

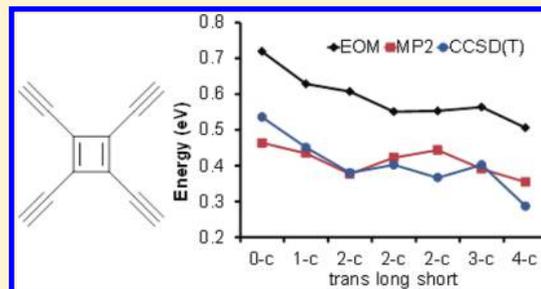
Effects of Ethynyl Substituents on the Electronic Structure of Cyclobutadiene

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S Supporting Information

ABSTRACT: The effects of ethynyl substitution on the electronic structure of cyclobutadiene are investigated in this work. Ethynyl substituted cyclobutadienes may be involved in Bergman cyclization reactions and are possible intermediates in the formation of fullerenes and graphitic sheets. Prediction of the electronic structure of cyclobutadiene is challenging for single-reference ab initio methods because of Jahn–Teller distortions and the diradical character of the singlet state. The equation-of-motion spin-flip coupled-cluster with single and double excitations (EOM-SF-CCSD) method accurately describes diradical states and is used to determine vertical and adiabatic singlet–triplet energy splittings in the substituted cyclobutadienes. The adiabatic singlet–triplet gaps decrease upon substituent addition, but the singlet states remain lower in energy. However, the results are affected by spin-contamination of the reference state and deteriorate when an unrestricted HF reference is employed. Additional insights in the electronic structure of cyclobutadienes are obtained by analyzing natural charges and spin densities. The substituents pull the charge out of the cyclobutadiene ring; however, the natural charges and spin densities are found to be nearly independent of the geometry and spin state.



INTRODUCTION

Because of their unique optical and electric properties, large ordered carbon systems such as graphene, fullerene, and carbon nanotubes are promising materials for developing new kinds of ultrasmall electronics. However, current production methods of graphene fail to provide consistent results in quality or size of the product. It has been proposed that carbon nanotubes and fullerene can be formed from alkyne chains that approach each other and form an antiaromatic cyclobutadiene ring.^{1–7} From there, the molecule can undergo Bergman cyclization and form a diradical cyclobutadiene-fused *p*-benzyne.⁷ Upon further cyclizations, fullerene or graphitic sheets are formed (Figure 1). In this work, we investigate the electronic structure and stability of the compounds involved in the initial step of this reaction scheme, namely, ethynyl substituted cyclobutadienes.

Cyclobutadiene has attracted extensive attention of theoreticians and method developers due to its intriguing characteristics such as antiaromaticity and diradical nature.^{8–39} Electronic structure of cyclobutadiene is challenging for ab initio methods because it undergoes Jahn–Teller distortions and has strong diradical character in the singlet state.²⁵ Therefore, standard single-reference methods such as Hartree–Fock (HF), second-order perturbation theory (MP2), or density functional theory (DFT) that lack nondynamical correlation fail to properly describe this system. Dynamical correlation is equally important for an accurate description of cyclobutadiene. While it is possible to employ multireference techniques that capture both nondynamical and dynamical correlation, such as CASPT2,^{40,41} MRPT2,^{42–45} or MRCl,⁴⁶ it

has been shown that the electronic structure of cyclobutadiene is accurately described by the spin-flip (SF) variant of the equation-of-motion coupled-cluster with single and double excitations (EOM-CCSD) method, i.e., EOM-SF-CCSD.³⁰ The SF variants of EOM-CC, configuration interaction (CI), and time-dependent (TD) DFT were developed by Krylov and co-workers to specifically target diradicals and bond-breaking.^{30,47–51} In this work, we employ EOM-SF-CCSD to investigate the electronic structure of ethynyl substituted cyclobutadienes. In particular, we determine how the substituents change the singlet–triplet energy splittings and whether these changes occur because of geometric distortions due to substituents or because of different stabilization of singlet and triplet states. The NBO analysis based on the EOM-SF-CCSD electron density is performed to characterize electron withdrawing effects and changes in spin-densities in singlet and triplet states.

COMPUTATIONAL DETAILS

For convenience, the substituted cyclobutadienes are labeled by the number of substituents, i.e., cyclobutadiene with zero substituents is called 0-c, ethynylcyclobutadiene is called 1-c, diethynylcyclobutadiene is 2-c, etc. Depending on the way of connecting substituents in the doubly substituted cyclobutadienes, one can distinguish between 2-c *trans* (two

