Ab Initio Study of the 1,3-butadienyl Radical Isomers

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Ab initio calculations at the B3LYP, QCISD, and MCSCF levels of theory and using the 6-311G(d,p) basis set were carried out on the ground state of the 1,3-butadiene derived radicals. The 1,3-butadien-1-yl and 1,3-butadien-2-yl radicals are obtained from 1,3-butadiene by abstraction of a hydrogen atom from a primary and secondary carbon, respectively. The 1,2-butadien-4-yl radical was also studied to examine the possibility of the relocalization of the unpaired electron from 1,3-butadien-2-yl. 1,2-Butadien-4-yl was consistently found to be the most stable isomer. The MCSCF relative energies are 29 kJ mol^{-1} for 1,3-butadien-2-yl and 35 kJ mol^{-1} for the most stable of the 1,3-butadien-1-yl configurational isomers. The 1,3-butadien-2-yl structure is found to be a local minimum in MCSCF calculations, but with an isomerization barrier of less than 1 kJ mol^{-1}, and deforms to the 1,2-butadien-4-yl isomer at all other levels of theory used. The energy of the most stable 1,3-butadien-1-yl isomer relative to 1,3-butadien-2-yl ranges from 6 to 18 kJ mol^{-1} across all levels of theory used, substantially lower than previous predictions by ab initio and semiempirical means. Optimized geometries, relative energies, permanent dipole moments, Fermi contact terms and harmonic vibrational frequencies are reported.

1. Introduction

The butadienyl radicals are possible intermediates in the pyrolysis of hydrocarbons and the formation of benzene in flames.[1−8] The radical isomers obtained by abstraction of a hydrogen atom from 1,3-butadiene are 1,3-butadien-1-yl and 1,3-butadien-2-yl, assuming that the geometry of the parent molecule is preserved. Both radicals have cis and trans configurational isomers due to the possibility of internal rotation about the CC single bond. The 1,3-butadien-1-yl radical can further be drawn in either a cis or trans form with respect to placement of the terminal hydrogen atom. The canonical structures of all these isomers are shown in Figure 1.

In combustion studies,[3,7] 1,3-butadien-1-yl is assumed to be the predominant C_4H_5 isomer in 1,3-butadiene flames, although it is thermodynamically less favorable than 1,3-butadien-2-yl. The secondary radical, 1,3-butadien-2-yl, has an entropy 2.9 J K^{-1} mol^{-1} larger than the primary radical, but an enthalpy 54 kJ mol^{-1} lower.[8] However, the rate of formation of 1,3-butadien-2-yl is only about 3−30% of the other isomer.[7] The secondary radical would enhance formation of branched hydrocarbon chains, which are not found.[4]

The 1,3-butadien-2-yl radical, a secondary radical with the double bonds conjugated, has another possible canonical structure: the 1,2-butadien-4-yl radical, with cumulated double bonds and the unpaired electron localized on the terminal carbon atom. The relocalization of the unpaired electron changes the hybridization of the radical center and the geometry: the CCC chain bends from the linear allene-type structure to roughly 135° for the planar isomer, as depicted in Figure 2. Although the sequence of atoms is the same, $H_2C_2HC_2H_2$, 1,3-butadien-2-yl, and 1,2-butadien-4-yl are not resonance structures of a single isomer, but distinct configurational isomers.

