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The molecular structure of *gauche*-1,3-butadiene: Experimental proof of non-planarity

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Abstract: The planarity of the second stable conformer of 1,3-butadiene – the archetypal diene for the Diels-Alder reaction, in which a planar conjugated diene and a dienophile combine to form a cycle – is not established. The most recent high level calculations predict the species to adopt a twisted, *gauche* structure due to steric interactions between the inner terminal hydrogens rather than a planar, *cis* structure favored by the conjugation of the doubled bonds. Here we unambiguously prove experimentally that the structure *cis*-1,3-butadiene is indeed *gauche* with a substantial dihedral angle of 34°, in excellent agreement with theory. Observation of two tunneling components indicates that the molecule undergoes facile interconversion between two equivalent enantiomeric forms. Comparison of experimentally determined structures for *gauche*- and *trans*-butadiene provides an opportunity to examine the effects of conjugation and steric interactions.

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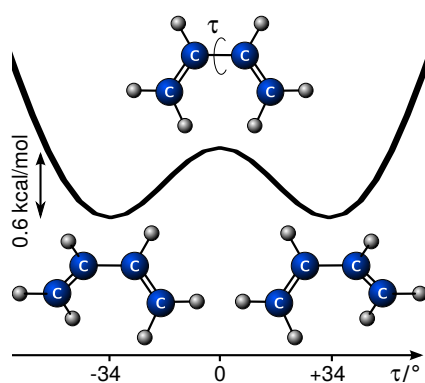
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The second stable conformer of 1,3-butadiene is nonplanar: The structure of *gauche*-butadiene has been determined using a combination of sensitive microwave experiments, unambiguously proving its non planarity with a twist angle of 34° . High level theoretical calculations show that the *cis* structure is a transition state between the two *gauche minima* on the potential energy surface (see figure).

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Cyclic structures play essential roles in organic and biological chemistry. Perhaps the most important ring forming reaction is the stereospecific Diels-Alder cycloaddition,^[1,2] where a conjugated diene and a dienophile combine; the classic example is the reaction of 1,3-butadiene and ethylene to form cyclohexene. While this clearly requires that butadiene contort from its most stable *trans* form^[3–5] to allow ring closure, there was substantial debate as to the nature of the lowest reaction pathway,^[6] which is notoriously opaque to the usual experimental tools of mechanistic analysis.^[7] The eventual consensus is that the reaction proceeds via a synchronous transition state within a concerted mechanism.^[8] For all the diversity of Diels-Alder transition state possibilities,^[9,10] butadiene is believed to adopt a planar structure in the lowest, aromatically stabilized, pericyclic transition state,^[11] no doubt because orbital considerations suggest a planar *cis* conformation for optimal overlap with the π -system of the dienophile.^[12]

It is therefore surprising that the planarity of *cis*-butadiene itself remains a topic of interest^[13] and even controversy. Although the planarity of *trans*-butadiene is well established and attributed to conjugation between the two double bonds, steric interaction between the inner terminal hydrogens of *cis*-butadiene is a competing factor that favors a non-planar *gauche* conformation. After the existence of a second conformer was first established in 1946,^[14] numerous studies were unable to determine its structure or even its symmetry definitively.^[15–27] The advent of modern electronic structure methods^[28–30] and careful examination of gas-phase Raman spectra^[31] have led to the prevailing view that *cis*-butadiene is in fact *gauche*.^[32–35] Despite this progress, conclusive detection and structural characterization of this elementary molecule have remained elusive for sixty years.^[36,37]

Here we report the first microwave spectrum of “*cis*” butadiene, which proves unambiguously that it possesses a nonplanar *gauche* structure. The experimental evidence for non-planarity, which includes not only a nearly complete equilibrium structure but also vivid observation of tunneling between equivalent *gauche* minima, was acquired with a combination of sensitive microwave techniques and high accuracy *ab initio* calculations. Examination of the structures and energetics obtained from both experiment and theory reveals detailed information about how the interplay of steric and conjugation effects determines the structure of this fundamental reaction intermediate.

