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Investigation of Conformationally Rich Molecules: Rotational Spectra of Fifteen Conformational Isomers of 1-Octene

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The rotational spectra of 15 conformational isomers of 1-octene have been measured in a molecular beam at a rotational temperature of less than 2 K using a pulsed-nozzle Fourier transform microwave spectrometer. The transition assignments are guided by rotational constant calculations based on moderate-level ab initio theory and on the relative energy minima on the MM3 molecular-mechanics force field. The number of conformers identified is slightly more than 10% of the 131 predicted from the MM3 molecular-mechanics force field of Allinger et al. Fourteen of the observed conformers are identified with 14 of the 15 lowest energy minima predicted from the MM3 molecular-mechanics force field. The observation of such a large number of conformers, with a MM3 calculated energy spread of 365 $\mathrm{cm^{-1}}$ for this subset of 14, is a consequence of the minimal conformational cooling in the molecular-beam expansion. Limiting this cooling are the relatively high barriers separating the conformers compared to the thermal energy, kT, of the preexpansion gas. In some cases, primarily for the higher energy conformers, the need to cross multiple internal-rotation barriers provides an additional bottleneck for conformer relaxation. The rotational spectra furnish values for the principal moments of inertia, which are sensitive to the conformational geometry and can be compared with predictions from future high-level ab initio calculations. Assuming no conformer relaxation in the expansion allows the use of the transition-intensity data to estimate the energy ordering of the conformers.

Introduction

There has been much recent interest in the structure and dynamics of unbranched hydrocarbon chains.[1] Saturated and partially unsaturated hydrocarbon chains, either alone or attached to other functional groups such as in a fatty acid, are an important component of various organic polymers, detergents, and self-assembled monolayers. In addition, they make up the hydrophobic ends of phospholipids that form the lipid bilayers of cellular membranes and aid in the anchoring of proteins to these membranes. Because of their conformational richness and the relative simplicity of their carbon and hydrogen force fields, unbranched alkanes provide simple model systems for the theoretical investigation of molecular conformation.

Critical to the quantitative molecular-level modeling of systems containing hydrocarbon chains is the ability of the intramolecular force field to accurately describe the conformer geometries and energetics. The large number of conformers possible for even small chains makes it difficult to provide both the experimental data and the theoretical results to test the hydrocarbon force field. For saturated, unbranched hydrocarbons, Tasi et al.[2] have theoretically enumerated the conformers using their scaled effective one-electron method (SEOEM) and found 2, 4, 12, 30, 95, 279, 876, and 2691 chemically distinct conformers for *n*-butane through *n*-undecane. (We use chemically distinct to refer to conformers not related by a symmetry operation, such as reflection through a mirror plane or proton interchange.) At present, however, there is no complementary experimental investigation to test the predictive capability of their model.

In principle, rotational spectroscopy could be used to provide structures and relative energies for the various conformers of the *n*-alkanes; however, the electric-dipole moments for these molecules are small to vanishing, making such measurements difficult. Alternatively, a polar functional group can be substituted terminally on the alkane chain to increase the intensity of the rotational spectrum. We have recently been undertaking such investigations by examining the rotational spectra of a series of 1-alkenes and the analogous isoelectronic aldehydes at a rotational temperature of <2 K using a pulsed-molecular-beam Fourier transform microwave spectrometer. We have reported results on two of the alkenes, 1-pentene[3] and 1-hexene.[4] For 1-pentene we observed four of the five conformers predicted by ab initio and molecular modeling calculations, while for 1-hexene we observed seven of the 13 expected conformers. The structures of the two lowest energy conformers of 1-hexene are shown in Figure 1.

The large number of conformers found in these systems, together with their estimated energies from the ab initio and molecular modeling calculations, indicates that there is minimal collisional relaxation of the conformers in the molecular-beam expansion. This result is anticipated from earlier studies[5−9] that, for instance, demonstrated the absence of conformer relaxation in molecular beams when the barrier between the two conformers is greater than approximately 400 $\mathrm{cm^{-1}}$,[6] or about a factor of 2 greater than the thermal energy, kT.