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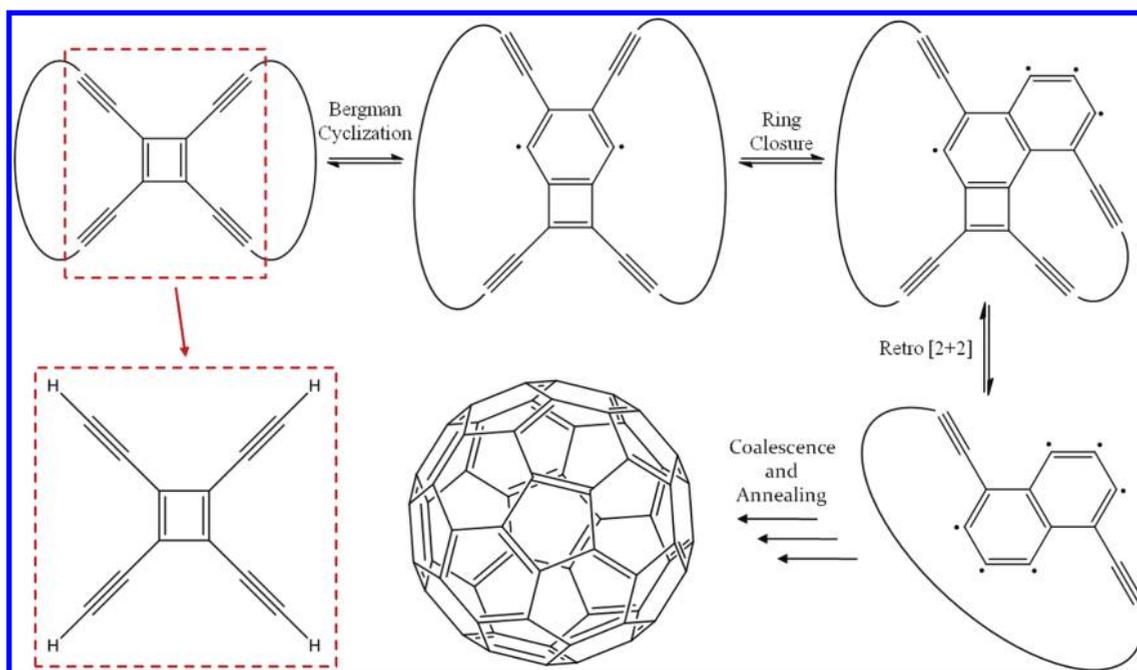


Figure 1. Proposed reaction pathway for fullerene formation.⁷ Ethynyl substituted cyclobutadienes are involved in the first step of the reaction.

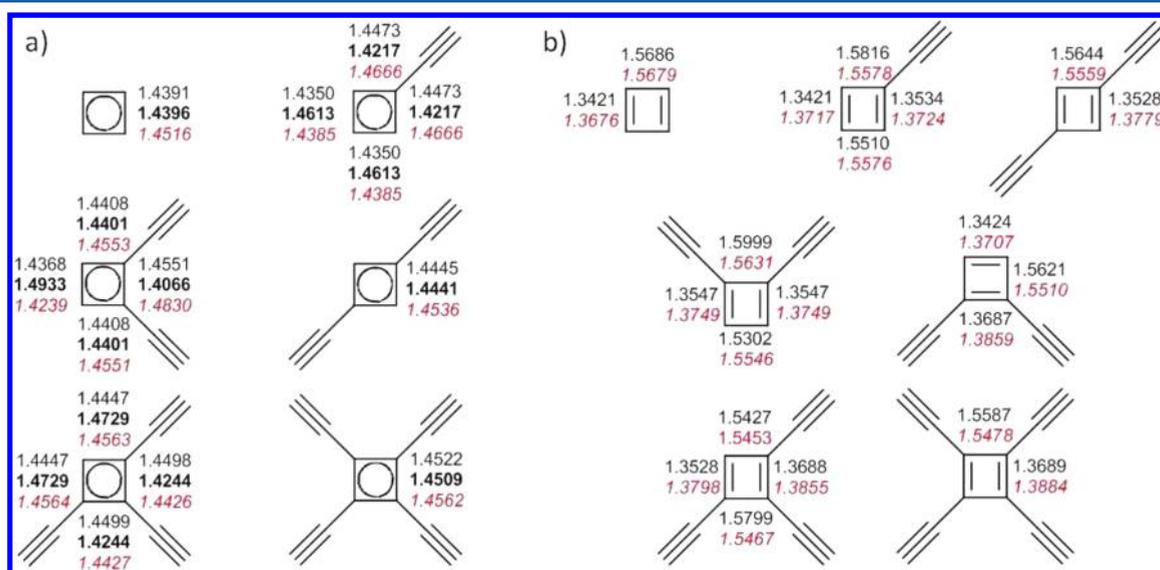


Figure 2. Bond lengths in cyclobutadiene ring in (a) triplet states of ethynyl substituted cyclobutadienes [ROMP2/cc-pVTZ, UMP2/cc-pVTZ (bold), UEOM-SF-CCSD/cc-pVDZ (red italics)] and (b) singlet states [RMP2/cc-pVTZ, UEOM-SF-CCSD/cc-pVDZ (red italics)].

substituents are attached to opposite sides of the ring in a trans position), **2-c short** (connection to a shorter carbon–carbon bond), and **2-c long** (connection to a longer carbon–carbon bond). In the symmetric triplet state, **2-c short** and **2-c long** are identical structures.