We have recorded the gas phase spectrum of *gauche*-1,3-butadiene using Fourier-transform microwave (FTMW) spectroscopy, a powerful technique capable of distinguishing isomers, conformers, and even enantiomers.^[38] A particular advantage of microwave spectroscopy in this case is its immunity to spectral interference from the *trans* conformer, which has no dipole moment. Prior attempts to detect *gauche*-butadiene by microwave techniques were unsuccessful presumably owing to a combination of several factors: this conformer

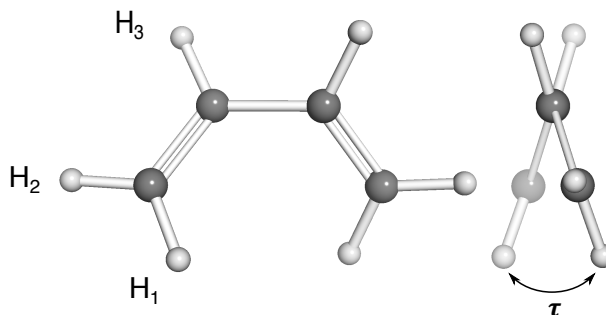


Figure 1: The structure of *gauche*-butadiene. The C_2 symmetry b -axis is vertical. The dihedral $\angle C=C-C=C$ is indicated (τ) on the right.

lies 2.93 kcal/mol above the ground state *trans* conformer,^[39] it possesses a very small dipole moment^[40] (calculated to be 0.09 D in this work), and its rotational transition frequencies are sensitive functions of the torsional $\angle C=C-C=C$ angle τ (Fig. 1). Observation of the microwave spectrum of *gauche*-butadiene in the present work required the use of two complementary experimental techniques: cavity enhanced FTMW combined with a supersonic expansion^[41] and chirped-pulse FTMW in a cryogenic buffer gas cell.^[42] The population of the minor conformer was increased by using a 1 kV electric discharge or a heated inlet capillary (245 °C) in the two experiments, respectively. In the buffer gas cell, butadiene molecules rapidly thermalize rotationally to the cell temperature (~ 10 K) through collisions with cold helium atoms, while the *gauche-trans* relaxation proceeds much more slowly. The molecules diffuse through the cold gas until they collide with the cell wall, where they freeze; during this time, the sample is repeatedly interrogated. The combination of a high repetition rate (30 kHz) and cryogenic low noise amplifiers (noise temperature of ~ 9 K) yields significantly higher signal-to-noise than in the cavity-enhanced pulsed jet experiment. The spectral resolution in the buffer gas cell is limited by collisional broadening with helium to ~ 80 kHz, while the cavity-enhanced pulsed jet work yields a time-of-flight broadening of ~ 5 kHz. Initial spectral searches were guided by high-level predictions of the rotational constants, and transitions were readily observed near the predicted frequencies. The large inertial defect (-2.5 amu \AA^2 , Table ??) is a clear sign of non-planarity, which was confirmed by the semi-experimental equilibrium structure^[43], r_e^{se} , derived from subsequent spectroscopy of five isotopically substituted species of butadiene ($^{13}\text{CH}_2\text{CHCHCH}_2$, $\text{CH}^{13}_2\text{CHCHCH}_2$, $\text{CH}_2\text{CDCDCH}_2$, $\text{CD}_2\text{CHCHCD}_2$, $\text{CD}_2\text{CDCDCD}_2$). Unfortunately, the lack of commercial asymmetrically deuterated samples precludes the determination of a complete structure at present, but efforts to remedy this are underway.

Conclusive evidence that the equilibrium structure of the species being probed is *gauche*, rather than *cis*, is the doublet structure of the measured transitions (Fig. 2). Such doublets can only arise from tunneling

between the two equivalent C_2 *gauche* minima on the potential energy surface, which causes the low-lying vibrational states to split into two components, e.g. $v = 0^+$ and $v = 0^-$ for the ground state, each of which has its own manifold of rotational levels.

