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Equilibrium Structures for Butadiene and Ethylene: Compelling Evidence for Π-Electron Delocalization in Butadiene

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Equilibrium structures have been determined for *s-trans*-1,3-butadiene and ethylene after adjusting the rotational constants obtained from rotational spectroscopy by vibration−rotation constants calculated from the results of quantum chemical calculations. For butadiene, the formal C═C bond length is 1.338 Å, and the formal C−C bond length is 1.454 Å. For ethylene, the C═C bond length is 1.3305 Å. These values appear to be good to 0.001 Å. It is shown for the first time that π-electron delocalization has the structural consequences of increasing the length of the formal double bond by 0.007 Å and decreasing the length of the formal single bond by 0.016 Å. Comparisons are made with structures computed with several quantum chemical models. The MP2/cc-pVTZ results agree best with the new r_e structure.

Introduction

The determination of the equilibrium structure of any molecule is a worthy objective for a structural investigation, but such a study for *s-trans*-1,3-butadiene (BDE) carries with it a special interest. This molecule occupies a key position in both the understanding and the exposition of certain basic principles of chemical bonding. Organic chemistry textbooks use a discussion of bonding in BDE to introduce the concept of π-electron delocalization. The $\sigma-\pi$ framework is as shown in Figure 1. Yet, the available experimental data provide confusing evidence for the expected structural adjustments of a lengthening of the formal double bonds and a shortening of the formal single bond in comparison with standard lengths for corresponding localized bonds.

Table 1 compares the published experimental data for the structure of BDE, together with standards for a localized $\sigma-\pi$ double bond and a localized sp^2-sp^2 single bond. The experimental data in Table 1 come from an electron diffraction investigation of BDE[1] and a microwave study of butadiene-1,1-d_2.[2] The table includes structures derived from a Hartree−Fock (HF) calculation that was used in conjunction with the microwave data,[3] an MP2/6-311G(2d,p) calculation,[4] an MP2/cc-pVTZ calculation,[5] and a DFT calculation done with the adiabatic connection method (ACM).[6,7] Many other quantum chemical (QC) calculations of the structure of BDE have been published. Table 1 includes but a sampling of the structures found with higher-level models. The benchmark for the length of a localized $\sigma-\pi$ bond comes from ethylene, which has been reinvestigated as part of the present work. Because no molecule has a simple sp^2-sp^2 single bond, this bond length was estimated by applying the difference between the sp^3-sp^3 bond in ethane and the sp^3-sp^2 bond in propene to shrink the sp^3-sp^2 single bond in propene to an sp^2-sp^2 bond. The same method for estimating the sp^2-sp^2 single bond length was applied by Dewar but with data of lower quality.[8] The C═C bond length in ethylene is a new equilibrium value, and the sp^2-sp^2 bond length is derived from near-equilibrium values.[9]

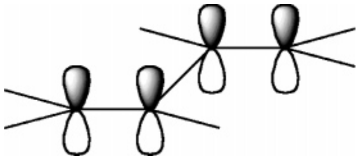

Figure 1. $\sigma-\pi$ framework of bonds for butadiene.

The lengthening by 0.018 Å of the C═C bond in BDE in comparison with ethylene, as found in the electron diffraction study, is unreasonably large. In contrast, the corresponding C−C bond shows little shrinkage. Electron diffraction gives questionable information about C−H bond parameters because hydrogen atoms are weak scatterers of electrons. For the microwave study, which used some bond parameters designated in brackets from the HF calculation and information from the electron diffraction study, a reasonable lengthening of the C═C bonds was a consequence of the structure fitting. However, the C−C bond length was fixed at the HF value. The three different CH bond lengths from the microwave investigation follow the pattern found in all the QC calculations. The two calculations with the MP2 method show a C═C bond length increase of 0.009 Å or 0.010 Å in comparison with ethylene and a C−C bond length decrease of 0.0016 Å or 0.017 Å in comparison with an sp^2-sp^2 single bond. Although the DFT calculation gives a reasonable C−C bond length, the C═C bond length seems too short. For all calculations other than the HF calculation, the three different C═C−H bond angles follow the same pattern.

For structures derived from most experimental data, bond lengths reported to better than 0.01 Å must be regarded as

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TABLE 1: Existing Structural Data for Butadiene

Reference Bond Lengths (Å)[a]	
ethylene C═C	1.330
sp^2-sp^2	1.470

	electron diff[b]	microwave[c]	HF calc[d]	MP2/6-311(2d,p) calc[e]	MP2/cc-pVTZ calc[f]	DFT calc[g]
			Bond Length (Å)			
C═C	1.348	1.337	1.322	1.339	1.340	1.333
C−C	1.468	[1.467]	1.467	1.454	1.453	1.450
trans C−H	1.107	1.085	1.075	1.083	1.080	1.081
cis C−H	1.107	1.087	1.077	1.085	1.082	1.084
α C−H	1.107	1.089	1.079	1.088	1.085	1.086
			Bond Angle (deg)			
C═C−C	124.3	123.5	124.0	123.6	123.5	124.2
trans H−C═C	120.7	[121.5]	121.5	121.5	121.5	121.6
cis H−C═C	120.7	[121.6]	121.6	120.9	120.8	121.3
α H−C═C	120.7	[119.6]	119.6	116.8	116.7	119.R

[a] See ref 9 and the discussion in the text. [b] Reference 1. [c] Reference 2; values in brackets fixed to the HF values. [d] Reference 3. [e] Reference 4. [f] Reference 5. [g] Reference 7.

uncertain. Zero-point vibrations of the atoms contribute to the ground state rotational constants obtainable from spectroscopic measurements. Thermally excited vibrations as well as ground-state vibrations are a complication for electron diffraction and X-ray diffraction. However, observing the structural consequences of interesting electronic effects requires bond lengths good to 0.001 Å. Such accuracy in bond parameters depends on having an equilibrium structure, in which the atoms are at rest. In addition, equilibrium structures are directly comparable with structures computed with standard QC methods.

