appears that the 13.4% Becke exchange contribution improves the relative energies, but experimental results are needed to confirm our suggestion. It is likely that the correct Δ*E* is between the CCSD(T)/cc-pVTZ value of −14.3 and the BXLYP prediction of −19.7 kcal/mol.

Analogous to the C_5H_4 linearity analysis at the MP2/cc-pVTZ level of theory, **5** and **6** were coerced into D_{2d} and C_{3v} symmetry to yield insight into the possible bent nature of these structures. When **5** was forced into D_{2d} symmetry, an imaginary frequency of 124*i* cm^{-1} emerged. Parallel to the C_5H_4 case, when **6** was placed in explicit C_{3v} symmetry a small positive carbon-chain bending frequency of 75 cm^{-1} remained.

The magnitude of the imaginary vibrational frequency increases with chain length (compare **3** and **5**: $\Delta\nu = 44$ cm^{-1}). This confirms the notion that as the length of carbon-chains increases the likelyhood of linearity decreases. Therefore, even though **4** and **6** in C_{3v} symmetry have all positive frequencies, the probability that **6** exists in a bent form is higher that of **4**. Likewise, **5** is more likely to have a nonlinear equilibrium geometry. Again, just as in the C_5H_4 case, the energetic differences between the approximate symmetry minima and the linearly constrained structures are extremely small (below 0.1 kcal/mol), and thus, CCC bending modes are easily accessible energetically.

V. Conclusions

We systematically investigated the relative energetics obtained when DFT is applied to cumulene and poly-yne isomers. We selected the C_3H_4 isomers allene (**1**) and propyne (**2**) as model systems because of the observed reversal in relative energetics. The study was extended to the larger C_5H_4 isomers penta-1,2,3,4-tetraene (**3**) and penta-1,3,5-diyne (**4**), as well as to C_7H_4 hepta-1,2,3,4,5,6-hexaene (**5**) and hepta-1,3,5-triyne (**6**).

Comparison of geometries obtained using various DFT approaches showed good agreement with MP2/cc-pVTZ, CCSD(T)/cc-pVTZ, and the experiment (when available). However, DFT energetics displayed significant differences when compared to the explicitly correlated theoretical and experimental results. The quintessential example is the erroneous energy separation, ΔE, of the C_3H_4 isomers **1** and **2**. We examined the problem more carefully with isodesmic reactions, DFT exchange analysis, and DFT energy decompositions. This revealed that appropriate isodesmic reactions can accurately predict both heats of formation and isomeric energy separations. We also found serious problems with the way DFT treated the exchange energy of cumulenes. One conclusion from the Gritsenko et al. work[69] stated that DFT should correctly treat systems with typical covalent bonding patterns (e.g., N_2). However, we discovered that DFT, as is the case with transition states, tends to overstabilize these covalently bonded delocalized cumulenes, thus introducing errors into energetic analyses. Therefore, a general statement about all covalent bonding patterns cannot be made, but instead, each type must be examined in more detail.

The DFT exchange energy errors that occurred with the C_3H_4 isomers appeared to extend to the larger cumulenes and poly-ynes. Here, we employed homodesmotic reactions and CCSD(T)/cc-pVTZ//MP2/cc-pVTZ computations to predict heats of formation and energy separations. The DFT computed ΔE values for C_5H_4 (**3** and **4**) and C_7H_4 (**5** and **6**) also were significantly underestimated compared to isodesmic and CCSD(T) results. This again appears to be due to overstabilization of the respective cumulene isomers.

The results of the C_3H_4 BXLYP analysis were fitted to a polynomial function, using the experimental ΔE (−1.4 kcal/mol) for C_3H_4, with the optimal Becke exchange energy contribution determined to be 13.4%. This value was tested with the C_5H_4 and C_7H_4 isomers and determined to be a fairly good approximation to the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ energy separations and isodesmic results. The 13.4% Becke exchange contribution, empirically determined as optimal for the C_3H_4 isomers, is in sharp contrast to the current implementation of B3LYP which includes 72% Becke, 20% Hartree−Fock, and 8% Slater exchange energy. From this, it is clear that the still most popular functional, B3LYP, is not able to accurately describe the relative energies of cumulene and poly-yne isomers.

