Calculating Cumulene/Poly-yne Isomerization Energies

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We report the isomerization energies of cumulene and poly-yne oligomeric sequences calculated using several different theoretical methods in an attempt to evaluate both the performance of these methods and their potential application to similar systems. We find that the recently developed KMLYP density functional theory method reproduces the CCSD(T) benchmark relative energies better than other commonly used quantum chemical methods. Furthermore, the KMLYP relative energies scale significantly better with molecule length with an average error of 0.6 kcal/mol per additional C_2 monomer. The B3LYP, B3PW91, *m*PW1PW91, and BXLYP methods scale with errors of 2.3, 2.4, 2.0, and 2.1 kcal/mol per additional C_2 monomer, respectively, while the MP2, MP4(SDQ), and CCSD methods scale with errors of 2.6, 1.4, and 1.4 kcal/mol, respectively. Consequently, these methods have large errors for chain lengths above C_5. The Hartree−Fock (HF) method is surprisingly successful in calculating the enthalpy difference between shortest cumulene/poly-yne isomers, allene and propyne. This appears to be the result of a fortuitous equivalence of correlation energies for these two molecules as HF adds an additional error of 5.1 kcal/mol per additional C_2 unit. We point out how this equivalence makes the allene/propyne system useful as a testing ground for the ability of quantum chemical methods to capture correlation energy.

Introduction

There has been a long-standing interest in determining the relative energies of large linear and cyclic unsaturated organic isomers with the goal of predicting their equilibrium distribution.[1] Unfortunately, the electronic effects giving rise to the energy differences are often subtle, and consequently, many methods fail to determine the relative energies accurately. This problem is exacerbated for longer oligomeric sequences, as the errors generally scale with the system size. The isomerization of $H_2C_{2n+1}H_2$ cumulenes to $HC_{2n+1}H_3$ poly-ynes is particularly interesting, as these species are present in the atmosphere of Saturn's moon Titan and may be indicative of the composition of the Earth's prebiotic environment.[2−5] Furthermore, because the cumulene/poly-yne relative energies, ΔE_{2n+1} (where $2n + 1$ is the number of carbon atoms), involve the approximately fixed effect of the sp^3−sp to sp^2−sp^2 termination and the increasing effect of the number of double bond/double bond pairs versus single bond/triple bond pairs, this system is relatively simple to analyze. Also, because these molecules are linear and thus involve neither ring strain nor variation of C−C−C bond angles, the isomerization energies should scale linearly from the shortest oligomers, allene and propyne.

Unfortunately, the longer cumulene/poly-yne oligomeric sequences are large enough to make study with highly accurate theoretical techniques, such as the QCISD(T) and CCSD(T) size-consistent methods or the Gaussian[6,7] or Complete Basis Set (CBS) compound methods,[8] impractical. Density functional theory (DFT) methods, on the other hand, are efficient enough to simulate molecules much larger than those that can practically be calculated with the methods mentioned above.[9,10] However, the energy differences between cumulene and poly-yne isomers may be difficult to describe correctly using DFT and less computationally intensive wave function methods such as MP2. Indeed, Houk and co-workers have observed that commonly used DFT methods such as BLYP and B3LYP incorrectly predict the relative stability of the smallest cumulene/poly-yne pair, allene and propyne.[11,12] The errors associated with these small molecules likely will be exacerbated for the long chain isomers, because the relative energies, and thus the errors in the predicted relative energies, scale with the size of the isomers. To address this issue, Woodcock et al.[13] recently developed a new DFT formulation that is optimized to reproduce the energy difference between the smallest cumulene and poly-yne, allene and propyne (ΔE_3). Their method was shown to be superior to a set of standard DFT techniques for calculations of the energy difference between larger cumulenes and poly-ynes.

Here we report the potential utility of the KMLYP method for describing the relative stabilities of cumulenes and poly-ynes.[14] Although this technique is a general method and was not optimized for these systems, it appears to outperform even Woodcock's technique for all cumulenes/poly-ynes other than allene/propyne. Here we compare the details of these two methods and discuss how these details affect the calculated energies for this system.

