J. Phys. Chem. A **2000,** *104,* 1141−1146

Rotational Spectra of Seven Conformational Isomers of 1-Hexene

G. T. Fraser,* R. D. Suenram, and C. L. Lugez

Optical Technology Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899-8441

Received: September 13, 1999

The rotational spectra of 7 of the expected 13 conformational isomers of 1-hexene have been measured and assigned at a rotational temperature of <2 K using a pulsed-molecular-beam Fourier transform microwave spectrometer. The rotational assignments were guided by predictions from the MM3 molecular mechanics force field of Allinger et al. and by ab initio electronic-structure calculations (MP2/6-31G*). Six of the seven observed conformers have C_1 symmetry, as verified by the observation of *a*-, *b*-, and *c*-type electric-dipole transitions. The remaining conformer has C_s symmetry, consistent with its small inertial defect, $\Delta \equiv I_{cc} - I_{bb} - I_{aa} = -12.65$ uÅ^2, and the observation of only *a* and *b*-type transitions. Here, $I_{\alpha\alpha}$ is the moment of inertia of the conformer about its α-principal axis. The inertial defects determined for the seven conformers range from −12.65 to −51.29 uÅ^2. Both the molecular mechanics and ab initio calculations indicate the observed conformers are associated with the seven lowest-energy conformational minima of 1-hexene. The ab initio calculated energy difference between the lowest and highest energy conformers observed is 326 cm^{-1}, including vibrational zero-point contributions, indicating that the conformational temperature is not equilibrated with the <2 K rotational temperature of the molecular-beam expansion.

Introduction

Normal alkanes have served as simple models for the investigation of conformationally complex systems because of the assumed simplicity of their force fields and the availability of spectroscopic, thermodynamic, and electron-diffraction data for the smaller members of the group. Moreover, the chainlike structure and flexible nature of the *n*-alkanes allow them to serve as prototypical systems for understanding the C/N/O backbones of the more conformationally complex molecules found in biological systems.

The lowest energy conformers for the shorter *n*-alkanes are expected to have extended linear zigzag geometries (Figure 1) with trans C−C−C−C configurations, that is, C−C−C−C dihedral angles of 180°.[1] The structures of the longer alkane chains are as yet unknown, and indeed the theoretical determination of the chain length at which the minimum-energy configuration becomes “nonlinear” is of considerable interest. This interest is due, in part, to the sensitivity of the chain length for the linear-to-nonlinear transition to the force-field model used. This transition can occur for chains as small as $C_{12}H_{26}$ in some models.[2]

In addition to being able to elucidate the structure of the lowest energy conformer, the ability to predict the numbers, energies, and geometries of the higher energy conformers is also important for calculating thermodynamic properties and modeling conformational isomerization. For even relatively small hydrocarbons the search for all the minima and the determination of their relative energies can be computationally challenging because the number of conformers grows between $3^n/3$ to $3^n/2$, where $n + 2$ is the number of C−C bonds.[3] In the case of decane, for example, Tasi et al.[3] found 3375 chemically distinct conformers using their scaled effective one-electron quantum mechanical model (SEOEM), of which a significant fraction is populated at room temperature. Gotô et al.[4] found a similar number, 3263, using the older MM2 molecular mechanics force field of Allinger et al.[5] This conformational complexity of the *n*-alkanes has led to their use as test systems in the development of computational algorithms that allow the sampling of the energies and configurations of large numbers of possible conformers.[2,4−7]

Undecane

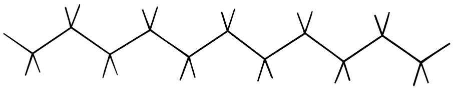

Figure 1. Structure of the lowest energy conformation for small *n*-alkanes. Shown is the expected structure for undecane.

We note that no quantitative experimental structural results exist for *n*-alkanes with more than seven carbon atoms to compare with the model predictions. Moreover, the experimental data for *n*-pentane through *n*-heptane, predicted to have 4, 12, and 30 distinct conformers, respectively,[3] are based primarily on electron-diffraction studies,[1,8] which are less reliable for molecules with several conformers. Indeed, in the electron-diffraction study of pentane, hexane, and heptane the ratio of the relative conformer energies were constrained in the data analysis by requiring the value for the gauche−trans C−C−C−C dihedral-angle energy difference to be independent of the position within the molecule or of the parent hydrocarbon.[1]

Limiting the availability of structural data on the *n*-alkanes is the vanishing or near-vanishing dipole moments for these molecules, which prevent their structural study by microwave rotational spectroscopy. In the present paper we report on the first part of an experimental structural study on a related group of hydrocarbon chains, the 1-alkenes, using molecular-beam Fourier transform microwave spectroscopy. The presence of the carbon−carbon double bond in these species increases their electric-dipole moment over the corresponding *n*-alkanes (which for some conformations have zero dipole moment), greatly aiding the observation of their rotational spectra. Rotational spectra have been measured in a supersonic molecular beam

