High Level ab Initio Energies and Structures for the Rotamers of 1,3-Butadiene

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High level ab initio calculations, utilizing coupled cluster theory with quasi-perturbative triple excitations and augmented quadruple ζ level basis sets, have been used to determine the structures and relative energies of the four stationary points on the 1,3-butadiene torsional potential curve. Corrections were applied in order to minimize the residual basis set error, as well as account for core/valence correlation and scalar relativistic effects. Higher order correlation recovery was also included to improve our estimate of the relative energies. The transition state separating the *trans* and *gauche* rotamers lies 26.8 kJ/mol above the *trans* global minimum. The *gauche* rotamer lies 12.6 kJ/mol above the *trans* rotamer and the *s-cis* form is a transition state 2.0 kJ/mol higher than the *gauche* rotamer (excluding zero point energies).

Introduction

The lowest energy form of 1,3-butadiene (BDE) possesses a planar *s-trans* conformation with C_{2h} symmetry.[1−3] Although a number of investigations of the potential surface corresponding to rotation about the central C−C bond have appeared in the literature, there remain open questions pertaining to the higher energy rotamers. Figure 1, which depicts the potential energy function as determined in this study, serves as a guide to the review of the earlier literature on the rotamers of butadiene.

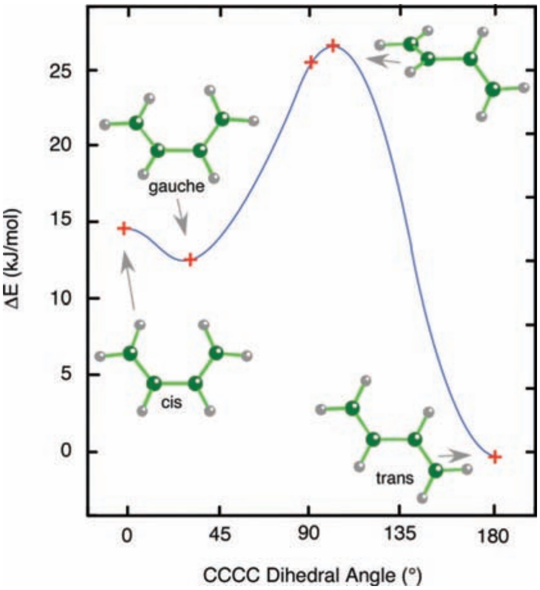

Figure 1. Vibrationless internal rotational potential function for butadiene based on the best available level of theory, as discussed in the text.

Very early work by Radom and Pople, based on restricted Hartree−Fock (RHF) calculations with the minimal STO-3G basis set, identified an *s-cis* (planar) conformer with C_{2v} symmetry as a minimum. It was reported to lie 8.6 kJ/mol (2.1 kcal/mol) higher in energy than the *trans* structure.[4] Unfortunately, due to the limitations of the computer hardware available at the time, only the CCC angles could be optimized. Slightly different geometries led to estimates of the *cis*/*trans* energy difference as high as 23.8 kJ/mol. Subsequent work by Skaarup et al. found *gauche* enantiomers with C_2 symmetry that were 2.5 kJ/mol (0.6 kcal/mol) lower in energy than the *cis* form, but once again only partial RHF geometry optimizations were possible.[5] The authors cautioned that such a small energy difference rendered their findings less than conclusive. De Maré found similar results with partially constrained RHF optimizations that included d polarization functions on the carbon atoms.[6] Schaefer and co-workers compared the *cis* and *gauche* conformers at the RHF and configuration interaction singles and doubles (CISD) levels of theory with basis sets of double-ζ (DZ) and double-ζ plus polarization (DZP) quality.[7] No constraints were imposed on the RHF geometry optimizations, which yielded a CCCC dihedral angle (τ) for the *gauche* conformer in the 33 − 38° range. (Throughout this paper we have adopted the convention that the *s-trans* rotamer corresponds to a torsion angle of 180° and the *s-cis* form corresponds to 0.0°.) The *cis* barrier height at their best level of theory (CISD/DZP) was reported to be 3.4 kJ/mol (0.82 kcal/mol).

In 1985, Feller and Davidson re-examined the *cis-gauche* portion of the rotational potential curve with a 10-orbital/10-electron complete active space self-consistent field (CASSCF) wave function with an unpolarized split valence basis set.[8] The active space consisted of the three C−C σ bonds, the two occupied π bonds and the five corresponding antibonding orbitals. At this level of theory, the *gauche* minimum disappeared, leaving the *cis* form as a minimum. When additional correlation recovery was introduced via multireference, singles and doubles CI (MR SD-CI) calculations and the basis set increased to the DZP level, the *gauche* minimum reappeared approximately 0.8−2.6 kJ/mol lower in energy than the *s-cis* conformer. Because it proved impossible to reoptimize the geometry at the highest level of theory or to gauge the impact of larger basis sets, the authors cautioned that the relative energies could easily be reversed with more sophisticated calculations.

