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The Substituted Alkyne 3-Heptyne is Eclipsed

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Although butane exists in staggered anti and gauche conformations, when the ethyl groups are separated by a C≡C triple bond (3-hexyne), the stable conformation changes to eclipsed,[1] C_{2v}. Using rotational microwave spectroscopy, we have studied another example, 3-heptyne, the C≡C elongated analogue of pentane. The most stable conformer of pentane has anti−anti (AA) conformations about the central C−C bonds (C_{2v}) and the next most stable has a gauche dihedral angle (GA, C_1). This microwave study determines that the extended analogue of the AA form is not staggered about the C≡C axis but eclipsed (C_s). Also, the elongated analogue of the GA conformer is also not staggered but nearly eclipsed. The conformations of low-polarity substituted acetylenes is determined by dispersion attractions between the end groups. A microwave study of the AA and GA conformers of pentane is also reported.

I. Introduction

Alkanes have staggered equilibrium structures. A consensus about the nature of the interactions favoring eclipsed over staggered forms remains elusive. In the case of ethane, a recent paper[2] emphasizes stabilization of the staggered form due to hyperconjugation between a C−H bonding orbital and the trans vicinal C−H antibonding orbital. That publication revived the discussion of the origin of the ethane barrier and prompted vigorous debate.[3−7] One group of authors[2−4,6] supports the hyperconjugation explanation, and other groups[5,7] favor a steric hindrance model. The most recent study,[7] using ab initio valence bond theory which formulates hyperconjugation differently, concludes that steric effects make the dominant contribution to the barrier in ethane and hyperconjugation interactions contribute about one-third of the barrier height. The controversy remains.

A distinguishing feature of the hyperconjugation and steric models is that hyperconjugation is sensitive to both separation and orientation of the interacting orbitals but steric interactions are sensitive only to separation. Butane is an analogue of ethane existing in anti and gauche conformations[1] consistent with the staggered conformation of ethane. In a previous study, we separated the two ethyl groups of butane by −C≡C− (3-hexyne, $CH_3-CH_2-C{\equiv}C-CH_2-CH_3$, or diethyl acetylene) and found that the compound has an eclipsed, C_{2v} structure. The ethyl groups in 3-hexyne have been separated by an additional 2.65 Å compared to butane, beyond the sums of the van der Waals radii between the atoms of the ethyl groups, and they take up an eclipsed configuration. Extensive ab initio calculations[9] support that model. In the elongated form of butane, which is 3-hexyne, any conformational control by hyperconjugation has disappeared. The steric/exchange repulsion from the close proximity of the ethyl groups in butane has also disappeared and been replaced by weak dispersion attraction.

In this study, we present another test of the results described for butane (anti and gauche staggered conformations) elongated to 3-hexyne (syn-eclipsed conformation). Pentane contains two central C−C bonds with anti (A) or gauche (G) configurations including AA, AG, GGtrans, and GGcis staggered conformations. We propose separating the ethyl and propyl groups which make up pentane by −C≡C− to form 3-heptyne ($CH_3-CH_2-C{\equiv}C-CH_2-CH_2-CH_3$ or ethyl propyl acetylene) (see Figure 1). In this compound, the ≡C−C−C−C dihedral angle is expected to exist in anti and gauche configurations. Determination of the structure of 3-heptyne will test whether the syn-eclipsed result in 3-hexyne is a general one (anti propyl form), and it will examine a new example when the opposing groups are asymmetrical (gauche propyl form).