Geometry optimizations and frequency calculations of the ethynyl substituted cyclobutadienes were performed using the second order Moller–Plesset (MP2) perturbation theory⁵² with a correlation consistent basis set of triple- ζ quality (cc-pVTZ)⁵³ utilizing the GAMESS^{54,55} electronic structure package. Both restricted open-shell (RO) and unrestricted (U) HF references were employed for the triplet states, i.e., ROMP2 and UMP2, respectively. Restricted (R) HF reference was used for the singlet states. The frequency analysis performed at the MP2/cc-pVTZ level acquired real frequencies

for all reported structures. Further geometry optimizations were performed starting from the optimized MP2 structures using the SF variant^{30,50,51,56} of EOM-CCSD^{57–60} with a cc-pVDZ basis set.⁵³ Unrestricted triplet HF reference was employed in EOM-SF-CCSD geometry optimizations (i.e., UEOM-SF-CCSD). EOM-SF-CCSD employing restricted open-shell reference (ROEOM-SF-CCSD) was also used for single-point energy calculations. Natural bond orbital (NBO) analysis^{61,62} was performed at the EOM-SF-CCSD/cc-pVDZ optimized geometries using UEOM-SF-CCSD, ROEOM-SF-CCSD, and HF densities (all with cc-pVDZ basis set). EOM-SF-CCSD calculations and NBO analysis were performed in the Q-Chem electronic structure package.⁶³ Additionally, for the investigation of the energetics of the isodesmic and homodesmotic reactions, geometry optimizations of involved species (Figure

5) were performed at the MP2/cc-pVTZ level, followed by single point energy calculations at the CCSD(T)/cc-pVTZ level (coupled cluster with single, double, and perturbative triple excitations method).⁶⁴ The CCSD(T) calculations were performed in the CFOUR computational package.⁶⁵

RESULTS AND DISCUSSION

Structures. It is well-known^{8–12,14–16,21–23} that the unsubstituted singlet cyclobutadiene exhibits a planar rectangular structure with alternating bond lengths of ~ 1.55 Å and ~ 1.37 Å, while the triplet state maintains a square planar structure with equal bond lengths of approximately 1.45 Å. The addition of ethynyl substituents does not change this main pattern (see Figure 2). That is, the singlet states exhibit rectangular-like structures with alternating bond lengths, and the triplets are approximately square. Analogous patterns were observed for cyano-, methyl-, and *t*-butyl-substituted cyclobutadienes.^{38,39}

At the square geometry, two nonbonded π orbitals of cyclobutadiene are exactly degenerate. In the triplet states, these two orbitals are singly occupied and the orbital degeneracy as well as the square geometry is preserved. The degeneracy between the orbitals is lifted in the singlet state, when one of the orbitals becomes doubly occupied and another empty, which leads to Jahn–Teller distortion to a rectangular geometry. However, even at rectangular geometries, the separation between diradical orbitals is small enough such that the second configuration (with two electrons occupying the higher orbital) has non-negligible weight. Thus, even though this singlet state of cyclobutadiene is of a closed-shell character, it is two-configurational and has diradical nature. Note that the open-shell singlet (not considered in this work) has two configurations of equal weights at any separations between the orbitals.⁶⁶

The ROMP2 and EOM-SF-CCSD triplet geometries of substituted cyclobutadienes are qualitatively similar. Slight distortions from square geometries are observed in both methods; with EOM-SF-CCSD showing larger deviations from square structures, see Figure 2. Typically, the bonds of the ring adjacent to a substituent lengthen and the opposite bonds become shorter. However, the deviations from the ring bonds in cyclobutadiene do not exceed 0.016 Å for MP2 and 0.03 Å for EOM-SF-CCSD and are often much smaller. The largest deviations occur in 2-c structures. Ring bond lengths in the fully substituted 4-c structure are by 0.05 Å and 0.013 Å longer (by MP2 and EOM-SF-CCSD, respectively) than in the cyclobutadiene. UMP2 optimized geometries exhibit larger deviations from the square structure than either ROMP2 or EOM-SF-CCSD. Strikingly, UMP2 patterns of shortening and lengthening of the bonds in the cyclobutadiene ring are opposite to the patterns observed in ROMP2 and EOM-SF-CCSD for structures 1-c, 2-c, and 3-c. In all of these structures, UMP2 tends to shorten the ring-bonds adjacent to a substituent and lengthen the opposite bond.

In the singlet state of cyclobutadiene, the double bonds are localized. The ratio of lengths of the double and single bonds provides an estimate of how diradical the molecule is at the given level of theory. For example, MP2 provides shorter double bonds and longer single bonds than EOM-SF-CCSD, suggesting that MP2 (along with many other single-reference techniques) underestimates the diradical character in the singlet state of cyclobutadiene. At the EOM-SF-CCSD level, the addition of substituents always results in the shortening of

single bonds and lengthening of double bonds; the maximum lengthening of a double bond is achieved in the fully substituted 4-c structure. This suggests that the substituents increase diradical character in the singlet cyclobutadienes and are expected to destabilize the singlet states. Generally, the MP2-optimized structures are in a qualitative agreement with the EOM-SF-CCSD structures. Several observed deviations include lengthening of one single bond while shortening of the other in 1-c, 2-c (long), and 3-c. However, in accord with the discussed trend, the double bonds at the MP2 level become longer in the substituted singlet molecules than the double bonds in the unsubstituted cyclobutadiene. For both singlets and triplets, the bond lengths in ethynyl substituents remain almost constant at all levels of theory.