We have undertaken an extensive computational study of the allene and propyne isomerization enthalpy. As Woodcock et al. have mentioned, there appear to be systematic errors in the calculated enthalpy difference between these molecules. We attempt to shed some light on the potential origin of these errors and discuss how this system could serve as a particularly useful testing ground for future quantum chemical theories.

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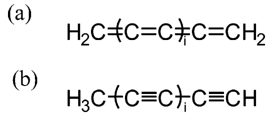

Figure 1. Generalized structures for (a) cumulenes and (b) poly-ynes. This work considers structures with $i = 0, 1, 2, 3, 4$.

Theoretical Methods

We have performed calculations on the cumulenes and poly-ynes with three, five, seven, nine, and 11 carbon atoms (see Figure 1). All calculations were performed using the Gaussian 98 quantum chemistry software package.[15] The most thorough calculations were performed for the simplest cumulene/poly-yne pair, allene and propyne. For this system, we calculated the enthalpy change of the isomerization reaction by subtracting the room-temperature enthalpies calculated for allene and propyne; this value can be compared to experiment.[16] We compare four different DFT methods and eight different wave function methods, with each method using 12 different Pople-type basis sets. In addition, we performed calculations using four Gaussian and three CBS compound methods. The calculations at each combination of method and basis set included a geometry optimization, an energy calculation, and a frequency calculation, with the exception that QCISD(T) and CCSD(T) energies and frequencies were calculated at the QCISD and CCSD geometries, respectively. A more limited set of calculations was performed for oligomers with five, seven, nine, and 11 carbon atoms. Experimental values for the enthalpies of these larger molecules are unavailable; consequently, we follow the approach of Woodcock et al. and use the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ energies as benchmark values, as this method is expected to be accurate, is size-consistent, and reproduces the experimental isomerization energy ΔE_3. We note that a computationally efficient basis set extrapolation procedure developed by Helgaker et al. can provide a more accurate benchmark.[17,18] Isomerization energies calculated with that benchmark lie within 0.1 kcal/mol of the isomerization energies calculated with the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ benchmark. Thus, the data presented here are essentially identical for both benchmarks. For each cumulene/poly-yne pair we used B3LYP, B3PW91, *m*PW1PW91, Woodcock's optimized hybrid reparametrization of B3LYP (BXLYP), the KMLYP method, and several wave function methods. The BXLYP method involves calculating energies with the 6-311+G(d,p) basis set for geometries optimized at the B3LYP/6-311+G(d,p) level; for the other DFT methods and for the Hartree–Fock (HF) method, energies were calculated at geometries optimized with the same method and basis set; however, the calculations for the correlated wave function methods were performed at the MP2 geometry.

The results of the allene and propyne calculations justify ignoring basis set effects and thermal corrections for calculations on the larger cumulenes and poly-ynes. We calculated the energies and room temperature enthalpies for allene and propyne using several DFT and wave function methods with each of the following 12 Pople-type basis sets: 3-21G, 6-31G, 6-311G, 6-31++G, 6-311+G, 6-31G(d), 6-31+G(d), 6-311+G(d), 6-311+G(d,p), 6-311++G(d,p), 6-31G(3df,2p), and 6-311+G(3df,2p). These basis sets were chosen to identify systematic effects on the system energy caused by the inclusion of specific basis functions, including diffuse functions and polarization functions. The result was that both the energy and enthalpy differences seem to be insensitive to the basis set used for basis sets that include polarization functions on both heavy and light atoms. No trend in energy or enthalpy differences corresponding to basis set size was observed, and the values for each basis set all fall within a range of approximately 2 kcal/mol. In addition, the thermal corrections are both small (0.5 kcal/mol) and almost identical (within 0.2 kcal/mol) for each theoretical method we tested. Thus, for this system, we conclude that errors introduced by ignoring thermal corrections are small relative to the differences in the calculated electronic energy. On the basis of these observations, we justify evaluating the methods by comparing the isomerization energies calculated with one large basis set to the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ isomerization energies.