In 1990, Wiberg and Rosenberg carried out third order Mϕller-Plesset perturbation theory (MP3) energy evaluations

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on the *s-cis* and *gauche* rotamers with the 6-311+G** basis set using second order (MP2) optimized geometries.[9] They found the *gauche* form to be energetically favored by 4.1 kJ/mol (0.98 kcal/mol). Similar conclusions were reached a year later by Guo and Karlpus in their MP2 study.[10]

The 1992 experimental work of Engeln et al. was the culmination of several investigations of the potential function of BDE.[11−13] They drew on observations of progressions of overtone transitions for the torsional modes of the *trans* and *gauche* rotamers in the gas-phase Raman spectrum to propose a complete potential function for internal rotation.[13]

More recently, Murcko et al.[14] studied the C−C rotational barriers in three hydrocarbons (butane, 1-butene and 1,3-butadiene) with the G2[15] and CBS-Q[16] theoretical composite methods. The first of these utilized MP2(full)/6-31G(d) optimized geometries, while the second used geometries obtained from frozen core (FC) MP2/6-31G† calculations. Both the G2 and CBS-Q approaches include empirically adjusted parameters. G2 predicted a *trans*-to-*gauche* zero-point-inclusive transition state (TS) that is 23.7 kJ/mol (5.7 kcal/mol) higher than the *trans* conformer and a *cis* transition state barrier of 2.2 kJ/mol (0.5 kcal/mol) relative to the *gauche* form. CBS-Q predicted a slightly higher energy transition state near $\tau = 100^\circ$ of 25.2 kJ/mol (6.0 kcal/mol) and a *cis* transition state that was essentially degenerate with the *gauche* conformer.

Sancho-Garcia et al. studied the butadiene torsional potential with a variety of correlated methods, ranging from MP2 through coupled cluster theory with singles and doubles (CCSD) and with quasi-perturbative triples (CCSD(T)).[17] Basis sets were chosen from the correlation consistent (cc-pVnZ) family of Dunning,[18] but the coupled cluster calculations were limited to the small cc-pVDZ basis. Values for the zero-point-exclusive barrier height near $\tau = 100^\circ$ ranged from 24.0 to 27.3 kJ/mol (5.7−6.5 kcal/mol), while the *cis* barrier was approximately 1.6 kJ/mol (0.4 kcal/mol) above the energy of the *gauche* rotamer.

The most recent high level theoretical study of the butadiene torsional potential was reported by Karpfen and Parasuk.[19] They carried out MP2 and density functional theory (DFT) geometry optimizations with basis sets as large as aug-cc-pVTZ and cc-pVQZ. Still larger basis set MP2 calculations (aug-cc-pVQZ and cc-pV5Z) were performed at the cc-pVQZ geometries. Higher level correlation corrections were obtained from frozen core CCSD(T) calculations with the cc-pVTZ basis set. Their best values combined MP2/cc-pV5Z and CCSD(T)/cc-pVTZ relative energies. This procedure yielded energies for the *gauche* rotamer and the *trans-gauche* transition state in acceptable agreement with those derived from the potential function proposed by Engeln et al.[13] However, Karpfen and Parasuk's zero-point-exclusive barrier of 2.4 kJ/mol (0.57 kcal/mol) for the *s-cis* transition state is only about half as large as the value derived from the potential function of Engeln et al. These findings cast doubt on the assignments for the *gauche* rotamer in the gas phase Raman spectrum and support the ambiguity between *gauche* and *cis* rotamers in the interpretation of the matrix isolation spectra. They also help to explain the difficulties encountered in attempts to observe microwave lines of the *gauche* rotamer. Unsuccessful searches have been made for microwave lines corresponding to the *gauche* rotamer of BDE.[20,21] A summary of selected theoretical literature values for the *s-cis* barrier height is presented in Table 1.

TABLE 1: Selected Theoretical Literature Values for the Zero Point Exclusive *gauche*-to-*cis* Barrier Height (kJ/mol).

year	barrier	method	reference
1976	2.5	RHF/Gaussian lobe	Skaarup et al.[5]
1984	3.4	CISD/DZP	Breulet et al.[7]
1985	0.8−2.6[a]	MR SD-CI/DZP	Feller and Davidson[8]
1990	4.1	MP3/6-311+G**	Wiberg and Rosenberg[9]
1991	2.1−4.2	RHF-MP3/6-31G*	Guo and Karplus[10]
1996	1.5−2.8[b]	CBS-Q and G2	Murcko et al.[14]
2001	1.6	CCSD(T)/cc-pVDZ	Sancho-Garcia et al.[17]
2004	2.4	CCSD(T)/cc-pVTZ+MP2/ cc-pV5Z	Karpfen and Parasuk[19]

[a] The smaller value resulted from the inclusion of an approximate correction for unlinked quadruple excitations.[56]

[b] Murcko et al. reported G2 (2.2 kJ/mol) and CBS-Q (0.0 kJ/mol) barriers that included the zero point vibrational energies. For the sake of consistency in this Table, the ZPEs have been removed.