For small or highly symmetrical molecules, equilibrium structures (r_e) can be obtained from purely spectroscopic data. Reference 9 includes a recent review of using such data for this purpose. For a molecule as large as BDE, obtaining an equilibrium structure from purely spectroscopic data is all but impossible.[9] However, the "semi-experimental" method of adjusting ground rotational constants,[10] obtained from rotational spectroscopy, to equilibrium rotational constants provides the route to an equilibrium structure. In this method the needed vibration−rotation constants, commonly called "spectroscopic" α's, are computed by QC methods. The relationship between equilibrium (e) and ground state (0) rotational constants is to first order,

$$B_e^\beta \approx B_0^\beta + {}^1\!/_2 \sum_k \alpha_k^\beta$$

where β stands for one of the principal axes of rotation (a, b, or c) and k indexes the normal vibrational modes.[11] The one-half-α sums are only approximately 1% or less of the rotational constants. Thus, QC calculation of α's at accessible levels of theory suffices. Recent examples of using the semi-experimental method to find equilibrium structures are represented by the work of Botschwina,[12] Demaison and co-workers,[10] Groner and Warren,[11] Kuczkowski, Stanton and co-workers,[13] and Craig and co-workers.[14] In the present report, we apply this method to solving the problem of the structural consequences of π-electron delocalization in BDE.

Because of a 0.004 Å difference between the C═C bond length in two near-equilibrium structures for ethylene,[9,15] we have reinvestigated the equilibrium structure of ethylene with this same semi-experimental method. As part of this investigation, a new quadratic force field has been fitted to the vibrational fundamentals of ethylene and its isotopomers.

Rotational constants are available for BDE and a number of its isotopomers. These include ground-state rotational constants for BDE,[16] BDE-2,3-d_2,[16] BDE-1,4-*trans,trans*-d_2,[17] BDE-1,4-*cis,cis*-d_2,[17] BDE-1,4-*cis,trans*-d_2,[17] BDE-1-$^{13}C_1$,[18] and BDE-2,3-$^{13}C_2$ [19] obtained from the analysis of rotational structure in high-resolution infrared spectra. Ground-state rotational constants of BDE-1,1-d_2, which has a tiny dipole moment, are available from the microwave investigation.[2] Ground-state rotational constants for BDE and BDE-1,1-d_2 are revised in the present paper. An extensive reinvestigation of the vibrational fundamentals of the isotopomers of BDE involved in the high-resolution infrared studies has yielded improved fundamental frequencies for use in a new normal coordinate analysis employed in the computation of α's as described elsewhere.[20]

For the reevaluation of the equilibrium structure of ethylene, ground-state rotational constants came from a number of investigations. The analysis of rotational structure in high-resolution infrared spectra gave rotational constants for ethylene,[21] ethylene-1-$^{13}C_1$,[22] ethylene-d_3,[23] and ethylene-d_4.[24] A microwave investigation of the slightly polar ethylene-d_1, ethylene-1,1-d_2, and ethylene-*cis*-1,2-d_2 species provided rotational constants for these substances.[25]

Computations

A number of computer programs were employed for the QC calculations in this work. Gaussian03 and 98 were used to compute equilibrium structures and quadratic and cubic force fields for the various MP2 and B3LYP models.[26] The tight convergence option was selected for both models in computing structures, and a grid of 99 shells each containing 302 points was applied for the DFT calculations.

A modification of Dr. Arthur Maki's ASYM program was used to fit rotational constants to spectroscopic transitions for asymmetric rotors. A Watson-type Hamiltonian was applied in the A-reduction and I^r representation.

The program ASYM40 was used to fit selected scale factors for the quartic force constants in symmetry coordinate space to vibrational fundamentals of various isotopomers of BDE and ethylene, to compute quartic centrifugal distortion constants, and to compute the harmonic contributions to the spectroscopic α's.[20,27]

The program VIBROT computed both harmonic and anharmonic contributions to the spectroscopic α's.[11] With this program the harmonic contributions depend on quadratic force constants from Gaussian scaled by a single factor. The cubic force constants from Gaussian were used unscaled with frequencies computed with scaled quadratic force constants.

TABLE 2: Ground State Rotational Constants for Butadiene and Butadiene-1,1-d_2

	butadiene	butadiene-1,1-d_2 [a]
A (cm^{-1})	1.3903838 (7)	1.2208141 (4)
B (cm^{-1})	0.1478858 (1)	0.13482502 (3)
C (cm^{-1})	0.1336939 (2)	0.12143848 (3)
$10^6\Delta_K$ (cm^{-1})	7.318 (3)	4.55 (7)
$10^7\Delta_{JK}$ (cm^{-1})	−2.443 (5)	−1.28 (6)
$10^8\Delta_J$ (cm^{-1})	2.923 (4)	2.41 (2)
$10^9\delta_J$ (cm^{-1})	3.585 (9)	2.96 (2)
$10^7\delta_K$ (cm^{-1})	1.34 (2)	1.27 (2)
$10^{11}\Phi_K$ (cm^{-1})	7.2 (4)	
$10^{12}\Phi_K$ (cm^{-1})	−9.4 (9)	
$\Delta\nu_{\text{rms}}$ (cm^{-1})	0.00245	0.000000212
κ	−0.977414	−0.97565
no. of transitions	2990[b]	13
max. K_a'	21[c]	4
max. J	66	41

[a] Refit of microwave data from ref 2 with the line at 12 914.705 MHz reassigned from $32_{3,30}-31_{4,27}$ to $38_{4,34}-37_{5,33}$ and the line at 17 275.345 MHz left unassigned. [b] 56.4% of the GSCDs are from the band at 525 cm^{-1}; the rest are from the band at 908 cm^{-1}. [c] Maximum $K_a' = 14$ for the 908 cm^{-1} band.