10.1021/jp993248n CCC: $19.00

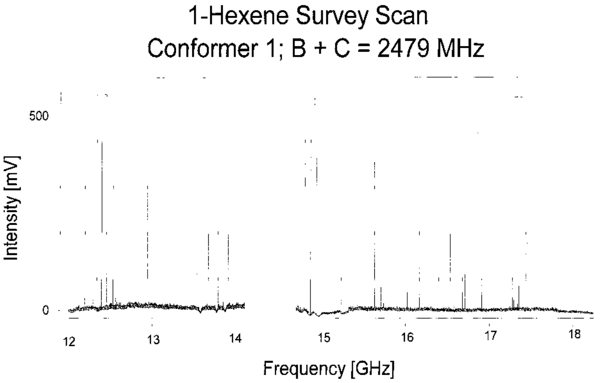

Figure 2. Survey spectrum from 12 GHz to just above 18 GHz for 1-hexene in a He/Ne carrier gas. The intense *a*-type $J = 5-4$, $6-5$, and $7-6$ transitions for conformer 1 spaced by approximately $B + C = 2479$ MHz are identified.

for 1-pentene through 1-dodecene at a rotational temperature of <2 K, with as many as 15 conformers observed for 1-octene.[9] Similar studies are also underway on the corresponding isoelectronic aldehydes to assess the affect of a very polar functional group on the observed conformations. Here, we discuss our results on 1-hexene, for which 7 conformers have been observed. The results are compared with predictions from the MM3 molecular mechanics force field of Allinger et al.[10,11] and from ab initio electronic-structure calculations.

Experimental Section

Rotational spectra of 1-hexene were recorded using pulsed-molecular-beam, Fourier transform microwave spectrometers described previously.[12,13] The molecular beam was formed by expanding a gas mixture consisting of 0.1−1 vol % of 1-hexene in an inert carrier gas (80% Ne and 20% He or 100% Ar by volume) through a 1.2-mm nozzle at expansion pressures up to approximately 70 kPa. The signal-to-noise ratio, *S/N*, was typically a factor of 2 larger for the He/Ne carrier gas compared to the Ar carrier gas.

Initial low-resolution survey spectra were recorded in 1 GHz intervals using frequency steps of 0.25−0.5 MHz. At each frequency step, the free-induction decays from 10 to 200 nozzle pulses acquired at a 5−10-Hz repetition rate are averaged. Up to 4 free-induction decays were acquired per nozzle pulse. The peak amplitude from the Fourier transform of the free-induction decay is plotted versus frequency. A partial survey spectrum for 1-hexene is shown in Figure 2.

Assigned lines have been measured at high resolution by recording the average free-induction decay from typically 50 to 2000 nozzle pulses and then Fourier transforming the result to obtain an amplitude spectrum. The standard uncertainties on the line positions extracted from the amplitude spectra, as inferred from previous studies, are approximately 2 kHz.

The rotational temperature of the expansion is less than 2 K, as suggested by previous studies under similar nozzle conditions. The conformational temperature is generally significantly higher and is a function of the energy differences and barriers between the various conformers and the carrier gas.[14] In the case of 1-butene, for example, both conformers[15] are observed in the He/Ne molecular beam. Here, the lower energy conformer is denoted “skew” or “gauche” and the higher energy one is denoted “cis” or “syn”. The ratio of the signal amplitudes for the $2_{02}-1_{01}$ transitions for these two conformers is skew:syn = 4.6:1, suggesting a syn−skew energy difference of approximately 1 cm^{-1}, if the conformer temperature is equilibrated with the rotational temperature, taken as 2 K, and the skew conformer is assumed to have twice as many states as the C_s-symmetry syn conformer. The energy difference between the two conformers has recently been determined from Raman gas-phase intensity measurements to be 14(4) cm^{-1}, that is, 20(6) K,[16] and from ab initio theory to be 126 cm^{-1}, that is, 181 K, by Murcko et al.[17] using essentially QCISD-(T)/6-311+G(3df,2p) energies at the MP4(SDQ)/6-31+G(2d,p) geometry.

Results

Ab Initio and Molecular Mechanics Modeling. The conformational minima of 1-hexene were examined using the MM3-(1996) molecular mechanics force field of Allinger et al.,[10,11] as implemented in the molecular-modeling program suite TINKER developed by Ponder et al.[18,19] Calculations were undertaken to find the number of minima and their geometries and energies. Starting from an initial reference configuration, all possible configurations differing by a rotation of a multiple of 60° about one or more C−C single bonds were examined, giving 6^{n-2} configurations for alkene C_nH_{2n}, or 1296 configurations for hexene. This number can be reduced by a factor of 3 by noting that the terminal methyl group only needs to be stepped through two of the six, 60° steps. A 60° torsional angle step size was found by Lipton and Still[7] to be sufficient for obtaining all the potential minima of *n*-hexane. Because the number of conformers increases faster than a factor of 3 per CH_2 group added to the alkene chain, the torsional sampling must be done on a grid finer than 120°. We note that a still further reduction in the number of structures sampled can be achieved by only considering one of the two mirror-image configurations.