DeMaré et al. investigated the rotational structure in an infrared band near 750 cm^{-1} at moderate resolution and attributed this band to the *gauche* rotamer.[22] However, a recent re-examination of this band with much higher resolution showed the band comes from a difference band of the *trans* rotamer.[23] In addition, no subbands with rotational structure of the *gauche* rotamer, which is only 5% *or less* abundant at room temperature,[24] could be identified in the high-resolution infrared spectrum.[23] The estimate of 5% for the *gauche* content of butadiene at room temperature appears to be an overestimate. Saltiel et al.[24] report $\Delta_r S^\circ_{320} = 16.6$ J/K mol for *gauche* - *trans*. This $\Delta_r S^\circ$ is too large. From Gaussian 03 (G03)[25] B3LYP[26,27]/aug-cc-pVTZ calculations, $\Delta_r S^\circ_{298} = 8.2$ J/K mol, including an R ln 2 contribution for the statistical weight of two *gauche* rotamers. With the $\Delta_r H^\circ_{320}$ value from Saltiel et al. and the new $\Delta_r S^\circ$ value, the *gauche* content at room temperature is estimated to be only 2%. The large value for $\Delta_r S^\circ_{320}$ probably reflects uncertainty in determining different absorption coefficients for the two rotamers.[24]

A number of matrix-isolation studies with infrared and Raman spectroscopy have been made of BDE, heated to high temperature in the incident beam or photolyzed in situ to increase the *gauche*/*cis* content. These experiments have recently been reviewed.[23,28−34] Although evidence for a *gauche* or *cis* rotamer is unmistakable in these spectra, uncertainty exists about the conformer present. The conformer could be *gauche* or *cis* or a floppy gauche rotamer sampling the two enantiomers.[33]

We have recently reported high level ab initio structures for the *s-trans* and the 90°-twisted rotamers of BDE. The structure found for the *trans* rotamer of BDE agrees within 0.001 Å with the semiexperimental equilibrium structure recently reported.[35] In the present work, we apply the same theoretical approach to the *trans-gauche* transition state, the *gauche* rotamer, and the *gauche*−*gauche* transition state. In addition, new predictions of the frequencies and intensities for the *gauche* rotamer are supplied.

Theoretical Section

The present approach closely follows the procedure used in our previous work on butadiene,[35] as well as the approach used in a recent survey of over 100 small molecules that found mean absolute deviations of 0.003 Å (AH bond lengths, 49 comparisons), 0.001 Å (AB bond lengths, 79 comparisons) and 0.2° (bond angles, 30 comparisons).[36] Although the survey just mentioned sometimes employed basis sets as large as aug-cc-pV7Z, in the context of the present work the first step is a series of three CCSD(T)(FC) geometry optimizations with the aug-cc-pVnZ, n = D, T, Q sequence of basis sets.[18,37] Although by current standards the aug-cc-pVQZ basis set is at the practical limit of what can be used in coupled cluster geometry optimizations, the resulting structures still contain a small but non-negligible, residual basis set truncation error. We further reduce this error by performing a three-parameter exponential extrapolation of the aug-cc-pVnZ optimized bond lengths in order to estimate the complete basis set (CBS) limit. In the case of the *trans* conformer, the CBS bond length extrapolation shortened the C=C bond by 0.0007 Å and the C−C bond by 0.0004 Å. With the aug-cc-pVQZ basis set, the bond angles were already converged to an accuracy of ± 0.1°, so no extrapolation was performed.

The second step in our procedure is a series of six CCSD(T) geometry optimizations intended to recover the core/valence correlation correction. These calculations made use of the correlation consistent weighted core/valence (CV) basis sets, cc-pwCVnZ, n = D,T,Q,[38] and were performed in matched pairs. One calculation employed the normal frozen core approximation in which the carbon (1s) electrons were excluded from the correlation treatment, while the other calculation in the pair involved all electrons. The CV correction was also extrapolated to the CBS limit.

The third step involves an additional pair of CCSD(T) geometry optimizations intended to account for scalar relativistic (SR) effects. The SR correction is defined as the difference between a conventional CCSD(T)(FC)/cc-pVTZ optimized structure and a corresponding structure optimized with a second order Douglas−Kroll−Hess (DKH) CCSD(T)(FC) calculation[39,40] using the cc-pVTZ_DK basis set.[41] For first and second row compounds, the scalar relativistic correction is generally an order of magnitude smaller than the CV correction, with the former typically falling into the 0.0001−0.0003 Å range. However, for third row or heavier elements the scalar relativistic correction may exceed 0.002 Å.

Zero point vibrational energies (ZPEs), based on harmonic frequencies, were obtained at the CCSD(T)(FC)/aug-cc-pVDZ level for the stationary points on the torsional potential.

All CCSD(T) calculations in the present work were performed with MOLPRO 2006.1.[42] Geometries were optimized using MOLPRO's default convergence criterion, i.e. the maximum component of the gradient is less than 3×10^{-3} au and the maximum energy change is less than 1 μE_h.

