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ARTICLES

Structure of the High-Energy Conformer of 1,3-Butadiene

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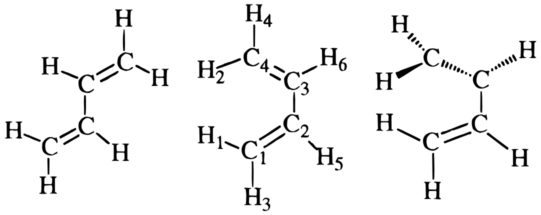
The experimental vibrational frequencies of *s-trans*-1,3-butadiene, for which the assignments are well-established, are used to determine the scale factors for its quantum mechanical force field obtained at the MP2/6-31G*//MP2/6-31G* level of theory. The scale factors are then transferred to the MP2/6-31G*//MP2/6-31G* force fields of the *s-cis* and *s-gauche* rotamers and their theoretical frequencies calculated. Comparison of the vibrational frequencies of these three species indicates a special region of the IR spectrum of 1,3-butadiene in the gas phase (720−790 cm^{-1}) in which only a band attributable to the *s-gauche* rotamer should be present; i.e., it should be free both of the observed IR bands of the *s-trans* and of the calculated vibrational frequencies of the *s-cis* conformer. Investigation of the medium- and high-resolution IR spectra of 1,3-butadiene in the gas phase reveals the presence of a band at 749.22(20) cm^{-1} possessing the typical B contour (consistent with A symmetry, C_2 group). Rotational analysis of the medium-resolution spectrum of this band yields the rotational constants $A'' - \bar{B}'' = 0.4478(27)$ cm^{-1} and $A' - \bar{B}' = 0.4455(25)$ cm^{-1}, only about one-third of the experimental values for *s-trans*-1,3-butadiene. This identifies the band as belonging to the high-energy conformer of 1,3-butadiene. The agreement between the experimental and theoretical values of the band center (749 vs 735 cm^{-1}), the clear B type contour, and the extremely complicated character of the high-resolution spectrum of the band at 749.22 cm^{-1} strongly suggest that the geometry of the high-energy conformer of 1,3-butadiene *in the gas phase* is nonplanar *s-gauche* and not planar *s-cis*.

Introduction

About 60 years ago Hückel predicted that both the planar *s-trans* (**1**) and *s-cis* (**2**) conformers of 1,3-butadiene (see Figure 1) should be stabilized by resonance, although only one form was known at that time.[1] Numerous subsequent experimental[2−20] and theoretical[20−29] studies have led to the conclusion that **1** is the predominant, lowest energy, structure of 1,3-butadiene. The presence of a higher energy rotamer has been proven experimentally (see below), but whether its structure in the gas phase is **2**, as predicted by Hückel,[1] or *s-gauche* (**3**), as proposed by Bastiansen in 1948 on the basis of an electron diffraction study,[30] has not yet been resolved.[14b,16,17b,31] The main reasons for this are the relatively low population of the high-energy rotamer (**2** or **3**) at ordinary temperatures and the reactivity of 1,3-butadiene at higher temperatures.

Early attempts to observe the high-energy conformer directly[2] and to determine its vibrational frequencies[3] were generally unsuccessful[2] or gave erroneous results.[3] In an apparent important advance in 1975, Carreira[32] observed 10 torsional overtones in the Raman spectrum of 1,3-butadiene, three of which he assigned to the high-energy rotamer. (Later, however, these three overtones were reassigned to **1**.[11] Also, in a recent Raman study, Engeln et al.[33] assign them to **3**, but there is a discrepancy between the observed and calculated intensities.)



1 **2** **3**

Figure 1. Structures **1**, **2**, and **3**: *s-trans, s-cis,* and *s-gauche* rotamers of 1,3-butadiene, respectively. The numbering on **2** corresponds to that used in Table 1 for the three structures. The out-of-plane angle, ϕ, is the dihedral angle $C_1{=}C_2{-}C_3{=}C_4$.

A breakthrough occurred in 1978 when Huber-Wälchli[14a] reported trapping significant amounts of the high-energy conformer in a low-temperature, solid matrix. Whereas this technique has allowed observation of the IR spectrum of the high-energy rotamer in the solid phase,[14−17] the similarity of the values of the calculated fundamental frequencies for **2** and **3** prevented the definite choice of either structure in the early studies.[14b,16] Furukawa *et al.*[16] confirmed the presence of IR bands[14b] due to the high-energy conformer at 982−983 cm^{-1} (ν_{10}) and at 727−732 cm^{-1} (ν_{12}) in the IR spectrum of 1,3-butadiene-h_6 and at 585−587 cm^{-1} (ν_{12}) for the perdeuterated species in Ar matrices. In the IR spectrum of the 1,1,4,4-d_4 isotopomer they observed the corresponding bands, ν_{10} at 927 cm^{-1} and ν_{12} at 594 cm^{-1}, respectively.[16] They concluded that "the second stable conformer probably exists in the *gauche* rather than in the *s-cis* form."[16] In both refs 14b and 16 it is pointed out that most of the bands attributed to the high-energy conformer of 1,3-butadiene and its isotopomers can be assigned

