FTIR spectra were measured by Dr. S. Muralidharan in the Strategic Metals Recovery Research Facility of the University of Arizona.

Supplementary Material Available: Stereoscopic view of the packing of the molecule in the unit cell, tables of final atomic positional and thermal parameters, bond length, bond angle, and selected torsion angle data (8 pages); listings of structure factor amplitudes for amino acid **1c** (10 pages). Ordering information is given on any current masthead page.

Ab Initio C_s Transition State for the Diels–Alder Reaction of Acetylene and Butadiene

James M. Coxon,* Stephen T. Grice, Robert G. A. R. Maclagan,* and D. Quentin McDonald

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Ab initio calculations are reported for the Diels–Alder reaction between acetylene and butadiene. An activation energy of 60.9 kJ mol^{-1} and an enthalpy of –287.8 kJ mol^{-1} have been calculated at the MP4SDQ/6-31G*// HF/6-31G* level of theory. A full set of vibrational frequencies, calculated at the 4-31G level, exhibited a single imaginary frequency for the transition structure with C_s symmetry. The geometry of this transition structure was almost identical with the critical point determined at the HF/6-31G* level of theory. An analysis of the distortion energy of the reactants in the forward reaction at infinite separation showed that the magnitudes of the repulsive and attractive electronic contributions to the transition barrier are approximately equal. The increase in energy of the filled π-orbital of acetylene not involved in bonding changes is a major contributor to the activation energy for the Diels–Alder reaction of butadiene with acetylene being greater than that of butadiene and ethylene.

The Diels–Alder [$_\pi 4 + _\pi 2$] cycloaddition continues to challenge experiment and theory. A concerted synchronous mechanism is now favored by the highest levels of theory[1] and supported by experiment,[2] however, controversy still exists. Ortega et al.[3] have argued that the inclusion of correlation energy contributions increases the tendency toward asynchronicity, but the validity of this result is limited by the restriction imposed in the calculation such that the sum of the lengths of the two σ-bonds being formed is 4.4 Å. Dewar,[4] from studies at the HF level of theory, considers open-shell singlet "diradical" configurations to be important in the transition state. This is supported by the AM1 study of Chai and Lee[5] on substituent rate trends. However, recent ab initio studies by Houk et al.[1e] using a 3-21G basis set and RHF procedures also reproduced substituent effects for the reaction of butadiene with substituted alkenes, and the transition states showed little or no asynchronicity despite the nature of the unsymmetrical dienophiles.

A study of the butadiene–ethylene hypersurface, which included calculations with both minimal and nonminimal basis sets and the inclusion of correlation energy by the multiconfiguration SCF (MCSCF) method, has been reported by Bernardi et al.[1a] With a minimal STO-3G basis set, a "asynchronous diradicaloid" mechanism involving two intermediates and three "transition states" of differing conformation was found to be thermodynamically favored to a concerted process. However, with use of an extended 4-31G basis set, the surface around the "diradicaloid" pathway is flattened and the synchronous process is favored. These calculations did not include zero-point vibrational energy (ZPVE) corrections.[6]

An ab initio study at the RHF/6-31G* level of theory has similarly given[1d] a symmetrical transition state for the reaction of ethylene and butadiene. This is the largest basis set used to date in a study of the Diels–Alder reaction. The inclusion of correlation energy and polarization functions gave a calculated activation energy (106.3 kJ mol^{-1}, MP4SDTQ/6-31G*//HF/6-31G*) close to the experimental value (115.1 kJ mol^{-1}).

The analogous reaction between *cisoid*-1,3-butadiene and acetylene has to date not been the subject of theoretical investigation despite the fact that numerous synthetic examples exist for which this reaction is the prototype and an industrial process for the parent reaction is patented.[7] We now report the first ab initio calculation and transition-state structure for the reaction of *cisoid*-1,3-butadiene and acetylene.