The fitting of structures to moments of inertia was done with the University of Michigan version of the program STRFIT, which was originally written by Professor Richard Schwendeman at Michigan State University.[28] Fits were made globally to the full set of moments of inertia (I_a, I_b, I_c) of all isotopomers for the ground state form (r_0) and for the equilibrium form (r_e), even though the relationship $I_a + I_b = I_c$ applies to the equilibrium structure of planar molecules. The r_s substitution structures were computed from ground-state rotational constants with Kraitchman-type expressions.[29]

Revisions in Rotational Constants

Rotational constants were refit for two species of BDE. For the normal form of BDE, the rotational structure in a second C-type band has been analyzed since our original publication on its high-resolution infrared spectrum.[16] Details of the structure and the analysis of this band will be reported separately. Table 2 presents the new ground state rotational constants for BDE fit to 2990 ground state combination differences (GSCDs) derived from the previously analyzed C-type band for ν_{11} at 908 cm^{-1} and the recently analyzed band for ν_{12} at 525 cm^{-1}. The new A, B, and C rotational constants differ from the previously published values by less than 0.0008%.

The other isotopomer of butadiene with a revised set of ground-state rotational constants is BDE-1,1-d_2. Rotational transitions for this molecule were investigated by microwave spectroscopy.[2] We found that the reported centrifugal distortion constants originally fit to the microwave data were in poor agreement with the predicted centrifugal distortion constants. Through refitting experiments, the microwave line at 12 914.705 MHz was reassigned to the transition $38_{4,34}-37_{5,33}$, and the line at 17 275.345 MHz was rejected as unassignable. With the revised data set a much tighter fit was obtained to a full set of quartic centrifugal distortion constants, and the agreement with the predicted constants became satisfactory.[20] The A, B, and C rotational constants changed by less than 0.00055% in the refitting. The new rotational constants for BDE-1,1-d_2 are in Table 2.

A comparison of the observed and predicted quartic centrifugal distortion constants for the isotopomers of BDE is supplied in conjunction with our paper on the normal coordinate analysis.[20] For the eight isotopomers of BDE, the agreement between the observed and predicted values is generally better than 10% except for some δ_J and δ_K terms and is regarded as satisfactory.

Table 3 compares observed and calculated quartic centrifugal distortion constants for the isotopomers of ethylene. Although ground-state rotational constants for ethylene-d_3 have been reported,[23] we have not used these constants because only one A-type band in the infrared spectrum was analyzed. Such bands, in which the Q branches of subbands pile up in the band center, yield a poor definition of the A rotational constant. In addition, this investigation was done with a resolution of only 0.07 cm^{-1}. The comparison of observed and predicted quartic centrifugal distortion constants for the other isotopomers of ethylene, supplied in Table 3, is satisfactory with only a few instances of differences greater than 8%. Of course, some of the difference could be due to comparison of observed centrifugal distortion constants for the ground state with centrifugal distortion constants for the equilibrium form. We expect these differences to be small.

Scaled Force Fields for Ethylene

To provide improved harmonic contributions to the α parameters for the six isotopomers of ethylene, four scaled QC force fields were determined. The approach followed exactly that adopted for BDE in the companion study.[20] The methods

TABLE 3: Comparison of Observed and Calculated Centrifugal Distortion Constants for Isotopomers of Ethylene

	parent[a]				1-^{13}C$_1$ [b]				1-d_1 [c]			
	obsd	calc (dcct)[d]	% diff (dcct)[e]	% diff (mcct)[e]	obsd	calc (dcct)[d]	% diff (dcct)[e]	% diff (mcct)[e]	obsd	calc (dcct)[d]	% diff (dcct)[e]	% diff (mcct)[e]
Δ_K/kHz	2592.6	2651.0	2.2	1.9	2594	2659	2.5	0.5	2116	2181	3.1	0.8
Δ_{JK}/kHz	306.75	323.89	5.6	8.0	302	318	5.3	7.6	180	192	6.7	10.6
Δ_J/kHz	44.076	46.249	4.9	3.0	41.8	44.1	5.5	3.6	39.0	40.6	4.1	2.6
δ_J/kHz	8.445	8.715	3.2	0.6	7.84	8.12	3.6	0.9	8.40	8.78	4.5	2.4
δ_K/kHz	304.56	303.12	−0.5	−1.4	287	293	2.1	1.0	244	240	−1.6	−2.0

	1,1-d_2 [c]				*cis*-2,3-d_2 [c]				d_4 [f]			
	obsd	calc (dcct)[d]	% diff (dcct)[e]	% diff (mcct)[e]	obsd	calc (dcct)[b]	% diff (dcct)[c]	% diff (mcct)[c]	obsd	calc (dcct)[b]	% diff (dcct)[c]	% diff (mcct)[c]
Δ_K/kHz	[1224][g]	1258	2.8	0.4	1458	1511	3.6	1.1	629.3	645.0	2.5	0.0
Δ_{JK}/kHz	192	205	6.8	9.9	117	118	0.9	6.8	81.87	86.24	5.3	10.0
Δ_J/kHz	32.7	34.3	4.9	3.7	36	37	2.8	0	23.6	25.2	6.8	5.9
δ_J/kHz	7.88	8.12	3.0	1.1	8.6	8.9	3.5	1.2	6.36	6.66	4.7	3.6
δ_K/kHz	206	208	1.0	1.0	197	194	−1.5	−2.0	113	118.6	5.0	4.4

[a] Reference 21. [b] Reference 22. [c] Reference 25. [d] Computed with the scaled B3LYP/cc-pVTZ force field (dcct), rounded to the precision of the observed value. [e] Calc − obsd as a percentage, for dcct or mcct (MP2/cc-pVTZ) predictions. [f] Reference 24. [g] Transferred from ref 30.