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TABLE 1: Calculated (MP2/6-31G*) and Experimental Structures (angstroms and degrees) of 1, 2, and 3 (See Figure 1)

	1						
	expt					**2**	**3**
structural parameter	MW[a]	ED[b]	ED[c]	ED[d] (r^0_α)	calc (this work)	calc (this work[e])	calc (this work[e])
r(C═C)	1.337	1.349	1.344	1.342	1.3425	1.3425	1.3415
r(C−C)	1.467[f]	1.467	1.467	1.463	1.4562	1.4697	1.4680
r(C1−H1)	1.087[f]	1.108	1.094	1.093	1.0863	1.0856	1.0856
r(C1−H3)	1.085[f]	1.108	1.094	1.093	1.0843	1.0842	1.0846
r(C2−H5)	1.089[f]	1.108	1.094	1.093	1.0897	1.0884	1.0893
∠C1═C2−C3	123.5	124.4	122.8	123.6	123.73	126.46	124.12
∠C2═C1−H1	121.6[f]	120.9	119.5	120.9	121.41	122.42	121.33
∠C2═C1−H3	121.5[f]	120.9	119.5	120.9	121.77	121.05	121.58
∠C3−C2−H5	116.9[f]	114.7	117.7	115.5	116.71	115.61	116.87
∠C1═C2−C3═C4					180.0	0.0	37.81
∠H3−C1═C2−C3					180.0	180.0	−178.48
∠H1−C1═C2−C3					0.0	0.0	2.37
∠H5−C2−C3═C4					0.0	180.0	−143.09
ΔE (in au)[g]					−0.44171	−0.43599	−0.43744

[a] MW = microwave; ref 12. [b] ED = electron diffraction; ref 10, all C−H bonds assumed to be equal. [c] Reference 4. [d] Reference 6. [e] The present results agree completely with those reported in ref 26c. [f] Fixed or adjusted ab initio values (see ref 12). [g] Add −155.0 au to obtain the total energy. Structure **2** is a transition state.

reasonably to the planar form **2**. Much controversy has arisen because, whereas the ν_{10} and ν_{12} modes belong to A_2 symmetry for **2** (C_{2v} group) and they are symmetry forbidden for an isolated molecule, they are allowed for **3** (C_2 group).[14b,16,17b] On the basis of their theoretical and experimental study and a reexamination of the available data, Wiberg and Rosenberg[20] concluded that the minor rotamer of butadiene is not planar, though it need not be significantly nonplanar to fit the data. Nevertheless, it must be pointed out that the A_2 modes of **2** may become allowed in a matrix because of intermolecular interactions.[34] Thus, the observed bands can be attributed to either **2** or **3**.[17b] This is similar to the observation of IR bands attributed to the parity-forbidden A_g modes of **1** in the Ar matrix spectra.[17c]

Further information on the structure of the high-energy rotamer in matrices was obtained from the observed red shift of its UV spectra (compared to that of **1**)[15] and from the polarized IR spectra.[17] Both sets of results seem to require that the high-energy conformer in the solid phase (or linearly oriented) be planar within 10−15°.[15,17a,b] Note that a recent classical molecular dynamics simulation of the behavior of the 1,3-butadiene molecule surrounded by an Ar matrix predicts that **2** may be stabilized enough in a low-temperature matrix to invert the relative stabilities of **2** and **3**.[35] Such a stabilization could also explain the apparent discrepancy between the UV spectra of the high-energy form in an Ar matrix ($\lambda_{\max} = 226$ nm[15]) and in the gas phase ($\lambda_{\max} = 216 \pm 2$ nm[19]). It is therefore possible that the structure of the high-energy conformer of 1,3-butadiene in a matrix is **2**, or nearly planar, and nonplanar (**3)** in the gas phase, the latter being in agreement with the best theoretical predictions for isolated molecules (see below).