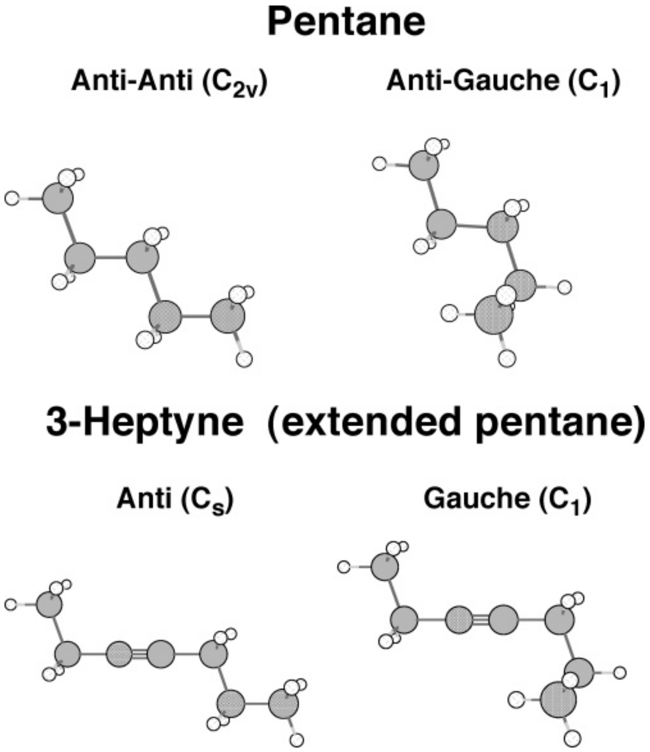

Figure 1. The two lowest-energy conformers of pentane and their formal C≡C elongated analogues in 3-heptyne.

The triple bond in acetylene is cylindrically symmetrical and thus has no barrier to internal rotation. Groups bonded to each end of the triple bond change that slightly. The few acetylenes

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TABLE 1: Assigned Frequencies of the Two Conformers of 3-Heptyne

J'	K_p'	K_o'	$\leftarrow J''$	K_p''	K_o''	C_s freq/MHz	C_s (obsd − calcd) /kHz	C_1 freq/MHz	C_1 (obsd − calcd) /kHz
						b-type			
1	1	1	0	0	0	8902.5510	−0.6		
2	1	2	1	0	1	10508.9978	−6.7	7795.2418	−2.1
3	1	3	2	0	2	12084.9334	6.8		
4	1	4	3	0	3	13630.8091	1.7		
5	1	5	4	0	4	15147.4340	−0.4	13256.9807	0.8
6	1	6	5	0	5	16635.8895	−4.6	14960.5120	1.1
7	1	7	6	0	6	18097.5750	2.3	16635.8895	1.7
5	0	5	4	1	4			7703.7808	2.5
7	0	7	6	1	6			12518.6360	0.2
8	0	8	7	1	7			14895.9769	−0.4
9	0	9	8	1	8			17232.1414	−0.9
2	2	0	1	1	1			15650.3790	−0.3
2	2	1	1	1	0			15468.7910	0.5
3	2	2	2	1	1			17447.9829	−2.8
1	1	0	1	0	1	7296.1608	2.4		
2	1	1	2	0	2	7358.0104	−3.3		
3	1	2	3	0	3	7451.5183	2.6		
4	1	3	4	0	4	7577.5262	1.0		
5	1	4	5	0	5	7737.1863	1.9		
6	1	5	6	0	6	7931.9049	−5.9		
7	1	6	7	0	7	8163.3879	1.7		
8	1	7	8	0	8	8433.5412	1.8	7783.7148	1.2
9	1	8	9	0	9	8744.5200	−0.8	8989.7286	2.2
2	2	1	2	1	2			11510.4222	4.2
3	2	2	3	1	3			11777.3802	−0.3
4	2	3	4	1	4			12135.3966	2.8
5	2	4	5	1	5			12585.8402	1.0
6	2	5	6	1	6			13129.9839	−1.7
7	2	6	7	1	7			13768.7277	−1.8
8	2	7	8	1	8			14502.3292	−1.2
9	2	8	9	1	9			15330.1736	1.7
10	2	9	10	1	10			16250.5718	−1.4
4	2	2	4	1	3			10473.9001	−3.3
11	3	8	11	2	9			16591.8416	0.0
						c-type			
5	1	4	4	0	4			15884.4204	−3.0
2	2	0	1	1	0			15474.9450	1.1
9	2	8	9	1	8			7560.4846	1.9
10	3	8	10	2	8			16878.8477	0.0

whose torsional barriers have been determined have barriers ranging from 2.2(1) cm^{-1} in tetrolyl fluoride[10] ($CH_3C{\equiv}CCOF$) to 10.1(1) cm^{-1} in 1-chloro-2-butyne[11] ($CH_3C{\equiv}CCH_2Cl$). These compounds and the few others so far characterized all involve threefold rotation of methyl groups. More massive rotating groups quench tunneling splittings, but we have observed obvious tunneling splittings of several megahertz in spectra of ethyl phenyl acetylene and isopropyl phenyl acetylene.[12] Tunneling splittings only occur with multiple equivalent minima (three in the case of methyl groups and two for phenyl). 3-Heptyne will not have multiple equivalent minima independent of the barrier height, so tunneling is not an issue. We have studied one substituted acetylene with a twofold barrier which does not display resolvable tunneling splittings, phenyl formyl acetylene,[12] but we believe this compound has a fairly large internal rotation barrier because of conjugation effects between the carbonyl and phenyl groups which are transmitted through the $C{\equiv}C$ triple bond.