In the present study we report on our investigation of the conformers of 1-octene. Molecular modeling and ab initio electronic-structure calculations predict 131 chemically distinct conformers for this molecule. Using a pulsed-molecular-beam Fourier transform microwave spectrometer and the model calculations for guidance, we have been able to observe and assign the spectra for 15 of these conformers. The identification of the experimental conformers with the theoretical conformers

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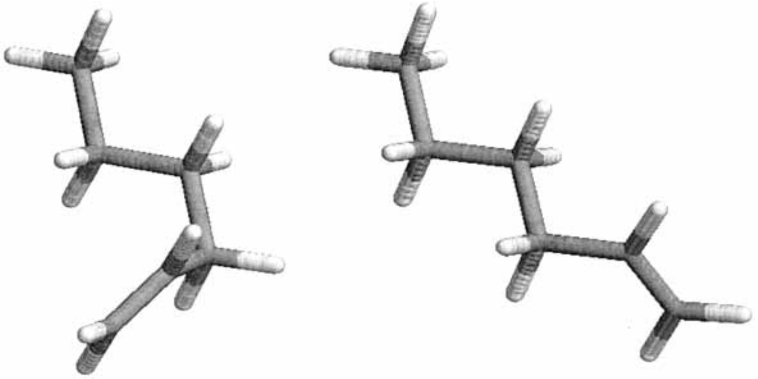

Figure 1. Two lowest-energy conformers for 1-hexene. The two conformers differ primarily by a rotation about the C_2-C_3 and C_3-C_4 carbon−carbon single bonds.

relies on the comparison of rotational constants, inertial defects, and relative intensities. The calculations are not of sufficient quality to provide an exact energy ordering and, indeed, the energy ordering of the two lowest energy conformers predicted by the ab initio calculations is reversed from that predicted by the experimental relative intensities. As an aside, we note that the 15 conformers observed here are by far the most conformers to ever be experimentally observed for a single molecule.

Experimental Section

Rotational spectra were recorded using a Balle-Flygare,[10] pulsed-molecular-beam Fourier transform microwave spectrometer, described previously.[11] Briefly, a molecular beam of a gas sample consisting of approximately 0.5% 1-octene in 20% He in Ne by volume is injected coaxially[12] into a high-*Q* Fabry−Perot microwave cavity using a 1.2 mm diameter nozzle, at a driving pressure of 200 kPa to 400 kPa. A short (≈1 μs) pulse of microwave radiation with center frequency coincident with a TEM_{00} mode of the cavity is injected into the cavity. If the molecules have a transition at a frequency that overlaps the bandwidth of the cavity, which is less than the bandwidth of the microwave pulse, a macroscopic polarization of the gas is induced and the resulting free-induction decay is detected with a super-heterodyne receiver. The signal is digitized, averaged, and then Fourier transformed to obtain an amplitude spectral window. In the frequency domain, a transition appears as a doublet about the true center frequency. The doubling is due to the Doppler effect arising from the two counterpropagating traveling waves making up the standing wave of the cavity, interacting with the coaxial unidirectional molecular beam. A “low-resolution” survey spectrum is obtained by systematically adjusting both the cavity length and microwave frequency and plotting the peak amplitude within the spectral windows as a function of center frequency. Initial broad survey scans were made using 10 nozzle pulses per frequency step of 250 or 500 kHz, depending on frequency, while higher sensitivity survey spectra were made using 100 to 200 nozzle pulses per frequency step. A section of a low-resolution survey spectrum for 1-octene is shown in Figure 2.

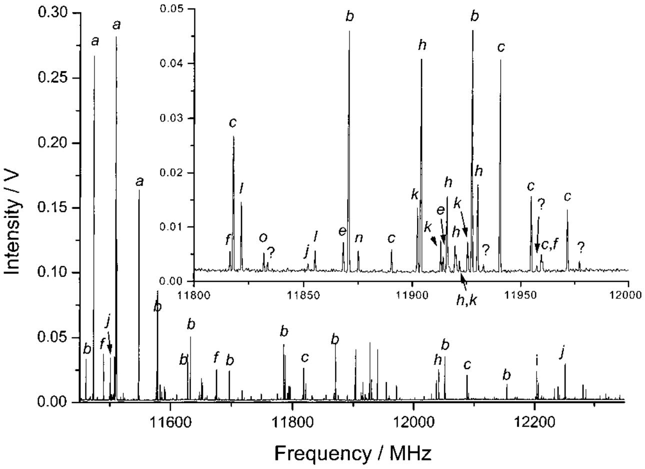

Figure 2. Part of the survey spectrum for 1-octene taken from 11.4 to 12.4 GHz. The lines are labeled a−o to identify the conformer from which they originate in Table 2. In the inset spectrum every line is labeled, with unassigned lines identified by a question mark. Because of space limitations, only the strong lines are labeled in the full 1 GHz spectrum.