The high-energy form of 1,3-butadiene is predicted to be **3** by the majority of recent quantum mechanical calculations (out-of-plane angle $\phi = 38 \pm 5^\circ$, see Figure 1) with the planar structure **2** representing a transition state between two equivalent *gauche* wells.[17b,20,24−29] (Note that for the related molecule, vinylcyclopropane, a three-well *gauche*−*trans* torsional potential for rotation about the formal single C−C bond between the vinyl group and the ring is substantiated both by experiment[36] and by theory.[36a,37]) There are a few notable exceptions where **2** is predicted to be the stable higher energy conformer of 1,3-butadiene. These are computations with a minimal basis set[22,25] and even a series of geometry optimizations using a multiconfigurational wave function without polarization functions.[38] In all cases the computed energy differences between **2** and **3** are small (2−4 kJ mol^{-1}),[17b,20,22−29] and tunneling between the two *gauche* minima or large scale vibrations may be important in the gas phase at ambient temperature.[39]

In light of all that work, it is therefore particularly important to obtain new experimental data (especially in the gas phase) in conjunction with computational quantum mechanical results to try to clarify the situation.

To the best of our knowledge, there has been no detailed rotational analysis of any of the IR spectral bands attributed to the high-energy conformer of 1,3-butadiene in the gas phase. Such an analysis is necessary to prove that the band is indeed due to the high-energy conformer and to give information on its structure (**2** or **3**). We shall proceed by predicting an IR region which should include an absorption band attributed to **3** but which should be free from any absorption bands belonging either to **1** or to **2**. To do this, structures **1**, **2**, and **3** must be optimized completely at the same, adequate, theoretical level,[40] their quantum mechanical force fields calculated and scaled, and their theoretical vibrational frequencies calculated.[41] When a suitable IR spectral region has been identified, it will be investigated thoroughly using medium- and high-resolution Fourier techniques.

Methods and Results

Computational Details. The geometries of **1**, **2**, and **3** were optimized completely with Gaussian 92[42] using second-order Møller−Plesset perturbation[43] and the standard split-valence 6-31G* (6d) basis set (MP2/6-31G*). The optimizations were carried out without any frozen core orbitals. The optimized geometrical parameters are collected in Table 1 with the corresponding experimental data for **1**.

The Cartesian force constants were calculated at the MP2/6-31G*//MP2/6-31G* level using analytical first derivatives and numerical second derivatives. The reasons for choosing this theoretical level for computation of the force field have been discussed.[40] The force constants were transformed into local (valence) symmetry coordinates[44] and scaled (according to Pulay's method,[40,45] without correction of the calculated geometry) by scale factors determined for **1** using the experimental frequencies listed in Table 2. The details of this calculation and the scaled quantum mechanical force fields of **1**, **2**, and **3**

TABLE 2: Experimental and Calculated Vibrational Frequencies (cm^{-1}) of 1, 2, and 3

	1			**2**^{a}		high-energy conformer			**3**	
ν, assign	sym	exp^b	calc	sym	calc	exp^c	exp^d	exp^e	sym	calc
1. $\nu(CH_2)$ a str	A_g	3100.3	3111	A_1	3114		3103	3070^f	A	3114
2. $\nu(C{-}H)$ str		3013.0	3024		3024		3014	3023		3018
3. $\nu(CH_2)$ s str		3013.0	3008		3035		2986	3010^f		3030
4. $\nu(C{=}C)$ s str		1643.9	1652		1634	1611.5^f	1612^f	1602		1619
5. $\delta(CH_2)$ sci		1440.8	1443		1437	1424	1425	1425		1433
6. $\delta(C{-}H)$ def		1291^g	1287		1327					1306
7. $\nu(C{-}C)$ str		1203.0	1209		858					866
8. $\rho(CH_2)$ rock		887.8	879		1046					1052
9. $\delta(C{=}C{-}C)$ def		511.6	510		305					274
10. $\chi(C{-}H)$ wag	A_u	1013.8^h	1022	A_2	985	982	983	984		984
11. $\chi(CH_2)$ wag		908.1	907		894	(915)	915	920		918
12. $\tau(CH_2)$ twist		524.5^h	518		712	732	727	730		735
13. $\tau(C{-}C)$ tors		162.5	159		(−165)					186
14. $\chi(C{-}H)$ wag	B_g	965.4	964	B_2	1004	996	996	996	B	1004
15. $\chi(CH_2)$ wag		908.0	908		909	914	914	914		919
16. $\tau(CH_2)$ twist		751.9	747		501	468	470	470		457
17. $\nu(CH_2)$ a str	B_u	3100.5^h	3111	B_1	3111		3103	3103		3112
18. $\nu(C{-}H)$ str		3054.7^h	3024		3015		3014	3023^f		3025
19. $\nu(CH_2)$ s str		3010^g	3015		3026		2986	2990^f		3010
20. $\nu(C{=}C)$ a str		1596.7^h	1591		1614	1632^f	1633^f	1633		1628
21. $\delta(CH_2)$ sci		1380.8^h	1380		1407	1401	1403	1403		1403
22. $\delta(C{-}H)$ def		1295.0^h	1290		1281					1274
23. $\rho(CH_2)$ rock		990.2^h	996		1105	1087	1087^f	1087		1093
24. $\delta(C{=}C{-}C)$ def		291^h	295		560	598	596	596^i		616