Results and Discussion

Most theoretical studies of the [$_\pi 4 + _\pi 2$] reaction have used small basis sets and not included polarization functions. The inadequacy of such calculations in comparing alternative reaction pathways is well-known. The use of

(1) (a) Bernardi, F.; Bottoni, A.; Field, M. J.; Guest, M. F.; Hillier, I. H.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1988**, *110*, 3050. (b) Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609. (c) Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190. (d) Bach, R. D.; McDouall, J. J. W.; Schlegel, H. B.; Wolber, G. J. *J. Org. Chem.* **1989**, *54*, 2931. (e) Houk, K. N.; Loncharich, R. J.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 9172.

(2) (a) Gajewski, J. J.; Peterson, K. B.; Kagel, J. R.; Huang, Y. C. J. *J. Am. Chem. Soc.* **1989**, *111*, 9078. (b) Gajewski, J. J.; Peterson, K. B.; Kagel, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5545. (c) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554.

(3) Ortega, M.; Oliva, A.; Lluch, J. M.; Bertrán, J. *Chem. Phys. Lett.* **1983**, *102*, 317.

(4) Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771.

(5) Choi, J. Y.; Lee, I. *J. Chem. Soc., Faraday Trans. 2.* **1989**, *85*, 867.

(6) A preliminary study of the ethylene–butadiene reaction has revealed that the less constrained asynchronous transition state has a lower ZPVE. Inclusion of zero-point vibrational energy brings the synchronous and asynchronous transition states to almost equal energy. The region around the synchronous transition state is very flat, and differences in vibrational energies should not be ignored.

(7) U.S. Patent 3,513,209, 1970.

Table I. Total Energies and Zero-Point Vibrational Energies for the Optimized Geometries of Acetylene, *cisoid*-1,3-Butadiene, *transoid*-1,3-Butadiene, and 1,4-Cyclohexadiene and the C_s Transition State for the Diels–Alder Reaction of Butadiene and Acetylene

|	RHF (hartrees)	MP2 (hartrees)	MP4SDQ (hartrees)	ZPVE (kJ mol^{-1})	ΔE^a (kJ mol^{-1})
		4-31G Basis Set			
acetylene	−76.711 41	−76.893 60	−76.905 83	78.6	
cisoid-1,3-butadiene	−154.694 46	−155.047 27	−155.086 99	241.4	
transoid-1,3-butadiene	−154.699 96	−155.052 07	−155.091 70	242.2	
1,4-cyclohexadiene	−231.498 56	−232.025 46	−232.079 50		−227.6^b
C_s transition state	−231.341 09	−231.907 11	−231.947 21	328.5	119.7^b
		6-31G* Basis Set			
acetylene	−76.817 83	−77.064 61	−77.079 99	77.3	
cisoid-1,3-butadiene	−154.913 46	−155.415 39	−155.457 35	293.6	
transoid-1,3-butadiene	−154.919 65	−155.421 12	−155.462 81	240.3	
1,4-cyclohexadiene	−231.833 52	−232.589 62	c		−287.8^d
C_s transition state	−231.663 50	−232.456 82	c		60.9^d

^{a} ΔE is the energy relative to acetylene and *cisoid*-1,3-butadiene. ^{b} Calculated at the MP4SDQ/4-31G//HF/4-31G level of theory. ^{c} A vibrational frequency calculation was not carried with the 6-31G* basis set—see text. ^{d} Calculated at the MP2/6-31G*//HF/6-31G* level of theory.

larger basis sets and the inclusion of correlation energy is important for calculating thermodynamic parameters; however, the inclusion of correlation energy can become prohibitively expensive. A best practical estimate of the transition-state energy can be calculated by optimizing with larger basis sets at the restricted Hartree–Fock (RHF) level of theory and then performing a single-point Møller–Plesset calculation to include correlation energy.

To enable calculation of the activation energy and reaction enthalpy for both the forward and reverse reactions, the geometries of acetylene, *cisoid*- and *transoid*-butadiene, and 1,4-cyclohexadiene were optimized at the HF level of theory with both 4-31G and 6-31G* basis sets and GAUSSIAN 82.[8] The energies were then calculated for these optimized geometries at the MP2//HF or MP4SDQ//HF levels of theory. Harmonic vibrational frequencies were calculated at the HF level of theory. The optimized geometries are displayed in Figure 1, and the energies at the various levels of theory are given in Table I.

