

## ARTICLES

## Singlet–Triplet Gap in 1,2,3-Butatriene and Its Consequences on the Mechanism of Its Spontaneous Polymerization

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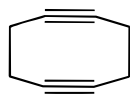
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Received: September 15, 1997; In Final Form: April 13, 1998

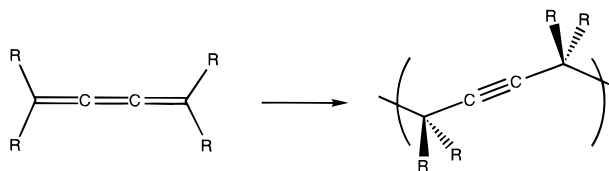
The reactivity of 1,2,3 butatriene,  $C_4H_4$ , has been postulated to be due to the presence of low-lying triplet states. However, there have been no experimental or theoretical determinations of the energy separations or geometries of these states. We have examined the structures, energetics, and possible mechanisms involved in the self-polymerization of the title compound using single-determinant ab initio molecular orbital theory. We find that the magnitude of the singlet–triplet gap for the monomer and its relatively high positive heat of formation does not allow for a mechanism involving the direct formation of an isolated triplet species. We speculate on an alternative mechanism and show its relationship to recent work on related reactive monomers.

## Introduction

As early as 1937, Carothers reported on the utility of 1,2,3-butatriene as a reactive monomer.<sup>1</sup> He observed that this material, when synthesized by elimination of hydrochloric acid from 1-chloro-2,3-butadiene, produced a white, fluffy, intractable polymeric material of unknown structure. It has been subsequently observed that 1,2,3-butatriene readily polymerizes to this unknown structure under almost all reaction conditions.<sup>2–5</sup> In a number of these studies, this polymer was also noted to undergo a color change from white to green and to black, even in the absence of air.<sup>2</sup> Additionally, there is a report in the literature<sup>3</sup> of a cyclic dimer, 1,5-cyclooctadiyne,



being extracted from the polymeric residue. The presence of free-radical inhibitors such as hindered phenols suppresses this reaction to some extent.<sup>2</sup> Recently, one of the authors<sup>6</sup> reported on the self-polymerization of the related compound 1,1,4,4-bis-(pentamethylene)-1,2,3-butatriene both as an intractable homopolymer and as a soluble high molecular weight alternating copolymer with maleic anhydride. The structure of the polymers were spectroscopically determined to be due to the 1,4 addition to form a poly(2-butyne-1,4-diyl) as the basic backbone.



This system was also inhibited by the presence of hindered phenols but required no initiator for polymerization to occur. As part of our ongoing interest in the polymer chemistry of butatrienes,<sup>7</sup> we have undertaken a study to understand the mechanism and energetics of this reaction as a means of predicting what structural features would allow for better control of the chemistry. The current study reports on molecular orbital theory based analysis of the reaction chemistry of the parent compound.

There have been some limited theoretical calculations on the ground-state structures of butatrienes, but we have been unable to locate any previously published work on the low-lying excited states of this species. Tantardini and Simonetta<sup>8</sup> have reported ab initio valence bond calculations for the valence ionization potentials using a contracted 6-31G basis. A comparative study of the structures, energetics, and bonding of butatriene and several other unsaturated hydrocarbons has been reported by Bock et al.<sup>9</sup> All geometries reported in that study were obtained at the Hartree–Fock level of theory, although single-point calculations at the MP2 level<sup>10</sup> were also reported. The most recent study of butatriene by Gundersen et al. reports results from higher-level calculations on the structure and quadratic force field of ground-state butatriene.<sup>11</sup>

The low-lying excited states of the linear isomer of butatriene have been suggested to play critical roles its reactivity.<sup>3,12</sup> However, none of the theoretical studies on butatriene that have been reported in the literature have focused attention on the relative energy ordering of the singlet and triplet excited states, their geometries, or harmonic vibrational frequencies. The objective of this research is to use the calculated energies, spin distributions, and harmonic frequencies for the lowest-lying electronic states of butatriene in order to understand its reactivity.