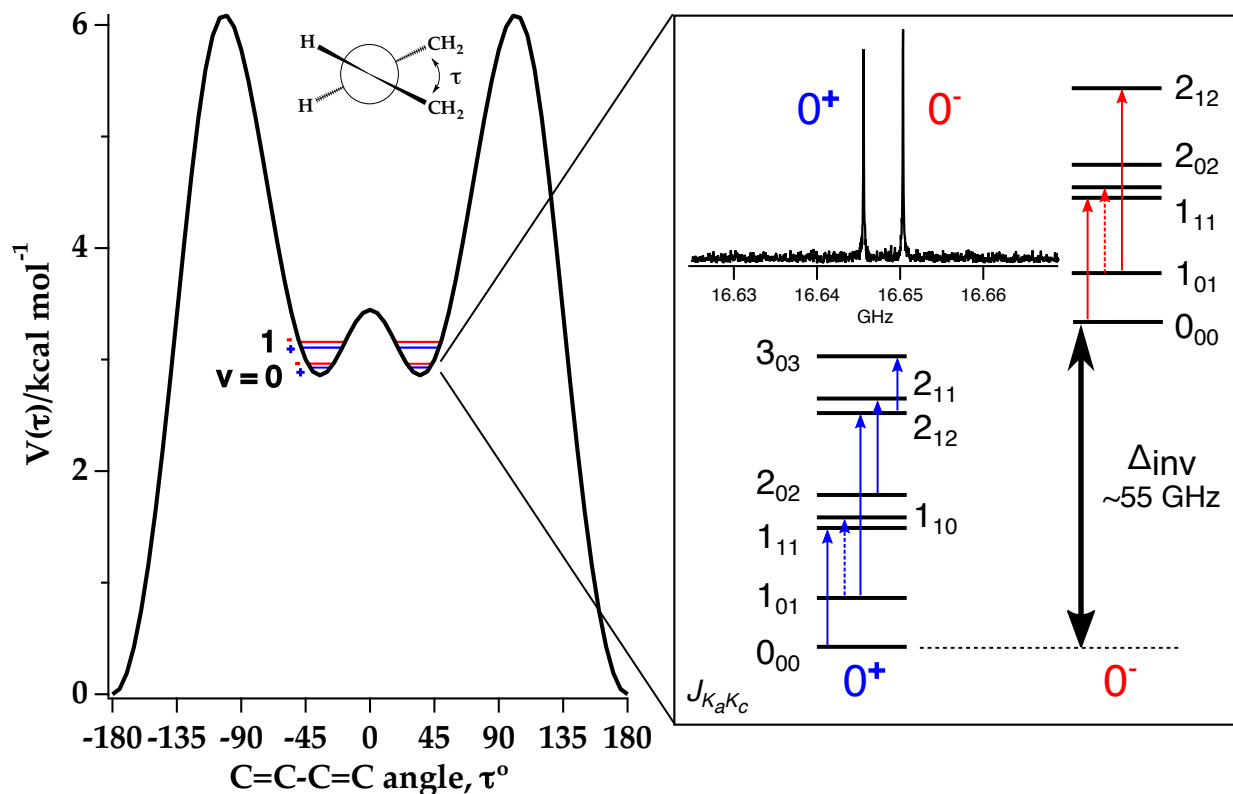


Figure 2: Torsional potential and rovibrational energy levels of butadiene. The potential was calculated at the FC-CCSD(T)/ANO1 level of theory. The expanded view on the right shows the rotational level structure of the ground state tunneling doublet and the b -type microwave transitions allowed within each tunneling component. Dashed arrows mark transitions in the inset spectrum, which consists of 2×10^6 averages collected in ~ 5 minutes, while flowing 0.7 sccm butadiene through a 245°C nozzle along with 6 sccm He into the cryogenic buffer gas cell.