The above configurations were used as trial guesses in the energy minimization program OPTIMIZE in the TINKER package, which implements an optimally conditioned, variable-metric method to minimize the energy with respect to the Cartesian coordinates. A total of 13 “chemically” distinct minima were found for the potential energy surface. Minima related through a symmetry operation, such as reflection through a plane or interchange of identical nuclei, are not considered chemically distinct. The minima were verified by vibrational normal-mode calculations. The normal-mode calculations ruled out a number of C_s-symmetry configurations as minima, and in fact, only one C_s-symmetry minimum could be established. The rotational constants (A, B, and C), relative energies (E_{rel}), and point-group symmetries for the 13 minima are listed in Table 1. Also listed are the inertial defects, $\Delta \equiv I_{cc} - I_{bb} - I_{aa}$, where $I_{\alpha\alpha}$ is the moment of inertia of the conformer about the α-principal axis. For 1-hexene, the magnitude of the inertial defect takes its smallest value for conformations with a plane of symmetry.

The presence of 13 minima on the 1-hexene potential energy surface is easy to rationalize. First, we will assume that the minima will be biased toward configurations having dihedral angles that minimize steric repulsions. From this viewpoint we expect 3 possible staggered configurations for each of the 2 single-bond C−C−C−C dihedral angles. The C=C−C−C dihedral angle will likewise have 3 minima. In this case the minima have the sp^2 hybridized carbon, C2, of the CH_2= group eclipsed with the sp^3 hybridized carbon, C4, or with one of the hydrogens, H8 or H9. The atom labels used are defined in Figure 3. From the above considerations we expect $3^3 = 27$ minima, of which one has C_s-point-group symmetry and the other 26 consist of 13 minima and their mirror images. This argument thus gives 14 chemically distinct minima compared to the MM3

TABLE 1: Molecular Mechanics, Ab Initio, and Experimental Rotational Constants, Inertial Defects, Symmetries, and Relative Energies for the 13 Conformers of 1-Hexene

conformer no.	1	2	3	4	5	6	7	8	9	10	11	12	13
						MM3							
symmetry	C_1	C_1	C_1	C_s	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1
A (MHz)	12626	6922	8728	9605	10663	5061	8598	7232	6344	9088	4730	5651	5325
B (MHz)	1253	1694	1482	1440	1395	2194	1496	1703	1857	1528	2427	1996	2123
C (MHz)	1231	1489	1403	1294	1348	1818	1384	1623	1595	1438	1820	1891	1708
Δ (uÅ^2)	−32.9	−32.0	−38.7	−12.9	−34.9	−52.2	−31.4	−55.3	−34.9	−34.9	−37.4	−75.3	−37.2
E_{rel} (cm^{-1})	0	43	161	265	292	294	296	424	525	576	673	828	951
						MP2/6-31G*							
symmetry	C_1	C_1	C_1	C_s	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1
A (MHz)	13177	7118	8940	9667	10835	5055	8974	7016	6419	9255	4891	5694	5409
B (MHz)	1257	1693	1496	1469	1408	2273	1500	1780	1890	1560	2338	2042	2136
C (MHz)	1235	1495	1414	1316	1361	1864	1390	1678	1619	1461	1794	1935	1714
Δ (uÅ^2)	−31.1	−31.5	−37.0	−12.5	−34.2	−51.1	−29.7	−54.8	−33.9	−32.7	−37.7	−75.0	−35.2
E_{rel}/cm^{-1}	0	−47	228	279	258	117	244	438	573	550	659	829	1059
rel. frac. pop. at 296 K[a]	1.00	1.26	0.33	0.13	0.29	0.57	0.31	0.12	0.06	0.07	0.04	0.02	0.01
						Observed[b]							
symmetry	C_1	C_1	C_1	C_s	C_1	C_1	C_1						
A (MHz)	13397	7247	9258	9698	10835	5177	8957						
B (MHz)	1251	1665	1470	1463	1402	2189	1494						
C (MHz)	1228	1479	1392	1313	1355	1823	1382						
Δ (uÅ^2)	−30.2	−31.6	−35.3	−12.7	−34.1	−51.3	−29.1						
E_{rel} (cm^{-1})	0	130(140)	840(140)	520(140)	570(140)	530(140)	480(130)						

[a] Estimated relative fractional populations of the conformers at 296 K considering only contributions from E_{rel} in the calculation. We also assume that the C_1 configurations have statistical factors of 2 relative to the C_s configuration. [b] The uncertainties on the experimental rotational constants are given in Table 4.