[a] Structure **2** is a transition state; thus ν_{13} is negative. [b] Except for those marked otherwise, the values were taken from ref 20. [c] Reference 14b; Ar matrix at liquid He temperature. [d] Reference 16; Ar matrix at 20 K. [e] Reference 17b; Ar matrix and neat solid at 28 K. [f] The symmetries are inversed compared to the assignments in the original work, giving better agreement between the experimental and calculated values of these bands. [g] Corrected for Fermi resonance. [h] Measured in this work. [i] In ref 17b, 596 cm^{-1} is assigned to ν_9 and a band at 530 cm^{-1} attributed to ν_{24} (see text).

TABLE 3: Rotational Constants (cm^{-1}) for 1,3-Butadiene

	experimental values		MP2/6-31G*	semiempirical $A'' - \bar{B}''$	
rotamer	$A'' - \bar{B}''$	$A' - \bar{B}'$	$A'' - \bar{B}''$	MW	ED
1	1.251(4)^a 1.245(2)^f 1.24782(9)^g	1.255(3)^b 1.226(2)^f	1.260^c	1.251^d	1.224^e
2			0.536^c	0.494^h	0.496^i
3	0.4478(27)^j	0.4455(25)^j	0.534^c	0.494^h	0.496^i

[a] Reference 47; weighted mean of $A'' - \bar{B}''$ for the ν_{11}, ν_{12}, and ν_{22} fundamentals. [b] Reference 47; from analysis of the ν_{22} band. [c] This work. [d], [e] Computed with Gaussian 92, using the structural parameters from refs 12 and 10, respectively. [f] Reference 5, from analysis of the ν_{11} band. [g] Reference 8. [h], [i] Values obtained for the semiempirical MP2/6-31G* geometries, adjusted using the ratio of the theoretical parameters for **1** and the experimental microwave (ref 12) and electron diffraction (ref 10) geometrical parameters, respectively. [j] This work; from analysis of ν_{12}. The numbers quoted in parentheses refer to one standard deviation (1σ) of the least-squares fit in the unit of the last quoted digits.

will be reported in a subsequent paper.[46] The vibrational frequencies calculated using the scaled force fields are listed in Table 2.

Theoretical rotational constants A'', B'', and C'' for the MP2/6-31G* optimized structures of **1**, **2**, and **3** were calculated with Gaussian 92.[42] The values of $A'' - \bar{B}''$, where in the symmetric top−rigid rotor approximation $\bar{B}'' = (B'' + C'')/2$, are given in Table 3. In addition, scale factors for the theoretical structural parameters were obtained using the theoretical values for **1** and its experimental microwave[12] and electron diffraction parameters.[10] The optimized geometrical parameters of **2** and **3** (Table 1) were then multiplied by these scale factors to obtain their semiempirical structures for which the corresponding rotational constants were also calculated. The latter are listed in Table 3.

Experimental Details. 1,3-Butadiene with a stated purity of >99.5% was purchased from Merck and used without purification. The sample used for the IR spectral analysis (about 9 hPa at constant temperature (295 K)) was contained in a 1.7 m long multipass absorption cell, adjusted for 16 transits (path = 27.2 m), and closed by two KBr windows. Its spectra were recorded between 550 and 1360 cm^{-1} with a Bruker IFS120HR spectrophotometer fitted with a Globar source, a KBr beam splitter, and a HgCdTe detector. The spectrum was recorded at unapodized resolutions of 0.64 and 0.005 cm^{-1}, apodized with a Norton-Beer weak function, and then ratioed against an empty cell background. Each spectrum is the result of the coaddition of 100 interferograms. The spectral range 715−785 cm^{-1} of the medium-resolution spectrum is presented in Figure 2.