Although CCSD(T) is one of the highest levels of theory that can routinely be applied in structural determinations of small (i.e., ≤ 24 atoms) molecules, there is a growing body of evidence about the impact of correlation recovery beyond CCSD(T) on bond lengths and angles.[43−46] For example, in a recent study of such effects carried out with the CCSDT(Q) and CCSDTQ methods, increases in C−C bond lengths on the order of 0.0002 Å (C_2H_6) to 0.0011 Å (C_2H_2) were reported.[36] Unfortunately, methods incorporating quadruple excitations are currently prohibitively expensive for optimizing the geometries of all stationary points on the BDE torsional potential. Nevertheless, we were able to perform single point CCSDT(Q) calculations at the stationary points in order to improve our estimate of their relative energies. We were also able to carry out full CCSDT(Q) geometry optimization on the *s-trans* conformer. All CCSDT(Q) calculations were performed with the MRCC program of Kállay and co-workers[47,48] interfaced to MOLPRO. Finally, the difference between CCSDT(Q) and full configuration interaction (FCI), which represents the exact solution of the Schrödinger equation for a fixed basis set, was estimated with a continued fraction approximant based on CCSD, CCSDT, and CCSDT(Q) energies.[36,49]

TABLE 2: Energies[a] and Torsion Angles for Rotamers of Butadiene

	theoretical					experimental	
	present work[b]			Karpfen and Parasuk[c]		Engeln et al.[d]	
	w/o ZPE	w ZPE[e]	τ/deg	w/o ZPE	τ/deg	energy	τ/deg
trans	0.0	0.0	180.0	0.0	180	0	180
T.S.	26.8	24.0	101.7	25.6	101	24.8	103
90°	25.8	23.1	90.0	24.5[f]	90	23.1	90
gauche	12.6	12.2	35.5	12.1	35	12.0	38
cis (TS)	14.6	13.5	0.0	14.5	0	16.5	0

[a] Relative to the *trans* rotamer in kJ/mol. [b] Based on CCSD(T)(FC)/CBS + CCSD(T)(CV)/cc-pwCVQZ + SR correction + CCSDT(Q)(FC)/cc-pVDZ correction. [c] Reference 19 based on MP2(FC)/cc-pV5Z + CCSD(T)(FC)/cc-pVTZ values. [d] Reference 13. We evaluated the reported potential function at various angles to obtain the energies and angles reported here, which are supplementary to the angles of Engeln et al. Only the parameters of the potential function and a graph were reported in the paper. [e] Including CCSD(T)(FC)/aug-cc-pVDZ zero point vibrational energies. [f] Karpfen and Parasuk did not report an explicit value for $\tau = 90°$. This value was derived from their potential function.

Results and Discussion

Table 2 compares our best relative energies (with and without zero point vibrational contributions) for the various rotamers with the theoretical results of Karpfen and Parasuk[19] and the experimental values derived from the potential function of Engeln et al.[13] We note here that the convention adopted in this paper for the torsion angle differs from the convention used by Engeln et al., who assigned the *trans* conformation an angle of 0°. The zero of energy in Table 2 is taken to be the *trans* rotamer global minimum. The 0°-, 90°-, and 102°-rotamers all possessed a single imaginary frequency. The gradient norm at the first and last of these was $\sim 10^{-4}\, E_h/a_0$ and the gradient norm at the 90° structure was $4 \times 10^{-4}\, E_h/a_0$, indicating that it is a near transition state. Figure 1 is a schematic potential function derived from the best available data. Inclusion of the CCSDT(Q) correction increases the 102° barrier height by 0.34 kJ/mol and stabilizes the *gauche* minimum by 0.12 kJ/mol, both relative to the *trans* conformer.

The present energies and torsion angles are in good agreement with those of Karpfen and Parasuk, who used a slightly lower level of theory, as previously discussed.[19] The energy difference between the *gauche* and the *trans* rotamers in the present work (12.2 kJ/mol, including the ZPE) is nearly the same as the experimental value of $\Delta H°_{320}$ of 12.0 kJ/mol.[24] The *cis* barrier height of 2.0 kJ/mol (excluding the ZPE) is slightly smaller than the 2.4 kJ/mol value reported by Karpfen and Parasuk. Nonetheless, the two theoretical values are sufficiently close to suggest that the corresponding experimental value (4.5 kJ/mol)[13] is likely too large.

Table 3 lists the optimized internal coordinates (bond lengths and bond angles) found for the various rotamers, while the atomic numbering convention is shown in Figure 2 for the *trans* rotamer. An equivalent numbering scheme was used with the other rotamers. Due to the excellent agreement between the theoretical and semiexperimental structures for the *trans* rotamer (bond lengths within ± 0.001 Å, bond angles within ± 0.2°),[35] we expect a similar level of accuracy in the theoretical predictions for the other three structures.

As reported previously, the C=C and C−C bond lengths in the 90°-twisted rotamer differ significantly from those in the *trans* rotamer, indicating localized bonds with negligible