We and other groups have studied several compounds which contain the $-C{\equiv}C-$ group in the alkyl chain $\equiv C-C_\alpha-C_\beta-C_\gamma-$. In all cases, the gauche configuration about the $C_\alpha-C_\beta$ bond is as stable or more stable than the anti configuration. This effect can be interpreted as a weak dispersion attraction between the π electrons of the triple bond and the methyl or methylene group in the γ position. The same effect occurs when $N{\equiv}C$ replaces $C{\equiv}C$. This gauche stabilization is seen in 1-pentyne[13−18] ($HC{\equiv}C-CH_2-CH_2-CH_3$), butyronitrile[19−21]($N{\equiv}C-CH_2-CH_2-CH_3$), 1-hexyne[22] ($HC{\equiv}C-CH_2-CH_2-CH_2-CH_3$), pentanenitrile[23,24]($N{\equiv}C-CH_2-CH_2-CH_2-CH_3$), 5-hexynenitrile[24]($N{\equiv}C-CH_2-CH_2-CH_2-C{\equiv}CH$), 1,6-heptadiyne[25] ($HC{\equiv}C-CH_2-CH_2-CH_2-C{\equiv}CH$), and 4-methyl-1-pentyne[26]($HC{\equiv}C-CH_2-CH(CH_3)_2$). Other examples of CH/$\pi$ attractive interactions involving π electrons of aromatic rings and $C{=}C$ double bonds have been recently reviewed by Nishio.[27]

Pentane is the benchmark compound for 3-heptyne. A search of the chemical literature did not reveal any microwave spectroscopic study of its structure. We carried out a study of pentane as well.

II. Experimental Section

A sample of 3-heptyne was purchased from GFS Chemicals. No significant impurity was detected by NMR. A 2 L tank was evacuated, 0.3 g (0.003 mol) of sample was distilled into it, and then it was filled to 4 atm with first-run neon (∼75% Ne/∼25% He) or pure He as the carrier gas. The vapor pressure of the sample is 9 Torr at room temperature. Pulses of this 0.3% mixture at 1 atm were fed at 5 s^{-1} into the pulsed jet Fourier transform microwave spectrometer[28] of the Southern New

TABLE 2: Spectroscopic Constants Derived from the Rotational Spectra of 3-Heptyne and Pentane

parameter	3-heptyne C_s	3-heptyne C_1	pentane C_{2v}	pentane C_1
A/MHz[a]	8099.325(4)*	4826.477(2)	16898.038(4)	11658.7534(8)
B/MHz	864.594(6)	1165.0310(2)	1944.6407(12)	2287.6459(3)
C/MHz	803.1954(19)	989.5941(2)	1844.5191(14)	2114.3980(3)
Paa/uÅ2	575.67	419.89	251.98	208.29
Pbb/uÅ2	53.54	90.81	22.01	30.72
Pcc/uÅ2	8.86	13.9	7.90	12.62
DJ/kHz	0.40(4)	0.661(2)	0.337(15)	0.618(7)
DJK/kHz	−16.9(10)	−2.48(2)		−3.55(4)
DK/kHz		15.0(5)		
d1/kHz	−0.121(30)	−0.1893(6)		−0.111(4)
d2/kHz		0.0184(6)		−0.016(6)
HK/kHz		−0.70(4)		
h3/kHz		0.000101(2)		
κ	−0.9832	−0.9086	−0.9867	−0.9637
no. lines	16	28	9	23
StdDev/kHz	5.6	2.3	6.0	2.2

[a] Values in parentheses are 1 std dev in the last printed digit.

England Microwave Consortium.[29] Rotational transitions were observed between 7 and 19 GHz, although the complete spectral range was not scanned. The rotational temperature of the expanded gas is estimated to be ~2 K.