**TABLE 2: Electronic Energy Difference and Classical Barrier Heights from QCISD/6-311G(2d)//MP2/6-311(2d) Single-Point Calculation**

level of theory	electronic energies (hartrees)		energy separation <sup>a</sup> (kcal mol <sup>-1</sup> )
	<sup>3</sup> B <sub>1g</sub>	<sup>1</sup> A <sub>g</sub>	T-S
HF	-153.717 61	-153.722 55	5
MP2	-154.212 44	-154.271 89	39
MP3	-154.238 77	-154.294 72	37
MP4D	-154.245 78	-154.310 68	42
MP4DQ	-154.235 71	-154.293 85	38
MP4SDQ	-154.241 86	-154.301 27	39
QCISD	-154.247 79	-154.303 12	36

## Computational Details

calculations do not lead to large corrections for the lowest singlet–triplet separation. The predicted sequence of states is a planar singlet ground state of  $^1A_g$  symmetry, a  $D_{2d}$  triplet state of  $^3A_1$  symmetry, and several closely spaced planar triplet states of  $^3B_{1g}$  or  $^3A_2$  symmetry. The singlet–triplet energy separation is calculated to be about 36 kcal/mol at the MP2 level of theory and 38 kcal/mol at the QCISDT single-point calculations using the MP2 optimized geometry. These values are in good agreement with experimental estimates of the singlet–triplet gap reported by Kloster-Jensen.<sup>3</sup> The classical barrier has been calculated by taking into account the difference in zero-point energies (ZPEs) for each structure at the MP2/6-31G(d) level of theory to be 56.6 kcal mol<sup>−1</sup>.

The spin distributions of the electronic states of  $C_4H_4$  were also examined by analysis of the Fermi contact terms and atomic-atomic spin densities. The same general localization pattern is observed for the spin densities of both planar triplet states ( ${}^3B_{1g}$  and  ${}^3A_2$ ). The spins in these stationary point structures are localized on the terminal carbons. This is consistent with resonance forms such as

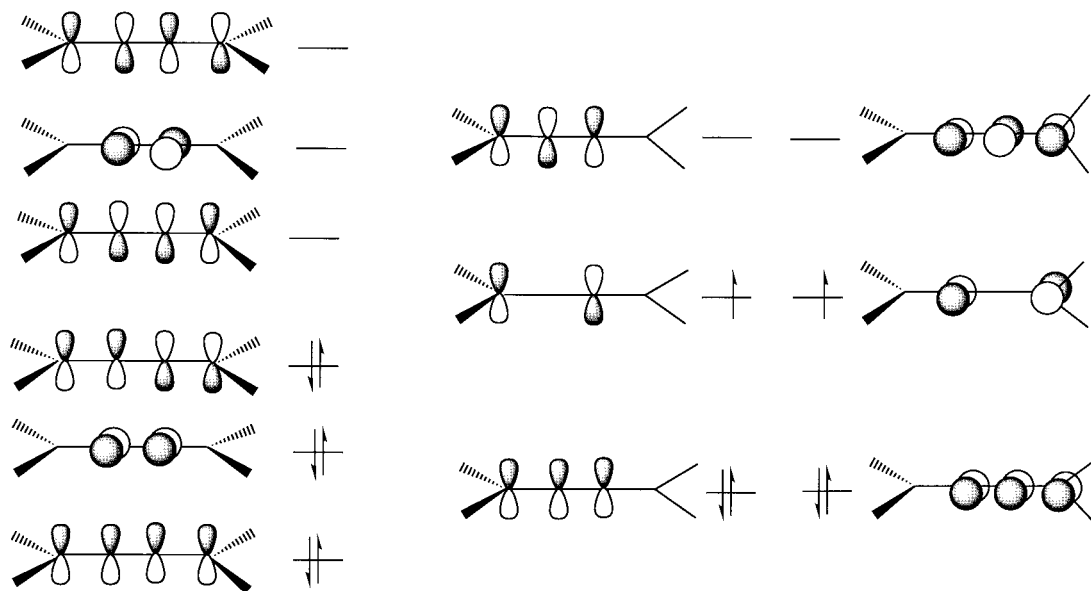
$$\text{H}_2\text{C}=\dot{\text{C}}=\dot{\text{C}}=\text{CH}_2 \longleftrightarrow \text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{CH}_2$$

The localization is stronger in the  ${}^3A_2$  state than in the  ${}^3B_{1g}$  state. From the optimized structural parameters and spin density information we have constructed schematics of the orbital structures. These are shown in Figure 1.