TABLE 4: Comparison of Observed and Calculated Frequencies (cm^{-1}) for Four Isotopomers of Ethylene

	C_2H_4			C_2D_4		
mode[a]	ν_{obs} [b,c]	ϵ_{dcct} [d]	ϵ_{mcct} [d]	ν_{obs} [b]	ϵ_{dcct} [d]	ϵ_{mcct} [d]
ν_1 A_g	3013.6* [e]	−13.9	−4.7	2261.6[f]	−2.5	−1.4
ν_2 A_g	_1631.05_	−5.7	−6.1	_1518.4_[e]	5.2	6.2
ν_3 A_g	_1350.55_	4.2	2.8	_984.6_[f]	−0.6	0.1
ν_4 A_u	_1025.59_	−1.9	−1.9	_729.96_[f]	3.2	3.2
ν_5 B_{1g}	_3083.5_[e]	2.3	0.0	2315.4[f]	−7.3	−10.7
ν_6 B_{1g}	_1219.51_	−5.8	−6.7	_1000_[e]	1.5	2.6
ν_7 B_{1u}	_948.77_	−1.1	−1.1	_719.77_[g]	1.2	1.2
ν_8 B_{2g}	_939.86_	−1.2	−1.8	_780_[e]	1.7	2.4
ν_9 B_{2u}	_3104.89_	−3.9	−4.0	2341.9[f]	2.2	1.0
ν_{10} B_{2u}	_825.93_	−0.2	−0.5	_593.34_[g]	−0.5	−0.4
ν_{11} B_{3u}	_3014.92_*	0.2	14.8	2201.0[f]	−0.5	11.0
ν_{12} B_{3u}	_1442.48_	−4.8	−4.4	_1076.99_[g]	4.9	4.6
ΣWSE		0.65	0.69		0.60	0.73

	H_2CCD_2			$HDCCH_2$		
mode[a]	ν_{obs} [b,h]	ϵ_{dcct} [d]	ϵ_{mcct} [d]	ν_{obs} [b]	ϵ_{dcct} [d]	ϵ_{mcct} [d]
ν_1 A_1, A′	3017.12	−4.1	7.7	3016.2* [e]	−4.5	7.6
ν_2 A_1, A′	_1586.05_	−1.7	−0.8	_1605.5_[i]	−2.6	−2.4
ν_3 A_1, A′	_1029.86_	1.9	2.2	_1288.79_[j]	−1.5	−2.3
ν_4 $A_{2,}$ A″	_888.71_	−1.2	−1.2	_1000.04_[k]	−1.9	−1.9
ν_5 B_1, A′	2335.02	3.9	1.6	_3061.56_[l]	3.6	7.3
ν_6 B_1, A′	_1142.27_	3.1	2.9	_1125.28_[k]	1.9	1.9
ν_7 $B_{2,}$ A″	_750.57_	0.8	1.2	_806.47_[k]	1.9	1.9
ν_8 $B_{2,}$ A″	_943.41_	−1.5	−1.8	_943.50_[k]	−1.3	−1.7
ν_9 B_1, A′	_3094.11_	−1.1	−2.3	_3096.09_[l]	−1.8	−2.3
ν_{10} B_1, A′	_684.64_	0.2	0.5	_732.14_[k]	0.3	0.3
ν_{11} A_1, A′	2230.54	−3.6	2.5	2273.8[l]	−5.9	−3.3
ν_{12} A_1, A′	_1383.93_	0.0	−0.8	_1400.73_[l]	−2.9	−3.0
ΣWSE		0.18	0.21		0.20	0.29

[a] Mode numbers as in ref 31. For the d_2 and d_1 isotopomers of lower symmetry, the symmetry species quoted are those for the appropriate C_{2v} or C_s point group. [b] In italics, frequencies used in the refinement. The asterisk denotes Fermi resonance correction applied. [c] Data from ref 32 except where otherwise indicated. [d] $\Delta\nu$(obs−calc) from the B3LYP/cc-pVTZ (dcct) or MP2/cc-pVTZ (mcct) methods. Calculated ν(CD) values have been multiplied by 1.011 for comparison with observed data. [e] Reference 31. [f] Reference 33. [g] Reference 24. [h] Reference 34. [i] Reference 35. [j] Reference 36. [k] Reference 37. [l] Reference 38.

used were B3LYP and MP2, with both the bases 6-311++G** (tz+) and cc-pVTZ (cct). Symmetry coordinates were analogous to those used for butadiene. Independent scale factors were determined for all symmetry coordinates, except for those involving CH stretching, by fitting frequency data from four isotopomers, parent (d_0), d_4, 1,1-d_2 and d_1.[24,31−38] For the CH stretches, a single factor was derived by refining to the higher CH stretching frequencies where Fermi resonances should be minor. Supplementary Table S1 shows the scale factors obtained. The frequency fit is shown in Table 4.

Spectroscopic α's

We have introduced the QC calculations of the harmonic contributions to the spectroscopic α's in two ways. In the first more elaborate method, these contributions were derived from a force field with a multiplicity of scale factors in symmetry coordinate space fit to the vibrational assignments of ethylene, BDE and their isotopomers. The values calculated for the harmonic contributions to the α's of BDE were reported in conjunction with the paper on the normal coordinate analysis.[20] For ethylene, the harmonic contributions to the α's computed from the multiply scaled quadratic force constants are in supplementary Table S2. In the second, simplified method, the contributions of quadratic force constants to the α's were computed with a single scale factor in VIBROT. In both methods, unscaled cubic force constants contributed to the α's. Although the cubic force constants are used unscaled, scaling of quadratic force constants has an indirect influence on the anharmonic contributions to the α sums. This contribution occurs because harmonic frequencies are in the denominator of the terms containing the cubic force constants, as seen in the equation for a_k^{β}(anh) on p 35 in ref 11. Although the α's computed by the second method are not reported, the equilibrium rotational constants, which depend on the α's computed with single scale factors, are given in supplementary Tables S3 and S4 for, respectively, ethylene and BDE.

For ethylene, α's were computed using the four QC models described in the previous section. Two of these models were of the Dunning type: B3LYP/cc-pVTZ and MP2/cc-pVTZ. Two were of the Pople type: B3LYP/6-311++G** and MP2/6-311++G**. For BDE, only the dcct, mcct, and dtz+ models were used for reasons explained in the paper on normal coordinate analysis.[20]

The anharmonic contributions to α sums for *A* rotational constants are about 3 times larger than the harmonic contributions. For the *B* and *C* rotational constants, the harmonic contributions to the α sums are only about 1 MHz, whereas the anharmonic contributions are up to 30 times larger. Differences in the two methods for computing harmonic contributions to α's affect principally the *A* rotational constant for the equilibrium form. Larger differences in the α sum contributions arise from the varying contributions of cubic force constants computed with the different QC models. Supplementary Table S5 gives an example of the various contributions of α's to the ground-state rotational constants of BDE computed with the dcct model.