Pentane was purchased from Aldrich Chemical Co. To an evacuated 4 L bulb was added 1.5 g pentane and 6.3 atm of first-run Ne to give a 2% sample mixture. Other experimental conditions used in the study of pentane were the same as for 3-heptyne. Measured rotational frequencies are estimated to be accurate to <2 kHz.

III. Results

3-Heptyne. A molecular structure model for 3-heptyne was extrapolated from a structure adjusted to fit the rotational constants of 3-hexyne.[1] The important parameters are 1.196 Å, 1.454 Å, 1.523 Å, and 1.09 Å for the C≡C, ≡C−C, aliphatic C−C, and C−H bond lengths, respectively, and 112.8° for bond angle C−C−C coupled with ≡C−C−C−C dihedral angles of 60° or 180° for the gauche and anti conformations of the propyl group. Rotational constants calculated for 3-heptyne with the gauche conformation of the propyl group predicted an intense pair of b-type transitions, $2_{21}-1_{10}$ and $2_{20}-1_{11}$, between 15 and 16 GHz separated by ~200 MHz. Strong lines seen at 15 468 and 15 650 MHz matched that expectation. The model also predicted an intense $6_{16}-5_{05}$ line about 500 MHz lower frequency. Assigning the observed line at 14 960 MHz to that transition produced a fit that predicted several other lines which had already been observed. A total of 28 lines, 24 b-type and 4 c-type, were measured, assigned, and fit by three rotational constant and seven centrifugal distortion constants of a conventional Hamiltonian[30] to a standard deviation of 2.3 kHz. The spectral assignment is shown in Table 1 and the derived spectral constants in Table 2. The observation of c-type transitions indicates that this structure cannot have C_s symmetry because the c-dipole of such a structure would be zero.

Assigning the second conformer was much more challenging. The transitions of this species are less intense than those of the first species assigned. The line at 15 147 MHz was the strongest remaining unassigned line. Rotational constants from the model described above but rotated into the C_s conformation predicted the most intense line of the C_s conformer, $5_{15}-4_{04}$, near 15 GHz, and this assignment was tentatively made. A weak line at 10 508 MHz was consistent with the expected corresponding R-branch line, $2_{12}-1_{01}$. A pair of weak lines at 7296 and 7451 MHz lay reasonably close to the expected Q-branch lines, $1_{10}-1_{01}$ and $3_{12}-3_{03}$. That assignment was valid and predicted other lines which were observed and measured. A total of 16 b-type lines were measured, assigned, and fit by three rotational constants and three centrifugal distortion constants of a conventional Hamiltonian[30] to a standard deviation of 5.6 kHz. The assignment is shown in Table 1 and the derived spectroscopic constants in Table 2.

Studies of other compounds containing the ≡C−C−C−C chain described above suggest that the anti and gauche conformations in 3-heptyne should have comparable energies. Although the C_s conformer has generally less intense transitions than the C_1 form, that may be due to a smaller dipole moment rather than a lower population, and our data provides no useful information about the relative energies.

A few unassigned lines were observed, all quite weak.

Pentane. Pentane can exist in four possible staggered conformations: anti−anti (AA, C_{2v} symmetry), anti−gauche (AG, C_1), gauche−gauche trans (GGtrans, C_2), and gauche−gauche cis (GGcis, C_s). The GGcis conformer is extremely crowded and was ignored. An electron diffraction study of a series of alkanes concluded that a gauche kink adds 0.6 kcal/mol to its room-temperature free energy[31] on average. That predicts a room-temperature composition for pentane of 51%, 36%, and 13% for the AA, AG, and GGtrans conformers, respectively, accounting for degeneracy. An MP2/6-311++G-(2d,2p) calculation predicted 0.55 kcal/mol higher energy for the gauche C_1 form than the C_{2v} form, in excellent agreement with the empirical value.

Alkanes are generally considered to be nonpolar, but most have small dipole moments sufficiently large to allow observation of rotational spectra. Propane's dipole moment, 0.085 D, is directed along its *b* principal axis.[32] We expect similar dipole moment values in pentane. A low-level ab initio calculation at the HF/6-31G(d,p) level estimates the b dipole moment value of 0.06 D for both the AA (C_{2v}) and GGtrans (C_2) conformers and 0.03, 0.02, and 0.03 D values along the *a*, *b*, and *c* axes of AG (C_1) pentane, respectively.