Results

Ab Initio and Molecular Modeling Calculations. The primary goal of the ab initio and molecular modeling was to provide approximate rotational constant and conformer relative energy estimates to guide the assignment of the complex microwave spectrum resulting from the overlap of a large number of individual conformer spectra. Estimates of the total number of conformers were first obtained by searching for all the minima of 1-octene using the MM3 molecular-mechanics potential energy surface.[13,14] The search was performed by independently varying all the rotatable dihedral angles in increments of 60°. A step size of 60° was found by Lipton and Still[15] to be sufficient to find all the minima of 1-hexane. For each set of dihedral angles, the energy was minimized using the OPTIMIZE computer program in the molecular modeling package TINKER developed by Ponder and co-workers.[16] This program implements an optimally conditioned, variable-metric method to minimize the energy with respect to the Cartesian coordinates of the nuclei.

For 1-octene, a total of 131 chemically distinct minima were found, only one of which has a plane of symmetry. The relative room-temperature populations of the 131 conformers are shown in Figure 3, normalized to unity for the lowest energy conformer. The populations are estimated by assuming similar rotational partition functions for the conformers and are proportional to $ge^{-E/kT}$, where g is the degeneracy (1 if the conformer has a plane of symmetry, 2 otherwise) and E is the relative conformational energy. In the figure, the conformers are indexed from 1 to 131 in order of increasing MM3 energy. The deviation in the relative population of conformer 4 from the trend is due to the presence of a plane of symmetry, which reduces its degeneracy, and thus its relative population, by a factor of 2. A number of conformers are predicted to have significant room-temperature population. From the plot we find that 22 conform-

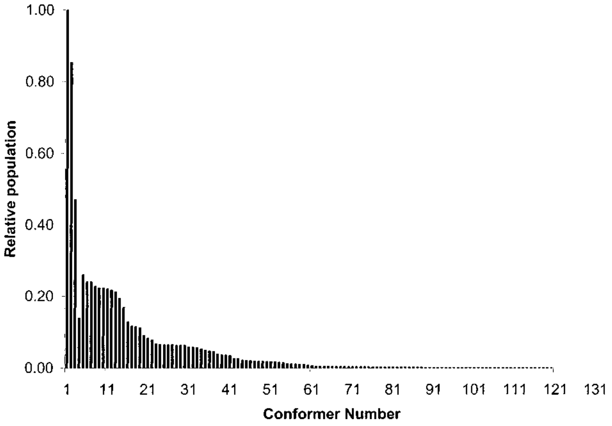

Figure 3. Relative populations of conformers 1−131 using energies from the MM3 potential-energy surface. The relative population is approximated by $g_i \exp(-E_i/kT)$, where g_i is a degeneracy factor of the *i*th conformer, taken as 1 except for conformer 4, which has a plane of symmetry where it is taken as $^1/_2$, E_i is the MM3 energy relative to the lowest energy conformer, and $T = 296$ K.

ers have a relative room-temperature population that is at least 10% of that of conformer 1.

The 131 MM3 configurations were further energy optimized using ab initio electronic-structure theory with a simple MP2 treatment of the electronic correlation energy and a modest 6-31G* basis set, as implemented in Gaussian 98.[17,18] Murcko et al.[19] found that this basis set gives conformer energy-level differences for *n*-butane in good agreement with higher level MP2/6-311++G(df,pd) and MP2/6-311++G(2df,2pd) calculations. To save computer time for the large number of conformations examined, calculations were done with the default convergence criterion set (i.e., no opt=tight). Tests revealed that this setting had minimal, 1−2 MHz, effect on the *A* rotational constant, and insignificant effect on the other rotational constants or conformational energy. The density-functional calculations (B3LYP/6-31G*) discussed later were more sensitive to this option and thus the opt=tight flag was set. Following others,[20] we denote the conformer configuration by the use of t (trans, 180°), g$^{\pm}$ (gauche, ±60°), c (cis, 0°), and s$^{\pm}$ (skew, ±120°) for the five C−C−C−C dihedral angels, starting from the C=C end of the molecule. Note that an equivalent configuration can be obtained by reversing the signs in a configuration. Also, in Table 1, we give the energies, rotational constants, and inertial defects ($\Delta = I_{cc} - I_{bb} - I_{aa}$, where I_{ii} are principal moments of inertia about the $i = a$, b, and c inertial axes) of the 25 lowest energy MM3 minima. The corresponding MP2/6-31G* energies (corrected for vibrational zero-point energy), rotational constants, and inertial defects are also given in the table.