Equilibrium Moments of Inertia

Ethylene. Table 5 supplies the ground state and equilibrium moments of inertia for ethylene and its isotopomers as computed with the four QC models. These equilibrium moments of inertia were obtained by the first method, i.e., with the use of multiply scaled quadratic force constants and unscaled cubic force constants to compute the α's. The inertial defects (Δ) for the ground state are small enough to confirm the planarity of ethylene, and the tiny inertial defects for the equilibrium form are close enough to zero to support the semi-experimental method of obtaining equilibrium rotational constants.

The α's computed from the four QC models differ somewhat but not to an extent that produces significant differences in bond parameters for ethylene. Differences in the α's from the four QC models cause discrepancies in only the third or fourth decimal place of the moments of inertia in Table 5. The two sets of moments of inertia derived from the cct models differ very little. The two sets of moments of inertia derived from the tz+ models differ more between themselves and from the cct values.

Supplementary Table S3 gives the equilibrium moments of inertia for ethylene computed with the single scale factor in the second method. In all cases inertial defects are larger, in some instances by a factor of two or three compared to those found with the first method. These discrepancies suggest that the second method is less reliable. However, see the subsequent discussion of bond parameters.

Butadiene. Table 6 contains ground state and equilibrium rotational constants for BDE. As for ethylene, the α's used to compute the equilibrium rotational constants in Table 6 were found by the first method, i.e., with multiple scale factors for

TABLE 5: Ground State and Equilibrium Moments of Inertia (amu Å^2) for the Isotopomers of Ethylene

	ethene[a]	ethene-1-$^{13}C_1$ [b]	ethene-1-d_1 [c]	ethene-1,1-d_2 [c]	ethene-*cis*-1,2-d_2 [e]	ethene-d_4 [d]
Ground State						
I_a	3.46535	3.46541	4.20821	5.18355	5.07066	6.90418
I_b	16.83984	17.27018	18.39699	19.68350	19.88334	22.93826
I_c	20.35832	20.78921	22.66503	24.93385	25.01991	29.91503
Δ^e	0.05313	0.05367	0.05982	0.06680	0.06591	0.07259
Equilibrium dcct						
I_a	3.42614	3.42626	4.16523	5.13627	5.02160	6.84609
I_b	16.71019	17.13884	18.26218	19.54329	19.74691	22.78385
I_c	20.13368	20.56287	22.42463	24.67658	24.76561	29.62654
Δ^e	−0.00264	−0.00224	−0.00278	−0.00298	−0.00290	−0.00340
Equilibrium mcct						
I_a	3.42612	3.42626	4.16492	5.13600	5.02121	6.84569
I_b	16.69879	17.12689	18.25220	19.53437	19.73827	22.77787
I_c	20.12284	20.55150	22.41485	24.66787	24.75707	29.62050
Δ^e	−0.00207	−0.00165	−0.00227	−0.00250	−0.00241	−0.00305
Equilibrium dtz+						
I_a	3.42741	3.42754	4.16659	5.13782	5.02309	6.84796
I_b	16.71564	17.14437	18.26803	19.54930	19.75310	22.79049
I_c	20.14113	20.57039	22.43262	24.68501	24.77415	29.63597
Δ^e	−0.00192	−0.00151	−0.00200	−0.00212	−0.00204	−0.00249
Equilibrium mtz+						
I_a	3.42497	3.42512	4.16326	5.13450	5.01948	6.84377
I_b	16.72309	17.15104	18.28042	19.56500	19.76997	22.81601
I_c	20.14718	20.57571	22.44272	24.69846	24.78850	29.65830
Δ^e	−0.00089	−0.00045	−0.00096	−0.00104	−0.00096	−0.00148

[a] Reference 21. [b] Reference 22. [c] Reference 25. [d] Reference 24. [e] Inertial defect where $\Delta = I_c - I_a - I_b$.

TABLE 6: Ground State and Equilibrium Moments of Inertia (amu Å^2) for the Isotopomers of Butadiene

	BDE[a]	BDE-1-$^{13}C_1$[b]	BDE-2,3-$^{13}C_2$[c]	BDE-1,1-d_2[a]	BDE-2,3-d_2[d]	BDE-*t*,*t*-1,4-d_2[e]	BDE-*c*,*c*-d$_2$[e]	BDE-*c*,*t*-d$_2$[e]
Ground State								
I_a	12.12444	12.13834	12.44557	13.80851	16.52122	12.58241	14.78903	13.76541
I_b	113.99086	117.33715	114.72426	125.03339	114.46214	128.98085	122.14284	125.41572
I_c	126.09124	129.44992	127.14698	138.81621	130.96630	141.53135	136.90897	139.15789
Δ^f	−0.02406	−0.02557	−0.02285	−0.02570	−0.01705	−0.03190	−0.02290	−0.02324
Equilibrium dcct								
I_a	11.97891	11.99256	12.29952	13.64977	16.35141	12.43524	14.61635	13.60505
I_b	113.26543	116.59569	114.00450	124.28047	113.73478	128.17166	121.45302	124.66870
I_c	125.24174	128.58460	126.30165	137.92815	130.08467	140.60344	136.06728	138.27330
Δ^f	−0.00261	−0.00364	−0.00237	−0.00209	−0.00152	−0.00346	−0.00209	−0.00044
Equilibrium mcct								
I_a	11.99302	12.00665	12.31403	13.66296	16.36935	12.44667	14.63149	13.61772
I_b	113.19027	116.51805	113.92940	124.20852	113.66691	128.10446	121.37666	124.59840
I_c	125.17978	128.51991	126.24016	137.86821	130.03345	140.54690	136.00465	138.21450
Δ^f	−0.00351	−0.00479	−0.00327	−0.00328	−0.00282	−0.00422	−0.00350	−0.00161
Equilibrium dtz+								
I_a	11.98306	11.99670	12.30368	13.65413	16.35667	12.43912	14.62109	13.60920
I_b	113.29019	116.62102	114.02903	124.30707	113.75788	128.20039	121.47828	124.69611
I_c	125.27033	128.61378	126.33004	137.95882	130.11270	140.63577	136.09700	138.30459
Δ^f	−0.00292	−0.00394	−0.00268	−0.00238	−0.00185	−0.00373	−0.00238	−0.00071