Table 1 shows the experimentally determined and calculated structures of *gauche*-butadiene. The *ab initio* geometry was extrapolated from optimizations at the (all-electron) AE-CCSD(T) level of theory with cc-pCVTZ through cc-pCV5Z basis sets, and supplemented by a perturbative quadruples correction calculated with the ANO0 basis set and the frozen core (FC) approximation. The (Q) correction for the dihedral τ is surprisingly large (almost 1°), presumably because of the complex electron correlation associated with conjugation. Together with zero-point corrections from second-order vibrational Møller-Plesset theory^[44] (VMP2) using FC-CCSD(T) calculations and the ANO1 basis set,^[45,46] this structure accurately predicted the rotational constants for all isotopologues – preliminary calculations prior to the experiments were within

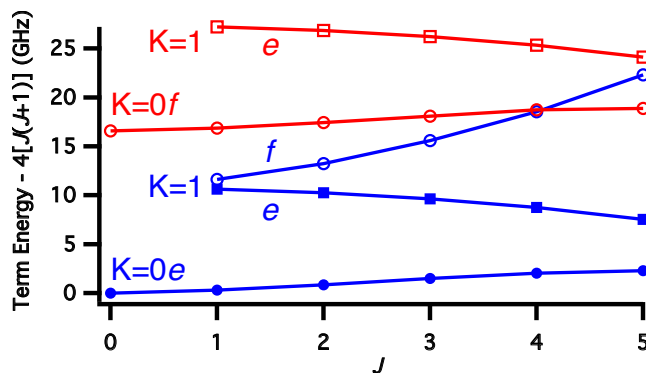


Figure 3: Reduced term value plot for d_6 butadiene, illustrating the near-resonant Coriolis interaction between tunneling components that allows the determination of Δ_{inv} from the microwave data. E+/O+/E-/O- rovibrational symmetries^[49,50] are represented by filled/open circles and squares, respectively. 0^+ levels (blue) from $K = 1f$ tune into resonance with 0^- levels (red) of the same O+ symmetry from $K = 0f$ at $J = 4$.

roughly 20 MHz, and the final calculations described here match all observed rotational constants to within 6 MHz. All electronic structure calculations were carried out with CFOUR;^[47] the VMP2 calculations were performed using NITROGEN.^[48] The resulting rovibrational energies were then reduced to spectroscopic constants for the $v = 0^+$ and 0^- *gauche*-butadiene levels.

While the observed transitions do not yield any direct measurement of the $0^+/0^-$ tunneling splitting, Δ_{inv} , a fit of Coriolis interactions between the two tunneling components allows us to determine Δ_{inv} (Fig. 3). The best fit results are obtained for the heaviest isotopologue available, d_6 , where $\Delta_{inv}=16577(16)$ GHz, within 5% of theory. Based on this agreement and a similar, preliminary fit for the normal isotopologue, we believe the *ab initio* value of 55 GHz is likely to be accurate to within 20%, corresponding to a tunneling lifetime of approximately 18 ps. This result is entirely compatible with the proposal of Michl *et al.*^[20,22] that rapid tunneling could cause the matrix infrared spectrum to appear as that of a planar C_{2v} *cis*-butadiene.

Two major factors influence the structure of *gauche*-butadiene: conjugation of the double bonds and steric interaction between the inner terminal hydrogens. The former favors planarity, as in the *trans* conformer, and the latter is destabilizing at the planar *cis* geometry; a compromise between the two effects leads to the *gauche* minimum. Conjugation of the two π bonds in planar butadiene imparts a stabilization of roughly 4 kcal/mol (Table ??), while twisting about the dihedral angle τ (Fig. 1) reduces the conjugation by a factor of roughly $\cos^2 \tau$, implying that the steric repulsion between the two *endo* hydrogens is decreased by at least 1.3 kcal/mol in *gauche*- relative to *cis* butadiene.