Microwave Spectra. Rotational assignments were made by comparing predicted spectra from the molecular modeling calculations with the observed spectrum, a 1 GHz window of which is shown in Figure 2. Assignments were further facilitated by looking for R-branch, $\Delta K_a = 0$, $\Delta J = \pm 1$ series in the observed spectrum, which are spaced by approximately $B + C$. Typically, *a*-type electric-dipole transitions were assigned first. Fitting of these transitions gave predictions for the *b*-type and *c*-type transitions. Spectra dominated by *b*-type transitions were generally difficult to assign because of the lack of identifiable spectral patterns. We note that most of the assigned conformers had relatively strong *a*-type spectra. A total of 15 distinct rotational spectra could be identified, and these are assigned to 15 different conformers of 1-octene, labeled as a−o. Some of the assigned lines for the conformers are identified in Figure 2. A significant number of weak unassigned lines remain, presumably due to other conformers that we could not identify.

The observed transitions were least-squares fit to the Watson asymmetric-rotor Hamiltonian[21] in the *A*-type, I^r representation, appropriate for prolate rotors such as 1-octene. The rotational constants and quartic distortion constants determined in the fit are listed in Table 2. Typically, if $K_a = 2 - 1$ or higher $\Delta K_a = 1$ progressions were not observed, primarily due to signal-to-noise limitations, the Δ_K constant was indeterminate and constrained to zero in the fit. Likewise, if only $K_a \leq 1$ lines were assigned, both the δ_K and Δ_K constants were indeterminate and fixed to zero in the fit. The quality of the least-squares fits

TABLE 1: Molecular Modeling and ab Initio Rotational Constants and Inertial Defects (Δ) for the 25 Lowest Energy Molecular Modeling Conformers of 1-octene

		molecular modeling (MM3)					Ab initio (MP2/6-31G*)				
no.	configuration	rel energy/cm^{-1}	*A*/MHz	*B*/MHz	*C*/MHz	Δ/u Å^2	rel energy/cm^{-1}	*A*/MHz	*B*/MHz	*C*/MHz	Δ/u Å^2
1	s$^-$tttt	0	9261	527	520	−42.2	0	9666	529	522	−39.8
2	s$^+$g$^-$ttt	33	4596	681	622	−40.7	−59	4689	682	625	−40.1
3	s$^-$g$^-$ttt	155	5835	610	587	−53.0	214	5975	616	591	−49.9
4	ctttt	264	7386	571	541	−19.4	278	7459	579	549	−18.7
5	s$^-$g$^+$g$^+$tt	277	3027	911	780	−74.2	61	2983	949	802	−71.6
6	s$^+$tttg$^+$	293	6478	588	570	−51.2	252	6735	591	572	−47.9
7	s$^-$tttg$^+$	294	7343	578	564	−46.9	250	7514	582	567	−45.2
8	s$^+$tg$^-$tt	304	6271	603	579	−46.1	237	6299	610	585	−44.7
9	S$^+$ttg$^-$t	309	4953	635	593	−45.3	239	5144	637	596	−43.6
10	s$^-$tg$^-$tt	309	4708	652	600	−39.0	219	4873	655	603	−36.7
11	s$^+$ttg$^+$t	311	5756	610	584	−51.0	240	5875	615	588	−47.7
12	s$^+$g$^-$ttg$^+$	314	3229	852	718	−45.7	176	3278	857	722	−43.6
13	s$^-$g$^+$ttg$^+$	320	3499	793	713	−72.9	188	3543	799	718	−70.7
14	s$^-$g$^+$tg$^+$t	337	4601	709	688	−88.3	187	4766	710	690	−85.9
15	s$^-$g$^+$tg$^-$t	365	5930	671	637	−45.0	196	6076	676	641	−42.9
16	s$^+$g$^+$g$^+$tt	422	4159	731	687	−77.4	396	3997	765	711	−76.3
17	s$^-$g$^-$ttg$^+$	443	3904	743	663	−48.1	463	3973	750	669	−45.9
18	s$^+$g$^+$ttg$^+$	445	4665	677	660	−89.0	460	4644	690	668	−84.7
19	s$^+$g$^+$tg$^+$t	451	4479	698	659	−70.5	447	4733	695	663	−71.4
20	s$^+$g$^+$tg$^-$t	496	6672	628	613	−55.5	501	6864	635	618	−52.2
21	cg$^-$ttt	512	4612	703	653	−54.1	557	4691	711	661	−53.6
22	s$^-$g$^+$g$^+$tt	524	2699	1096	873	−69.8	275	2753	1104	892	−74.4
23	ctttg$^+$	557	6343	619	592	−42.3	529	6440	629	600	−39.3
24	s$^-$ttg$^+$g$^+$	561	3853	745	684	−70.4	432	3923	757	695	−68.7
25	s$^+$tg$^+$g$^+$t	565	3035	866	728	−56.1	393	3076	884	741	−54.1