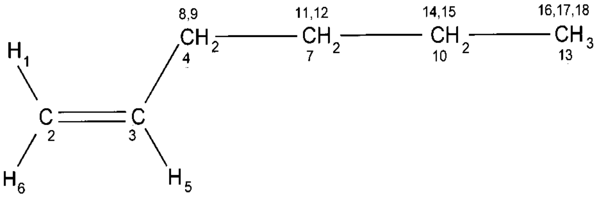

Figure 3. Definition of the atom labels for 1-hexene used in Figure 4 and Table 2.

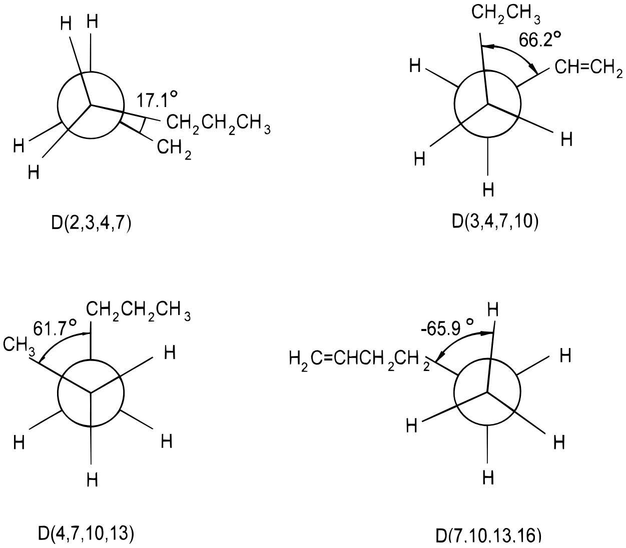

Figure 4. Definition of the ab initio (MP2/6-31G*) dihedral angles of Table 2. The values shown are for conformer 12 of Table 2.

result of 13. The extra minimum corresponds to values for the dihedral angles in Figure 4 of $D(2,3,4,7) \approx 0$, $D(3,4,7,10) \approx \pm 60°$, and $D(4,7,10,13) \approx \mp 60°$, and it does not exist for the MM3 force field or any other reasonable force field because it is almost cyclic, leading to strong steric repulsions between the two ends of the molecule.

TABLE 2: Ab initio (MP2/6-31G*) Dihedral Angles (in Degrees) as Defined in Figures 3 and 4 for the 13 Conformational Isomers of 1-Hexene

conformer no.	D(2,3,4,7)	D(3,4,7,10)	D(4,7,10,13)	D(7,10,13,16)
1	−116.8	−178.6	−179.8	179.9
2	118.6	−64.2	−179.3	−60.0
3	−110.7	−62.7	−176.2	−59.6
4	0.0	180.0	180.0	−59.8
5	116.5	−177.8	−64.5	−175.7
6	120.9	−58.6	−61.0	66.0
7	116.6	174.4	63.1	−64.5
8	109.0	57.9	59.7	55.3
9	13.3	70.6	−178.8	60.8
10	−2.2	−176.5	−64.3	64.7
11	−127.2	67.0	−80.1	63.1
12	17.1	66.2	61.7	−65.9
13	−107.9	−58.5	91.2	−57.4

The Cartesian coordinates for each of the MM3 minima were used as trial guesses in a full Gaussian 98[19,20] geometry optimization at the MP2/6-31G* level. Vibrational normal-mode calculations were used to verify that the stationary points are minima on the conformational potential energy surface. In all cases the ab initio calculations found minima close to the minima of the MM3 force field. The calculated relative energies (corrected for zero-point vibrations), rotational constants, and inertial defects are also listed in Table 1 and the resulting structures are summarized in Table 2, where values for the C−C−C−C dihedral angles are listed. The definition of the dihedral angles can be found in Figures 3 and 4. To minimize steric repulsions, the dihedral angles $D(3,4,7,10)$, $D(4,7,10,13)$, and $D(7,10,13,16)$ are biased toward values near the staggered configurations of ±60° and ±180°.

Spectroscopic Measurements. Guided by the MM3 and ab initio rotational constant predictions, seven conformers have been identified in the rotational spectrum of 1-hexene. A number of unassigned lines remain and are attributed to impurity molecules, van der Waals complexes, ^{13}C isotopic forms or vibrationally excited states of 1-hexene, and other conformers. A list of the assigned transitions is presented in Table 3.