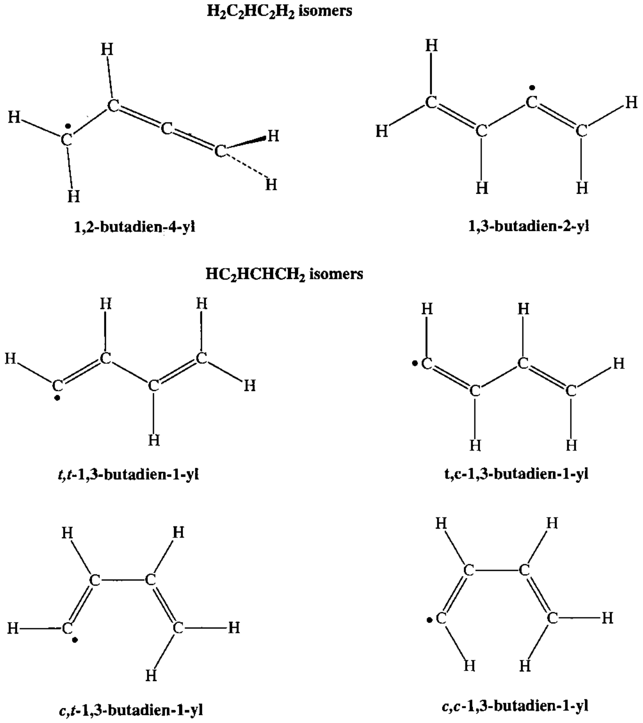

Figure 1. Canonical structures of the butadienyl radicals investigated.

Previous ab initio calculations[9] support the greater stability of the secondary radical, but find no local minimum near the 1,3-butadien-2-yl geometry. Instead, the 1,2-butadien-4-yl radical is the most stable, 58 kJ mol^{-1} more stable than 1,3-butadien-1-yl. These calculations used up to third order in perturbation theory, and a maximum basis set of 6-31G(d).[9]

Other previous calculations are semiempirical studies. The radical formed by abstraction of a hydrogen atom from a secondary carbon in 1,3-butadiene is consistently found to be more stable than the primary 1,3-butadien-1-yl radical. Kühnel and co-workers[10,11] found at the MINDO level that the enthalpy gap between these radicals is 41.8 kJ mol^{-1}. Wang and Frenklach[12] carried out an exhaustive study of radical-acetylene reaction rates that included Hartree−Fock and AM1 character-

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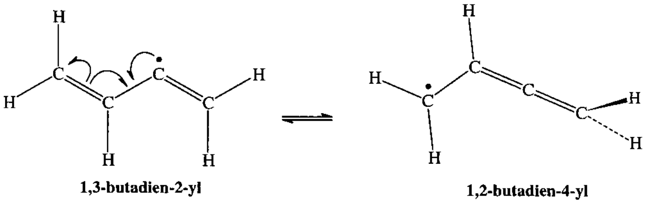


Figure 2. Electron relocalization path between 1,3-butadien-2-yl and 1,2-butadien-4-yl.

izations of 1,3-butadien-1-yl (n-C_4H_5) and the secondary radical (i-C_4H_5), nominally 1,3-butadien-2-yl. Using an empirical $=CH-H$ dissociation energy, the enthalpy of formation of 1,3-butadien-1-yl was predicted to be greater by 33.5 kJ mol^{-1}.

Previous calculations on the ground-state vibrational potential surfaces on carbon chain radicals have established a tendency toward very flat potential surfaces along the bending coordinates.[13-15] This is due to the existence of multiple favorable, nonequivalent canonical geometries, corresponding to the same structural isomer, but with the unpaired electron localized on different atoms. Our goal is to determine the existence or absence of multiple minima for the 1,3-butadienyl radicals and to calculate the relative energies of the radical isomers. In this paper we report optimized geometries, relative energies, Fermi contact terms, dipole moments, harmonic vibrational frequencies, and potential energy curves for the 1,3-butadienyl radicals. A parallel ab initio study of the other C_4H_5 structural isomers is underway and will be reported elsewhere.

2. Computational Methods

Unrestricted Hartree−Fock (UHF), configuration interaction (CI), coupled cluster (CC), and density functional method calculations were carried out using the Gaussian 94 system of programs[16] on Silicon Graphics Power Challenge L and Cray Y-MP, J90 and C90 computers. Calculations based on multi-configuration self-consistent field (MCSCF) wave functions were carried out using Gamess 5.4[17] on Silicon Graphics workstations and Cray Y-MP and J90 computers. The 6-311G(d,p) basis set[18,19] was used for all calculations because it has been proven to be well-converged in previous studies of HC_3O and similar molecules.[13]