Adiabatic Energy Gaps. The adiabatic singlet–triplet (ST) energy splittings in substituted cyclobutadienes are shown in Figure 3. The adiabatic ST splitting in the unsubstituted

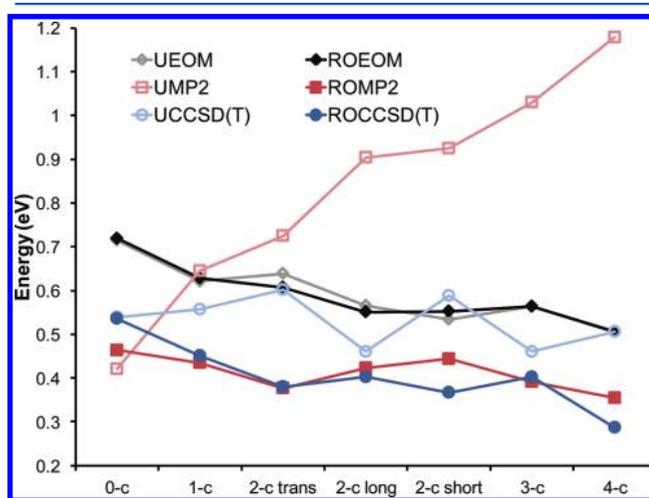


Figure 3. Adiabatic ST energy gaps (eV) calculated using UMP2//UMP2, UCCSD(T)//UMP2, ROMP2//ROMP2, and ROCCSD(T)//ROMP2 with a cc-pVTZ basis set and UEOM-SF-CCSD//UEOM-SF-CCSD [UEOM] and ROEOM-SF-CCSD//UEOM-SF-CCSD [ROEOM] with a cc-pVDZ basis set.

cyclobutadiene has been previously investigated by a number of computational methods.^{8,12,16,30,33,35–37} CCSD(T) (calculated at the MP2 optimized geometries) provides the adiabatic ST splitting of ~ 0.54 eV; EOM-SF-CCSD overestimates the ST splitting with respect to CCSD(T) and results in 0.72 eV energy separation, while MP2 underestimates this value and gives 0.42 and 0.46 eV separations, for UMP2 and ROMP2, respectively. It has been shown that the triple corrections decrease the EOM-SF-CCSD values of the ST splitting in cyclobutadiene, bringing it to a better agreement with the CCSD(T) values.⁶⁷

At the EOM-SF-CCSD level, the ST energy differences are the largest for the unsubstituted cyclobutadiene and decrease with the addition of substituents. The decrease in the adiabatic ST energies between structures 0-c and 4-c is 0.21 eV both with UHF and ROHF references. CCSD(T) employing ROHF reference for the triplet state (calculated at the ROMP2 geometries) has a similar trend of decreasing the ST gaps with increasing the number of substituents. The ROCCSD(T) difference in ST gaps between 0-c and 4-c is 0.25 eV. Interestingly, ROMP2 ST gaps agree very well with the ROCCSD(T) results, the largest discrepancy of ~ 0.08 eV being

observed for **2-c short**. However, ROMP2 exhibits a smaller decrease in the adiabatic energy gaps between structures **0-c** and **4-c** (~ 0.11 eV). The most striking observation from Figure 3 is a stark disagreement of UMP2 with the other methods. Indeed, UMP2 predicts a large ~ 1.3 eV increase of the ST gaps with the addition of substituents. We attribute this effect mainly to increasing spin-contamination and inaccuracy of UMP2 geometries for the triplet states. CCSD(T) calculations on top of the UMP2 geometries [UCCSD(T)] significantly improve the accuracy of UMP2. However, even at the CCSD(T) level, large unsystematic oscillations in the ST gaps with adding the substituents are observed. Thus, we ascribe the main source of errors in the UMP2 adiabatic ST energy splittings to inaccuracies in UMP2 geometries.

Spin-contamination of the triplet reference slightly affects the EOM-SF-CCSD results. While the coupled-cluster wave function is much less spin-contaminated than the HF reference, the remaining spin-contamination may lead to inaccuracies in excitation energies, as is observed in doubly substituted cyclobutadienes (**2-c long**, **2-c trans**, and **2-c short**) where the differences between the UEOM and ROEM ST splittings are of the order of several hundredths of an electronvolt. As been suggested previously,^{68,69} the most accurate results are obtained when restricted open-shell HF reference is employed in correlated calculations of open-shells.

The decrease in the adiabatic ST gaps upon adding substituents indicates that either the triplet state is stabilized or the singlet state is destabilized by the substituents. As discussed above, geometrical changes due to substituents (increasing lengths of the double bonds and decreasing lengths of the single bonds in the ring) indicate that the singlet states gain diradical character and become destabilized with respect to the triplets.

Vertical Excitation Energies. In order to separate the geometrical effects caused by ethynyl substitutions from the effects on the electron density of the cyclobutadiene ring and the stability of the singlet and triplet states, the vertical ST energy gaps are analyzed in this section. Since the singlet state is the ground state, it is expected that the vertical ST energy gaps are larger than the adiabatic ones at the singlet geometries and smaller than the adiabatic ones at the triplet geometries. The MP2 vertical ST energy gaps are provided in the Supporting Information (Figure SF1). MP2 cannot properly describe the diradical singlet states at the triplet geometries where two π orbitals of the cyclobutadiene ring are (nearly) degenerate, resulting in unpredictable behavior of the vertical ST gaps. At the singlet geometries, the diradical character of the singlet state decreases, and it is valid to employ single-reference methods such as MP2 or CCSD(T). As expected, the ROMP2-based singlet-geometry vertical ST splittings decrease with adding substituents. However, UMP2-based singlet-geometry ST gaps increase but lack any clear pattern. This dubious performance of UMP2 for the vertical ST gaps can be attributed only to the spin-contamination of the triplet states.