Discussion

Theoretical Analysis. With the exception of only ν_9, ν_{11}, ν_{12}, ν_{16}, and ν_{24}, the calculated vibrational frequencies of **2** and **3** are very close to each other (see Table 2). However, of the five exceptions, three are probably not suitable for our purposes: the predicted values of ν_9 and ν_{11} are rather close to the intense IR bands ν_{24} and ν_{11} of **1**, respectively. We do not have a suitable detector for the range in which ν_{16} should fall. This leaves ν_{24} and ν_{12}, and our first choice has been the latter for the following reasons: (a) The frequency ν_{12} = 712 cm^{-1} for **2** (Table 2) belongs to A_2 symmetry, and it is thus forbidden in the gas phase IR spectrum. (b) The computed MP2/6-31G* IR intensity for the ν_{12} = 735 cm^{-1} band of **3** is 6.4% of that computed for its most intense IR band (ν_{15} = 919 cm^{-1}). In Table XIV of ref 20, Wiberg and Rosenberg use a different numbering of the fundamental modes of **3**; thus, the relative intensities of $\nu_{12}/\nu_{15} = \nu_{11}(733\ \text{cm}^{-1})/\nu_{22}(946\ \text{cm}^{-1}) = 6.36/91.11 = 7.0\%$. This is very close to our calculated value and well within the uncertainties of theoretical intensities. (d) The only bands observed between 535 and 898 cm^{-1} in the Ar matrix spectra are attributed to the high-energy conformer. (See, for example, the experimental spectra in ref 14b.

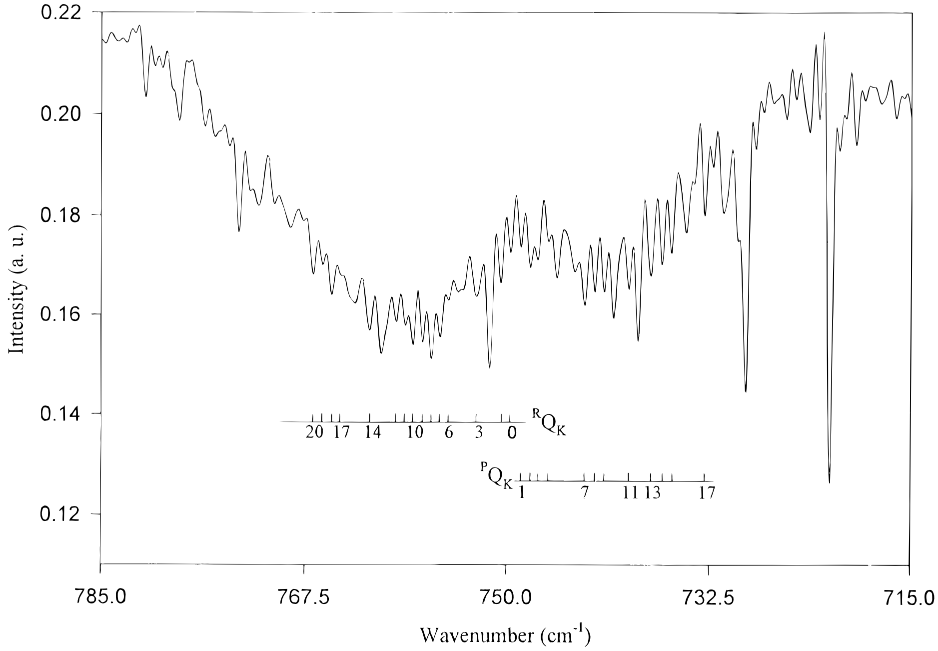

Figure 2. IR absorption spectrum of 1,3-butadiene in the gas phase at 295 K, recorded at a resolution of 0.64 cm^{-1}.

Assignment of the Experimental Spectrum. Figure 2 covers the range where the ν_{12} band of **3** is predicted to be situated (see above). As can be seen, an absorption band is clearly present, centered around 749 cm^{-1}, thus agreeing well with the theoretically predicted position of 735 cm^{-1} for the ν_{12} band and the value of about 730 cm^{-1} in the low-temperature matrices. The observed band is assigned to ν_{12} of **3** because no IR-active fundamental band for either **1** or **2** is predicted to be situated in this spectral region in the gas phase. (See below for possible alternate explanations which have been raised by the reviewers.) The quite high pressure and long absorption path length required to allow its observation are consistent with the low relative population of the second rotamer but do not allow one to choose between structures **2** and **3.** However, because the mode is of A symmetry (C_2 group), the ν_{12} band of **3** should be of B type, which is consistent with the observed band shape (Figure 2).

Two other features appear in Figure 2 which merit our attention. The narrow absorption peak near 729.3 cm^{-1} is easily identified as the Q branch of the strong ν_5 band of acetylene. The acetylene concentration is calculated to be $\leq$300 ppm. This is somewhat higher than is supposed to be present in the 1,3-butadiene sample. The second Q-branch-like feature at about 722 cm^{-1} is tentatively assigned to the C type, $\nu_8-\nu_{13}$ band of **1** ($888 - 163 = 725$ cm^{-1}, Table 2).