Before discussing the results, we briefly describe each method being compared. HF is the well-known, self-consistent field technique that includes electron–electron interactions only in an average way. B3LYP is currently the most commonly applied DFT method for finite systems, such as molecules and clusters. It is a hybrid method that corrects the combination of the HF and Slater exchange functionals with the Becke88 gradient correction to exchange. The B3LYP correlation energy is a weighted combination of the VWN and LYP correlation functionals. The weights on the exchange and correlation functionals are determined by minimizing the root mean square error over the G1 molecular set.[19] The B3PW91 hybrid method uses the same exchange functions as B3LYP but employs the Perdew/Wang 91 nonlocal correlation functional.[20,21] *m*PW1PW91 uses the same correlation function but employs the modified Perdew-Wang 1991 one-parameter hybrid function to calculate the exchange energy.[22] BXLYP is another hybrid DFT method that uses a weighted sum of HF and Becke exchange functionals to calculate the exchange energy. The weights were chosen to reproduce exactly the energy difference between the C_3 cumulene/poly-yne pair allene and propyne, in an attempt by Woodcock et al.[13] to develop a DFT method able to predict accurately the energy differences between cumulenes and poly-ynes.

KMLYP is a hybrid DFT formulation that attempts to reduce self-interaction errors inherent in other DFT methods.[14] This method employs the HF and Slater exchange functionals to calculate the exchange energy and the VWN and LYP functionals for the correlation energy. Unlike many of the other DFT methods examined here, it does not include the Becke88 gradient correction to exchange. The weights were chosen to reproduce exactly the ground-state energy of atomic hydrogen, to minimize the self-interaction energy, and the electron affinity of atomic oxygen, to include exchange and correlation effects in systems with significant electron–electron interactions that are not present in atomic hydrogen, except as a self-interaction error. This technique was designed to be general and was not optimized for cumulenes or poly-ynes in particular. KMLYP has been shown to be successful in calculating molecular structures, transition-state barriers, and thermochemical properties,[14,23–26] although this method can overestimate activation enthalpies for some systems when it is paired with a relatively small basis set.[27]

Results and Discussion

Table 1 and Figure 2 compare the calculated energy differences of five cumulene/poly-yne pairs. The tabulated values are the errors of each method for each cumulene/poly-yne pair. This error is defined as the difference between the isomerization energy calculated with a particular method and the isomerization energy calculated with the benchmark CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory. We have calculated these errors for the following methods:

TABLE 1: Difference between ΔE_n (kcal/mol) for DFT and Wave Function Methods from the CCSD(T) Benchmark for C_3−C_{11} Cumulene/Poly-ynes[a]

method	C_3	C_5	C_7	C_9	C_{11}
HF	−0.8	−5.2	−10.1	−15.4	−20.9
B3LYP	2.8	5.7	8.1	10.2	12.3
B3PW91	3.0	6.0	8.4	10.6	12.7
*m*PW1PW91	2.8	5.3	7.3	9.2	10.9
BXLYP	**0.1**	−1.7	−3.9	−6.0	−8.1
KMLYP	1.5	**1.3**	**0.7**	**0.0**	**−0.8**
MP2	−3.5	−6.8	−9.5	−11.9	−14.1
MP4(SDQ)	−0.4	−1.8	−3.2	−4.6	−6.0
CCSD	−0.2	−1.5	−2.9	−4.3	−5.7

[a] The lowest errors are boldfaced.

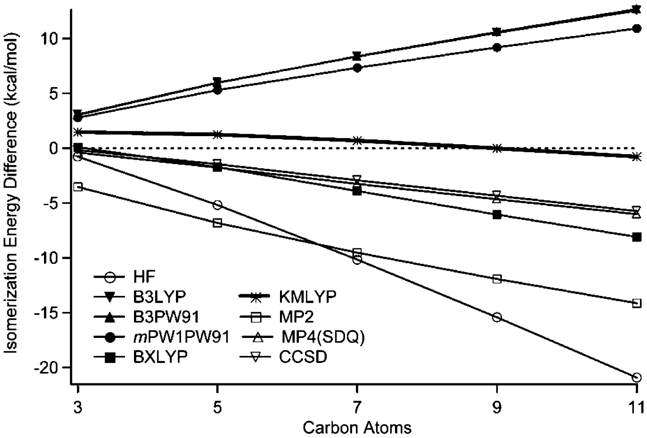

Figure 2. Deviations of cumulene/poly-yne isomerization energy (ΔE_n) from the CCSD(T) benchmark as a function of the number of carbon atoms.