TABLE 3: Internal Coordinates for Rotamers of Butadiene[a]

parameter	*trans*	102° (TS)[b]	90°[c]	*gauche*	*cis* (TS)[b]
r(C1C2)/Å	1.3377 (1.3389)[d]	1.3327	1.3329	1.3362	1.3371
r(C2C3)/Å	1.4548 (1.4549)	1.4824	1.4818	1.4682	1.4696
r(H1C1)/Å	1.0823 (1.0825)	1.0820	1.0819	1.0821	1.0819
r(H2C1)/Å	1.0799 (1.0799)	1.0807	1.0808	1.0802	1.0799
r(H3C2)/Å	1.0846 (1.0848)	1.0850	1.0852	1.0841	1.0833
α(C1C2C3)/deg	123.5 (123.5)	123.8	123.8	124.4	126.3
α(H1C1C2)/deg	120.8 (120.8)	121.3	121.2	121.3	122.1
α(H2C1C2)/deg	121.5 (121.5)	121.1	120.2	121.1	120.8
α(H3C2C1)/deg	119.8 (119.8)	117.0	119.3	116.6	118.2
τ(C1C2C3C4)/deg	180.0 (180.0)	101.7	90.0	35.5	0.0
τ(H1C1C2C3)/deg	0.0 (0.0)	−0.5	0.0	2.1	0.0
τ(H2C1C2C3)/deg	180.0 (180.0)	179.8	180.0	181.3	180.0
τ(H3C2C3H4)/deg	180.0 (180.0)	−79.1		−145.7	0.0

[a] Dihedral angles (τ) are as normally defined and used in the calculation. [b] T.S. stands for transition state. [c] The dihedral angles involving CH bonds were constrained to planar values with 0.0° or 180.0° in this calculation. These torsion angles were relaxed in the calculation of the 102° transition state and were found to be little different from the planar values. [d] Values in parentheses include a CCSDT(Q)(FC)/cc-pVDZ correction.

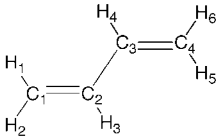

Figure 2. Schematic for the trans rotamer of butadiene showing the numbering of atoms.

TABLE 4: Theoretical Harmonic Vibration Frequencies (cm^{-1}), Raman Activities (Å^4/u) and IR Intensities (km/mol) for the *gauche* Rotamer of Butadiene

sym	freq.	CCSD(T)[a]	B3LYP[b]	Raman activity[b]	IR intensity[b]
a	ω_1	3233.4	3221.0	138.7	5.2
	ω_2	3155.7	3142.1	301.5	0.45
	ω_3	3134.2	3132.7	30.7	25.6
	ω_4	1655.6	1670.4	212.0	2.6
	ω_5	1452.8	1469.1	35.8	9.5
	ω_6	1317.1	1347.2	32.0	0.037
	ω_7	1049.7	1070.7	2.7	0.012
	ω_8	971.2	1022.1	18.5	1.9
	ω_9	908.2	952.5	7.3	6.6
	ω_{10}	880.3	884.9	4.2	0.64
	ω_{11}	723.7	759.2	1.7	3.1
	ω_{12}	264.9	275.0	9.3	0.008
	ω_{13}	158.1	161.0	2.9	0.29
b	ω_{14}	3231.9	3219.3	5.0	14.9
	ω_{15}	3142.3	3136.9	15.1	4.2
	ω_{16}	3132.3	3121.8	58.7	7.7
	ω_{17}	1653.5	1693.2	2.9	7.5
	ω_{18}	1420.0	1444.8	6.3	1.9
	ω_{19}	1287.2	1315.9	15.7	0.28
	ω_{20}	1084.5	1111.3	4.0	4.5
	ω_{21}	991.6	1035.4	0.59	27.1
	ω_{22}	912.2	954.7	1.2	76.0
	ω_{23}	604.3	621.2	0.25	9.5
	ω_{24}	453.0	474.9	0.61	15.2

[a] CCSD(T)/aug-cc-pVDZ. Torsion angle = 36.1°. [b] B3LYP/aug-cc-pVTZ. Torsion angle = 32.6°.

π-electron delocalization. The lengths of the two C=C double bonds in the *trans* and *cis* rotamers are comparable, indicative of significant π-electron delocalization in both. However, the C−C bond in the *cis* rotamer is considerably longer than in the *trans* rotamer. Thus, it seems that the C−C bond in the *cis* rotamer must be lengthened in response to repulsion of the H1 and H5 hydrogen atoms rather than because of the absence of π-electron delocalization. The significant increase in the C1C2C3 bond angle in the *cis* rotamer also reflects the H1H5 repulsion. The pattern in CH bond lengths and bond angles seen in the *trans* rotamer is essentially preserved in the other rotamers with the exception of the shortening of the C2H3 and C3H4 bonds and the increase in the C1C2H3 and C4C3H4 bond angles in the *cis* rotamer. The C−C bond length in the gauche rotamer is closer to that of the *cis* rotamer than the *trans* rotamer. Supporting Information Tables S1−S5 supply the current Cartesian coordinates for the five rotamers.

The leftmost column in Table 4 gives new predictions of the harmonic vibrational frequencies of the *gauche* rotamer obtained at the CCSD(T)/aug-cc-pVDZ level of theory. Earlier predictions for the *gauche* rotamer were made by De Maré et al.[22] by transferring to the *gauche* rotamer scale factors for internal coordinate force constants fitted to the experimental data for the *trans* rotamer.[50,51] Their predictions, which are listed in Table 6, include the effects of anharmonicity and are thus not directly comparable to the harmonic frequencies in Table 4. DFT Raman activities and infrared intensities were obtained from B3LYP/aug-cc-pVTZ calculations using the G03 program.[25] The corresponding B3LYP harmonic frequencies are in column two in Table 4. The DFT set of frequencies is generally larger than the first set and differ more than might be expected. The torsion angle (relative to the *cis* rotamer) of only 32.6° in the DFT calculation compared to 36.1° in the CCSD(T) structure undoubtedly causes the difference in frequencies, which are all larger except in the CH stretching region.