The origin of the 749 cm^{-1} band (around 730 cm^{-1} in the solid phase) has been questioned. Notably, it might be due to an impurity (in spite of indications to the contrary[15-17]); it might be a combination band or even consist exclusively of torsional hot bands of ν_{12} of **2** which become allowed because of the distortion of the molecule in the higher torsional levels populated at room temperature. We will now consider these possibilities.

An Impurity. No further purification of the sample by gas chromatography (GC) is feasible because 1,3-butadiene is a volatile substance (1 atm at −4.5 °C) and purification by GC, involving its low-temperature trapping and further transport to the absorption cell, is beyond our present technical means. Merck lists the following impurities: 2-butene (0.3%, without indication of whether it is *cis* or *trans*); butane (50 ppm); propane (20 ppm); propene (10 ppm); inhibitor (*tert*-butyl-4-pyrocatechol; 50−100 ppm); and acetylene (50 ppm). Thus, one must consider the possibility that the 2-butenes could be responsible for the band at 749 cm^{-1}, even though they do not have CH_2 moieties. The rotational constants computed for the HF/6-31G* optimized geometries of *trans*- and *cis*-2-butene yield $A'' - \bar{B}'' = 1.058$ and 0.399 cm^{-1}, respectively, thus eliminating *trans*-2-butene from consideration (see Table 3). We recorded the IR spectrum of *cis*-2-butene and found that there is a broad window extending from 715 to 930 cm^{-1} with no discernible absorption. To avoid further polemics on this subject, we also obtained a GC/mass spectral (GC/MS) analysis of the 1,3-butadiene on a 120 m capillary column (i.d. 0.32 mm) coated with a 2 μm film of methylpolysiloxane. In addition to the stated impurities, the analysis reveals the presence of ~0.05% of an isomer of 1,3-butadiene with a longer retention time and base peak $m/z = 54$. From the MS data base it corresponds to 1,2-butadiene, for which $A'' - \bar{B}''$ is expected to be nearer to that of *trans*-1,3-butadiene. Indeed, for the HF/6-31G* optimized geometry of 1,2−butadiene, $A'' - \bar{B}'' = 1.007$ cm^{-1}, and on this basis alone, it can be excluded as a possible source of the observed 749 cm^{-1} IR band. Thus, the high-resolution GC/MS analysis reveals no impurities which could be responsible for the 749 cm^{-1} band.

A Combination Band. Wiberg and Rosenberg[20] have examined the possibility that the 733 cm^{-1} band is a combination band of **2**. They concluded that only the combination of the ν_{13} (torsion, if a real frequency) and ν_{24} would give the required frequency. They found that this does not fit their predictions as well as the fundamental band and that the intensity is quite strong for a combination band. They thus favor ν_{12} of **3**.

Torsional Hot Bands of **2***.* At room temperature, the lower torsional levels of the higher energy rotamer will be populated whether it is **2** or **3**. It is possible, although we do not accept this, that the forbidden A_2 modes of **2** become permitted due to the distortions brought about by these large-scale movements from planarity. The entire band centered at 749 cm^{-1} would then be the result of torsional hot bands ν_{12} of **2** ($\nu_{12} + n\nu_{13} - n\nu_{13}$). This seems highly unlikely.

Spectral Analysis. As already mentioned in the Experimental Section, the band under investigation has also been recorded at high resolution. Unfortunately, several factors prevent carrying out its complete rotational analysis at this time: (a)

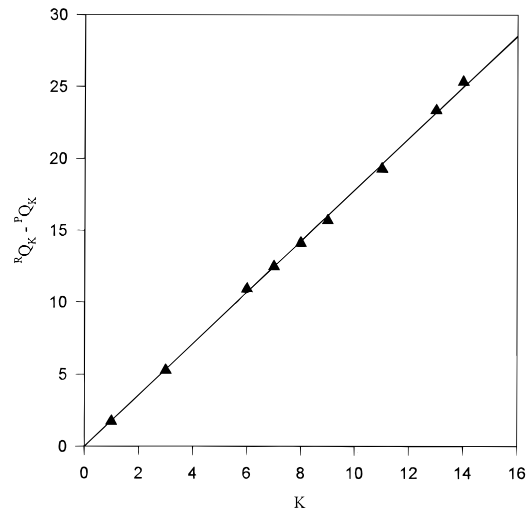

Figure 3. Plot of the combination differences $^{R}Q_{K} - {}^{P}Q_{K}$ versus K (eq 1).

the spectrum is extremely dense; (b) there are practically no discernible branchlike structures (except for a few Q-branches in the P-branch side of the band); (c) there are no known experimental values for the individual rotational constants, A'', B'', C'', A', B', and C' for the minor conformer of 1,3-butadiene. Also, the anharmonicity of the ν_{12} band is unknown.