Geometry optimizations were performed initially at the UHF level, starting with the geometries of the canonical structures. In most cases, the UHF optimized structures were used as input for the QCISD calculations. This method adds single and double substitutions to the Hartree−Fock determinant and a quadratic term to restore size-consistency.[20] QCISD was also used to search for minima that did not optimize at the UHF level. CCSD(T) calculations of the relative energies were carried out at the QCISD optimized geometries. In these single reference calculations, the value of $\langle S^2 \rangle$ prior to annihilation is 1.1 for 1,2-butadien-4-yl and about 1.3 for the 1,3-butadien-1-yl isomers, although all the ground-state species have doublet spin multiplicity. MCSCF[21] calculations were therefore carried out to test the impact of the spin contamination. This method also tests the importance of very high substitutions in the CI wave function, but has the disadvantage of considering those substitutions only for a limited number of electrons and orbitals. First- and second-order CI terms were included in the MCSCF expansion in selected cases for comparison and verification. Quoted results are for active spaces consisting of nine molecular orbitals housing nine electrons. Density functional method calculations with the B3LYP Hamiltonian were also performed.[22,23]

Harmonic vibrational analysis was carried out at optimized geometries to test for imaginary frequencies and to assess zero-point corrections to the relative energies.

In addition to the configurations drawn in Figure 1, several additional initial geometries were obtained by rotation of the CH_2 groups around the CC single bond axis. These were not found to be minima on the UHF potential energy surface.

3. Results and Discussion

The most stable configurational isomers are those with structural formula $H_2C_2HC_2H_2$: 1,2-butadien-4-yl and *trans*-1,3-butadien-2-yl, with *trans*-1,3-butadien-2-yl roughly 30 kJ mol^{-1} higher in energy. The 1,3-butadien-1-yl radicals, with structural formula HC_2HCHCH_2, are less stable by an added 6−20 kJ mol^{-1}. These relative energies are listed in Table 1. Although the UHF relative energies are lower and the B3LYP higher than those predicted by the other methods, the energy ordering of these isomers is the same at all levels of theory. All the isomers with the canonical structures shown in Figure 1 are minima at the UHF, B3LYP, and QCISD levels, except 1,3-butadien-2-yl.

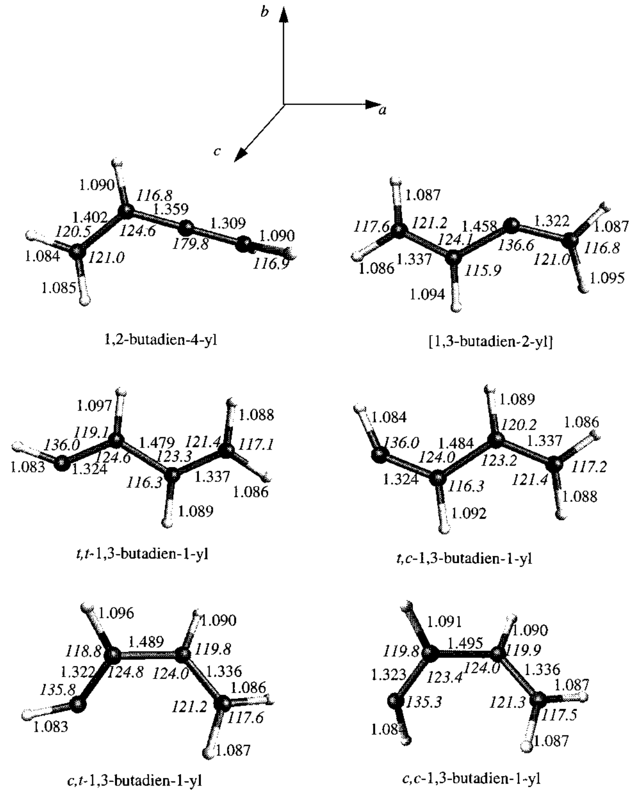
The QCISD results are supported by the single point CCSD(T) energies, which agree within 2.5 kJ mol^{-1}. Qualitative agreement is also found between the QCISD and MCSCF results, but with one significant discrepancy: *trans*-1,3-butadien-2-yl is a local minimum only on the MCSCF potential energy surface. *cis*-1,3-Butadien-2-yl is not stable under any of the theory levels used, optimizing instead to 1,2-butadien-4-yl.