B3LYP and CCSD(T) harmonic frequencies for the *trans* conformer obtained with the aug-cc-pVDZ and aug-cc-pVTZ basis sets are compared in Table 5 in order to illustrate the sensitivity of the values to the quality of the basis set. Although DFT in general converges more rapidly with respect to improvements in the basis set, for this particular collection of frequencies the total variation in the CCSD(T) frequencies as a function of the basis set size was slightly less than the variation observed for B3LYP. Studies comparing CCSD(T)-based frequencies with experimental values in diatomic molecules lead us to expect that this level of theory should ultimately be capable of achieving very high accuracy and excellent agreement with experiment.[36] Achieving this level of accuracy would require the same sequence of steps used in determining the structures, i.e. frozen core calculations with large basis sets corrected for core/valence and scalar relativistic effects and possibly for higher order correlation effects. Frequency evaluations at that level are currently intractable with present day software and hardware for a molecule the size of butadiene. For example, the CCSD(T)/

TABLE 5: Comparison of B3LYP and CCSD(T) Harmonic Frequencies (cm^{-1}) and Zero Point Vibrational Energies (kJ/mol) for *s-trans*-1,3-Butadiene

	aug-cc-pVDZ		aug-cc-pVTZ	
sym.	B3LYP	CCSD(T)	B3LYP	CCSD(T)
a_u	180.9	169.2	174.5	157.5
b_u	300.9	289.5	299.7	285.8
a_g	518.1	505.1	519.4	505.8
a_u	537.8	524.9	538.5	524.1
b_g	778.1	748.6	781.0	751.7
a_g	899.7	890.2	901.5	893.9
a_u	946.9	906.8	943.4	913.8
b_g	948.7	908.3	945.3	914.8
b_g	997.9	960.3	1002.0	964.7
b_u	995.6	982.6	1007.2	989.6
a_u	1046.2	1014.1	1056.6	1027.3
a_g	1222.8	1212.6	1229.0	1219.4
a_g	1307.7	1293.5	1317.5	1304.3
b_u	1312.1	1297.7	1324.1	1307.3
b_u	1404.1	1394.5	1419.6	1406.4
a_g	1464.2	1461.6	1479.5	1472.0
b_u	1647.9	1618.3	1651.2	1628.7
a_g	1703.4	1681.3	1702.1	1689.5
a_g	3137.3	3132.8	3124.7	3133.7
b_u	3142.1	3134.3	3134.6	3136.3
a_g	3146.5	3146.1	3137.3	3144.1
b_u	3151.5	3152.0	3137.4	3148.6
a_g	3236.5	3233.8	3220.8	3230.8
b_u	3236.9	3234.2	3221.1	3231.1
ZPE	222.9	220.7	222.9	221.2

aug-cc-pVTZ normal mode calculation on *s-trans*-1,3-butadiene required 27 days on two Opteron cores.

Despite the differences in the B3LYP and CCSD(T) frequencies, the predictions of Raman activities and infrared intensities in the DFT calculation (Table 4) are regarded as qualitatively useful. These predictions lead to a revised interpretation of the assignments for the *gauche* rotamer in the gas phase Raman spectrum made by Engeln et al.[13] A keystone in their interpretation was assigning a feature at 269.9 cm^{-1} as the 2−0 transition of ν_{13} for the *gauche* rotamer. We now suggest this feature is the ν_{12} fundamental of the *gauche* rotamer, which has a predicted frequency of ~265 cm^{-1} and a predicted Raman activity of 9.3 Å^4/u. The overtone of ν_{13}, the torsional mode at about 285 cm^{-1} would have a very small Raman activity unless it gains intensity by Fermi resonance with ν_{12}. Engeln et al. expressed concern about the anomalously high intensity of the feature at 269.9 cm^{-1}, assigned to the overtone of the torsion.[13] Even if $2\nu_{13}$ gains intensity by Fermi resonance, this band would be less intense than ν_{12}. We conclude that the gas-phase Raman spectrum of butadiene needs to be reevaluated.

The small energy difference between the *gauche* rotamer and the *cis* transition state supports the expectation that tunneling through the barrier between the two *gauche* rotamers will be a signature feature of the rotational spectrum of the *gauche* rotamer. Thus, tunneling splitting will significantly influence the frequencies of the rotational transitions.