TABLE 3: Measured Transition Frequences in MHz for Seven Conformers of 1-Hexene; The Estimated (Type B) Standard Uncertainties on the Frequencies Is ≈2 kHz

conformer no.	1	2	3	4	5	6	7
$1_{10}-0_{00}$			10727.8203		12237.9834		10450.3906
$1_{10}-1_{01}$	12168.9673						
$1_{11}-0_{00}$			10649.8223		12191.0078		10338.6914
$1_{11}-1_{01}$	12146.2820						
$2_{11}-1_{01}$		12242.4795	13668.2256		15041.3662	11742.6680	13437.4424
$2_{11}-2_{02}$	12191.7280						
$2_{11}-1_{10}$						8388.6035	
$2_{12}-1_{01}$		11684.9238	13434.2012	13635.5820	14900.4404	10645.5146	13102.3672
$2_{12}-2_{02}$	12123.6710						
$2_{20}-2_{11}$		16750.2647					
$3_{03}-2_{02}$		9414.6934		8317.6855		11909.4268	
$3_{12}-2_{02}$		15667.2559					
$3_{12}-2_{11}$		9708.8633		8549.4043		12562.0186	
$3_{12}-3_{03}$	12225.9307						
$3_{13}-2_{12}$		9151.4082				11466.7178	
$3_{13}-3_{03}$	12089.8081						
$3_{13}-2_{02}$				16186.7480		14120.9492	
$3_{21}-2_{20}$		9451.3975				12159.0293	
$3_{22}-2_{21}$		9433.1670				12034.3809	
$4_{04}-3_{03}$	9915.7627	12531.6801	11443.3506	11080.7822	11023.8242	15742.9102	
$4_{04}-3_{13}$						13531.3887	
$4_{13}-3_{12}$	9961.4702	12939.5449	11604.1553	11396.7783	11119.1797	16707.9609	
$4_{13}-4_{04}$	12271.6421						
$4_{14}-3_{03}$		17334.1963		18666.2891			
$4_{14}-3_{13}$	9870.7266	12196.6445	11292.1709	10797.2266	10931.2863	15255.6992	
$4_{14}-4_{04}$	12044.7705						
$4_{22}-3_{21}$		12619.3716	11455.1553	11119.7891		16323.0166	
$4_{22}-4_{13}$		16172.6221					
$4_{23}-3_{22}$	9916.4131	12573.9131	11449.3311	11099.5283		16020.9229	
$5_{05}-4_{04}$	12394.4326	15630.8603	14299.7017	13835.8232	13778.4312		14351.6933
$5_{14}-4_{13}$	12451.7465	16165.2138	14503.9492	14242.0195	13898.6026		14650.2568
$5_{14}-5_{05}$	12328.9551						
$5_{15}-4_{14}$	12338.3154	15237.6055	14114.0293	13492.8203	13663.7509		14092.0254
$5_{15}-5_{05}$	11988.6526						
$5_{23}-4_{2\,2}$		15801.9521	14322.4600	13912.2969	13785.0908		14398.8242
$5_{24}-4_{23}$	12395.4229	15711.5400	14310.8096	13871.8467	13781.5928		14373.9907
$6_{06}-5_{05}$	14872.9200		17153.0791	16580.9102	16532.1406		17208.3652
$6_{06}-5_{15}$		14299.3637					
$6_{15}-5_{14}$	14941.9590		17402.8984	17084.5285	16677.7764		17576.6440
$6_{15}-6_{06}$	12397.9960						
$6_{16}-5_{15}$	14805.8428		16935.1143	16186.0342	16395.9766		16907.0556
$6_{16}-6_{06}$	11921.5728						
$6_{24}-5_{23}$	14875.4859				16543.6572		17289.7793
$6_{25}-5_{24}$	14874.3862				16537.5332		17246.4111
$7_{07}-6_{06}$	17351.1924				19284.7734		
$7_{16}-6_{15}$	17432.0972				19456.6474		
$7_{17}-6_{16}$	17273.2969				19127.9209		
$7_{25}-6_{24}$	17355.0722						
$7_{34}-6_{33}$	17354.5264						
$7_{35}-6_{34}$	17354.5264						
$8_{08}-7_{07}$	19829.2110						
$8_{18}-7_{17}$	19740.6641						
$8_{26}-8_{17}$		14716.4004					

All of the conformers exhibit *a*- and *b*-type electric-dipole transitions. For six of the seven conformers *c*-type transitions are also observed, establishing that these six conformers have C_1-point-group symmetry. The spectra for all the conformers are well characterized by a near-prolate-top asymmetric-rotor Hamiltonian. The effects of the terminal methyl-top internal rotation are also observed, particularly on the *b*- or *c*-type transitions which in some cases are broadened or partially split from internal-rotation splitting of the lines into *A* and *E* symmetry components. Qualitatively, this effect is more pronounced for the conformers with the larger *A* rotational constants.