EOM-SF-CCSD vertical ST energy splittings are shown in Figure 4. This data shows nice agreement with the physical picture of the singlet state being lower in energy than the triplet state. Singlet-geometry vertical ST energy gaps decrease as substituents are added, while the triplet-geometry ST gaps remain almost constant. This may indicate that either the singlet and triplet energy surfaces become flatter or that the singlet geometries become closer (more similar) to the triplet geometries with adding substituents. The geometrical changes

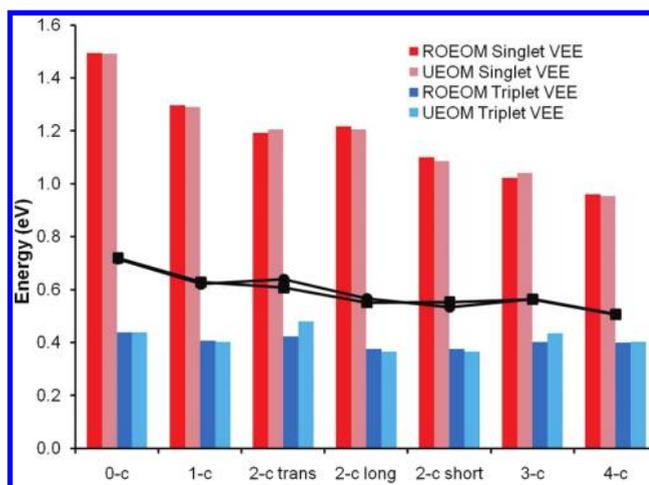


Figure 4. Vertical ST excitation energies (VEE) in eV calculated at the singlet (blue) and triplet (red) UEOM-SF-CCSD optimized geometries by ROEOM-SF-CCSD and UEOM-SF-CCSD in the cc-pVDZ basis set. Black lines show adiabatic ST gaps at the same levels of theory.

in the structure of the cyclobutadiene ring suggest that the later assumption (more similar singlet and triplet geometries) is valid.

Isodesmic and Homodesmotic Reactions. Stabilization energies of substituents can be related to heats of formation and calculated from energetics of the corresponding reactions. However, calculation of heats of formation is challenging because of differences in electron correlation in reactants and products. In order to simplify this task, various types of reactions that preserve the number and type of particular bonds were suggested and discussed in literature.⁷⁰ In this work, we analyze heats of formation energies associated with adding ethynyl substituents by using isodesmic and homodesmotic reactions (reactions 1 and 2–5, respectively, in Figure 5). The

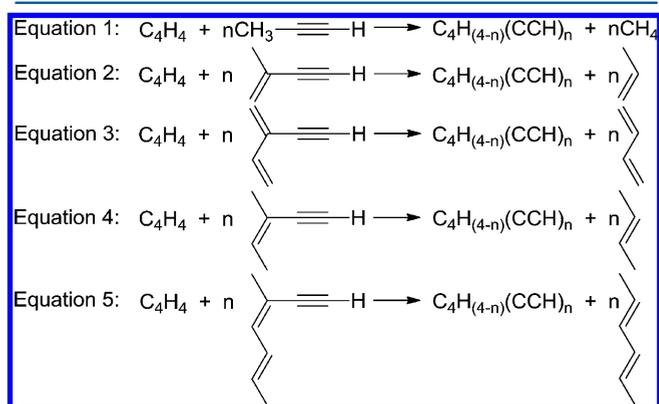


Figure 5. Isodesmic (1) and homodesmotic (2–5) reactions.

isodesmic reactions preserve the number and type of bonds (single, double, and triple).⁷⁰ The homodesmotic reactions preserve the hybridization, the number and types of bonds of the carbon atoms, and the number of hydrogen atoms bonded to individual carbon atoms in reactants and products.⁷⁰ Therefore, homodesmotic reactions are expected to provide more accurate estimates of stabilization energies. Reaction 1 is similar to reactions employed by Balci³⁸ and Menke³⁹ for methyl, *t*-butyl, and cyano substituted cyclobutadienes and is

Table 1. Total and Incremental Substituent Stabilization Energies (kcal/mol) Calculated Using Reactions 1–5 (see Figure 5) at the MP2/cc-pVTZ Level^a

singlet RMP2	reaction 1		reaction 2		reaction 3		reaction 4		reaction 5	
	total	incr.	total	incr.	total	incr.	total	incr.	total	incr.
1-c	-11.74	-11.74	-3.73	-3.73	-4.26	-4.26	-2.40	-2.40	-1.71	-1.71
2-c short	-24.73	-12.25	-8.69	-4.23	-9.77	-4.77	-6.05	-2.91	-4.66	-2.22
2-c long	-24.17		-8.14		-9.22		-5.49		-4.10	
2-c trans	-23.08		-7.04		-8.12		-4.40		-3.01	
3-c	-36.75	-12.76	-12.70	-4.74	-14.32	-5.28	-8.73	-3.42	-6.65	-2.72
4-c	-50.01	-13.26	-17.95	-5.25	-20.11	-5.79	-12.66	-3.93	-9.88	-3.23
triplet ROMP2	reaction 1		reaction 2		reaction 3		reaction 4		reaction 5	
	total	incr.	total	incr.	total	incr.	total	incr.	total	incr.
1-c	-12.07	-12.07	-4.05	-4.05	-4.59	-4.59	-2.73	-2.73	-2.04	-2.04
2-c short	-26.38	-13.34	-10.35	-5.33	-11.42	-5.87	-7.70	-4.01	-6.31	-3.31
2-c long	-26.38		-10.35		-11.42		-7.70		-6.31	
2-c trans	-23.48		-7.45		-8.53		-4.80		-3.41	
3-c	-37.92	-12.51	-13.87	-4.49	-15.49	-5.03	-9.91	-3.17	-7.82	-2.48
4-c	-51.70	-13.78	-19.63	-5.76	-21.79	-6.30	-14.34	-4.44	-11.56	-3.74
triplet UMP2	reaction 1		reaction 2		reaction 3		reaction 4		reaction 5	
	total	incr.	total	incr.	total	incr.	total	incr.	total	incr.
1-c	-4.48	-4.48	3.54	3.54	3.00	3.00	4.86	4.86	5.56	5.56
2-c short	-8.37	-4.76	7.66	3.25	6.58	2.71	10.31	4.58	11.70	5.27
2-c long	-8.37		7.66		6.58		10.31		11.70	
2-c trans	-10.98		5.05		3.97		7.69		9.08	
3-c	-14.62	-5.38	9.43	2.64	7.81	2.10	13.40	3.96	15.48	4.66
4-c	-20.56	-5.95	11.50	2.07	9.34	1.53	16.79	3.39	19.57	4.09