In previous sections, our discussion referred to harmonic frequencies obtained from a variety of theoretical methods. On current computer hardware, harmonic frequencies can be readily obtained from applications such as G03[25] and MOLPRO,[42] although large basis set CCSD(T)(FC) normal mode calculations are quite time-consuming, even for as small a molecule as butadiene. Until recently, theoretical reports of anharmonic fundamental frequencies were largely limited to molecules with six or fewer atoms where it was possible to construct complete

TABLE 6: Comparison of Anharmonic CCSD(T)(FC) and Experimental Fundamental Frequencies (cm^{-1}) for *s-trans*-1,3-Butadiene and *gauche*-1,3-Butadiene[a]

s-trans-1,3-Butadiene

sym.	aug-cc-pVDZ	aug-cc-pVTZ	aVTZ + CV[b]	PD scaled[c]	expt.[d]
a_u	157.9	163.1	163.5	159	162.2
b_u	291.1	301.3	301.2	295	299
a_g	502.4	516.7	517.3	510	513
a_u	507.2	520.8	520.8	518	524.6
b_g	724.7	757.0	758.4	747	749
a_g	876.4	887.7	889.9	879	889
a_u	876.3	912.9	914.4	907	908.1
b_g	879.0	916.0	917.5	908	908
b_g	929.9	971.6	973.1	964	966
b_u	970.3	994.9	995.4	996	990
a_u	982.6	1025.1	1026.4	1022	1013.8
a_g	1188.0	1204.4	1205.7	1209	1204
a_g	1273.7	1297.7	1298.4	1287	1285
b_u	1272.2	1298.6	1299.4	1290	1281
b_u	1360.1	1385.2	1386.5	1380	1380.6
a_g	1420.9	1438.8	1439.6	1443	1442
b_u	1576.1	1609.3	1611.9	1591	1596.5
a_g	1633.9	1654.7	1657.8	1652	1644
a_g	2978.7	2970.6	2977.5	3008	3012
b_u	3012.0	3012.3	3019.3	3015	3011.4
a_g	2999.3	2990.5	2997.3	3024	3025[e]
b_u	3011.5	2996.9	3003.6	3024	3026
a_g	3087.9	3074.9	3082.2	3111	3100
b_u	3088.2	3075.1	3082.4	3111	3099.7
ϵ_{rms}	20.7	16.4	14.1	5.8	

gauche-1,3-Butadiene

sym.	aug-cc-pVDZ	aVDZ + CV	PD scaled[c]	expt.
a	140.9	142.8	186	136[f]
a	262.5	263.6	274	NA
b	445.9	446.9	457	470[g]
b	595.2	596.4	616	596[g]
a	707.6	709.1	735	730[g]
a	861.8	863.5	866	NA
a	887.8	890.5	918	920[g]
b	889.4	891.8	919	914[g]
a	949.0	950.6	984	984[g]
b	970.4	971.7	1004	996[g]
a	1033.2	1034.5	1052	1034[h]
b	1064.8	1065.7	1093	1087[f]
b	1260.4	1261.3	1274	NA
a	1284.2	1285.1	1306	NA
b	1380.9	1381.8	1403	1403[g]
a	1405.1	1408.5	1433	1425[g]
a	1602.5	1605.2	1619	1612[i]
b	1610.3	1613.0	1628	1633[g]
b	3020.3	3026.3	3025	3010[g]
a	3017.4	3023.3	3030	2990[g]
b	2998.3	3004.4	3114	3070[g]
a	3013.4	3019.4	3025	3023[g]
b	3085.5	3091.7	3112	3103[g]
a	3086.8	3092.9	3018	3035[g]
ϵ_{rms}	28.7	27.9	20.3	

[a] Anharmonic corrections were computed at the MP2(FC)/aug-cc-pVDZ level of theory. [b] Based on CCSD(T)(FC)/aug-cc-pVTZ + a scaled core/valence correction obtained from CCSD(T)(CV)/cc-pwCVDZ calculations. [c] Panchenko and DeMaré MP2 values based on 8 scaling factors.[51] [d] Gas phase values reported by McKean et al. (unless otherwise noted).[50] [e] Furukawa et al.[30] [f] Gas phase value taken from Carriera.[11] [g] Low temperature argon matrix IR taken from Arnold et al.[32] [h] Argon matrix Raman taken from Choi et al.[33] [i] This value was reported by Arnold et al. as 1602 cm^{-1}, but that value is a misprint.

quartic (or better) force fields.[52,53] Results from an alternative approach which exploits the different rates of convergence of the harmonic frequencies and the anharmonic corrections has recently been reported.[36] This approach combines CCSD(T)/aug-cc-pVnZ (n = D, T, or Q) harmonic frequencies with DFT or MP2 anharmonic corrections determined with the smaller basis sets. Although the number of critical evaluations of the combination approach is still limited, the available comparisons with quartic force field or well-established experimental fundamentals suggest that the technique can achieve accurate results at greatly reduced computational expense.