The QCISD optimized geometries are shown in Figure 3; these agree with the MCSCF (9,9) optimized geometries to within 0.026 Å for bond lengths and 2.7° for bond angles. The differences between QCISD and B3LYP optimized geometries are within 0.018 Å for bond lengths and 3.1° for bond angles. Comparison with Somasundram's earlier ab initio calculations[9] shows qualitative agreement. Although the energy ordering of the isomers in that work is the same, the energy difference between 1,2-butadien-4-yl and *t,t*-1,3-butadien-1-yl is 61 kJ mol^{-1} at the MP3 level, higher by 15 kJ mol^{-1} than our QCISD results.

TABLE 1: Absolute ab Initio Energy in hartree of 1,2-butadien-4-yl and Relative Energies (kJ mol^{-1}) of 1,3-Butadienyl Radicals[a]

	UHF	B3LYP	QCISD	CCSD(T)	MCSCF (9,9)	MP3/6-31G[c]
1,2-butadien-4-yl	−154.33144	−155.37086	−154.89854	−154.92103	−154.43110	−154.57477
1,3-butadien-2-yl[b]	[16.8] (16.2)	[39.4] (39.8)	[35.0] (36.6)	[31.8]	28.6	
t,t-1,3-butadien-1-yl	23.1 (25.2)	55.0 (57.6)	43.4 (46.5)	40.9	34.6	57.9
t,c-1,3-butadien-1-yl	24.2 (26.8)	57.5 (60.4)	45.5 (49.0)	43.0	36.0	
c,t-1,3-butadien-1-yl	32.7 (34.1)	68.2 (69.7)	52.8 (55.9)	51.1	44.0	
c,c-1,3-butadien-1-yl	34.6 (36.5)	70.1 (72.6)	52.8 (56.6)	51.1	45.2	

[a] The zero point vibrational corrected relative energies are given in parentheses. CCSD(T) energies are evaluated at the QCISD optimized geometry. The basis set is 6-311G(*d,p*) for all listed results, unless otherwise stated. [b] Square brackets denote values for saddle point structures obtained by constraining the radical to be planar. [c] From ref 9.



1,2-butadien-4-yl [1,3-butadien-2-yl]

t,t-1,3-butadien-1-yl *t,c*-1,3-butadien-1-yl

c,t-1,3-butadien-1-yl *c,c*-1,3-butadien-1-yl

Figure 3. QCISD/6-311G(d,p) optimized geometries of the butadienyl radicals studied. Bond lengths are in angstroms, and angles (in italics) are in degrees. The principal inertial axes are shown.

All structures tested at the QCISD level converged to C_s structures, except the *c,t*-and *c,c*-1,3-butadien-1-yl isomers. The ground electronic state is $^2A''$ for all C_s isomers except 1,2-butadien-4-yl, which has a $^2A'$ ground state. While the energy gap between $^2A''$ 1,2-butadien-4-yl and the most stable $^2A'$ isomer is larger by 8 kJ mol^{-1} at the QCISD level than at the MCSCF level, the energy differences among the different $^2A'$ isomers at all levels of theory agree to within 3.4 kJ mol^{-1}. Extension from a (9,9) to (9,10) and (11,11) active spaces does not considerably change the MCSCF relative energies. The inclusion of first- and second-order CI terms for a (9,7) active space with 20 external orbitals yields absolute energies higher than the corresponding energies for a (9,9) active space. This indicates that at this level the variational stabilization energy is more dependent on the size of the complete active space than on the number of orbitals available for limited CI.

The MCSCF wave function is a truncated CI expansion, in which the expansion coefficient of the UHF reference wave function for the single-reference QCISD and CCSD(T) calculations is C_0. The 1,2-butadien-4-yl radical has a low C_0 coefficient of 0.66, compared to the lowest C_0 of 0.76 for the other isomers. This indicates that the single-reference calculations are based on an initial wave function significantly worse than the initial wave functions for the other structures. Although the contribution from the UHF reference was quite small, the UHF reference wave function and its single and double substitutions accounted for over 93% of the final MCSCF wave function. Since the MCSCF calculations are not sensitive to the quality of the UHF reference wave function, we believe these results are more reliable than the QCISD results.