A starting geometry for high-level calculations of the C_s transition state of the butadiene–acetylene reaction was provided by RHF-AM1[9] calculations of the transition geometry. The distance between the carbon centers undergoing bonding was systematically varied while all other variables were optimized. The potential energy surface in the region of the col was found to be almost flat, and only a symmetric exit channel to product exists. Optimization of the transition state with respect to the 18 independent geometrical variables constrained with C_s symmetry was carried out at a RHF level of theory with both 4-31G and 6-31G* basis sets. Because of the flatness of the potential energy surface, it was necessary to calculate numerically those parts of the second-derivative matrix for the variables contributing most to the reaction coordinate.

Calculation of harmonic vibrational frequencies with the 4-31G basis set revealed a single imaginary frequency associated with a symmetric reaction coordinate (see Figure 2a). A frequency calculation was not performed at the 6-31G* level because it would have required more than 0.5 Gbyte of disk space. However, the geometry of the HF/6-31G* synchronous pathway critical point (see Figure 2b) was remarkably similar to that of the 4-31G transition-state geometry, and so we conclude that the critical
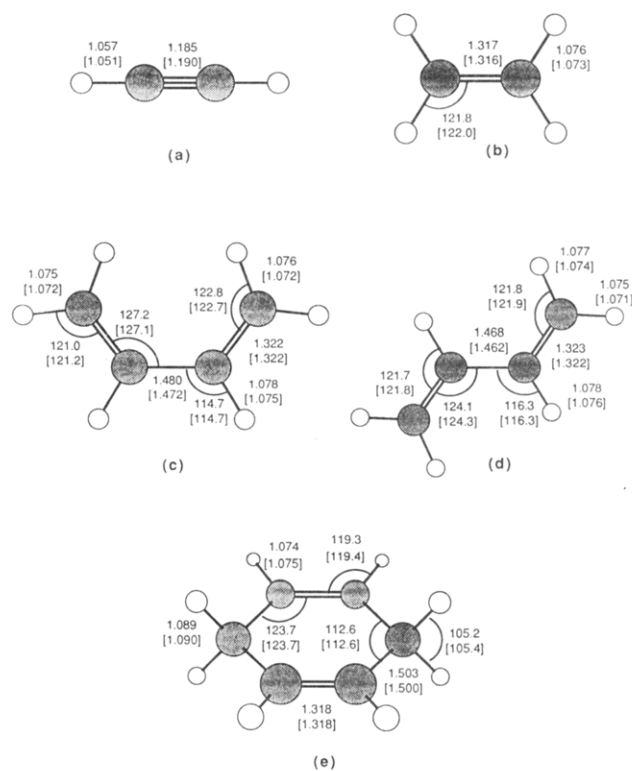
Figure 1. 4-31G [brackets] and 6-31G* optimized geometries for (a) acetylene, (b) ethylene, (c) *cisoid*-1,3-butadiene, (d) *transoid*-1,3-butadiene, and (e) 1,4-cyclohexadiene.
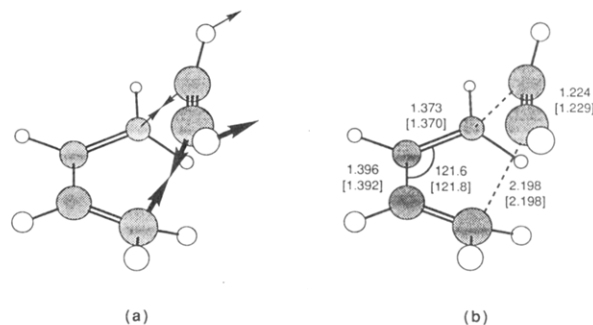
Figure 2. (a) C_s transition-state dominating vectors of the symmetric vibrational mode of the single imaginary frequency. (b) 4-31G C_s transition state [brackets] and 6-31G* C_s transition state for the acetylene–1,3-butadiene reaction.

(8) Binkley, J. S.; Firsch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. *Gaussian 82*; Carnegie-Mellon University: Pittsburgh, PA, 1983.