TABLE 2: Spectroscopic Constants for the 15 Observed Conformers of 1-Octene (Standard Uncertainties in Parentheses, As Determined from the Least-Squares Analysis (Type *A* Analysis) of the Frequency Measurements)

no.	A/MHz	B/MHz	C/MHz	Δ_J/kHz	Δ_{JK}/kHz	Δ_K/kHz	δ_J/kHz	δ_K/kHz	σ^a/kHz	$\mu_a, \mu_b, \mu_c{}^b$	Δ/u Å^2
a	9810.11683(73)	526.60750(96)	519.81622(96)	0.01873(11)	−2.3943(18)	169.24(19)	0.000226(57)	−1.03(48)	2.1	70, 11, 7	−39.0
b	4751.5790(18)	673.99928(19)	619.62769(16)	0.09082(47)	−1.3096(41)	21.23(37)	0.01658(21)	0.573(89)	2.3	34, 20, 0	−40.6
c	5967.75582(42)	611.390618(53)	584.340564(50)	0.05821(19)	−3.0518(48)		0.007468(90)		0.7	17, 2, 2	−46.4
d	7481.7321(11)	577.77175(10)	547.489459(93)	0.01736(17)	−0.6846(64)		0.00255(17)		1.0	23, 4, 0	−19.2
e	3022.64313(50)	922.67605(28)	785.56264(28)	0.5558(16)	−2.169(19)	9.115(57)	0.15121(71)	1.744(84)	1.7	0, 23, 0	−71.6
f	6742.62044(83)	588.520210(66)	569.914313(65)	0.03886(24)	−1.944(25)		0.00169(11)		1.0	15, 3, 3	−46.9
g	7543.2(10)	578.90329(32)	564.96981(30)	0.02533(22)	−0.628(12)		0.00239(60)		1.2	21, 0, 0	−45.5
h	6247.904(88)	608.591961(97)	583.221865(91)	0.04405(11)	−2.0467(43)		0.00699(18)		0.3	16, 0, 0	−44.8
i	5198.03310(74)	632.074727(71)	592.479713(53)	0.07872(14)	−3.1134(44)		0.01630(14)		0.5	18, 3, 0	−43.8
j	4854.9889(21)	652.91794(22)	600.33348(19)	0.07525(79)	−2.459(27)		0.01293(39)		2.9	18, 2, 1	−36.3
k	6149.40(21)	607.54228(12)	583.95522(11)	0.07785(19)	−4.0080(82)		0.00843(25)		0.6	19, 0, 0	−48.6
l	3303.62628(32)	843.69534(14)	713.87472(12)	0.23658(73)	−1.1812(87)	5.332(40)	0.05974(35)	0.700(37)	1.1	19, 14, 0	−44.0
m	4673.16(35)	708.68755(18)	687.74168(17)	0.17978(41)	−4.819(16)		0.02728(50)		0.9	16, 0, 0	−86.4
n	6164.2929(17)	668.00924(16)	635.85992(14)	0.06263(27)	−1.4923(86)		0.00806(50)		0.9	19, 3, 0	−43.7
o	4096.258(29)	757.43078(13)	690.992478(93)	0.24488(34)	−4.688(16)		0.05848(36)		0.6	15, 0, 0	−59.2

[a] Standard deviation of the least-squares fit. [b] Number of observed *a*, *b*, and *c* type electric-dipole transitions.

is high, as judged by the standard deviations, σ, of the fits of 0.6−2.9 kHz, which are close to the estimated standard uncertainties on the line positions of 1−2 kHz. The small values for σ and the large number of degrees of freedom in the fits, i.e., number of observed lines minus number of fitted parameters, of between 9 and 80, makes it highly unlikely that the quantum-state labels are incorrect. Furthermore, all the fits were validated by demonstrating their ability to correctly predict a previously unobserved transition within several kilohertz of observation.