A. $H_2C_2HC_2H_2$ Isomers. The most stable isomer, according to all levels of theory used, is 1,2-butadienyl, in agreement with Somasundram's results.[9] The stability of this isomer is attributable to delocalization of the spin over an allylic-type structure. The total atomic spin densities at the terminal carbon atoms of the allylic structure are 0.8 and 0.6, showing substantial delocalization. The next most stable isomer, *trans*-1,3-butadien-2-yl, is a local minimum at the MCSCF level, but not on the QCISD potential energy surface; nor is it a minimum in the previous calculations.[9] Geometry optimizations at the QCISD level with an initial 1,3-butadien-2-yl geometry optimized to the 1,2-butadien-4-yl configuration. It is important to note that the most stable radical obtained by abstraction of a hydrogen atom from 1,3-butadiene is 1,2-butadien-4-yl, an isomer that does not maintain the geometry of its parent hydrocarbon.

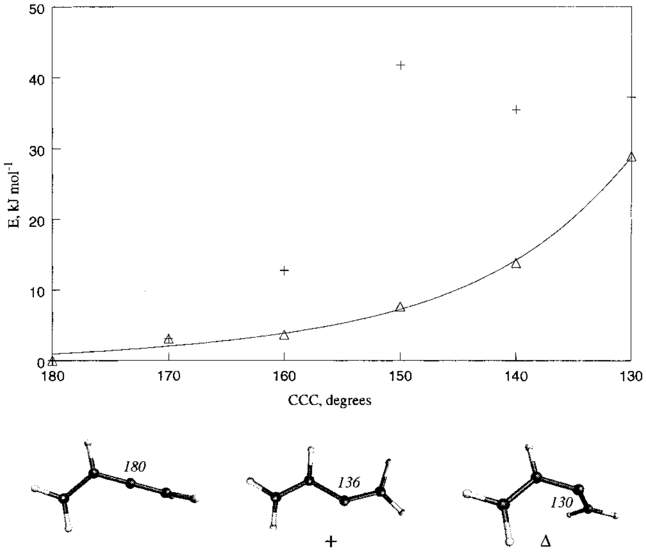


Figure 4. Plot of the effective vibrational potential energy as a function of the CCC bond angle for the isomerization of 1,2-butadien-4-yl to constrained planar 1,3-butadien-2-yl (+) or the unstable, nonplanar structure (Δ) at the QCISD level.

The QCISD energy of the 1,3-butadien-2-yl radical optimized by enforcing a planar geometry, a saddle point on the potential energy surface, is 35.0 kJ mol^{-1} higher than the energy of 1,2-butadien-4-yl. At the MCSCF level, for which 1,3-butadien-2-yl is a minimum, this relative energy is 28.6 kJ mol^{-1}. The lifetime of 1,3-butadien-2-yl on the MCSCF potential surface depends on the barrier height of its isomerization to 1,2-butadien-4-yl. This isomerization was modeled by simultaneously fixing the CCC bending angle and an HCCH dihedral angle in 5° increments while optimizing the other geometric parameters. A very small energy barrier, less than 1 kJ mol^{-1}, was found for the isomerization from 1,3-butadien-2-yl to 1,2-butadien-4-yl at the MCSCF (9,9) level. Such a small barrier indicates that this minimum is unlikely to contain more than a single vibrational state. The qualitative conclusion from MCSCF and QCISD results is therefore the same: of these two configurations, only the 1,2-butadien-4-yl radical is likely to be observable.