The observed transition frequencies listed in Table 3 have been fit to the Watson asymmetric-rotor Hamiltonian[21] in the I^r representation to yield the rotational and centrifugal distortion constants given in Table 4. For six of the seven conformers, no $K = 2-1$ or higher *K*, *b*- or *c*-type transitions were observed, preventing the determination of the Δ_K centrifugal distortion constant. The standard deviations, σ, of the fits are close to the expected measurement precision of 2 kHz and are also listed in the table. The larger uncertainty for conformer 1 is attributed to the effects of internal rotation, which partially splits and broadens a number of the lines, making it more difficult to precisely specify the line center. The surprisingly larger value of δ_K for conformer 1 and our inability to determine δ_J for this conformer may also be further manifestations of the internal-rotation effects.

The possibility that one or more of the conformers are not distinct, but should be identified with a monosubstituted ^{13}C form or vibrational hot band of one of the other conformers, can be ruled out by consideration of the relative intensities and inertial defects. In Table 4 we list the relative intensities for

TABLE 4: Spectrocopic Constants Determined for the Seven Observed Conformers of 1-Hexene; Statistical (Type A) Standard Uncertainties Are Given

conformer no.	1	2	3	4	5	6	7
symmetry	C_1	C_1	C_1	C_s	C_1	C_1	C_1
A (MHz)	13397.1224(18)	7247.2173(13)	9257.6162(14)	9697.54376(62)	10836.29147(45)	5176.9104(16)	8956.8636(20)
B (MHz)	1250.931(26)	1665.10247(79)	1470.17321(58)	1462.59435(12)	1401.6871(20)	2188.6118(11)	1493.51829(99)
C (MHz)	1228.101(26)	1479.23724(85)	1392.16456(57)	1312.67678(13)	1354.7195(20)	1822.8601(11)	1381.82504(96)
δ_J (kHz)		0.2114(37)	0.0666(44)	0.0296(10)	0.01992(91)	0.982(11)	0.0507(66)
δ_K (kHz)	36(13)	2.00(32)			−2.1(10)	2.98(46)	
Δ_J (kHz)	0.2061(64)	0.8383(46)	0.6755(50)	0.16059(88)	0.2042(15)	3.153(20)	0.3756(90)
Δ_{JK} (kHz)	−10.397(56)	−9.825(39)	−18.876(51)	−1.9562(99)	−1.267(15)	−12.721(96)	−5.676(61)
Δ_K (kHz)		56.17(30)					
σ (kHz)	5.1	1.8	2.6	0.5	0.9	2.4	3.5
no. transitions	33	23	17	18	20	15	14
Δ (uÅ^2)	−30.2	−31.6	−35.3	−12.7	−34.1	−51.3	−29.1
transition types	a,b,c	*a,b,c*	a,b,c	a,b	a,b,c	a,b,c	a,b,c
μ_a [MP2/6-31G*] (D)	0.31	0.12	0.26	0.22	0.35	0.12	0.32
relative intensity in Ar	69	14	1	2	5	2	7
relative intensity in He/Ne	>68	11	1	2	5	3	8

the $5_{05}-4_{04}$ transitions for conformers 1−5 and 7 and for the $4_{04}-3_{03}$ transition for conformer 6 in an Ar carrier gas and in the 20 vol % He in a Ne carrier gas. As can be seen in the table, the relative intensities vary by nearly 2 orders of magnitude among the conformers. Measurements of ^{12}C:^{13}C isotopic ratios in 1-pentene suggest that the intensity ratio for two lines is accurate to within a factor of 2. Moreover, the relative insensitivity of the intensity ratios to the carrier gas suggests that the observed transitions are not due to vibrational hot bands, which are more efficiently collisionally relaxed in an Ar carrier gas than in a Ne:He carrier gas.

The relative intensities in Table 4 demonstrate that only conformer 1 has a sufficiently intense spectrum to have a ^{13}C spectrum that could be identified with conformers 3, 4, or 6. However, the A rotational constant for conformer 1 is predicted to change by ≤1.1% upon monosubstitution with ^{13}C, which is significantly smaller than the A rotational constant differences between conformer 1 and conformers 3, 4, and 6. Also, modeling calculations using the MM3 determined structures indicate that the magnitudes of the inertial defects should change by ≤1.5 uÅ^2 for all the conformers upon monosubstitution with ^{13}C. Only conformers 1 and 2 and conformers 3 and 5 have inertial defects sufficiently close to be isotopic partners. Again, the large differences in the A rotational constants for these conformers rule out this possibility.

Examination of the A rotational constants and inertial defects demonstrate that the identification of the observed conformers with predicted conformers 1−7 as given in Table 1 is the only reasonable choice. Examination of the A rotational constants alone suggests that conformer 2 could be assigned to conformer 8, conformer 3 could be assigned to conformer 7 or 10, and conformer 6 could be assigned to conformers 11, 12, or 13. The inertial defects, though, are sufficiently different among these conformer sets to require the conformer assignments given in the bottom of Table 1.