When accurate energy separations and heats of formation of cumulenes and poly-ynes are desired the theoretical method of choice is CCSD(T). As the size of the system of interest increases, CCSD(T) optimizations quickly become too computationally expensive and MP2 and DFT geometries, which are good approximations to CCSD(T) and experimental structures for many covalently bonded systems, become a viable alternative. However, when accurate energetics are required most currently implemented DFT functionals no longer are valid. To correct this problem, we suggest two possible solutions. The first is to use MP2 or DFT geometries and obtain CCSD(T) energetics with at least a triple-ζ quality basis set. A second possibility is to perform a functional analysis (analogous to the current BHLYP analysis) on a related system and fit to known experimental data. Using these results a unique functional can be designed for use with the system of interest.

From the results of constrained symmetry optimizations, it seems clear that as the carbon-chain length of cumulenes and poly-ynes increases the probability that bending modes are energetically accessible increases. Therefore, it is probable that the C_5H_4 and C_7H_4 cumulenes (**3** and **5**) are bent, whereas poly-ynes (**4** and **6**) are more likely to be linear.

In general DFT, as shown in the current and previous studies, may be problematic when invoked to study delocalized linear systems. Therefore, when accurate energetics of carbon-rich systems are desired, one must be very careful in choosing the scheme (i.e., isodesmic reactions), theoretical method, and basis set for theoretical studies.

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Supporting Information Available: Tables 1−9 and Figures 8−11 showing experimental data and DFT energy separations and optimized geometries, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(2) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.

(3) Cooper, D. L.; Wright, S. C.; Gerratt, J.; Raimondi, M. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 255.

(4) Baeyer, A. *Ber.* **1885**, *2269*, 2277.

(5) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 9751.

(6) de Meijere, A.; Blechert, S. *Strain and Its Implications in Organic Chemistry, Vol. 273 of NATO ASI Series*; Kluwer Academic Publ.: Dordrecht, The Netherlands, 1989.

(7) Grimme, S. *J. Am. Chem. Soc.* **1996**, *118*, 1529.

(8) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

(9) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.

(10) Dewar, M. J. S. *Adv. Chem. Phys.* **1965**, *8*, 65.

(11) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349.

(12) Katritzky, A. R.; Jug, K.; Oniciu, D. C. *Chem. Rev.* **2001**, *101*, 1421.

(13) Krygowski, T. M.; Cryanski, M. K. *Chem. Rev.* **2001**, *101*, 1385.

(14) Schleyer, P. v. R. *Chem. Rev.* **2001**, *101*, 1115. This entire issue is devoted to aromaticity.

(15) Scott, L. T.; Siegel, J. S. *Tetrahedron* **2001**, *57*, 3507.

(16) Bender, C. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 4984.

(17) Pople, J. A.; Curtiss, L. A.; Raghavachari, K. *J. Chem. Phys.* **1991**, *94*, 7221.

(18) Pople, J. A.; Curtiss, L. A.; Raghavachari, K. *J. Chem. Phys.* **1998**, *109*, 7764.

(19) Dunning, T. H.; Peterson, K. A. *J. Chem. Phys.* **1994**, *100*, 7410.

(20) Császar, A. G.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1998**, *108*, 9751.

(21) East, A. L. L.; Allen, W. D. *J. Chem. Phys.* **1993**, *99*, 4638.

(22) Allen, W. D.; East, A. L. L.; Császar, A. G. *Structures and Conformations of Non-Rigid Molecules*; Laane, L., Dakkouri, M., van der Verken, B., Oberhammer, H., Eds.; Kluwer Academic Publ.: Dordrecht, The Netherlands, 1993, 343−373.

(23) Sham, L. J.; Kohn, W. *Phys. Rev. A* **1965**, *140*, 1133.

(24) Yang, W.; Parr, R. G. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(25) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley: New York, 2001.

(26) Ignatyev, I. S.; Xie, Y.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1997**, *107*, 141.

(27) Xie, Y.; Schaefer, H. F. *Mol. Phys.* **2000**, *98*, 955.

(28) King, R. A.; Crawford, T. D.; Stanton, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 10788.

(29) Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322.

(30) Iijima, S. *Nature* **1991**, *354*, 56.

(31) Tans, S. J.; Devoret, M. H.; Dai, H. J.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekkar, C. *Nature* **1997**, *386*, 474.

(32) Hutter, J.; Lüthi, H. P.; Diederich, F. *J. Am. Chem. Soc.* **1994**, *116*, 750.

(33) Raghavachari, K.; Strout, D. L.; Odom, G. K.; Scuseria, G. E.; Pople, J. A.; Johnson, B. G.; Gill, P. M. W. *Chem. Phys. Lett.* **1993**, *214*, 357.

(34) Kroto, H. W.; McKay, K. *Nature* **1988**, *331*, 328.