(9) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

point is a first-order saddle point. The energies at the transition-state geometries with the two basis sets are given

in Table I. The optimized geometry of the transition state for the acetylene–butadiene reaction at the HF/6-31G* level of theory has an angle of attack of acetylene to the plane of butadiene of 124.8°, and the forming σ-bond has lengths of 2.198 Å. In the transition state for the forward reaction, the C_1–C_2 and C_3–C_4 bonds of *cisoid*-1,3-butadiene and the C_5–C_6 bond of acetylene are lengthened by 0.051 and 0.039 Å, respectively, and the C2–C3 bond of *cisoid*-1,3-butadiene is shortened by 0.084 Å relative to the calculated reactant bond lengths.

In analogous HF/6-31G* calculations[1d] for the ethylene–butadiene reaction, the C_1–C_2/C_3–C_4 bonds of butadiene were lengthened by 0.055 Å and the C2–C3 bond was shortened by 0.087 Å. The extent of perturbation of the *cisoid*-1,3-butadiene bonds in the reaction with acetylene and ethylene will reflect the relative position of the transition state in the reaction pathway, and while these differences are small in absolute terms, the general trends in the parameters are consistent with a transition state for the acetylene reaction occurring earlier in the reaction coordinate.

At the MP4SDQ/4-31G//HF/4-31G level of theory, ΔE is calculated[10] for the reaction of acetylene and butadiene to be −227.6 kJ mol^{-1}, and at the MP2/6-31G*//HF/6-31G level of theory, ΔE is −287.8 kJ mol^{-1}. This compares with a value of ΔH = −205.4 kJ mol^{-1} (MP4SDTQ/6-31G//HF/6-31G*) for the reaction of butadiene and ethylene.[1d] The greater exothermicity of the acetylene reaction is consistent with an earlier transition state for the acetylene–butadiene reaction.

For butadiene–acetylene, ΔE for the transition state was calculated to be 119.7 kJ mol^{-1} at the MP4SDQ/4-31G/HF/4-31G level of theory. Inclusion of zero-point vibrational energy increases the barrier by 8.4 to 128.2 kJ mol^{-1} (Table I). This compares with a value of 77.1 kJ mol^{-1} for the reaction of ethylene and butadiene at the MP4SDTQ/6-31G* level of theory.[11] The difference in these ΔE's is in line with the experimentally observed difficulty of butadiene–acetylene cycloaddition reactions. For the trimerization of acetylene,[12] a reaction that has much in common with the Diels–Alder reaction of butadiene and acetylene, the estimated ΔE at the MP2/6-31G* level was notably higher than for the acetylene Diels–Alder reaction.

The acetylenic hydrogens at the transition state for butadiene and acetylene are distorted by 26.5° and 26.9° for the 4-31G RHF and the 6-31G* RHF calculations, respectively. These values are comparable to those reported for the transition state of the acetylenic carbons in the trimerization of acetylene[12] to benzene. For the trimerization reaction, a 3-21G SCF calculation showed that the acetylenic hydrogens are distorted 28.0° from linearity at the D_{3h} transition state. Bond lengthening between acetylenic carbons at the transition state in the butadiene–acetylene reaction of 0.039 Å is somewhat greater than calculated for the trimerization of acetylene (0.029 Å).