HF/6-311+G(3df,2p), B3LYP/6-311+G(3df,2p), B3PW91/6-311+G(3df,2p), *m*PW1PW91/6-311+G(3df,2p), BXLYP, KMLYP/6-311+G(3df,2p), MP2/cc-pVTZ, MP4(SDQ)/cc-pVTZ//MP2/cc-pVTZ, and CCSD/cc-pVTZ//MP2/cc-pVTZ. We note that our calculations using BXLYP differ by approximately 1 kcal/mol from the original Woodcock results, with our BXLYP calculations being slightly in error for allene and propyne but being in better agreement with the benchmark than Woodcock's results for the larger cumulene/poly-yne pairs. We attribute these small differences to variations in the numerical integration methods between the Gaussian 98, Q-Chem, and ACESII programs (the latter two being used by Woodcock et al.).

Our results confirm those of Woodcock's that the BXLYP method indeed improves upon the common B3LYP, B3PW91, and *m*PW1PW91 formulations of DFT and on the HF method. BXLYP reproduces the allene/propyne energy difference (by design), but it has increasingly larger errors for the longer oligomeric sequences. KMLYP, on the other hand, has a larger error than BXLYP for allene/propyne (1.5 kcal/mol), yet as shown in Figure 2, KMLYP produces lower errors than BXLYP for all cumulene/poly-yne pairs with five or more carbon atoms (see below) and lower errors than B3LYP, B3PW91, and mPW1PW91 for all chain lengths. Figure 2 also presents the performance of four wave function methods. HF produces a very accurate result for allene/propyne, but the error grows quickly with chain length. MP2 produces the largest error for allene/propyne, although the increase of the error with chain length is less severe than for HF. MP4(SDQ) and CCSD are almost indistinguishable, both producing small errors that grow steadily with chain length. Of all the methods considered here, KMLYP proves to be the most accurate at reproducing the CCSD(T) isomerization energies, comparing favorably even against wave function methods that are much more computationally demanding.

TABLE 2: Error Per C_2 Monomer and Termination Error (kcal/mol) for DFT and Wave Function Methods[a]

method	error per C_2 monomer	termination error
HF	−5.1	4.3
B3LYP	2.3	0.7
B3PW91	2.4	**0.6**
*m*PW1PW91	2.0	0.8
BXLYP	−2.1	2.2
KMLYP	**−0.6**	2.0
MP2	−2.6	−0.9
MP4(SDQ)	−1.4	1.0
CCSD	−1.4	1.2

[a] The lowest errors are boldfaced.

For all methods considered, the size of the isomerization error grows linearly with the number of carbon atoms in the species of interest. We note that all methods considered here are size-consistent. We attribute this linear growth in error to each method having a fixed error associated with calculating the relative energy of a single bond/triple bond pair versus a double bond/double bond pair. Consequently, as more bond pairs are added, the error increases according to the number of bond pairs, and interactions with the rest of the molecule do not introduce any significant nonlinearities. Thus, we can calculate the additional error introduced for each added pair of carbon atoms (C_2 monomer). The magnitudes of these errors for each additional bond pair from C_3H_4 to $C_{11}H_4$ are on average 2.3, 2.4, 2.0, 2.1, and 0.6 kcal/mol per bond pair for B3LYP, B3PW91, *m*PW1PW91, BXLYP, and KMLYP, respectively, and 5.1, 2.6, 1.4, and 1.4 kcal/mol for the HF, MP2, MP4(SDQ), and CCSD wave function methods, respectively (see Table 2). Subtracting these values from the error for the allene/propyne isomerization energy error allows us to estimate the residual error that is not due to the difference between a single bond/triple bond pair and two double bonds. This residual or termination error can be attributed to the inherent error in describing sp^3 and sp C−H bonds versus sp^2 C−H bonds and the interaction of these bonds with neighboring C−C bonds and with each other. This error is essentially constant, except for the decreasing effect of interaction between the C−H bonds on different terminal C atoms as the oligomer chain lengthens. We find a termination error of 0.7, 0.6, 0.8, 2.2, and 2.0 kcal/mol for B3LYP, B3PW91, *m*PW1PW91, BXLYP, and KMLYP, respectively, for DFT methods and 4.3, 0.9, 1.0, and 1.2 kcal/mol, respectively, for the HF, MP2, MP4(SDQ), and CCSD wave function methods (see Table 2).