There are a couple observations about the constants listed in Table 2 that are of interest. First, we see that conformer a has the largest *A* rotational constant of the 15 observed conformers, suggesting that it has the most elongated structure. Conformer d, on the other hand, has the smallest inertial defect of the group, $\Delta = -19.2$ u Å^2. This value for the inertial defect indicates that the heavy atoms of conformer d lie in a plane; i.e., the conformer has a plane of symmetry. The absence of any *c*-type transitions is consistent with a plane of symmetry for this conformer.

Discussion

The identification of the 15 experimentally characterized conformers with the 131 predicted conformational minima is based on the measured relative intensities and comparisons of the observed and calculated rotational constants and inertial defects. The measured relative intensities and predicted isotopic shifts indicate that none of the observed conformers can be attributed to an isotopic variant of one of the higher intensity conformers. Also, the significant rotational constant differences between the conformers effectively rules out the possibility that one or more of the observed conformers are vibrational hotbands of the other conformers. The possibility of different methyl-top internal-rotor states being responsible for the large number of observed conformers is also ruled out. Internal-rotation splittings, which scale with the magnitude of the rotational constants assuming a fixed internal-rotation barrier height, are expected to be the greatest for 1-pentene, in the series 1-pentene through 1-octene. In the case of 1-pentene, however, the splittings are only of the order of 100 kHz. For 1-octene, we do attribute some line broadening, most apparent on *b*- or *c*-type transitions, to unresolved methyl internal-rotation tunneling splittings. Finally, we have also explored the possibility of contamination of the spectra from other octenes, such as *cis*- and *trans*-2-octene, which would have rotational constants similar to those of 1-octene. Spectra recorded for 2-octene revealed that none of the assigned conformers could be attributed to this species. Moreover, the methyl top associated with C1 gives resolvable and easily identifiable internal-rotation splittings, which were not seen in the present 1-octene spectrum.

We will now present some of our justifications for the identification of the experimentally observed conformers a−o, with the theoretically predicted conformers 1−131, labeled by increasing MM3 energy. Conformer a has the most intense spectrum of the experimentally identified conformers. Additionally, it has the largest *A* rotational constant. The MM3 and experimental *B* and *C* rotational constants agree with each other to three significant digits, although the *A* rotational constant and inertial defect do not agree as well. The ab initio inertial defect for this minimum is in much better agreement with experiment. These observations lead us to unambiguously assign conformer a with MM3 conformer 1. We note (see Table 1) that the MP2/6-31G* energy for conformer 1 is 59 cm^{-1} higher than that of conformer 2. The structure of conformer a is built from the lowest energy conformer for 1-hexene, shown in Figure 1a, by continuing for carbons 7 and 8 of 1-octene the zigzag trans−trans alkane pattern established for carbons 3−6 of 1-hexene.

Conformer b has the second most intense spectrum of the series a−o. The rotational constants and inertial defect are in good agreement with the predictions for conformer 2 from the MM3 force field, although the *B* and *C* constants do not agree as closely as in the case of MM3 conformer 1 and experimental conformer a. Upon examining the rotational constants and inertial defects for the 25 MM3 minima listed in Table 1, it is clear that the best agreement is obtained between MM3 conformer 2 and experimental conformer b. We note that the MP2/6-31G* basis set gives MM3 conformer 2 as the absolute minimum. However, it should be noted that this level of theory may not be as reliable for energy differences as it is for geometries and dipole moments. Analogous to conformer 1 or a, the structure for conformer 2 or b is obtained by extending the zigzag alkane pattern for the hexene conformer shown in Figure 1b. We note that the relative energy ordering for the two lowest energy conformers of 1-octene, as inferred by the MM3 force field and experiment, is similar to that observed for 1-hexene; i.e., the energy for the Figure 1a conformer is less than that of the Figure 1b conformer. The MP2/6-31G* energy ordering for the two 1-hexene conformers in the figure is likewise reversed from the experimental and MM3 results.