The three fundamentals in H_2O were chosen as a test case to explore the capabilities and limitations of this approach. CCSD(T)(FC) harmonic frequencies were obtained from basis sets up through aug-cc-pV6Z.[54] CV corrections to the harmonic frequencies were determined from weighted core/valence basis sets up through cc-pwCV5Z. The scalar relativistic corrections for the harmonic frequencies were based on CCSD(T)-DK/cc-pVTZ_DK calculations. Higher order correlation effects on the harmonic frequencies were obtained from CCSDTQ(FC)/cc-pVDZ calculations. Very few CCSDTQ frequencies for polyatomic molecules have been reported due to their high computational cost. In the case of H_2O, higher order correlation effects shift the CCSD(T) harmonic frequencies by $\pm$ 6 cm^{-1} or less. Anharmonic corrections were evaluated at the MP2(FC)/aug-cc-pVnZ, n = D,T,Q levels of theory. The largest of these basis sets yielded the following fundamentals, with corresponding experimental[55] values in parentheses, $\nu_1(a_1) = 3663$ (3657), $\nu_2(a_1) = 1603$ (1595) and $\nu_3(b_2) = 3759$ (3756) cm^{-1}. By extrapolating the CCSD(T) frozen core and core/valence components to the complete basis set limit and increasing the CCSDTQ basis set to aug-cc-pVDZ quality, near perfect agreement with experiment is possible. However, such extensive calculations are well beyond what is affordable for butadiene. If the water basis sets are reduced to a size that is practical for butadiene, namely aug-cc-pVTZ for the CCSD(T) harmonic frequencies, cc-pwCVDZ for the CV corrections and aug-cc-pVDZ for the MP2 anharmonic corrections, the resulting fundamentals are in only slightly poorer agreement with experiment: $\nu_1(a_1) = 3625$ (3657), $\nu_2(a_1) = 1596$ (1595) and $\nu_3(b_2) = 3722$ (3756) cm^{-1}.

CCSD(T) theoretical values for the anharmonic frequencies of *trans* and *gauche* butadiene are compared in Table 6 with the available experimental values. The anharmonic frequency corrections obtained from G03 are weakly dependent on the choice of the axis system. All of the anharmonic calculations performed as part of the present work were carried out in the principal axis system (PAS). In the case of *trans*-butadiene, the PAS differs from the G03 default choice of axis system by 23°. At the MP2(FC)/aug-cc-pVDZ level of theory, the largest difference in anharmonic corrections observed between values based on the G03 default axis system and those based on the PAS was only 0.9 cm^{-1}. Larger differences may be observed at other levels of theory. For example, differences as large as 10 cm^{-1} were found with B3LYP/cc-pVTZ and differences of up to 8 cm^{-1} were found in the *gauche* conformer. In addition to the choice of axis system, the details of how G03 treats Fermi resonances has changed with various versions of the code. The present results were obtained with the C.02 version.

The small rms error shown in Table 6 for the Panchenko and DeMaré[51] *trans* rotamer frequencies reflects the effects of multiple empirically adjusted scale factors for the theoretical internal-coordinate force constants. These scale factors, which were obtained by fitting to the observed *trans* frequencies, were then applied to the theoretical force constants used to derive the *gauche* anharmonic frequencies. In part, the increase in the CCSD(T) and "PD Scaled" rms errors for the *gauche* structure is thought to result from comparing theoretical gas phase frequencies with experimental matrix isolation values. In the case of the "PD Scaled" values, the adoption of the *trans* scaling factors is also a contributor.

For the *trans* rotamer, the level of agreement between theory and experiment[50] is quite good (see Table 6). Increasing the basis set from aug-cc-pVDZ to aug-cc-pVTZ decreases the root-mean-square (rms) deviation by 4.3 cm^{-1} (~20%). A further increase in the size of the basis set, to aug-cc-pVQZ, proved intractable with our current resources. Nonetheless, tests on prototype hydrocarbons such as ethylene and ethane suggest that the use of the larger aug-cc-pVQZ basis set would produce a further small reduction in the rms error as a result of increases in the high frequency stretching modes above 3000 cm^{-1}. All results in Table 6 are based on MP2(FC)/aug-cc-pVDZ anharmonic corrections. Tests on ethylene and ethane also indicated that improving the basis set used for the anharmonic correction from aug-cc-pVDZ to aug-cc-pVTZ would result in additional small increases in the high frequency stretches, but such calculations were prohibitively expensive for butadiene.

As seen in Table 6, core/valence corrections to the harmonic frequencies at the CCSD(T)/cc-pwCVDZ level of theory further reduces the rms deviation to 14.1 cm^{-1} for the *trans* conformer. A scale factor of 1.39 was applied to the anharmonic corrections for frequencies above 3000 cm^{-1} based on cc-pwCVTZ calculations conducted on ethylene and ethane. Scalar relativistic corrections to the harmonic frequencies of ethylene averaged less than 0.2 cm^{-1} and, therefore, were expected to be unimportant for small hydrocarbons such as butadiene.

Due to the lower C_2 symmetry and greater cost of obtaining harmonic frequencies in the *gauche* conformer, we were unable to perform a CCSD(T) normal-mode analysis with the aug-cc-pVTZ basis set. Nonetheless, the CV-corrected values are still in reasonable agreement with the available matrix-isolation fundamentals for that conformer,[11,32,33] with an rms deviation of 28 cm^{-1}.

In conclusion, we believe the present structures and relative energies of the butadiene rotamers to be the most accurate theoretical values reported, to date. Furthermore, based on their ability to reproduce the available experimental data for the well-characterized *trans* rotamer, we expect our predictions for the other stationary points to be similarly reliable and thus should guide the search for improved experimental data. The predictions of frequencies for the *gauche* rotamer should also guide the search for this rotamer in gas-phase spectra.

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Supporting Information Available: Tables S1−S5 supplying the current Cartesian coordinates for the five rotamers. This material is available free of charge via the Internet at http://pubs.acs.org.

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