The error per C_2 monomer is the more important of the two errors in evaluating the performance of these methods for larger cumulene/poly-yne pairs. While the termination error is significant for allene/propyne, this error becomes small compared to the error in the n C_2 monomer units for the calculation of the cumulene/poly-yne $C_{2n+1}H_4$ isomerization energies as more monomers are added (i.e., the most significant error scales with chain length). The KMLYP error per C_2 monomer is significantly smaller than the error per C_2 monomer for all other methods considered here; consequently, KMLYP appears to be the most accurate method for calculations of the relative energies of cumulene/poly-yne chains.

For the shorter cumulene/poly-yne oligomeric sequences, the termination error plays a more important role. We note that HF has the largest termination error, although because it is nearly equal in magnitude and opposite in sign to the error per C_2 monomer, the HF isomerization error is a minimum for C_3H_4

TABLE 3: Allene/Propyne Isomerization Enthalpies (kcal/mol) for (a) DFT and Wave Function Methods at the Listed Basis Sets and (b) Compound Methods

(a) DFT and Wave Function Methods at the Listed Basis Sets

basis set	HF	BLYP	B3LYP	B3PW91	KMLYP	MP2	MP4	CISD	QCISD	QCISD(T)	CCSD	CCSD(T)
3-21G	−2.8	2.3	1.2	1.2	−0.4	−8.6	−4.4	−3.6	−3.4	−2.9	−3.4	−2.9
6-31G	−0.8	4.2	3.0	2.9	1.4	−6.9	−2.5	−1.6	−1.4	−0.9	−1.4	−0.9
6-311G	−2.4	2.8	1.6	1.7	−0.1	−6.6	−2.5	−2.3	−1.5	−1.0	−1.5	−1.0
6-31++G	−0.5	3.9	2.9	2.8	1.4	−5.9	−1.6	−1.2	−0.7	−0.2	−0.6	−0.2
6-31G(d)	−1.6	4.3	3.1	2.9	1.2	−4.9	−2.0	−1.4	−1.0	−0.6	−0.9	−0.5
6-31+G(d)	−1.3	4.0	2.9	2.8	1.2	−4.1	−1.5	−1.0	−0.5	−0.1	−0.5	−0.1
6-31G(3df,2p)	−1.5	3.8	2.7	2.6	1.0	−4.7	−2.0	−1.5	−1.0	−0.7	−1.0	−0.6
6-311+G	−2.3	2.7	1.6	1.6	−0.1	−6.4	−2.3	−3.7	−1.3	−0.8	−1.3	−0.8
6-311+G(d)	−2.1	2.9	1.8	1.8	0.1	−5.3	−2.7	−2.1	−1.6	−1.3	−1.5	−1.2
6-311+G(d,p)	−1.8	3.2	2.1	2.1	0.5	−4.8	−2.4	−1.8	−1.4	−1.1	−1.3	−1.0
6-311++G(d,p)	−1.8	3.2	2.1	2.1	0.5	−4.7	−2.3	−1.8	−1.3	−0.9	−1.2	−0.9
6-311+G(3df,2p)	−1.4	3.4	2.3	2.3	0.8	−4.3	−2.1	−1.5	−1.2	−0.8	−1.1	−0.7