^aRMP2 is used for singlets; ROMP2 or UMP2 is used for triplets. Zero point vibrational energies are included. The incremental stabilization energies for the doubly substituted cyclobutadienes are averaged.

isodesmic because the hybridization of the ethynyl group changes from sp^3 to sp^2 .⁷⁰

Table 1 provides total and incremental stabilization energies due to adding ethynyl substituents at the MP2/cc-pVTZ level. Cyclobutadienes are considered both in singlet and triplet states. Stabilization energies in the singlet reactions decrease from reaction 1 to reaction 5, with a large jump occurring from isodesmic reaction 1 to the homodesmotic reaction 2. The same trend is observed for the triplet reactions calculated at the ROMP2 level. For all the considered reactions, stabilization of the triplet is larger than the stabilization of the singlet and, as discussed above, leads to a decrease of the singlet–triplet energy separation upon substitutions.

Both the singlet and triplet states are stabilized monotonically with adding the ethynyl substitutions. Incremental stabilization energies for **2-c short**, **2-c long**, and **2-c trans** differ between reaction 1 and reactions 2–5, but doubly substituted cyclobutadienes are energetically always between **1-c** and **3-c**. These results are contrary to the results reported for cyano-substituted cyclobutadienes using the homodesmotic reaction similar to reaction 1, where a nonmonotonic increase of stabilization energies upon substitutions was observed.³⁹ Increase of incremental stabilization energies in cyclobutadienes with more substituents suggests that some nonadditive stabilization effects are present in these systems.

Triplet stabilization energies at the UMP2 level contradict the ROMP2 trends. In particular, UMP2 results for reactions 2–5 suggest that the triplet state is destabilized with substituent addition. This destabilization effect agrees with the increasing adiabatic ST energy gaps observed at the UMP2 level upon substituent addition (Figure 3).

On the basis of the MP2 results, homodesmotic reaction 2 is sufficient for an accurate description of the substituent stabilization energies. CCSD(T)/cc-pVTZ stabilization energies using MP2/cc-pVTZ geometries and zero point energy corrections for reactions 1 and 2 are summarized in Table 2. The CCSD(T) results for the singlet states and the ROCCSD(T) results for the triplet states match the energies and trends observed at the equivalent MP2 levels. Large differences are observed between the UCCSD(T) and UMP2 as CCSD(T) reduces the effects of spin-contamination but still suffers due to inaccurate UMP2 geometries.

NBO Analysis. NBO analysis is employed for understanding the substituent effects on the electronic structure of cyclobutadiene. Natural charges based on the EOM-SF-CCSD density show that in both the singlet and triplet states, the total charge on the cyclobutadiene ring (carbon atoms only) is reduced as substituents are added, see Figure 6. Interestingly, the total charge is insensitive to the level of theory, structure, or spin state of the molecule, as the total ring charges for the singlet and triplet states are nearly identical. The total charge on the ring decreases linearly by ~ 0.20 electron per substituent, going from -0.841 for unsubstituted cyclobutadiene to -0.048 for **4-c**. The atom on the ring attached to the substituent loses the most charge. Carbons adjacent to the carbon with a substituent lose 1/5 of their charge. This trend is very similar to the effects caused by cyano substitutions.³⁹ For the antiaromatic system, partial loss or increase of charge on the ring is expected to stabilize the molecule. The singlet state of the cyclobutadiene is considered to be antiaromatic, while the triplet state is aromatic.^{31,32,34,71,72} Thus, electron-withdrawing effects of ethynyl substituents should stabilize the singlet state by decreasing the antiaromatic character and destabilize the