We initially attempted to assign the AA conformer (b-type selection rules) without success. Once we observed the transitions between 17 and 18 GHz and noted that they appear like an a-type R-branch pattern of the AG (C_1) conformer, assignment was trivial. We observed 23 lines (10 a-type, 5 b-type, and 8 c-type) which were fit to 3 rotational constants and 4 centrifugal distortion constants to a standard deviation of 2.2 kHz.

Once the lines of that conformer were assigned, a molecular model was adjusted to fit the spectrum. That AG model was converted to an AA model and the b-type Q-branch transitions of the AA (C_{2v}) conformer were predicted between 15 and 16 GHz. They were quickly found, although they are less intense than the transitions of the C_1 conformer. A search from 18 700 to 18 800 MHz revealed the 18 742 line as a candidate for the 111−000 transition. Fitting the first three Q-branch lines around 15 050 MHz with the 18 742 MHz line predicted the rest of the spectrum. The remaining lines were found with very short 1−2 MHz scans about the predicted frequencies. The nine measured lines are the most intense lines for this species at ~2 K, and we did not attempt to integrate over many more shots to measure weaker lines. All of the observed transitions (except 7375 MHz) appear as barely resolved triplets, doublets, or broadened lines consistent with internal rotation splittings of terminal methyl groups with barriers near 3 kcal/mol. We did not analyze this fine structure but merely selected the most

TABLE 3: Assigned Transitions of the AA (C_{2v}) and AG (C_1) Conformers of Pentane.

						C_{2v}		C_1	
J'	K_p'	K_o'	$\leftarrow J''$	K_p''	K_o''	freq/MHz	(obsd − calcd) /kHz	freq/MHz	(obsd − calcd) /kHz
						a-type			
2	0	2	1	0	1			8801.6871	−0.9
2	1	1	1	1	0			8977.3224	−4.0
2	1	2	1	1	1			8630.8356	−2.1
3	1	3	2	1	2			12944.7483	−0.5
3	1	2	2	1	1			13464.4482	0.1
4	0	4	3	0	3			17584.2502	3.2
4	1	4	3	1	3			17256.8812	2.0
4	1	3	3	1	2			17949.1634	1.8
4	2	3	3	2	2			17606.2829	−0.4
4	2	2	3	2	1			17630.0452	−0.5
						b-type			
1	1	1	0	0	0	18742.5558	−0.8	13773.1554	−1.1
2	1	2	1	0	1			18001.9523	−0.5
2	0	2	1	1	1	−7375.5833	7.2		
6	0	6	5	1	5	8450.5397	−7.8		
7	0	7	6	1	6	12515.8502	4.8		
1	1	0	1	0	1	15053.5212	1.5	9544.3622	0.1
2	1	1	2	0	2	15154.1410	−1.4	9720.0030	2.4
3	1	2	3	0	3	15306.0204	5.4	9987.8962	−4.2
4	1	3	4	0	4	15510.2634	1.9		
5	1	4	5	0	5	15768.3722	−2.5		
						c-type			
1	1	0	0	0	0			13946.4056	2.1
6	0	6	5	1	4			15505.6702	−1.5
1	1	1	1	0	1			9371.1145	−0.6
2	1	2	2	0	2			9200.2651	0.2
3	1	3	3	0	3			8948.4652	−0.2
4	1	4	4	0	4			8621.0975	−0.1
5	1	5	5	0	5			8225.3248	−0.9
6	1	6	6	0	6			7770.0354	1.3

intense component of each transition for the fit shown in Table 3. Nine lines were measured and fit to a standard deviation of 6.0 kHz using only the rotational constants and one centrifugal distortion constant. The assigned transitions for both conformers are listed in Table 3 and the spectral constants in Table 2. We did not search for lines of the GGtrans conformer. Except for the continuous 17−18 GHz scan, the remaining spectral observations on pentane covered only spotty intervals of the 7−19 GHz range. All lines observed were assigned.