Discussion

Both the MM3 force field and ab initio theory at the MP2/6-31G* level accurately predict the rotational constants for the seven conformers of 1-hexene. Indeed, in many cases, the calculations guided the spectral assignments. The relative errors [(obs. − calc.)/obs.] of the ab initio calculations for the A, B, and C rotational constants and the inertial defect, Δ, are −0.2% to 3.4%, −3.9% to −0.4%, −2.2% to −0.3%, and −4.6% to 1.6%, respectively. For the MM3 calculations the relative errors are slightly larger at 1.0% to 5.8%, −1.7% to 1.6%, −0.8% to 1.5%, and −10.0% to −1.3%, respectively.

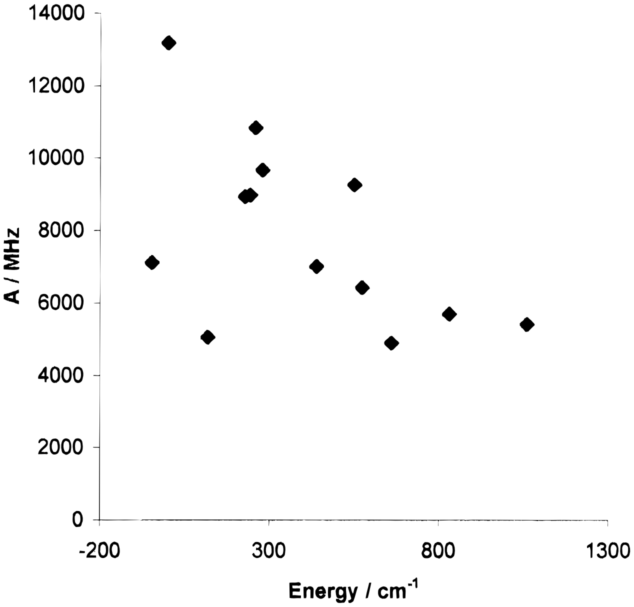

Figure 5. Plot of the ab initio (MP2/6-31G*) calculated A rotational constant versus energy (corrected for zero-point vibrations) for the 13 conformers of 1-hexene.

The lower-energy conformations of 1-hexene are also generally predicted to have the larger A rotational constants. This trend can be seen in Figure 5 where we plot the ab initio A rotational constant as a function of calculated energy. This observation implies that the lower energy configurations have more extended structures, such as those seen for the minimum-energy configuration of the n-alkanes (see Figure 1). Indeed, the alkane part of conformer 1 has all the C−C−C−C single-bond dihedral angles near ±180° (see Table 2), as found in the n-alkanes.

The fact that we have not observed conformers 8−13 of Table 1 is consistent with the conformer energies calculated by the MM3 and ab initio models, which both predict a significant energy jump of >125 cm^{-1} between conformers 1−7 and 8−13. In general, the relative conformer energies predicted by the MM3 and ab initio calculations are in reasonable agreement. We note, though, that the MM3 calculations give conformer 1 as the overall conformational minimum while the ab initio calculations give conformer 2 as the absolute minimum. However, the calculated energy differences between conformers 1 and 2 is small, <50 cm^{-1}, and is beyond the expected accuracy of the theories.

Unfortunately, the present measurements do not provide precise quantitative information on the relative energies of the observed conformers. Such data would furnish a further critical test of the calculations. Some insight on the conformer energetics can be obtained from a comparison of the intensities of the rotational transitions for the different conformers listed in Table 4. If we assume no conformer relaxation occurs during the expansion, then the above intensities can be used to estimate the relative populations of the conformers at room temperature. This information can then be used to derive the relative energies of the conformers. Our justification for ignoring conformer relaxation is based on the work of Ruoff et al.[14] who examined conformer relaxation in molecular beams for molecules with two conformers separated by barriers of various heights. They found that when the barriers between the conformers are greater than $\approx$400 cm^{-1}, no conformer relaxation occurs. Estimates of these barriers in 1-hexene using the MM3 force field and the SADDLE transition-state searching program in the TINKER package[18] give barriers on the order of 650 cm^{-1} or greater separating conformers 1−7, suggesting that essentially no cooling will occur among these conformers during the supersonic expansion. Further evidence for the absence of cooling is seen in the similar relative intensities of the transitions in Ar and He/Ne. We note that Ruoff et al.[14] found that Ar is approximately twice as efficient as Ne at inducing conformer relaxation for molecules with barriers below $\approx$400 cm^{-1}.