(b) Compound Methods

G1	G2 MP2	G2	G3	CBS-4M	CBS-Q	CBS-QCI-APNO
−0.8	−0.6	−0.8	−0.6	0.8	0.4	−1.1

(see below). B3LYP, on the other hand, has a relatively small termination error; however, because its error per C_2 monomer group is of the same sign and relatively large, B3LYP has a relatively large error for C_3H_4 and the error increases significantly for larger cumulene/poly-yne pairs. B3PW91 and *m*PW1PW91 both give results similar to each other and to B3LYP. BXLYP behaves similarly to HF in that its error per C_2 monomer group is nearly equal in magnitude but of opposite sign to the termination error, so that the error for C_3H_4 is small. As mentioned above, the error per C_2 monomer is significantly smaller for BXLYP than for HF and comparable to the error per C_2 monomer for the common formulations of DFT. KMLYP has a termination error of 2.0 kcal/mol, but the error per C_2 monomer (−0.6 kcal/mol) is of opposite sign to the termination error; the termination error is too large to be canceled completely by the error per C_2 monomer for C_3H_4. However, even without complete cancellation of errors, KMLYP already outperforms all methods considered here for oligomeric sequences C_5H_4 and longer. This cancellation of errors helps to make KMLYP the most accurate method for calculating the isomerization energies of C_5H_4 through $C_{11}H_4$, while its exceptionally low error per C_2 monomer unit ensures that the error scales substantially better than other methods. These qualities make KMLYP the most accurate method (with a reasonable computational cost) considered here for long $C_{2n+1}H_4$ molecules. Although the MP4(SDQ) and CCSD methods are extremely computationally intensive relative to KMLYP, their error per C_2 monomer is more than twice as big as KMLYP, and thus for large oligomeric sequences, their errors in cumulene/poly-yne relative energies will be more than twice that of KMLYP. For CCSD this is due to the lack of connected triples, as this is the difference between CCSD and CCSD(T). The lack of connected triple excitations is also most likely the source of the error for MP4(SDQ); however, we have not performed MP4 calculations to confirm this. Although adding connected triples in CCSD and MP4(SDQ) will make these methods more accurate than KMLYP, the computational cost of improving these methods is high.

It is interesting to note the large difference in performance of the five DFT methods studied here. These methods produce different results because each one employs different functionals for the calculation of exchange and correlation energies. Errors associated with the calculation of exchange energy are in general an order of magnitude larger than errors in the correlation energy, so we focus our discussion on the exchange energy. B3LYP, which is the most common DFT method for finite systems, performs the worst of the DFT methods here; B3LYP calculates exchange energy with a weighted sum containing 20% HF and 80% Slater exchange with a 72% contribution of the Becke88 gradient correction. B3PW91 calculates exchange energy using the same functionals as B3LYP; thus, their similar performance is not surprising. BXLYP improves on the B3LYP method for cumulene/poly-yne systems by dramatically decreasing the contribution of Becke exchange; BXLYP uses a weighted sum of only 13.4% Becke exchange (consisting of Slater exchange and the Becke88 gradient correction) and 86.6% HF exchange. KMLYP employs 55.7% HF and 44.3% Slater exchange, but it does not include the Becke88 gradient correction. Thus, we find that B3LYP, which employs 20% HF and 80% Slater exchange, overstabilizes the cumulenes relative to the poly-ynes, and BXLYP, which employs 86.6% HF and 13.4% Slater exchange, overstabilizes the poly-ynes relative to the cumulenes. KMLYP employs a more balanced mixture at 55.7% HF and 44.3% Slater exchange; this results in a cancellation of errors that produces a more accurate result for these systems and likely for systems involving similar bonding. Furthermore, we note that the Becke88 gradient correction is not needed for accurate calculations of these isomerization energies. Finally, we also evaluate the performance of the modified Perdew-Wang exchange functional. Like the Slater functional, this functional systematically overstabilizes the cumulenes. The errors in this functional are slightly less than in B3LYP but are much larger than in the more balanced KMLYP hybrid.