(35) Kroto, H. W. *Nature* **1987**, *329*, 529.

(36) Rodrigo, R. J.; Lara, L. M.; Lellouch, E.; LopezMoreno, J. J. *Geophys. Res.* **1996**, *101*, 261.

(37) McKay, C. P.; Toublanc, D.; Parisot, J. P.; Brillet, J.; Gautier, D.; Raulin, F. *Icarus* **1995**, *113*, 2.

(38) Pinto, J. P.; Yung, Y. L.; Allen, M. *Astrophys. J. Suppl.* **1984**, *55*, 465.

(39) Yung, Y. L. *Icarus* **1987**, *72*, 468.

(40) Lunine, J. I. *Mercury* **1997**, *10*, 10.

(41) Brunston, P.; Khlifi, M.; Benilan, Y.; Raulin, F. *J. Biol. Phys.* **1994**, *20*, 39.

(42) Kass, D. M.; Yung, Y. L. *Science* **1996**, *274*, 1932.

(43) Trinajstic, N.; August, J.; Kroto, H. W. *Astrophys. Space Sci.* **1986**, *128*, 411.

(44) Arnau, A.; Moreno, R.; Tunon, I.; Silla, E. *Astrophys. J.* **1994**, *437*, 532.

(45) Ochsenfeld, C.; White, C. A.; Head-Gordon, M. *J. Chem. Phys.* **1998**, *109*, 1663.

(46) Feller, D.; Dixon, D. A. *J. Phys. Chem.* **2000**, *104*, 3048.

(47) Pedley, J. B. *Thermodynamic Data and Structures of Organic Compounds*; Thermodynamic Research Center: College Station, TX, 1994; Vol. 1.

(48) Kafafi, S. A. *J. Phys. Chem. A* **1998**, *102*, 10404.

(49) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1873.

(50) Liang, C.; Xie, Y.; Schaefer, H. F.; Kim, K. S.; Kim, H. S. *J. Am. Chem. Soc.* **1991**, *113*, 2452.

(51) Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

(52) Kong, J.; White, C. A.; Krylov, A. I.; Furlani, T. F.; Lee, M. S.; Lee, A. M.; Ochsenfeld, C.; Gilbert, A. T. B.; Kedziora, G. S.; Maurice, D. R.; Nair, N.; Shao, Y.; Dombroski, J. P.; Dachsel, H.; Zhang, W.; Byrd, E. F. C.; Voorhis, T. V.; Oumi, M.; Ishikawa, N.; Florian, J.; Warshel, A.; Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. Q-Chem 2.0: A High-Performance Ab initio Electronic Structure Program Package. *J. Comput. Chem.* **2000**, *21*, 1532.

(53) Stanton, J. F.; Gauss, J.; Watts, J. B.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Kucharski, S. A.; Gwaltney, S. R.; Beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K. K.; Rozyczko, P.; Sekino, H.; Hober, C.; Almlöf, J.; Taylor, P. R.; Helgaker, T.; Jensen, H. J.; Jørgensen, P.; Olsen, J.; Bartlett, R. J. *ACESII* (a program product of the Quantum Theory Project); University of Florida, Gainesville, FL, 1998.

(54) Becke, A. D. *Phys Rev. A* **1988**, *38*, 3098.

(55) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(56) Becke, A. D. *J. Phys. Chem.* **1993**, *98*, 5648.

(57) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(58) Møller, C.; Plesset, M. S *Phys. Rev.* **1934**, *46*, 618.

(59) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(60) Raghavachari, K.; Trucks, G. W.; Pople, J. A. *Chem. Phys. Lett.* **1989**, *157*, 479.

(61) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(62) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(63) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.

(64) Pulay, P.; *In Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4, pp 153−185.

(65) Yamaguchi, Y.; Osamura, Y.; Goddard, W.; Schaefer, H. F. *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*; Oxford University Press: New York, 1994.

(66) Allen, T. A.; Scheiner, A. C.; Schaefer, H. F. *Inorg. Chem.* **1994**, *29*, 1930.

(67) Kuchitsu, K., Ed.; *Landolt-Börnstein Structure Data of Free Polyatomic Molecules*; Springer-Verlag: New York, 1992; II/7 and II/5.

(68) Qvibs: Program to perform vibrational animation of Q-Chem frequency analysis. Woodcock, H. L. http://www.ccqc.uga.edu/∼hlwood/qvibs.html, 2002.

(69) Gritsenko, O. V.; Ensing, B.; Schipper, P. R. T.; Baerends, E. J. *J. Phys. Chem. A* **2000**, *104*, 8558.