The lowest energy path from 1,3-butadien-2-yl to 1,2-butadien-4-yl consists of rotation about the CC single bond, which breaks the planar symmetry, followed by straightening of the CCC bond angle to give the nominal 180° bond angle characteristic of 1,2-butadien-4-yl. As a hydrogen atom is abstracted from one of the central carbon atoms in 1,3-butadiene, this path represents the likeliest route for reorganization of the remaining radical to form 1,2-butadien-4-yl. Figure 4 shows the QCISD potential energy as a function of the CCC bond angle, both for a constrained planar geometry and with that constraint lifted. The lowest energy path is clearly through the nonplanar geometries. Indeed, when the CCC bond angle is

TABLE 2: QCISD/6-311G(d,p) Dipole Moments μ (D) and ^{13}C Fermi Contact Terms *a* (MHz) for Butadienyl Radicals. Carbon Atoms Are Labeled a−d as They Appear from Left to Right in Figure 1

	1,2-butadien-4-yl	*t,t*-1,3-butadien-1-yl	*t,c*-1,3-butadien-1-yl	*c,t*-1,3-butadien-1-yl	*c,c*-1,3-butadien-1-yl
μ_a	−0.01	0.00	0.51	−0.24	0.61
μ_b	0.08	0.59	0.47	0.47	0.00
μ_c	0.00	0.00	0.00	0.25	0.21
$a(C_a)$	116 (145)[a]	635 (538)	687 (577)	1012 (585)	1030 (598)
$a(C_b)$	−121	−36	−28	−314	−292
$a(C_c)$	88	95	158	309	363
$a(C_d)$	−75	3	14	−202	−197

[a] Values in parentheses indicate *a* values per unit of atomic spin density.

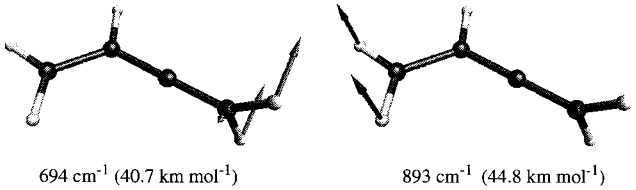
TABLE 3: Ab Initio QCISD/6-311G(d,p) Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) for the Most Stable Butadienyl Radicals

1,2-butadien-4-yl			*t,t*-1,3-butadien-1-yl			*t,c*-1,3-butadien-1-yl		
a″	182	5.7	a″	144	0.1	a″	135	0.1
a′	213	1.2	a′	299	6.8	a′	292	0.8
a″	508	0.7	a′	514	2.7	a′	488	1.9
a″	514	2.9	a″	561	45.8	a″	574	1.6
a′	569	6.1	a″	755	12.2	a″	744	22.8
a″	694	40.7	a′	819	13.8	a′	869	28.8
a′	893	44.8	a″	855	0.3	a″	910	30.9
a′	903	0.7	a″	938	38.4	a″	935	40.8
a″	931	21.8	a′	956	2.0	a′	945	8.7
a″	997	1.4	a″	1036	20.6	a″	1033	31.9
a′	1083	1.6	a′	1188	4.2	a′	1171	0.3
a′	1191	1.3	a′	1262	1.1	a′	1268	1.3
a′	1385	0.9	a′	1325	1.5	a′	1327	1.8
a′	1474	1.0	a′	1459	1.6	a′	1457	1.9
a′	1510	2.7	a′	1637	3.0	a′	1628	2.7
a′	1917	8.4	a′	1717	4.6	a′	1707	6.2
a′	3120	11.5	a′	3082	9.2	a′	3147	4.3
a′	3169	6.5	a′	3162	6.8	a′	3162	8.1
a′	3177	4.8	a′	3189	5.7	a′	3182	7.7
a″	3193	7.1	a′	3254	14.2	a′	3254	12.9
a′	3281	8.5	a′	3270	0.3	a′	3254	1.1

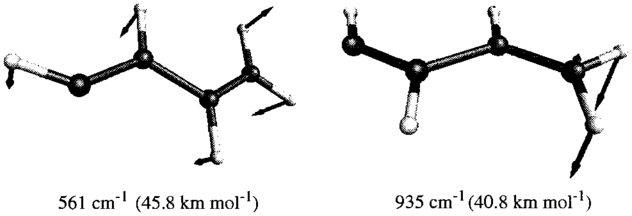
fixed to 130°, the molecule is more stable nonplanar than at the planar geometry corresponding to 1,3-butadien-2-yl, even though this sacrifices conjugation of the π bonds. The 1,3-butadien-2-yl radical easily twists, preferring partial conjugation of the unpaired electron to π bond−π bond conjugation. This tendency contrasts with that of the analogous H_2C_2HCO configurations 3-propenal-1-yl (conjugated π bonds) and 1-propenon-3-yl (allylic system),[24] which are both minima on the potential surface separated by a nonplanar transition state.