The activation barrier in a Diels–Alder reaction is the net effect of distortion energy of the reactants to the transition-state geometry, exchange repulsion, and stabi-
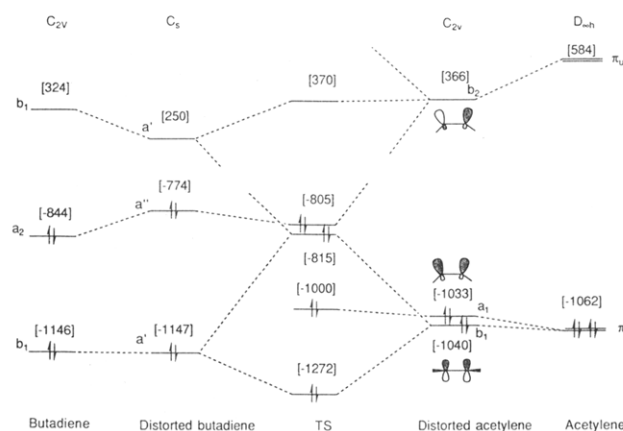
Figure 3. Electron correlation diagram for the C_s transition state for the reaction of acetylene and butadiene. One-electron orbital energies calculated at the RHF 6-31G* level of theory (kilojoules per mole).
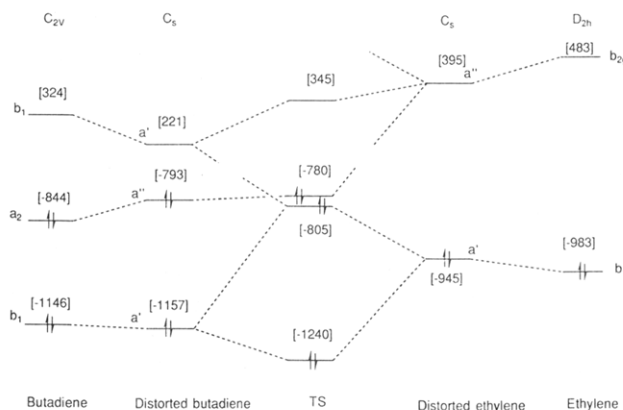
Figure 4. Electron correlation diagram for the C_s transition state for the reaction of ethylene and butadiene. One-electron orbital energies calculated at the RHF 6-31G* level of theory (kilojoules per mole).

lizing charge–transfer interactions. For the reaction of acetylene and butadiene the distortion energy for the reactants at infinite separation, but at their transition-state geometries, was established by single-point calculation as −106.2 kJ mol^{-1} at a MP4SDQ/4-31G level of theory. This value is comparable with the transition-state energy of −119.7 kJ mol^{-1} at the same level of theory, indicating that the magnitudes of exchange repulsion and charge-transfer interactions in this reaction at the transition state are almost equal.

For the trimerization of acetylene Houk et al.[13] have reported the distortion energy for the acetylenes to the transition-state geometry at the STO-3G level of calculation as 251 kJ mol^{-1}. The activation barrier for the forward reaction calculated at the same level of theory was 335 kJ mol^{-1}, and the 84 kJ mol^{-1} difference in energy was attributed to the excess of exchange repulsion over charge-transfer stabilization. This contrasts with the acetylene–butadiene reaction where the repulsive and attractive electronic interactions are approximately balanced at the transition state and the energy required to distort the reactants is approximately equal to the activation barrier for the reaction. Our calculations for the Diels–Alder reaction of ethylene and butadiene indicate that this is also the case with the repulsive and attractive electronic interactions approximately balanced.[14]

---

(10) ΔE is calculated relative to the energy of *cisoid*-1,3-butadiene and acetylene. A ΔH value is not available since a frequency calculation was not carried out for 1,4-cyclohexadiene.

(11) The ΔE for the transition state in the acetylene–butadiene reaction was 60.9 kJ mol^{-1} at the MP2/6-31G* level of theory compared with a value of 54.3 kJ mol^{-1} for the MP2/6-31G* calculation for the reaction of ethylene and butadiene.

(12) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837.

(13) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

The electron correlation diagrams, calculated at the RHF 6-31G* level of theory, for the C_s transition states for the reaction of butadiene with acetylene and ethylene[15] and including calculated energies of the reaction fragments distorted to the transition-state geometry, but at infinite separation, are shown in Figures 3 and 4. For the acetylene Diels–Alder reaction (Figure 3) there is 120 kJ mol⁻¹ net destabilization resulting from distortion to the transition-state geometry. Interaction of the distorted fragments results in a two-electron stabilization between the distorted butadiene HOMO a″ and the distorted acetylene LUMO b_2. The net destabilization shown of 222 kJ mol⁻¹ is a result of the four-electron three-orbital interaction between the a′ orbitals of distorted butadiene and the b_1 orbital of distorted acetylene.