IV. Discussion

Pentane. Since pentane is a small molecule with correspondingly large rotational constants, only a limited number of transitions are accessible in the 7−19 GHz range with the sample cooled to ∼2 K. The identity of the C_{2v} (AA) conformer is unambiguous. Its symmetry allows only a b-dipole moment, and only b-type transitions were found. Since only nine lines were observed, we chose to fit the data with only the three rotational constants and a single centrifugal distortion constant, D_J, with an rmsd of 5.6 kHz. This could be reduced to 2 kHz, our estimated experimental uncertainty, by adding a few more centrifugal distortion constants, but we chose not to do so because of the small data set. The second moment, P_{cc}, includes only contributions from the five pairs of H atoms extending out of the ab plane. Its value, 7.90 uÅ^2, corresponds to an average contributions of 1.58 uÅ^2 per H-atom pair. A survey of such values for a host of compounds shows the range to be 1.45 to 1.82 uÅ^2 for a pair of H atoms out of the plane of otherwise heavy-atom-planar structures,[33] the larger values occurring in less rigid compounds. The rotational constants for this conformer are consistent with values predicted from model structures.

The GA conformer of pentane is similarly unambiguously identified. The GA conformer is the only possible conformer with C_1 symmetry, with the others having C_{2v}, C_2, or C_s symmetry. Only C_1 symmetry allows nonzero dipole moment components along all three principal axes. Transitions obeying a-, b-, and c-type selection rules were observed and assigned. The rotational constant values are consistent with those predicted from model structures.

3-Heptyne. One conformer of 3-heptyne has a heavy-atom-planar structure with C_s symmetry for the following reasons. The P_{cc} second moment, 8.86 uÅ^2, is only slightly larger than the value in C_{2v} pentane, 7.90 uÅ^2, consistent with the fact that 3-heptyne has a much larger out-of-plane torsional amplitude due to the very small torsional barrier about $C\equiv C$. This is similar to the result found in 3-hexyne (four pairs of H atoms out of the plane) where P_{cc} is 7.31 uÅ^2 for the planar C_s form vs the value 6.39 uÅ^2 in AA 1-fluorobutane,[34] for example. Only b-type transitions were observed. A C_s structure can have a- and b-dipole moment components but no c dipole moment. No c-type transitions were found. We were unable to find a-type transitions probably because the a-dipole in 3-heptyne (ethyl propyl acetylene) is very small. The *a*-axis is almost parallel to the $C{-}C{\equiv}C{-}C$ axis. The rotational constants of the C_s conformer are very different from any other possible conformer and agree with rotational constant values predicted from model structures with an anti configuration of the propyl group. If the configuration were nonplanar, there would be a symmetrical torsional minimum for the mirror image form. These forms would present a double minimum in the torsional potential and tunneling perturbations would be evident. They are not present. There is also the possibility of a heavy-atom-planar C_s structure with the ethyl and propyl groups anti to each other rather than

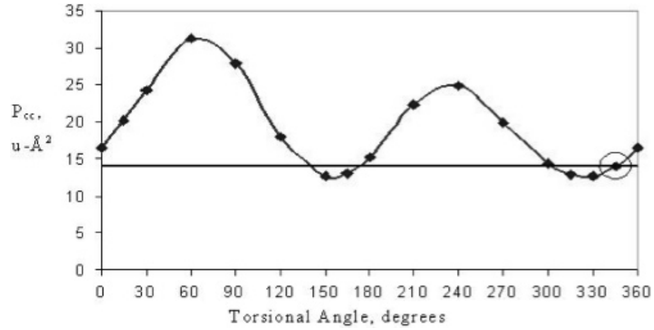

Figure 2. The second moment, P_{cc}, as a function of rigid rotation of a gauche propyl group vs an ethyl group about the C−C≡C−C axis of 3-heptyne.

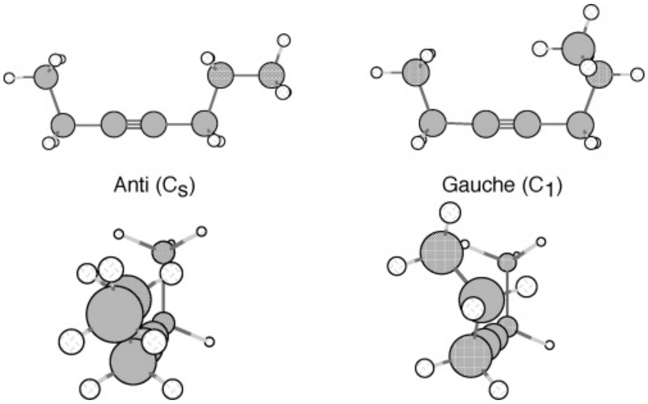

Figure 3. Structures of the species observed in 3-heptyne.

syn eclipsed. However, predicted rotational constants for a reasonable model of that structure are very different from the values observed.