We have also undertaken more in-depth studies of the allene/propyne system. It has been noticed previously that some common formulations of DFT predict allene to be more stable than propyne,[11−13] while experiment has shown propyne to be more stable by 0.9 ± 0.5 kcal/mol.[16] To further investigate this discrepancy, we calculated the room temperature enthalpy difference between allene and propyne using the HF method, four different general DFT methods, and seven correlated wave function methods, using 12 Pople-type basis sets for each method. We also calculated the allene and propyne enthalpy differences using four Gaussian and three CBS compound methods (see Table 3). Figure 3 shows those calculated enthalpy differences with the 6-311G+(3df,2p) basis set for the DFT methods and wave function methods and the calculated enthalpy differences for the Gaussian and CBS compound methods, along with the experimental value. Of these four general DFT methods, KMLYP most accurately reproduces the allene/propyne enthalpy

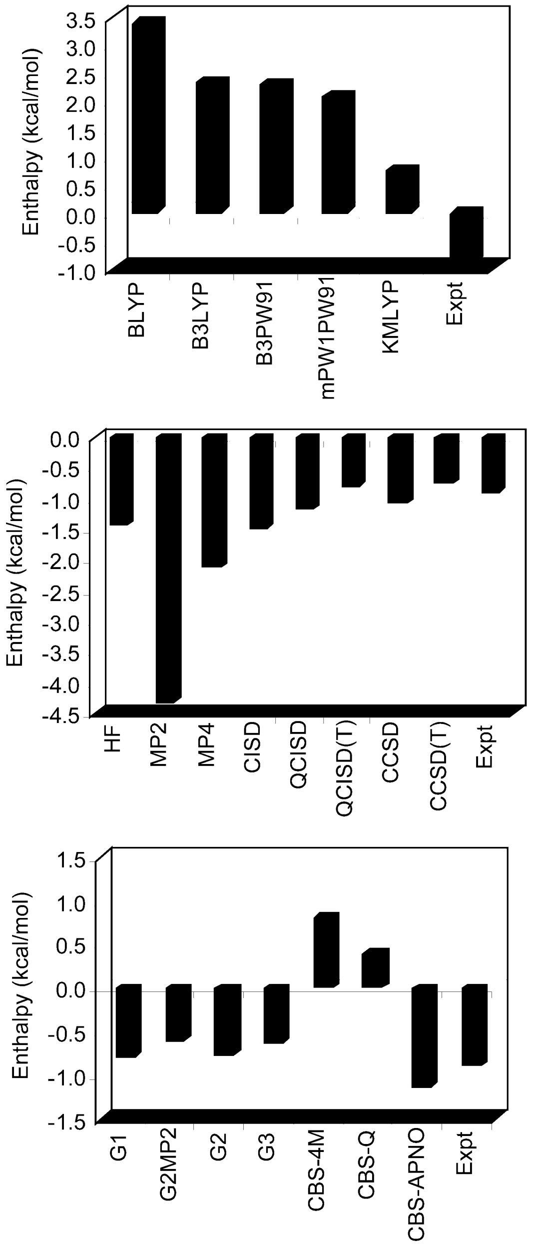

Figure 3. Calculated allene/propyne isomerization enthalpies for (a) DFT, (b) wave function, and (c) compound methods. The experimental isomerization enthalpy is also shown.[16]

difference. As previously stated, our calculations show that the general DFT methods predict the wrong sign for the enthalpy difference, confirming previous results.[11−13] Thus, this error seems to be common to several DFT methods. However, this error is not restricted to DFT methods: two of the three CBS methods also produce the wrong sign, although the most advanced CBS method (CBS-QCI-APNO) agrees well with experiment. The correlated wave function methods all predict the correct sign of the enthalpy difference and perform well overall, although MP2 is the worst performing method studied for C_3H_4.