In Table 1 we list the relative energies for conformers 1−7, as derived from the relative intensity measurements in Ar, where the free-induction decay signal for transition 1 is not saturating our data acquisition system. In calculating the relative energies, we have assumed that the intensity for conformer i is proportional to $\mu_{ai}d_i \exp(-E_i/kT)$, where μ_{ai} is the projection of the total dipole moment on the a inertial axis, taken from the ab initio values listed in Table 4, d_i is the conformer degeneracy (1 for the C_s-symmetry conformer 4, 2 otherwise), and E_i is the energy of the conformer relative to conformer 1. The signal intensity scales linearly with μ_a because the amplitude spectrum of the electric field associated with the free-induction decay is recorded. In practice, we could have measured μ_a for each of the conformers using the rotational Stark effect; however, for the weaker intensity conformers this would be difficult to impossible because of signal-to-noise requirements. For the relative energies, we have ignored the less than 10% variation in rotational partition functions, the slight differences in transition frequencies, and the small variation in direction cosine matrix elements for the rotational transitions for the conformers. The uncertainties in the energies are estimated on the basis of our results for ^{12}C:^{13}C isotopic intensity ratios for 1-pentene discussed above and assume that the relative intensities for conformer 1 to conformers 2−7 are known to within a factor of 2.

The relative energies estimated in Table 1 indicate that either conformer 1 or conformer 2 is the lowest in energy, consistent with the MM3 and ab initio calculations. Surprisingly, the experimental results strongly suggest that conformer 3 is the highest energy conformer of the seven studied. One possible explanation for this discrepancy between theory and experiment is that the ab initio value for the μ_a dipole moment component for conformer 3 is too high relative to the other conformers, requiring a larger value for the energy to bring its calculated intensity in line with observations.

Limiting, in part, the assignment of additional conformational isomers is the plethora of weak lines from the mono-^{13}C-substituted 1-hexenes overlapping the weaker lines of the higher energy conformers. Using a 1-hexene sample depleted of ^{13}C could eliminate this problem. Alternatively, efforts could be made to assign the spectra for the 42 monosubstituted ^{13}C species of conformers 1−7. Such a study would have the added advantage of furnishing more quantitative information on the geometries of conformers 1−7. Heating the gas prior to the expansion could also increase the population of the higher-energy conformers. When these approaches are used, future observation and assignment of spectra for conformers 8 and beyond should be possible.

References and Notes

(1) Bartell, L. S.; Kohl, D. A. *J. Chem. Phys.* **1963**, *39*, 3097.

(2) Goodman, J. M. *J. Chem. Inf. Comput. Sci.* **1997**, *37*, 876.

(3) Tasi, G.; Mizukami, F.; Pálinkó, I.; Csontos, J.; Gyorffy, W.; Nair, P.; Maeda, K.; Toba, M.; Niwa, S.; Kiyozumi, Y.; Kiricsi, I. *J. Phys. Chem. A* **1998,** *102*, 7698.

(4) Gotô, H.; Ôsawa, E.; Yamato, M. *Tetrahedron* **1993**, 49, 387.

(5) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(6) Nair, N.; Goodman, J. M. *J. Chem. Inf. Comput. Sci*. **1998**, *38*, 317.

(7) Lipton, M.; Still, W. C. *J. Comput. Chem.* **1988**, *9*, 343.

(8) Bonham, R. A.; Bartell, L. S.; Kohl, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4765.

(9) Fraser, G. T.; Suenram, R. D., unpublished results.

(10) Allinger, N. L.; Yuh, Y. H.; Li, J.-H. *J. Am. Chem. Soc*. **1989**, *111*, 8551.

(11) Allinger, N. L.; Li, F.; Yan, L. *J. Comput. Chem.* **1990**, *7*, 848.

(12) Suenram, R. D.; Lovas, F. J.; Pereyra, W.; Fraser, G. T.; Hight Walker, A. R. *J. Mol. Spectrosc*. **1997**, *181*, 67.

(13) Suenram, R. D.; Grabow, J.-U.; Zuban, A.; Leonov, I. *Rev. Sci. Instrum*. **1999**, *70*, 2127.

(14) Ruoff, R. S.; Klots, T. D.; Emilsson, T.; Gutowsky, H. S. *J. Chem. Phys.* **1990**, *93*, 3142.

(15) Van Hemlrijk, D.; Van den Enden, L.; Giese, H. J.; Sellers, H. L.; Schäfer, L. *J. Am. Chem. Soc.* **1980**, *102*, 2189.

(16) Gallinella, E.; Cadioli, B. *Vib. Spectrosc*. **1997**, *13*, 163.

(17) Murcko, M. A.; Castejon, H.; Wiberg, K. B. *J. Phys. Chem*. **1996**, *100*, 16168.

(18) Ponder, J. W. *TINKER: Software Tools for Molecular Design*, Version 3.6; Washington University School of Medicine, 1998.

(19) Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification neither implies recommendation or endorsement by the National Institute of Standards and Technology nor implies that the materials or equipment identified are necessarily the best available for the purpose.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc., Pittsburgh, PA, 1998.

(21) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York, 1977; Vol. 6, p 1.