Table 2. Total and Incremental Substituent Stabilization Energies (kcal/mol) Calculated Using Reactions 1–2 (Figure 5) at the CCSD(T)/cc-pVTZ Level^a

singlet RCCSD(T)	reaction 1		reaction 2	
	total	incr.	total	incr.
1-c	-10.71	-10.71	-3.42	-3.42
2-c short	-22.05	-10.92	-7.48	-3.63
2-c long	-21.67		-7.10	
2-c trans	-21.16		-6.58	
3-c	-32.74	-11.12	-10.88	-3.83
4-c	-44.21	-11.46	-15.06	-4.18

triplet ROCCSD(T)	reaction 1		reaction 2	
	total	incr.	total	incr.
1-c	-12.34	-12.34	-5.05	-5.05
2-c short	-26.85	-13.11	-12.27	-5.82
2-c long	-26.85		-12.27	
2-c trans	-22.65		-8.07	
3-c	-37.03	-11.58	-15.16	-4.29
4-c	-49.12	-12.10	-19.97	-4.81

triplet UCCSD(T)	reaction 1		reaction 2	
	total	incr.	total	incr.
1-c	-8.22	-8.22	-0.93	-0.93
2-c short	-15.89	-8.34	-1.31	-1.05
2-c long	-15.89		-1.31	
2-c trans	-17.91		-3.33	
3-c	-25.43	-8.87	-3.57	-1.58
4-c	-35.40	-9.97	-6.25	-2.68

^aRCCSD(T) is used for singlets; ROCCSD(T) or UCCSD(T) is used for triplets. MP2/cc-pVTZ zero point vibrational energies are included.

aromatic triplet state, thus increasing the singlet–triplet gaps. However, the electron-withdrawing effect of substituents is apparently weaker than the geometric effect as the latter plays a dominant role in energetics of the electronic states.

NBO analysis of spin densities is performed based on the HF and EOM-SF-CCSD densities. The total HF spin density of the triplet states should sum to two since $m_s = 1$ and to zero for the singlet states. EOM-SF-CCSD describes both singlet and triplet as $m_s = 0$ states, so the total spin density in both states is zero. A unique feature of EOM-SF-CCSD is that it provides an

opportunity to analyze the spin-density of the singlet states that is exactly zero in RHF singlets.

The triplet spin densities at the UHF level (see Figure 7) show trends and values similar to the ones observed for the

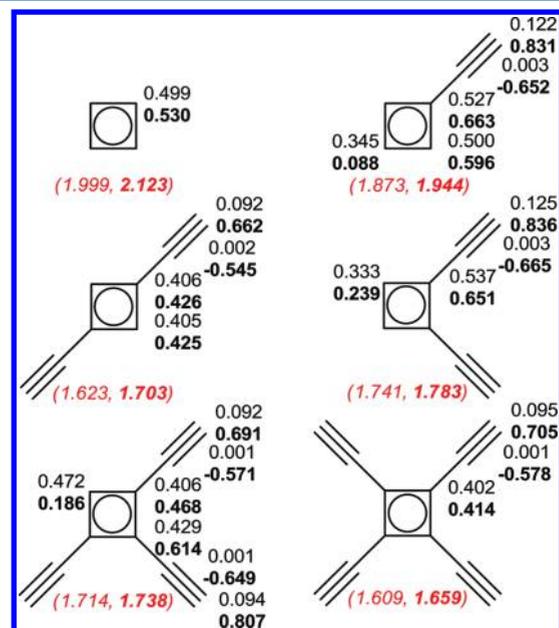


Figure 7. Spin density (atomic units) on each symmetry unique atom in the triplet substituted cyclobutadienes calculated at the ROHF/cc-pVDZ and UHF/cc-pVDZ (bold) levels of theory. The total spin density of the ring is given in red italics. Double bonds correspond to shorter sides of rectangular singlet cyclobutadienes.

cyano substituted cyclobutadienes.³⁹ Namely, there is a large spin polarization on the substituents and a removal of spin density from the ring carbons not adjacent to a substituent. At the ROHF level, there is no spin polarization on the substituents and there is little spin density on them. Both ROHF and UHF show a decrease of the total spin density on the ring upon adding substituents, but otherwise, ROHF and UHF provide very different spin density pictures.

Both ROHF-based and UHF-based EOM-SF-CCSD densities in the triplet states show spin polarization on the ethynyl substituents, see Figure 8a. However, the total spin density on the ring increases as substituents are added. This is qualitatively

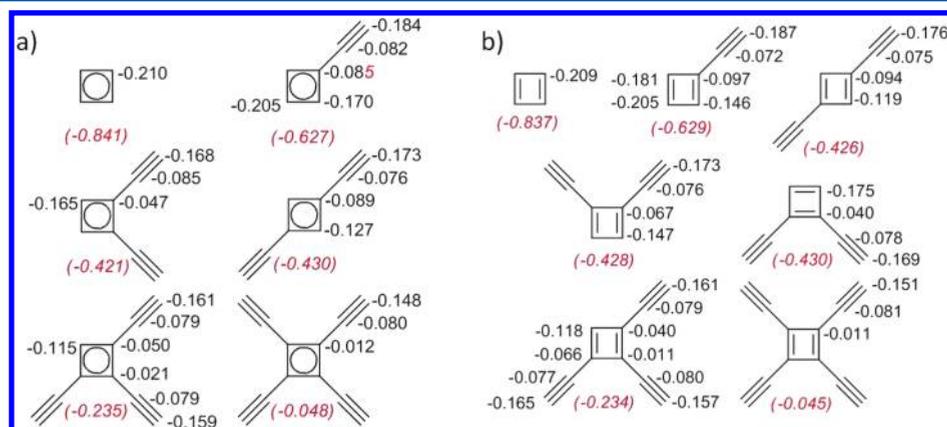


Figure 6. NBO charges on symmetry unique atoms, in atomic units, in (a) triplet and (b) singlet substituted cyclobutadienes calculated at the ROEOM-SF-CCSD/cc-pVDZ level of theory. The total charge of the ring is given in red italics.