## Results and Discussion

**Geometries.** Table 3 shows the optimized geometrical parameters from the UHF and MP2/6-31G\* and the MP2/6-311G\* and MP2/6-311G(2d) calculations, respectively. The electronic-state designations and planarity of each structure are also listed for reference. Structures for each multiplicity were constrained in both planar and orthogonal configurations. Since free optimizations of the angles between the planes containing the two CH<sub>2</sub> moieties resulted in perpendicular orientations, the planes containing the methylenic hydrogens were fixed perpendicular to each other in all nonplanar structures. Both the planar and nonplanar geometries possessed linear carbon backbones. In general, each optimization used a single parameter for the CH bond lengths and the HCH angles. The CC bond lengths were optimized with either two or three independent parameters. When two were used, a single parameter was used to represent the terminal CC bonds and another to represent the internal CC bond.

The energy separations for the lowest-lying states do not appear to be a strong function of basis, and the single-point



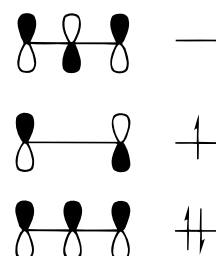
**Figure 1.** Orbital diagrams for the  $D_{2h}$  singlet (left) and  $D_{2d}$  triplet (right) forms of butatriene.

**TABLE 3: Optimized Geometrical Parameters: Bond Lengths  $R$  (Å) and Bond Angles  $A$  (deg)**

	$^1A_g$ (planar)	$^3B_{1g}$ or $^3A_1$ ( $D_{2d}$ )	$^3A_2$ or $^3B_{1u}$ (planar)
MP2/6-31G*			
$R(\text{CH})$	1.0869	1.0833	1.0835
$R(\text{C1C2})$	1.3239	1.3389	1.3388
$R(\text{C2C3})$	1.2758	1.2275	1.3074
$R(\text{C3C4})$	1.3239	1.3389	1.3390
$A(\text{HCC})$	121.50	121.01	120.52
MP2/6-311G*			
$R(\text{CH})$	1.0863	1.0826	1.0811
$R(\text{C1C2})$	1.3249	1.3902	1.4234
$R(\text{C2C3})$	1.2738	1.2258	1.2289
$R(\text{C3C4})$	1.3249	1.3902	1.4234
$A(\text{HCC})$	121.21	120.82	121.55
MP2/6-311G(2d)			
$R(\text{CH})$	1.0844	1.0805	1.0787
$R(\text{C1C2})$	1.3203	1.3861	1.4201
$R(\text{C2C3})$	1.2702	1.2214	1.2243
$R(\text{C3C4})$	1.3203	1.3861	1.4201
$A(\text{HCC})$	121.00	120.61	120.36

In addition to the expected trends of longer  $\text{H}_2\text{C}_2\text{--C}_2\text{H}_2$  bond lengths and shorter  $\text{C--CH}_2$  bond lengths for the singlet geometries in comparison to the triplet stationary point geometries, there are a few other interesting observations to be made from Table 3. The CC bond lengths in the planar geometries are significantly shorter than the nonplanar bond lengths for all basis sets. The same trend is observed for the triplet stationary point structures with the 6-311G(d) and 6-311G(2d) basis sets. However, at the MP2/6-31G\* level of theory this trend is reversed. This is likely due to the inclusion of correlation effects to describe the diradical nature of triplet  $\text{C}_4\text{H}_4$ . This basis set has been shown in previous studies to be adequate for geometry prediction of small hydrocarbons.<sup>16</sup> It is also interesting to compare the singlet-state geometry of the cumulene to related hydrocarbons. For 2-butyne, the central  $\text{C--C}$  bond length (determined at the MP2/6-31G\* level) is 1.2212 Å, and the other CC bonds are 1.4639 Å. The triple bond length is shorter than

observed for the central CC bond in the planar singlet state of the cumulene, as Lewis structures would predict. However, it is comparable to the length of the central CC bond of the cumulene in the  $D_{2d}$  triplet state. This is consistent with resonance forms exhibiting the 2-butyne-1,4-diyl type structure. For the doublet state of 2-butyne-1-yl ( $\text{CH}_3\text{--C}\equiv\text{C--CH}_2^*$ ), the lengths for the  $\text{CH}_3\text{--C}$ ,  $\text{CC}$ , and  $\text{C--CH}_2$  bonds are 1.4590, 1.2031, and 1.3937 Å, respectively. The shortening of the central CC bond and the  $\text{C--CH}_2$  bond is consistent with a simple Walsh orbital picture for the linear three-electron, three- $\pi$  system.