[a] This work. [b] Reference 18. [c] Reference 19. [d] Reference 16. [e] Reference 17. [f] Inertial defect where $\Delta = I_c - I_a - I_b$.

the quadratic force constants. The inertial defects from the ground state moments of inertia of the isotopomers of BDE are somewhat smaller than those for the isotopomers of the smaller ethylene molecule and provide unmistakable support for a planar structure for BDE. The inertial defects from the equilibrium rotational constants are comparably close to zero for BDE and ethylene.

The ground-state rotational constants obtained through fitting spectroscopic lines are what Watson has called "determinable combinations of coefficients".[39] These determinable constants are not the true ground-state constants; they contain contributions from centrifugal distortion. As a test of the effect of neglecting the corrections to the determinable rotational constants, we computed the corrections with the B3LYP/6-311++G** model and a single scale factor for the quadratic force constants for BDE.[11] The largest corrections were 7 kHz. These corrections were applied to the determinable ground-state rotational constants, and new equilibrium rotational constants were computed. When a structure was fitted to the new set of rotational constants, the bond parameters for BDE were indistinguishable from those obtained without correcting the determinable constants at the accepted level of accuracy. Thus, the correction of determinable rotational constants has been neglected in fitting r_e structures in this work.

Supplementary Table S4 contains the moments of inertia of the isotopomers of BDE computed by the second method with the single scale factor. As is true for ethylene, the inertial defects are larger for the equilibrium moments of inertia computed by the second method. The inertial defects for BDE are approximately six times larger for the second method.

TABLE 7: Bond Parameters for Ethylene[a]

				B3LYP		MP2	
parameter	r_s[b]	r_0[c]	r_e[d]	dtz+	dcct	mtz+	mcct
r(C=C)/Å	1.333 (3)	1.339 (1)	**1.3305 (10)**	**1.3289**	1.3241	1.3391	**1.3320**
r(C−H)/Å	1.085 (2)	1.085 (2)	**1.0805 (10)**	1.0850	1.0826	1.0854	**1.0804**
α(CCH)/deg	**121.4** (1)	121.1 (1)	**121.45 (10)**	121.74	121.74	**121.40**	**121.34**
α(HCH)/deg	**117.2 (1)**	117.8 (1)	**117.10 (10)**	116.53	116.52	**117.20**	**117.33**

[a] In boldface type are r_e bond lengths and bond angles and those other values that agree with them within 0.002 Å and 0.2°, respectively. [b] Costain uncertainties. [c] Statistical uncertainty in the fit. [d] Uncertainties span range caused by variation of α's with QC models.

TABLE 8: Bond Parameters for Butadiene[a]

	r_0[b]	r_s[c]	r_e[d]	MP2/cc-pVTZ	B3LYP/cc-pVTZ	B3LYP/6-311++G**
r(C=C)/Å	1.346 (3)	1.344 (6)	**1.3376 (10)**	**1.3401**	1.3339	**1.3384**
r(C−C)/Å	1.458 (3)	1.451 (4)	**1.4539 (10)**	**1.4533**	**1.4527**	**1.4562**
r(C−H$_\alpha$)/Å	**1.086 (2)**	1.088 (4)	**1.0847 (10)**	**1.0845**	**1.0859**	1.0882
r(C−H$_c$)/Å	1.085 (2)	1.088 (13)	**1.0819 (10)**	**1.0819**	**1.0832**	1.0856
r(C−H$_t$)/Å	**1.081 (3)**	**1.080 (8)**	**1.0793 (10)**	**1.0797**	**1.0809**	1.0833
α(C=C−C)/deg	**123.4 (1)**	**123.6 (6)**	**123.62 (10)**	**123.54**	124.36	124.33
α(C=C−H$_\alpha$)/deg	**119.8 (3)**	119.5 (6)	**119.91 (10)**	119.60	119.34	119.33
α(C=C−H$_c$)/deg	120.4 (1)	120.3 (6)	**120.97 (10)**	**120.84**	121.43	121.46
α(C=C−H$_t$)/deg	**121.3 (2)**	121.8 (11)	**121.47 (10)**	**121.47**	**121.68**	**121.66**
Δr(C−H$_{(\alpha-c)}$)/Å	0.001	0.000	**0.0028**	0.0026	0.0027	0.0026
Δr(C−H$_{(\alpha-t)}$)/Å	0.005	0.008	**0.0054**	0.0048	0.0050	0.0049
Δr(C−H$_{(\alpha-E)}$)/Å[e]			**0.0042**	0.0041	0.0033	0.0032
Δr(C−H$_{(c-E)}$)/Å[e]			**0.0014**	0.0015	0.0006	0.0006
Δr(C−H$_{(t-E)}$)/Å[e]			**−0.0012**	−0.0007	−0.0017	−0.0017

[a] In boldface type are r_e bond parameters and others that agree within 0.002 Å and 0.2°. Hydrogen atom *gem* to the vinyl group is α, the hydrogen cis is c, and the hydrogen trans is t. [b] Statistical uncertainties in the fit. [c] Costain uncertainties. [d] Uncertainties span the range caused by variation in α's with QC models. [e] E represents ethylene.