The HF method surprisingly predicts an allene/propyne enthalpy difference that is only 0.03 kcal/mol outside the experimental error bars. This performance is significantly better than that of MP2, MP4, and even CISD. The differences in the abilities to predict the allene/propyne relative enthalpies do not originate from inaccuracies in the predicted geometry, as all methods produce very similar geometries. Thus, the fact that HF accurately predicts the isomerization enthalpy indicates that the total error inherent in the self-consistent field approximation of the HF calculation is nearly identical for both allene and propyne. The HF error within the basis set expansion is the correlation energy, and consequently, the fact that HF reproduces the experimental isomerization enthalpy shows that allene and propyne have very similar correlation energies. Unfortunately, this fortuitous result does not extend to the larger C_{2n+1} chains; the HF error is 0.8 kcal/mol for ΔE_3 with an additional error of 5.1 kcal/mol per additional C_2 group. However, the fortuitous cancellation of correlation energies for C_3 may allow this system to be used in directly evaluating the performance of various theories. For wave function methods that perform worse than HF (MP2, MP4, and CISD) for C_3H_4, their inferior performance is due to errors introduced in their attempt to capture the correlation energy. These methods introduce a bias in which they capture correlation energy more efficiently for propyne than for allene, thereby overstabilizing propyne and producing inaccurate allene/propyne relative energies. These results suggest that this bias is strong for MP2 but is corrected in more advanced theories to such an extent that the CCSD(T) result falls within the experimental error bars. For DFT methods there is an additional complication because errors arise in calculating both the correlation and exchange energies. In any case, this system represents two isomers with nearly identical correlation energies, thereby providing a useful benchmark to measure the biases of various methods in determining correlation energies.

Conclusion

We have examined the performance of various quantum chemical methods in calculating the energy difference between cumulene/poly-yne isomers. The tailored BXLYP DFT method outperforms both HF and the common DFT method B3LYP in all cases. Both B3LYP and BXLYP are hybrid methods, and the difference between them is that they use different weights on the HF and Slater functionals in calculating the exchange energy. B3LYP consists of mainly gradient corrected Slater exchange with a small contribution from HF exchange and systematically overstabilizes the cumulenes; BXLYP consists mainly of HF exchange with a small contribution of gradient corrected Slater exchange and systematically overstabilizes the poly-ynes (although to a smaller extent than B3LYP overstabilizes cumulenes). This observation implies that KMLYP, which uses roughly equal mixtures of HF and Slater (without the Becke88 gradient correction), may be well-suited for this application. We find that KMLYP significantly outperforms both B3LYP and BXLYP for calculating the $C_{2n+1}H_4$ cumulene/poly-yne energy differences for C_5H_4 and longer chains. This result is due to the fact that the roughly equal errors in HF and Slater exchange cancel to a much better degree in KMLYP than in B3LYP and BXLYP and is manifested by KMLYP having the smallest isomerization error per C_2 monomer unit. These results indicate that the KMLYP method is particularly useful for describing large systems that involve subtle competition between localization and delocalization within the π-orbital subspace. For many large systems (greater than 10 carbon atoms), sophisticated methods such as QCISD(T) and CCSD(T) necessary to accurately describe the relative energies between various isomers are not practical. However, DFT methods and second-order perturbation theory methods are in general too inaccurate to describe these relative energies correctly. In fact, even methods such as MP4(SDQ) and CCSD have relatively large errors in the isomerization energies even for short oligomeric sequences, such as C_9H_4 and $C_{11}H_4$. The results presented herein provide evidence that KMLYP is well-suited for studying systems similar to the cumulene/poly-yne systems, such as large unsaturated annulenes, where DFT methods generally perform poorly and where other methods required to attain accurate results, most like CCSD(T), are impractical.

We have also performed more thorough calculations on the simplest cumulene/poly-yne pair, allene and propyne. We notice that DFT methods routinely predict the wrong sign for the enthalpy difference between these two molecules, although KMLYP is more accurate than the BLYP, B3LYP, B3PW91, and *m*PW1PW91 DFT methods. The wave function methods all produce the correct sign (albeit some with significant error) as do the compounds methods, excluding CBS-4M and CBS-Q. Furthermore, some advanced wave function methods are considerably less accurate than HF in reproducing the experimental value for allene/propyne isomerization enthalpy. We attribute this success of HF to a fortuitous equivalence of correlation energies between allene and propyne. Errors in higher wave function methods seem to be derived from biases in capturing correlation energy in propyne versus allene. Calculations on this system can provide a good means of evaluating the biases inherent to quantum chemical theories, so this system may be used to evaluate and characterize new electronic structure methods.

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