There were two low-lying planar triplet states of  $^3B_{1g}$  and  $^3A_2$  symmetry predicted at the Møller–Plesset level of theory. The primary structural difference between the equilibrium geometries is that the  $\text{C2--C3}$  bond length in the  $^3B_{1g}$  state is predicted to be much longer ( $\sim 0.08$  Å) than in the  $^3A_2$  state. This is consistent with the spin distributions where the elongated bond in the  $^3B_{1g}$  state acts to minimize repulsion between unpaired electrons, which are more delocalized along the entire carbon backbone. The results from geometry optimizations performed at both semiempirical levels of theory as well at higher levels (MP4 and QCISD) maintain this trend.

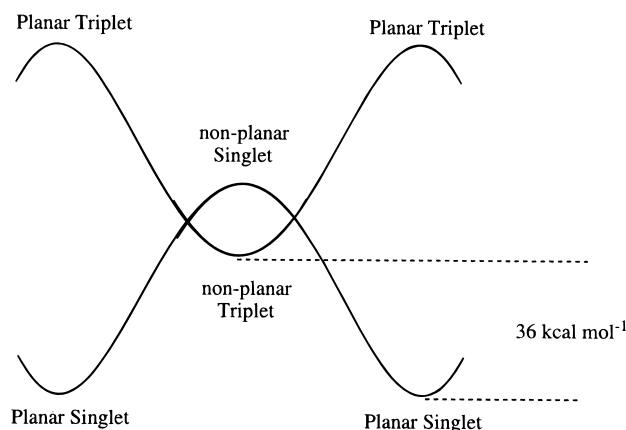
**Harmonic Frequencies.** The harmonic frequencies of the ground singlet and first two excited triplet states of 1,2,3-butatriene are presented in Table 4. These calculations were performed on the geometries optimized at the MP2/6-311G\* level of theory. The  $^3B_{1u}$  planar triplet structure exhibits an excessively large harmonic frequency for the 18th mode of vibration corresponding primarily to a  $\text{C--H}$  stretching vibration. This mode is a degenerate mode in the nonplanar triplet and is nearly degenerate in the ground-state singlet. This reproducible feature is likely indicative of deficiencies in the perturbation

**TABLE 4: MP2/6-311G\* Harmonic Frequencies (cm<sup>-1</sup>) for Butatriene**

mode	<sup>3</sup> A <sub>1</sub> <i>D</i> <sub>2d</sub> triplet	<sup>3</sup> B <sub>1u</sub> planar triplet	<sup>1</sup> A <sub>g</sub> planar singlet
1	226.3	169.6	227.9
2	226.3	204.9	229.9
3	409.6	213.0	350.2
4	409.6	352.5	514.7
5	522.7	427.3	790.9
6	598.7	446.2	879.8
7	598.7	479.3	882.4
8	826.5	812.8	903.7
9	1059.4	1055.8	1044.0
10	1059.4	1069.3	1070.9
11	1277.6	1483.8	1450.1
12	1504.1	1512.6	1511.8
13	1512.8	2259.6	1689.5
14	2149.2	3180.1	2205.1
15	3227.0	3246.1	3195.0
16	3230.3	3354.1	3197.0
17	3330.6	3354.3	3281.8
18	3330.6	6813.8	3282.8

treatment of symmetry breaking afforded by MP2 calculations. Linear arrangements of atoms such as found in this system tend to cause degeneracies in the orbitals that perturbative treatments cannot handle properly. In summary, since MP2 harmonic frequencies for small organic molecules tend to be larger by about 7%, these values may be of use in guiding future experimental observations of the low-lying triplet states. Coupled-cluster calculations are underway to improve the values and to remove the uncertainty due to the symmetry-breaking due to torsional motions in these C<sub>4</sub>H<sub>4</sub> structures.