For the ethylene Diels–Alder reaction (Figure 4) there is 78 kJ mol⁻¹ net destabilization resulting from distortion to the transition-state geometry. Interaction of the distorted fragments results in a two-electron interaction between the distorted butadiene HOMO a″ and the distorted ethylene LUMO a″, which is for this reaction destabilizing.[16] This two-electron destabilization combined with the four-electron three-orbital interaction between the a′ orbitals of distorted butadiene and the a′ orbital of distorted ethylene gives the net 148 kJ mol⁻¹ destabilization.

For the acetylene Diels–Alder reaction there is 42 kJ mol⁻¹ more destabilization resulting from distortion to transition-state geometry and 32 kJ mol⁻¹ more transition-state destabilization from the distorted fragments than for the corresponding reaction with ethylene. These differences contribute to the calculated net electronic energy difference between the reactions of 74 kJ mol⁻¹, the reaction of acetylene having the higher transition-state barrier.

A study of the valence orbitals not undergoing bonding changes shows that a significant contribution to the greater activation energy for the acetylene–butadiene reaction compared with the ethylene–butadiene reaction is a result of destabilization of the a_1 orbital of the distorted acetylene in the transition state. The a_1 orbital of acetylene as it distorts is raised in energy. A further increase in energy of this orbital occurs at the transition state, a result of

geometry constraints that force the a_1 orbital to overlap with filled orbitals in the butadiene fragment. This increase in energy (62 kJ mol⁻¹) is a major contributing factor to the difference in the transition barrier of the acetylene and ethylene Diels–Alder reactions (Figure 3).

For the trimerization of acetylene to benzene, a pseudo $[_\pi 4 + _\pi 2]$ reaction, the activation barrier is 259 kJ mol⁻¹ calculated[12] at the MP3/3-21G level of theory. The calculated[17] activation barrier for the $[_\pi 2 + _\pi 2]$ cycloaddition of acetylene and ethylene to cyclobutene is in excess of 300 kJ mol⁻¹. Both reactions have calculated activation barriers considerably greater for the butadiene–ethylene and butadiene–acetylene reaction. The activation barriers for butadiene–ethylene, butadiene–acetylene, and the trimerization of acetylene increase as we go across this series, and it is notable that the number of filled π-valence orbitals not directly undergoing bonding changes increases. As we go across this series of reactions, there is a trend toward greater reactant character at the transition state. This is indicated by the comparison of the calculated transition-state geometries reflected in the different bond deformations calculated for these reactions.

The transition-state calculations for the reaction of butadiene–acetylene demonstrate the existence of a synchronous concerted pathway for this reaction at this level of theory. Whether this is the energetically favored mechanism compared with an asynchronous or diradicaloid mechanism as proposed for the ethylene–butadiene reaction is still under investigation.

Conclusions

For the reaction of butadiene–acetylene, ab initio calculations at the HF/6-31G* level have shown the existence of a transition state consistent with a synchronous mechanism for cycloaddition. The higher activation barrier to that calculated for the reaction of ethylene–butadiene is consistent with presence of filled π-shell interactions at the transition state, and this is supported by an increase in the activation barrier for the trimerization of acetylene. For the reaction of butadiene with acetylene, the calculated distortion energy is comparable to the activation barrier, requiring that the charge transfer and exchange repulsion interactions are of comparable magnitude.

Registry No. Acetylene, 74-86-2; butadiene, 106-99-0.

(14) For ethylene and butadiene at the 6-31G* geometry reported for the transition state,[1d] E(HF) = -78.011 61 and -154.866 01 hartrees, respectively.

(15) The 6-31G* one-electron orbital energy calculations in Figure 3 are based on the 6-31G* geometry reported for the transition state.[1d] Ethylene optimized at 4-31G HF level: R(C–C) = 1.316, R(C–H) = 1.073 Å; E(HF) = -77.922 16, E(MP2) = -77.922 16, E(MP3) = -78.101 88, E(MP4SDQ) = -78.125 90 hartrees.

(16) A related comment has been made by Bach[1d] who noted that the butadiene HOMO – ethylene LUMO interaction was destabilizing.

(17) Hess, B. A., Jr.; Schaad, L. J.; Reinhoudt, D. N. *Int. J. Quantum Chem.* **1986**, *29*, 345.