As noted previously, conformer d has a small inertial defect of −19.2 u Å^2, which implies that the minimum has a plane of symmetry. The molecular modeling calculations indicate that

TABLE 3: Comparison of the Experimental, MM3, and ab Initio Calculated Rotational Constants (*A*, *B*, and *C*) and Inertial Defects (Δ)

observed					molecular modeling (MM3)					ab initio (MP2/6-31G*)			
label	*A*/MHz	*B*/MHz	*C*/MHz	Δ/u Å^2	no.	*A*/MHz	*B*/MHz	*C*/MHz	Δ/u Å^2	*A*/MHz	*B*/MHz	*C*/MHz	Δ/u Å^2
a	9810	527	520	−39.0	1	9261	527	520	−42.2	9666	529	522	−39.8
b	4752	674	620	−40.6	2	4596	681	622	−40.7	4689	682	625	−40.1
c	5968	611	584	−46.4	3	5835	610	587	−53.0	5975	616	591	−49.9
d	7482	578	547	−19.2	4	7386	571	541	−19.4	7459	579	549	−18.7
e	3023	923	786	−71.6	5	3027	911	780	−74.2	2983	949	802	−71.6
f	6743	589	570	−46.9	6	6478	588	570	−51.2	6735	591	572	−47.9
g	7543	579	565	−45.5	7	7343	578	564	−46.9	7514	582	567	−45.2
h	6248	609	583	−44.8	8	6271	603	579	−46.1	6299	610	585	−44.7
I	5198	632	592	−43.8	9	4953	635	593	−45.3	5144	637	596	−43.6
j	4855	653	600	−36.3	10	4708	652	600	−39.0	4873	655	603	−36.7
k	6149	608	584	−48.6	11	6271	603	579	−46.1	6299	610	585	−44.7
l	3304	844	714	−44.0	12	3229	852	718	−45.7	3278	857	722	−43.6
m	4673	709	688	−86.4	14	4601	709	688	−88.3	4766	710	690	−85.9
n	6164	668	636	−43.7	15	5930	671	637	−45.0	6076	676	641	−42.9
o	4096	757	691	−59.2	28	4188	738	678	−59.8	4119	761	695	−59.3

only one of the 131 MM3 minima, number 4, has a plane of symmetry. These observations allow us to make the association of MM3 conformer 4 with experimental conformer d. Consistent with this identification, the rotational constants are also similar for d and 4 as well.

For the remaining set of experimentally observed conformers, the relative intensity information is not as striking, so that the identification of the experimental conformers with the MM3 conformers will be based on the observed rotational constants and inertial defects. It is clear that anyone using these criteria will come up with results similar to what has been obtained in Table 3.

The main concern with the assignments given in Table 3 is associated with the identification of experimental conformer o. The lowest energy MM3 conformer that we could identify with o is number 28, with a MM3 relative energy of 569 cm^{-1} and a MP2/6-31G* relative energy of 422 cm^{-1}. This assignment appears unlikely since we have not been able to identify MM3 conformers 16−27 in the spectrum, although we note a number of unassigned lines remain. We note, though, that the relative room-temperature population for this conformer based on the MM3 energies is only a factor of 2−4 less than that predicted for conformers 6−20. Most striking for this conformer is the similarity between the MP2/6-31G* and experimental values. The possibility that the spectrum of o is due to an impurity, such as 2-octene, has also been considered, as discussed previously when we pointed out that none of the absorptions could be identified with lines from *cis*- or *trans*-2-octene. Additionally, the stated purity of the 1-octene sample of 98% makes it unlikely that contaminants are responsible for any of the conformer signals.

Since the assignments are heavily guided by the molecular modeling and ab initio calculations it is interesting to examine some of the theoretical results in detail. For the 50 lowest energy MM3 conformers, the MP2/6-31G* ab initio energies, after correcting for the zero-point vibrational energy, are systematically lower than the MM3 energies by approximately 93 cm^{-1}. We note that Allinger et al.[14] comment in their work on the extension of the MM3 force field to alkenes that the MM3 barrier between the two gauche conformers of 1-butene is 2.11 kcal/mol, compared to the experimental value of 1.73 kcal/mol. Likewise, they note that the MM3 barrier to internal rotation for propene is 1.74 kcal/mol, compared to the experimental value of 1.994 kcal/mol. The observations of Allinger et al.[14] suggest a tendency for the MM3 force field to overestimate the relative energy minima and maxima of 1-alkenes for rotation about the C−C bond neighboring the C═CH$_2$ group. These numbers can be contrasted with the case of ethane, where Allinger et al.[13] noted that the MM3 barrier to internal rotation is 2.41 kcal/mol compared to the higher experimental value of 2.88 kcal/mol.