A structural comparison between *gauche*- and *trans*-butadiene is particularly illustrative of the competition between these two effects (Table 1). It has been shown^[51] that conjugation in *trans*-butadiene shortens

Table 1: Butadiene geometries. Bond lengths in Å, angles in degrees. The experimental structures are semi-experimental equilibrium structures, r_e^{se} , obtained by correcting experimental rotational constants for zero-point rotation-vibration effects calculated *ab initio*.

Parameter	Calc. ^a	Expt.	<i>trans</i>		<i>cis</i>
			Calc. ^a	Expt. ^[51]	Calc. ^a
C–C	1.4673	1.48(2)	1.4542	1.4539(10)	1.4684
C=C	1.3369	1.33(1)	1.3385	1.3376(10)	1.3379
∠C–C=C	124.51	124.1(5)	123.57	123.62(10)	126.16
∠C=C–C=C (τ)	33.87	33.8(13)	planar		planar
r_{CH_1}	1.0817	1.08(1)	1.0819	1.0819(10)	1.0814
∠H ₁ –C=C	121.21	123(2)	120.94	120.97(10)	122.11
∠H ₁ –C=C–C	2.07	2(1)	planar		planar
r_{CH_2}	1.0798	[1.07983] ^b	1.0796	1.0793(10)	1.0795
∠H ₂ –C=C	121.10	118(1)	121.48	121.47(10)	120.75
∠H ₂ –C=C–H ₃	2.41	[2.410] ^b	planar		planar
r_{CH_3}	1.0837	1.083(5)	1.0843	1.0847(10)	1.0829
∠H ₃ –C–C	116.54	116.2(6)	116.69	116.47(10)	115.66
∠H ₃ –C–C=C	-147.26	-146.4(7)	planar		planar

^a Extrapolation of optimized all electron CCSD(T)/pCVTZ-5Z geometries, supplemented by a higher order perturbative quadruples correction calculated with the ANO0 basis set and the frozen core approximation. ^b Numbers in brackets were fixed to the *ab initio* values.

the C–C bond (relative to propene^[52] or a formal sp^2-sp^2 bond length^[53]) and slightly elongates the C=C bonds (relative to ethylene or propene).^[51,54] To minimize the steric interaction between the inner hydrogens (H₁, Fig. 1), *gauche*-butadiene adopts a surprisingly large twist angle of 34° for the C=C–C=C skeleton, over a third of the way to where conjugation would be completely destroyed. The C–C bond nearly returns to the canonical sp^2-sp^2 value because this displacement directly increases the H₁–H₁ distance; by contrast, the C=C bond is only slightly shorter than in the *trans* conformer. Other more subtle distortions with similar effects are also evident: for example, the ∠C–C=C angle opens by almost 1° compared to *trans*-butadiene. In general, modes with small force constants experience larger distortions, which relieves strain most efficiently.

The determination of the structure of *gauche*-butadiene advances our experimental knowledge of the quintessential Diels-Alder reaction pathway. The stereochemistry of this reaction has been established by reacting 1,1,4,4-tetradeutero-1,3-butadiene with both *cis*- and *trans*-1,2-dideuteroethylene, with the results supporting a concerted mechanism.^[55] The activation energy has been determined by kinetics studies to be 27 kcal/mol, both by examining the Diels-Alder reaction itself^[56] and by combining data on the *retro*-Diels-Alder reaction^[57,58] with the known enthalpy of reaction^[59]. Especially since the threshold energy is likely to be several kcal/mol lower^[60], this implies that the *trans-gauche* conformational change in butadiene accounts for a substantial portion of the total energy required to initiate the Diels-Alder reaction with ethylene. We

believe that the detection and characterization of the reactive conformation of butadiene points the way towards studying the pre-reaction complex^[61] and transition state of this important reaction.

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