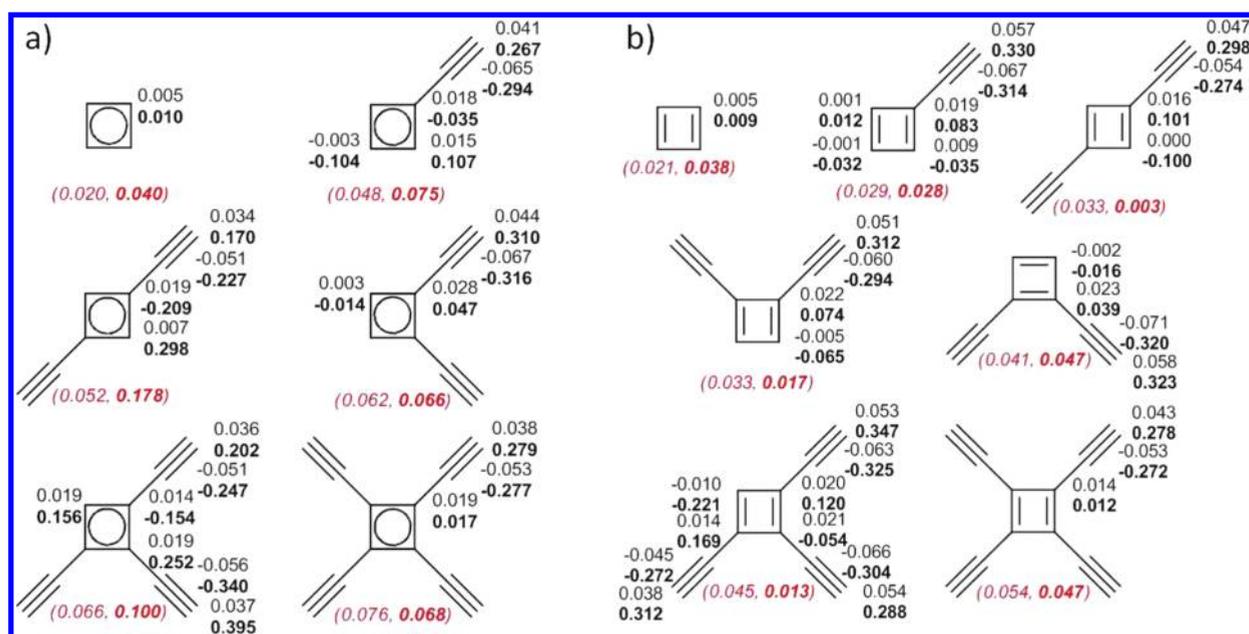


Figure 8. Spin density (atomic units) on each symmetry unique atom in (a) triplet and (b) singlet substituted cyclobutadienes calculated at the ROEOM-SF-CCSD/cc-pVDZ and UEOM-SF-CCSD/cc-pVDZ (bold) levels of theory. The total spin density of the ring is given in red italics. Double bonds correspond to shorter sides of rectangular singlet cyclobutadienes.

different from ROHF and UHF results. The absolute values of the spin densities by UEOM are larger than those by ROEOM, by as much as a factor of 10, suggesting a larger spin-contamination in the UEOM wave function. It is interesting to see that the spin-density of the singlet states has similar trends and absolute values as the spin-density of the corresponding triplet states (Figure 8b).

Overall, we observe significant differences in spin-density patterns calculated at different levels of theory. A correlated method is needed for an even qualitatively accurate NBO analysis. It would be noteworthy to investigate whether the patterns observed for ethynyl substituted cyclobutadienes are preserved with other substituents.

CONCLUSIONS

The effects of ethynyl substitutions on the electronic structure of cyclobutadiene are investigated. Substituents significantly increase the spin-contamination of the triplet states, making MP2 and CCSD(T) strongly dependent on the HF reference employed. Using the UHF reference results in striking overestimation and erroneous trend of the singlet–triplet gaps with increasing the number of substituents. With the ROHF references, the singlet states remain lower in energy than the triplet states in all considered cyclobutadienes, but the adiabatic singlet–triplet energy gaps decrease with adding the ethynyl substituents. Direct calculations of the ST gaps agree with analysis of the heat of formations using isodesmic and homodesmotic reactions that show that the triplet states are more stabilized than the singlet states, resulting in a decrease of the adiabatic splitting upon adding substituents. The decrease of the ST gaps may be explained by geometric effects of substituents, namely, by lengthening the double and shortening the single bonds in the cyclobutadiene ring, which increases diradical character of the singlet states and makes them less stabilized than the triplets.

Employing the NBO analysis reveals that, as expected, the substituents pull the electron density out of the cyclobutadiene

ring. The natural charges and spin densities are nearly independent of the geometry and spin state of the cyclobutadienes; however, they are strongly dependent on the level of theory and the HF reference employed. The spin-flip version of EOM-CCSD is a useful tool for analysis of spin-densities in diradicals as it allows calculation of spin-densities in singlets and comparing them to those in triplets.

ASSOCIATED CONTENT

Supporting Information

Spin-squared values of the HF references in substituted cyclobutadienes, MP2 vertical ST energy differences, and comparison of MP2 energies for the triplet states are provided. 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.

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