**Reactivity.** Kloster-Jensen<sup>3</sup> and Cyvin<sup>12</sup> both proposed that the reactivity of 1,2,3-butatriene was due to the isomerism of the planar singlet to a *D*<sub>2d</sub> symmetry triplet state followed by reaction of the triplet with a planar singlet. Thus, the activation barrier to this process is the conversion from planar singlet to perpendicular triplet.

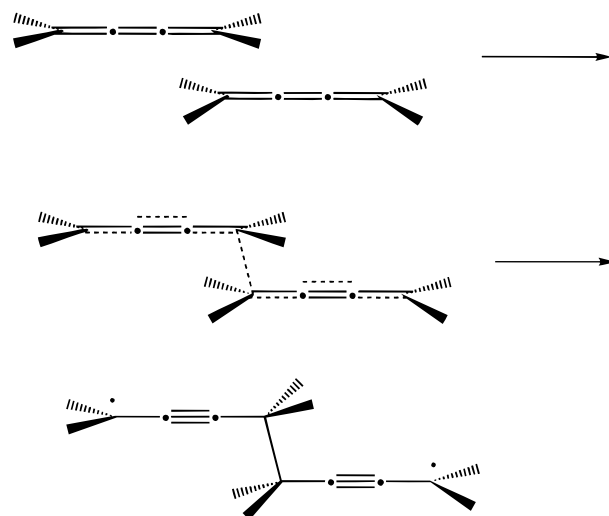


Taking the 36 kcal mol<sup>-1</sup> as an activation barrier at room temperature and by use of a preexponential factor consistent with a unimolecular reaction, the predicted value for the rate constant would be inconsistent with the observed nearly explosive reaction rate. Hence, it is highly unlikely that facile dimerization or polymerization of the 1,2,3-butatriene of monomer occurs at room temperature through such a mechanism.

The molecule *p*-xylylene has been postulated to polymerize through a similar mechanism, that is, conversion from the planar singlet form to a diradicaloid *D*<sub>2d</sub> symmetry state, followed by exothermic reaction with other monomers. Re-



cently, Li<sup>17</sup> demonstrated through trapping experiments that no monomeric diradical was formed, but rather, a diradical dimer was the dominant radical species. Presumably, the conversion from two planar, closed-shell singlet molecules to an  $\alpha,\omega$ -diradical has a low-energy pathway available.



Similarly, this type of mechanism could explain both the formation of the cyclic dimer found by Kloster-Jensen<sup>3</sup> as well as the high reaction rates for polymerization observed experimentally.

We are currently undertaking a study to determine if the spontaneous dimerization reaction postulated as an alternative mechanism is energetically feasible. We hope to report these results in the near future.

## Conclusions

One of the remaining questions to be addressed is the torsional profile of the methylene groups and how intersystem crossing may be mediated by this molecular motion. A rigorous ab initio treatment of this must involve a multideterminantal wave function in order to accurately describe the multiplicity of both states, since the surfaces cross as the methylene group twists out of plane. Calculations that allow for the relaxation of the orbital occupations as the CH<sub>2</sub> moiety is rotated out of plane are currently underway. The geometrical parameters of the entire molecule will be reoptimized at each point in order to provide a better estimate of the true torsional barrier. In addition, we will be studying the spontaneous dimerization pathway to determine its energetics.

The work presented above provides a consistent picture of the energetic ordering, spin distributions, and geometries of the lowest-lying singlet and triplet states of butatriene. Taken at face value, we estimate the first triplet state to lie ~40 kcal/mol above the ground singlet state.

**Acknowledgment.** We thank the Air Force Office of Scientific Research (Grant No. F49620-95-1-0223) for partial financial support. We also acknowledge the Joint Research Advisory Council for providing the authors with support in the form of a Howard University Faculty Research Support Grant (FRSG 300299). Finally, we thank Profs. Paul Lahti (University

of Massachusetts, Amherst) and Michelle Francl (Bryn Mawr College) for their helpful suggestions on open-shell calculations. The authors also thank Bridgette McGhee and Reyna Lewis for their assistance in the calculations and preparation of the tables and figures.

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