Equilibrium Structures

Ethylene. Table 7 presents the new structural information for ethylene derived from the α's found by the first method. The bond lengths and the bond angles for the equilibrium structure, r_e, were fitted to the equilibrium moments of inertia shown in Table 5. The uncertainties given with the r_e bond parameters span the range of values obtained with the four different QC models and include our estimate of the uncertainty in the method. The four QC models gave α's (supplementary Table S2), which though different, produced bond parameters within 0.001 Å or 0.1°. In support of these estimates of uncertainty, supplementary Table S6 gives the results of fitting the structure of ethylene with the two methods and the four models. The concurrence of these results gives us confidence that the new values of the bond parameters of the equilibrium structure are good within these close limits. For comparison with the r_e structure, Table 7 includes bond parameters found by a global fit of ground-state moments of inertia, designated r_0, and from the Kraitchman-type substitution method, r_s. The uncertainties associated with the r_0 values are the statistical uncertainties in the global fit. The uncertainties in the r_s values are the Costain uncertainties.[40] The table also contains the bond parameters found in the geometry optimizations with the four different QC models. The equilibrium bond parameters are in boldface type as are other values that agree with the r_e values within 0.002 Å or 0.1°.

When the bond parameters for ethylene were fitted to equilibrium moments of inertia (supplementaryTable S3) derived from α's computed by the second method, the uncertainties in the fitting were about twice as large as for the first method. However, the bond parameters differed negligibly (supplementary Table S6). We conclude that using the simpler, second method with a single scale factor is satisfactory with QC models at the triple-ζ level of theory.

Although the r_s and r_0 values provide estimates of the equilibrium bond parameters within 0.01 Å and a few tenths degree, for the most part the values and their uncertainties do not encompass the r_e values. The r_s values are the better approximation.

A recent estimate of r_e for the C=C bond in ethylene comes from the QC calculations of Martin et al.[41] They used coupled cluster models. With a CCSD(T)/cc-pCVTZ model they obtained 1.3313 Å for the C=C bond length. The latter value, adjusted for core electron correlation by the authors to 1.3307 Å and given an uncertainty of 0.0003 Å, agrees with our value for the C=C bond length. Their adjusted value for the C−H bond of 1.0809 ± 0.0003 Å and the C=C−H bond angle of 121.44 ± 0.03° also agree with our results.

Experimental estimates of r_e values for the C=C bond length are Duncan's value of 1.334 Å and Berry and Harmony's value of 1.3297 Å.[15,42] The first value was derived from spectroscopic data by standard methods; the second came from the scaled-moments-of-inertia method championed by Harmony. In a recent review of structural data, Harmony gave the average value of 1.332 Å for the C=C bond in ethylene.[9] Duncan's value for the C−H bond length was 1.081 (2) Å, whereas Berry and Harmony's value was 1.0801 (2) Å. For the C=C−H bond angle, Duncan's value was 121.3 (3)°, and Berry and Harmony's value was 121.4 (8)°. Our new data vindicate Harmony's method.

The new r_e structure may be compared directly to the structures found with QC calculations. The agreement is best with the MP2/cc-pVTZ model. In the past, most of the structures derived from experiments have not been directly comparable to the QC structures. The present results appear to give an advantage to the semi-experimental method over a range of QC calculations even with triple-ζ basis sets.

Butadiene. Table 8 gives the r_e bond parameters for BDE found with α's calculated by the first method with multiple scale factors for the quadratic force constants. These tables include r_s parameters from a substitution analysis and r_0 parameters from a global fit to the ground-state moments of inertia. Uncertainties in the parameters for the several types of structures have the same significance as for ethylene. These tables also have the bond parameters predicted by three different QC models. Our structure computed with the MP2/cc-pVTZ model agrees with the published one reported in Table 1.[5] The r_e values are in boldface type as are other values that agree within 0.002 Å or 0.2°.

Because the r_e bond parameters vary less than 0.001 Å across the calculations of α's made with the three QC models, we regard these parameters as good to 0.001 Å and 0.1°. In addition, equilibrium moments of inertia were obtained from α's computed with the second method, in which a single scale factor was used for the quadratic force constants. The bond parameters were then fitted to the moments of inertia obtained by this second method. These moments of inertia are in supplementary Table S4. The results of these second-method fits agreed with values computed by the first method even though the statistical uncertainties were about 4 times greater than for the fits with the first method. Supplementary Table S7 gives the results of fitting with the two methods and three models. As was found for ethylene, computing the α's by the simpler method with the single scale factor is adequate for bond parameters good to 0.001 Å.

The r_s parameters along with their sizable Costain uncertainties overlap with the r_e parameters. However, the statistical uncertainties for the r_0 values are not sufficient to bridge the differences with the r_e values in most cases. Lacking r_e values, there is a mild preference for r_s values even though they cannot be regarded as much better than 0.01 Å and 1.0° approximations to r_e values.

With accurate semi-experimental r_e values for the bond parameters, the structural predictions of the three QC models can be evaluated. Boldface type in Table 8 for predicted bond parameters that agree with the r_e values within 0.002 Å or 0.2° shows that the MP2/cc-pVTZ model comes closest to the r_e structure. For bond lengths, the B3LYP/cc-pVTZ model does almost as well. The exception is the critical C═C bond length. Bond angles are less satisfactory. The B3LYP/6-311++G** model does better in predicting the C═C bond length but less well on the C−H bond lengths.

Structural Implications for Butadiene

We now have good r_e structural data with which to answer the question about the influence of π-electron delocalization on the bonds in *s-trans*-butadiene. Comparing the C═C bond length for BDE in Table 8 with the localized C═C bond length for ethylene in Table 7 shows that the formal C═C bond in BDE has increased in length by 0.007 Å. For the C−C bond, the adjustment in the formal sp^2-sp^2 bond length is −0.016 Å, as is seen by comparing the value at the top of Table 1 with the entry in Table 8. The evidence linking π-delocalization to an observable effect on the CC bond lengths is now consistent with expectations about the consequences of π-bonding.