Carbon-13 Fermi contact hyperfine constants are listed in Table 2 for 1,2-butadien-4-yl. The Fermi contact hyperfine constant on the terminal carbon atom where the unpaired electron is primarily localized is 116 MHz, and on the opposite end of the allylic structure is 88 MHz. A high value of the hyperfine constant indicates a significant s character of the unpaired electron; in this case, the electron is localized in a pure p orbital.

The harmonic vibrational frequencies of the three most stable configurations are given in Table 3. Prospects for spectroscopic identification based on the predicted geometries are not very good. The strongest vibrational mode, a CH_2 wag, predicted at 893 cm^{-1}, has an IR intensity of only 45 km mol^{-1} and is depicted in Figure 5. The largest infrared intensity for the parent 1,3-butadiene is predicted to be over 100 km mol^{-1}. Determination of the molecular geometry by rotational spectroscopy will also be challenging. Table 2 lists the QCISD predicted dipole moment components along the *a*, *b*, and *c* inertial axes; the largest predicted dipole moment, along the *b* axis, is 0.08 D.


694 cm^{-1} (40.7 km mol^{-1}) 893 cm^{-1} (44.8 km mol^{-1})

1,2-butadien-4-yl


561 cm^{-1} (45.8 km mol^{-1}) 935 cm^{-1} (40.8 km mol^{-1})

t,t-1,3-butadien-1-yl *t,c*-1,3-butadien-1-yl

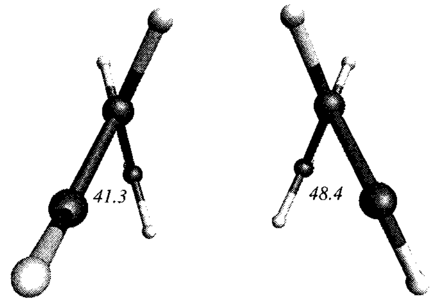
Figure 5. Strongest vibrational modes for the most stable butadienyl isomers.

B. H_2C_2HCHCH Isomers. All four configurational isomers of 1,3-butadien-1-yl, are found to be minima at the QCISD level. The energy ordering is as expected, the *tt* isomer, with *trans*-CCCC and *trans*-CCCH chains, being most stable. Relative energies of the *tt* isomer above the 1,3-butadien-2-yl isomer range from 6.0 (MCSCF) to 9.9 (QCISD) kJ mol^{-1}, substantially lower than the 34−44 kJ mol^{-1} values obtained in previous studies.[10−12]

These isomers do not present the opportunity for electron relocalization, and the unpaired electron is situated in a sp^2 hybrid orbital. The spin density indicates little delocalization of the unpaired electron; the value for the total atomic spin density on the terminal carbon atom is 1.18 for the *tt* isomer and 1.19 for the *tc* isomer. The Fermi contact terms at the radical center have large values, 635 and 687 MHz, respectively, indicative of the relatively high s character of the unpaired electron orbital. The singly occupied MO has roughly 20% s character at this atom, consistent with hybridization of the bonding orbitals intermediate between sp^2 and sp. This is also reflected by the 136° CCH bond angles at the radical centers.

The two radicals derived from *cis*-1,3-butadiene retain their planarity only at the UHF level; at all the other levels they twist about the single CC bond to reduce the steric interaction between the terminal groups. A side view of these radicals is presented in Figure 6. The CCCC dihedral is 41.3° at the QCISD level and 24.5° at the MCSCF level for *c,t*-1,3-butadien-1-yl, as well as 48.4° at the QCISD level and 37.1° at the MCSCF level for *c,c*-1,3-butadien-1-yl.