That the other conformer has C_1 symmetry is required by the assignment of a-, b-, and c-type transitions consistent with any model of 3-heptyne with a gauche propyl group. There is a mirror image form, but conversion of one into the other requires crossing a high-energy, ethane-like torsional barrier. With such a barrier and the large masses of the moving fragments, any tunneling perturbation would be quenched. Tunneling splittings are not observed. The question remains as to the value of the dihedral angle between the ethyl and propyl groups. The second moment, P_{cc}, is particularly sensitive to this angle. If we adjust a reasonable molecular model to fit the rotational constants of GA pentane, transfer those parameters to 3-heptyne, i.e., merely separate the ethyl and gauche propyl fragments by −C≡C, an added 2.65 Å, one can predict the rotational constants and P_{cc} in particular as a function of dihedral angle by rotating the ethyl and propyl groups around the −C≡C− axis. A rigid rotation is probably not exactly correct, but since the torsional potential is expected to be quite small, little structural relaxation is likely. A plot of P_{cc} vs dihedral angle is shown in Figure 2. The observed value, 13.9 uÅ^2, intersects the curve at four points. However, only at the ∼345° configuration do the other spectroscopic constants also agree with the model. The approximations in this determination are significant, so we estimate the dihedral angle to be −15(5)°. This structure is shown in Figure 3. It is clear that the dihedral angle, C−(C−C≡C−C)−C, is neither zero nor a symmetry related angle like 60°, a value consistent with hyperconjugative control of conformation. Rather, it appears to be a value consistent with the ethyl group on one end of the triple bond "eclipsing" the approximate electron density center of the opposite asymmetric gauche propyl group. This structure is consistent with the model that the conformation is determined by the dispersion attractions between the groups at each end of the C≡C triple bond. The separation between the ethyl and propyl endgroups is beyond the sums of the van der Waals radii of any of the atoms, and the observed conformations are consistent with bringing those groups as close to each other as possible to maximize the weak dispersive attractions.

From one perspective, 3-heptyne is a substituted propane and therefore expected to have gauche and anti forms characterized above. Are there other conformers arising from other torsional energy minima about the C≡C axis? In the smaller compound, 3-hexyne, we found only a single species.[1] The torsional barrier is so small that even our most exhaustive calculation [MP2/aug-cc-pVQZ//(TZ)][9] shows a variation of energy with torsion in the range of 40 cal/mol, a barrier so small that it is probably unreliable. It was a struggle in those computations to find a method and basis set which would predict the correct torsional minimum at the observed C_{2v} conformation rather than another. We did not attempt similar calculations on 3-heptyne with its extra CH_2 group.

The Illinois microwave group has shown that conformational isomers relax in the expansion of a pulsed jet to thermal equilibrium (∼2 K) if the barrier separating them is smaller than about 1 kcal/mol.[35] The barrier about the C≡C bond in 3-heptyne is expected to be 1 or 2 orders of magnitude smaller, so other possible conformational isomers would relax to the most stable form. The barrier to rotation within the propyl group is on the order of 2 kcal/mol, so the gauche and anti species are frozen at their room-temperature populations and do not relax in the expansion.

V. Summary

Two conformers of 3-heptyne, ethyl propyl acetylene, have been identified and characterized by microwave spectroscopy. One has a syn-eclipsed heavy-atom-planar structure analogous to the structure of the previously studied 3-hexyne. The second conformer, with the propyl moiety in a gauche configuration, has the ethyl and gauche-propyl groups essentially eclipsed. These structures are consistent with the model that, in relatively nonpolar substituted acetylenes, dispersion attractions between the end groups determine the conformation. Also, the two lowest-energy conformers of pentane, AA (C_{2v}) and GA (C_1), have been characterized.

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References and Notes

(1) Bohn, R. K. *J. Phys. Chem. A* **2004**, *108*, 6814.

(2) Pophristic, V.; Goodman, L. *Nature (London)* **2001**, *411*, 565.