The basis for the standards of comparison of the C═C and sp^2-sp^2 bond lengths should be considered. We have reevaluated the r_e structure for ethylene and thus have confidence in the value for the C═C bond length in ethylene. However, the double bond in propene might be regarded as a preferable standard. Harmony and co-workers report 1.333 Å for a near-equilibrium value of the C═C bond in propene found by the scaled-moment-of-inertia method.[43] (Some compromises were necessary in this analysis.) We suspect the above value is a trifle long. Nonetheless, on the basis of this value from propene, the formal C═C bond lengthens in butadiene by at least 0.005 Å. Given the method we used to estimate a standard for the single sp^2-sp^2 bond, as described in the Introduction, some doubt attends this standard. However, the shrinkage in the formal C−C bond length is so large with respect to the localized standard that we have no doubt that such an effect occurs. Clearly, a reevaluation of the r_e structure of propene with the semi-experimental method would be a timely contribution.

The shrinkage in the formal single bond in butadiene is about twice the increase in the formal double bonds. This adjustment seems reasonable because the single bond experiences the effect of delocalization from two directions. We emphasize that observing the effects of π-electron delocalization on butadiene depends on obtaining an r_e structure good to about 0.001 Å and 0.1°.

Along with the adjustments in the formal CC bond lengths, we find that the 123.6° C═C−C bond angle is appreciably larger than the expectation of 120° for sp^2 hybridized carbon atoms. It seems likely that this adjustment reflects accommodation to the repulsion of α and cis hydrogen atoms.

As shown in Table 8, the three types of CH bonds in BDE follow a pattern that is confirmed in the new more accurate structure. The CH_α bond is gem to the second vinyl group, the CH_c bond is cis to the vinyl group, and the CH_t bond is trans to the vinyl group. This pattern is emphasized in the bond length differences given near the bottom of the table. A striking feature of the Δr(C−H) differences is the pleasing, apparently unprecedented agreement to within about 0.0006 Å or better between our semi-experimental results and those derived wholly from MP2 or B3LYP calculations. These results suggest that wider applications of this semi-experimental method for finding equilibrium structures may reveal details, which up to now have been obscured in previous studies of molecules where only r_0 or r_s structures have been available. For example, a challenge of this nature would be represented by the two molecules of propene and dimethylamine, where there are respectively five and three types of C−H bond present, at present imperfectly characterized except by their ν^{is}(CH) values.[44,45] It would seem that any system in which inertial constants have been determined from an adequate number of isotopomers should be amenable to treatment, providing of course that key atoms do not lie close to principal axes of inertia.

To return to a consideration of the pattern in CH bond lengths, the data confirm that the CH_α bond is the longest and the CH_t bond is the shortest. This pattern in CH bond lengths has been explored in our paper on the normal coordinate analysis.[20] Suffice it to say here that the bond length sequence $CH_\alpha > CH_c > CH_t$ is reflected in expected differences in force constants as well as in the QC structures for the three types of CH bonds. The C═C−H bond angles also follow the same pattern of $C{=}C{-}H_\alpha < C{=}C{-}H_c < C{=}C{-}H_t$ in the r_e structure and in the QC structures. The strongest and shortest bond, CH_t, is associated with the largest C═C−H angle. This observation is reasonable because a stronger CH bond should have greater s character in the carbon orbital and thus be associated with the larger bond angle.

Table 8 includes the incremental change between the different r_e CH bond lengths in butadiene with the r_e CH bond length of ethylene, as obtained with the semi-experimental method and QC models. "E" designates ethylene in the subscripts. The CH bond length in ethylene is intermediate between the CH_t and CH_c bond lengths in BDE, as seems appropriate. The $H_t{-}C{-}H_c$ bond angle in BDE of 117.56° compared to the corresponding 117.10° bond angle in ethylene reflects the greater p character in the carbon orbital of the longer CH_c bond.

Summary

Equilibrium structures have been found for butadiene and ethylene. These r_e structures show for the first time that, compared to standards, the formal double bonds in BDE increase in length and the formal single bond decreases in length owing to partial delocalization of π electrons. These structures were obtained by the semi-experimental method, in which QC-calculated spectroscopic α's were combined with experimental ground state rotational constants to obtain equilibrium rotational constants. Quadratic contributions to the α's were based on a force field with many scale factors. A structure was then fit to the equilibrium moments of inertia for eight isotopomers of butadiene. These isotopomers included isotopic substitution for each chemically different atom. A similar analysis was done for ethylene with six isotopomers. The equilibrium structures are believed to be good to 0.001 Å and 0.1° because the use of MP2 and B3LYP theory with both Dunning-type and Pople-type basis sets gave spectroscopic α's, which, though differing some, led to the same outcomes for structures.

When a single scale factor was applied in computing the quartic contributions to the α's, the fit to moments of inertia was somewhat looser but the bond parameters agreed with those from the more rigorous method within the quoted uncertainties. Thus, we conclude that the simpler method of computing the α's with a single scale factor for the quartic contributions is adequate for QC models at the triple-ζ level.

These new r_e structures provide a sound basis for evaluating structures computed with quantum chemical models. QC structures found with the different models are in general agreement with the r_e structure. The structure from the MP2/cc-pVTZ model agrees best with the r_e structure.

With this work on the equilibrium structures of butadiene and ethylene, we have demonstrated that r_e structures with bond parameters good to 0.001 Å and 0.1° can be obtained for interesting small molecules. These structures can be used to assess subtle electronic effects on bonds and the quality of structures computed by QC methods.

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Supporting Information Available: Scale factors for QC force fields of ethylene (Table S1); harmonic contributions (MHz) to α parameters for six isotopomers of ethylene (Table S2); equilibrium moments of inertia (amu Å^2) for the isotopomers of ethylene based on a single scale factor for the quadratic force constants (Table S3); equilibrium moments of inertia (amu Å^2) for the isotopomers of butadiene based on a single scale factor for the quadratic force constants (Table S4); VIBROT and ASYM40 estimates of contributions to α's for BDE with the B3LYP/cc-pVTZ model (Table S5); structural parameters for ethylene from the two methods and four QC models (Table S6); structural parameters for BDE from the two methods and three QC models (Table S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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