TABLE 4: Rotational Constants, Inertial Defects, and Relative Conformation Energies for 10 Conformers of 1-Octene As Calculated from Density-Functional Theory (B3LYP/6-31G*)

conformer no.	*A*/MHz	*B*/MHz	*C*/MHz	Δ/u Å^2	rel energy/ cm^{-1}
1	9892.26	519.98	513.18	−38.2	0
2	4776.45	660.38	608.60	−40.7	105
3	6159.53	597.79	575.16	−48.8	345
4	7495.55	570.53	540.77	−18.7	263
5	3101.78	868.06	751.40	−72.5	405
6	6737.18	580.08	561.91	−46.8	343
7	7595.59	570.03	556.55	−45.1	317
8	6297.98	597.68	573.72	−44.9	327
9	5174.56	622.85	584.28	−44.1	334
10	4900.43	639.75	589.86	−36.3	314

To further explore the relative energy differences for the few lowest energy conformers through a more complete treatment of electron correlation, we have also undertaken density-functional calculations using the standard B3LYP functional with a 6-31G* basis set. Because of the lack of intramolecular hydrogen bonding in these systems, density-functional calculations are expected to have a high degree of reliability. Rotational constants, inertial defects, and relative conformational energies form the density-functional calculations (B3LYP/6-31G*) for the conformers 1−10 are listed in Table 4. As seen by comparing the results in Tables I, III, and IV, the density-functional rotational constants are also in reasonable agreement with experiment. The *B* and *C* rotational constants appear to be systematically lower than the MM3, MP2/6-31G*, and experimental values. Additionally, we see that both the density-functional calculations and the MM3 potential energy surface give the correct energy ordering of conformers 1 and 2. Of course, energy differences between the conformers are small, and are not expected to be accurately predicted by any of these models. It is clear, however, that to reliably predict the conformational processes in bigger systems, such as biomolecules, where the force fields are significantly more complex, it is critical to understand the ability of the various models to correctly estimate relative conformational energies.

The ability to observe a variety of conformers in the present study is due to the lack of collisional relaxation of the large number of room-temperature thermally populated conformational minima in the molecular-beam expansion. Moreover, the small cross sections for collisional relaxation are a consequence of the relatively high barriers between the conformational minima, the large reduced mass associated with the torsional motion necessary to cross the barriers, and the small transition-dipole matrix elements for torsional excitation. The torsional reduced mass is greatest for the torsional coordinates in the middle of the hydrocarbon chain. The large reduced masses give rise to low frequencies for the torsional vibrations, increasing the number of vibrational quantum, as well as the energy, that must be exchanged (primarily with the translational and rotational degrees of freedom in the gas expansion) to cross the rotational isomerization barriers. Examination of the lowest 10 minima (1−10) reveals that most of these conformers can relax to the conformational minimum (number 1), by a single approximately 120° rotation about a C−C single-bond dihedral angle. Indeed, only one of these conformers, number 5, requires rotation about two dihedral angles. These observations suggest that the lower energy conformers do not collisionally relax through several conformational isomers on the way to the conformational minimum. The collisional relaxation bottleneck of having to sample several conformational minima is only operative for the higher energy conformers, which have reduced thermal population in the room-temperature preexpansion gas.

The ability to use molecular beams to study conformationally rich systems at quantum-state resolution offers many opportunities, some of which have been explored for systems that only display a few conformers. Such studies include the investigation of the electronic spectra of conformers,[22] the trapping of conformers in liquid-He droplets,[23] and the spectroscopic investigation of the matrix elements coupling different conformers in vibrationally excited states.[24] We hope the present study, with the myriad of conformers observed, will provide a new tool for the investigation of rotational isomerization that may improve our understanding of conformational processes important in biomolecules, polymers, and other conformationally rich systems. In particular, we hope that the present study will motivate higher quality theoretical calculations, which will provide a more meaningful comparison with experiment than the present calculations.

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