Nevertheless, the few Q-branch features that could be identified at high resolution were also (and more easily and extensively) observable at medium resolution. Thus, a partial analysis of the ν_{12} band was performed, based on the medium-resolution spectrum presented in Figure 2. The analysis was carried out in the symmetric top−rigid rotor approximation. It involved assignment of the absorption peaks observed on the ν_{12} band contour to $^{\Delta K}Q_{K}$, with $\Delta K = -1$ or $+1$ (represented below by "P" and "R", respectively). The measured positions of these absorption peaks are listed in Table 4. The combination differences

$$^{R}Q_{K} - {}^{P}Q_{K} = 4(A' - \bar{B}')K \qquad (1)$$

were used to assign these Q-branches. The requirement that a plot of these differences versus K should yield a straight line passing through the origin (see eq 1) was found to be sensitive enough to allow unambiguous assignment of the Q branches. The assignments adopted here yield the plot shown in Figure 3. They are listed in Table 4 and noted in Figure 2. Once assigned, the positions of the Q-branches were fitted to the following symmetric top−rigid rotor expression:

$$\nu(^{\Delta K}Q_{K}) = \nu_{0} + (A' - \bar{B}')(K + \Delta K)^{2} - (A'' - \bar{B}'')K^{2} \qquad (2)$$

where ν_0 is the band origin and A and $\bar{B}$ are the rotational constants. The results of the fit are given in Table 3 under the heading "experimental values". The calculated Q-branch positions and the corresponding residuals are listed in Table 4. The standard deviation is 0.23 cm^{-1}. The fit yields $\nu_{12} = 749.22$ (20) cm^{-1}. (The number in brackets equals 3σ and applies to the last digits.)

Rotational Constants. The theoretical value, $A'' - \bar{B}'' = 1.260$ cm^{-1}, obtained here for **1** is quite close to the experimental values (Table 3). Note also that the experimental values of $A'' - \bar{B}''$ for **1** are not very different from those for $A' - \bar{B}'$. The theoretical rotational constants $A'' - \bar{B}''$, calculated for **2** and **3** differ by only 0.2%. However, whereas their values are 2.4 times smaller than those for **1**, they are within 20% of our experimental value. Thus, although the value of the rotational constants does not permit us to choose between structures **2** and **3** for the high-energy rotamer, they allow us to assign the 749.22 cm^{-1} band to it.

TABLE 4: Identification, Observed, and Calculated Wavenumbers and Residuals (in cm^{-1}) for the Absorption Peaks Observed in the Band at 749.22(20) cm^{-1} (Assigned to the ν_{12} Band of 3)

	$\nu(^{P}Q_{K})$			$\nu(^{R}Q_{K})$		
K	obsd	calc	obsd − calc	obsd	calc	obsd − calc
0				749.65	749.67	−0.02
1	748.77	748.77	0.00	750.49	750.55	−0.06
2	747.96	747.87	0.09		751.44	
3	747.32	746.97	0.35	752.60	752.32	0.28
4	746.39	746.06	0.33		753.19	
5	745.62	745.15	0.47		754.06	
6	744.08	744.24	−0.16	755.01	754.93	0.08
7	743.24	743.32	−0.08	755.73	755.79	−0.06
8	742.38	742.39	−0.01	756.50	756.65	−0.15
9	741.56	741.46	0.10	757.25	757.50	−0.25
10		740.53		758.09	758.34	−0.25
11	739.45	739.59	−0.14	758.74	759.19	−0.45
12		738.64		759.56	760.03	−0.47
13	737.54	737.69	−0.15		760.86	
14	736.56	736.74	−0.18	761.88	761.69	0.19
15	735.75	735.78	−0.03		762.51	
16		734.82			763.33	
17		733.85			764.15	
18				765.15	764.96	0.19
19				765.94	765.76	0.18
20				766.75	766.56	0.19