(3) Weinhold, F. *Nature (London)* **2001**, *411*, 539.

(4) Schreiner, P. R. *Angew. Chem.* **2002**, *114*, 3729; *Angew. Chem., Int. Ed.* **2002**, *41*, 3579.

(5) Bickelhaupt, F. M.; Baerends, E. J. *Angew. Chem.* **2003**, *115*, 4315; *Angew. Chem., Int. Ed.* **2003**, *42*, 4183.

(6) Weinhold, F. *Angew. Chem.* **2003**, *115*, 4320; *Angew. Chem., Int. Ed.* **2003**, *42*, 4188.

(7) Mo, Y.; Mu, W.; Song, L.; Lin, M.; Zhang, Q.; Gao, J. *Angew. Chem.* **2004**, *116*, 2020; *Angew. Chem., Int. Ed.* **2004**, *43*, 1986.

(8) Compton, D. A. C.; Montero, S.; Murphy, W. F. *J. Phys. Chem.* **1980**, *84*, 3587. Heenan, R. K.; Bartell, L. S. *J. Chem. Phys.* **1983**, *78*, 1270.

(9) Churchill, G. B.; Michels, H. H.; Bohn, R. K. *Int. J. Quantum Chem.* **2006**, *106*, 3364.

(10) Hensel, K. D.; Gerry, M. C. L. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3023.

(11) Stolwijk, V. M.; van Eijck, B. P. *J. Mol. Spectrosc.* **1987**, *124*, 92.

(12) Bohn, R. K. unpublished results.

(13) Damiani, D.; Mirri, A. M. *Chem. Phys. Lett.* **1971**, *10*, 351.

(14) Wodarczyk, F. J.; Wilson, E. B. *J. Chem. Phys.* **1972**, *56*, 166.

(15) Traetteberg, M. T.; Bakken, P.; Hopf, H. *J. Mol. Struct.* **1999**, *509*, 213.

(16) Crowder, G. A. *J. Mol. Struct.* **1986**, *147*, 17.

(17) Bell, S.; Guirgis, G. A.; Li, Y.; Durig, J. R. *J. Phys. Chem. A* **1997**, *101*, 5987.

(18) Durig, J. R.; Drew, B. R. *J. Mol. Struct.* **2001**, *560*, 247.

(19) Hirota, E. *J. Chem. Phys.* **1962**, *37*, 2918.

(20) Wlodarczak, G.; Martinache, L.; Demaison, J.; Marstokk, K.-M.; Møllendal, H. *J. Mol. Spectrosc.* **1988**, *127*, 178.

(21) Traetteberg, M. T.; Bakken, P.; Hopf, H. *J. Mol. Struct.* **2000**, *556*, 189.

(22) Atticks, K.; Bohn, R. K.; Michels, H. H. *Int. J. Quantum Chem*. **2001**, *85*, 514.

(23) Bohn, R. K.; Pardus, J. L.; August, J.; Brupbacher, T.; Jäger, W. *J. Mol. Struct.* **1997**, *293*, 413−414.

(24) Atticks, K.; Bohn, R. K.; Michels, H. H. *Int. J. Quantum Chem*. **2002**, *90*, 1440−1447.

(25) Restrepo, A.; Bohn, R. K. *J. Mol. Struct.* **2006**, *833*, 189.

(26) Churchill, G. B.; Milot, R.; Bohn, R. K. *J. Mol. Struct.*, in press.

(27) Nishio, M. *Cryst. Eng. Commun.* **2004**, *6*, 130.

(28) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33.

(29) Hight-Walker, A. R.; Lou, Q.; Bohn, R. K.; Novick, S. E. *J. Mol. Struct.* **1995**, *346*, 187.

(30) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1977; Vol. 6, pp 1−89.

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

(32) Muenter, J. S.; Laurie, V. W. *J. Chem. Phys.* **1966**, *45*, 855.

(33) Bohn, R. K.; Farag, M. S.; Ott, C. M.; Radhakrishnan, J.; Sorenson, S. A.; True, N. S. *J. Mol. Struct.* **1992**, *268*, 107.

(34) Favero, L. B.; Maris, A.; Esposti, A. D.; Favero, P. G.; Caminati, W.; Pawelke, P. *Chem.*−*Eur. J.* **2000**, *6*, 3018.

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