The Fermi contact terms at the radical center are very large, 1012 MHz for *c,t*-1,3-butadien-1-yl and 1030 MHz for the *c,c* isomer, but the values for the total atomic spin densities are also very large: 1.73 and 1.72, respectively. The increased values of the Fermi contact terms for the *c,t* and *c,c* isomers are proportional with the values for the *t,t* and *t,c* isomers, and they are consistent when normalized to unit spin density.



c,t-1,3-butadien-1-yl *c,c*-1,3-butadien-1-yl

Figure 6. Side view of the QCISD/6-311G(d,p) optimized geometries for *c,t*- and *c,c*-1,3-butadien-1-yl radicals.

All four structures are good candidates for detection by rotational spectroscopy: the dipole moment components have values comparable to those of similar molecules with observable rotational spectra, such as HC_4[25] and HC_3O.[14] Selected vibrational frequencies are given in Table 3, and the strongest vibrational modes are shown in Figure 5. The strongest vibrational modes, predicted at 561 cm^{-1} for *t,t*-1,3-butadien-1-yl and at 935 cm^{-1} for *t,c*-1,3-butadien-1-yl, have low intensities of 45.8 and 40.8 km mol^{-1}, respectively. For *c,t*-1,3-butadien-1-yl, the strongest vibrational mode is even weaker, 35.5 km mol^{-1} at 954 cm^{-1}, but for *c,c*-1,3-butadien-1-yl the vibrational intensity is 49.2 km mol^{-1} at 903 cm^{-1}.

4. Conclusions

The most stable of the 1,3-butadienyl radicals is conclusively predicted to be 1,2-butadien-4-yl, an isomer that does not maintain the conjugated four-electron system of the parent 1,3-butadiene. The main cause for the stability of this isomer is the allylic spin delocalization, which surpasses the stabilization due to double bond conjugation in the other isomers. On the basis of the predicted dipole moment and vibrational transition strengths, we anticipate the spectroscopic observation of this isomer to be difficult. The energy difference between this isomer and the next, *trans*-1,3-butadien-2-yl, is much larger than that between any of the 1,3-butadienyl isomers.

The low energy gap between the 1,3-butadien-1-yl and 1,3-butadien-2-yl radicals appears to contradict earlier semiempirical estimates,[10−12] but this may be attributable to a blurred distinction between the 1,2-butadien-4-yl and 1,3-butadien-2-yl radicals in the previous work. The HF/6-31G(d,p) properties reported by Wang and Frenklach[12] for their *i*-C_4H_5 radical are for 1,3-butadien-2-yl, but this radical is not a minimum at the AM1 level, deforming instead to the 1,2-butadien-4-yl radical. The vibrational frequencies indicate their *n*-C_4H_5 structure to be the *t,c*-1,3-butadien-1-yl isomer. The 35.5 kJ mol^{-1} stability of *i*-C_4H_5 relative to *n*-C_4H_5, which is based on their AM1 relative energies, is therefore to be compared with our 36.0 MCSCF relative energy of *t,c*-1,3-butadien-1-yl in Table 1. The prior MINDO calculations,[10] also nominally for the 1,3-butadien-2-yl radical, report an allylic electronic structure and a 166.4 degree CCC bond angle, consistent with the 1,2-butadien-4-yl radical rather than with 1,3-butadien-2-yl.

The QCISD results predict that the relocalization of the unpaired electron from 1,3-butadien-2-yl to form 1,2-butadien-4-yl occurs without any energy barrier. In the case of the MCSCF calculations, both 1,2-butadien-4-yl and 1,3-butadien-4-yl are minima, but the 1,3-butadien-2-yl minimum is extremely shallow, with an isomerization barrier of less than 1 kJ mol^{-1}.

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Supporting Information Available: Tables of vibrational frequencies for 1,3-butadien-2-yl, *c,t*- and *c,c*-1,3-butadien-1-yl (1 page). Ordering information is given on any current masthead page.

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