In an attempt to determine the effect of eventual differences between the optimized theoretical and the real (unknown) experimental geometrical parameters on the values of the rotational constants, semiempirical structures were obtained. The data in Table 1 show that the theoretical geometrical parameters for **1** are in fairly good agreement with the corresponding experimental data.[4,6,10,12] This suggests that the computed trends in the geometrical changes for **2** and **3** with respect to the geometry of **1** can be considered to be fairly reliable. The ratios of the experimental/theoretical geometrical parameters of **1** were therefore used to adjust the corresponding parameters of **2** and **3**. The values of $A'' - \bar{B}''$ of **2** and **3** calculated with each of these semiempirical geometries are fortuitously close, being equal within 0.1% for a given experimental set (see Table 3). Using these semiempirical geometries lowers the values of $A'' - \bar{B}''$ by about 7%, bringing them reasonably close to our experimentally determined value. Part of the discrepancy between our theoretical and experimental values for the high-energy rotamer can be explained by the presence of hot bands due to the low-energy fundamentals. Indeed, for the 908 cm^{-1} band of **1**, Cole, Mohay, and Osborne determined $A'' - \bar{B}'' = 1.245$ cm^{-1} for the main series and $A'' - \bar{B}'' = 1.204$ and 1.18 cm^{-1} for the first and second hot band series, respectively.[5] A similar decrease in the rotational constants $A' - \bar{B}'$ was observed for the excited state (1.226 to 1.188 cm^{-1}, respectively).[5]

In our investigation of the region of the recorded IR spectrum which should be free from active fundamental bands of **1** and **2**, and where another band of **3** (ν_{24}) should appear (see above), we found two very weak bands at 602 and 612.9 cm^{-1}. The latter is easily assigned to the ν_4 band of acetylene which is present as an impurity in the sample (see above). The 602 cm^{-1} band is attributed to ν_{24} of **3**; indeed, the band origin agrees well with the predicted value of 616 cm^{-1} (see Table 2). This assignment is in contradiction with that in ref 17b where the absorption band observed at 596 cm^{-1} in the IR spectrum of 1,3-butadiene in an Ar matrix (at 601 cm^{-1} according to ref 17a was reassigned from ν_{24} to ν_9 (both are C═C−C deformation modes). This reassignment was based on the degree of polarization of the absorption band of 1,3-butadiene in the Ar matrix.[17b] However, the value 596 cm^{-1} disagrees strongly with the computed values for ν_9 for both **2** and **3** in ref 17b and in this work (Table 2).

The values of the frequencies for the symmetrical vibrations of the C=C bonds, i.e., 1632 and 1612 cm^{-1} (refs 14 and 16), respectively, may serve as a measure of the conjugation of the high-energy conformer of 1,3-butadiene. For the planar conjugated structure **1**, the corresponding frequencies are 1644 and 1597 cm^{-1} (see Table 2). This seems to indicate that the resonance splitting in the minor conformer is only half that in **1**. Such a small splitting is characteristic of nonplanar conjugated systems.[48] In addition, the relative frequencies of $\nu(C{=}C)_{sym}$ and $\nu(C{=}C)_{asym}$ are inverted for **3** compared to those observed for **1** and those calculated for **2** (Table 2).

There is thus much evidence indicating that the high-energy conformer of 1,3-butadiene in the gas phase is the nonplanar structure **3**. Perhaps the torsional vibration can be described as a large-amplitude vibration because of the low barrier between the two equivalent energy minima. The corresponding nonrigid molecular symmetry group (supergroup S) is isomorphic to C_{2v}.[39] In this case the true behavior of the high-energy conformer in the gas phase lies, in general, somewhere between that predicted for the rigid C_2 conformation and that of the completely free rotating structure, supergroup S. The manifestation of peculiarities of the appropriate symmetry group depends upon the shape and the height of the barrier for **3** → **2** rotation. In a matrix at very low temperature this large-amplitude vibration must be hindered, and except for matrix effects,[17b,c,34,35] it should adopt an *s-gauche* structure.

The presence of hindered rotation could be one of the reasons why the gas phase spectrum of the ν_{12} band is so dense, with little obvious structure. Indeed, a low barrier to internal rotation can lead to a splitting of the rotational levels which complicates the spectrum. Furthermore, the presence of a low-frequency vibration must lead to the observation of hot bands which overlap, leading to an even more dense spectrum.

Conclusions

The observation of the IR absorption band in the gas phase at 749.22(20) cm^{-1} in the spectral region which should be free from the fundamental bands of both **1** and **2**, the agreement of its observed frequency and the $A'' - \bar{B}''$ rotational constant with the predicted theoretical values allow us to assign it to the high-energy rotamer of 1,3-butadiene. Furthermore, its typical B contour in the gas phase, medium-resolution spectrum (consistent with A symmetry, C_2 group) and the very complicated structure in the high-resolution spectrum are strong evidence in favor of the nonplanar structure **3** in the gas phase. However, in order to provide a more definite proof of the nonplanarity of the high-energy structure, it is necessary to perform the complete rotational analysis of one of its vibrational bands. Indeed, if the three rotational constants, A'', B'', and C'', were known, the inertial defect could be calculated, giving a good indication of the planarity or nonplanarity of the conformer. Nevertheless, even if our results only partially answer this question, they represent the first experimental determination of the rotational parameters of the minor conformer of 1,3-butadiene.

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