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A Butane Analogue, 3-Hexyne, Is Eclipsed

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In ethane the facts of a staggered equilibrium structure and a 2.9 kcal/mol torsional barrier are established.[1] However, the origin of the barrier to internal rotation in ethane remains controversial. This debate centers around the relative importance of hyperconjugation vs steric/exchange interactions in determining the staggered structure and torsional barrier. A distinction between the competing models is that steric interactions primarily depend on the distance between interacting atoms, whereas hyperconjugation depends also on the symmetry (orientation) of the interacting orbitals. The orbital orientation distinction suggests another perspective on the barrier. The staggered gauche and trans conformers of butane are a corollary of the staggered ethane structure. 3-Hexyne ($CH_3CH_2C{\equiv}CCH_2CH_3$) is butane elongated by a cylindrically symmetrical C≡C spacer, which separates the ethyl groups. If hyperconjugation were the dominant interaction in this butane analogue, the equilibrium structure would be staggered. But if steric interactions were dominant, the structure would be eclipsed. The equilibrium conformation of 3-hexyne is experimentally determined and its structure is syn-eclipsed, C_{2v}, not staggered.

I. Introduction

Ethane has a staggered equilibrium structure, and the torsional barrier is 2.9 kcal/mol.[1] A consensus about the origin of the barrier remains elusive. A recent paper by Pophristic and Goodman,[2] which emphasizes stabilization of the staggered form of ethane due to hyperconjugation between a C−H bonding orbital and the trans vicinal C−H antibonding orbital, has revived the discussion of the origin of the ethane barrier and prompted vigorous debate.[3−7] The key result of Pophristic and Goodman is that if $\sigma_{C-H}-\sigma^*_{C-H}$ hyperconjugation is excluded from the quantum chemical calculation, then the eclipsed form becomes more stable. Inclusion of hyperconjugation restores the stability of the staggered form, which is the experimental result. Their conclusion is challenged by other authors[5,7] who favor a steric hindrance model.[8] One group[5] factors ethane energetics into three terms: Pauli repulsion, arising from orbital antisymmetrization, electrostatic interactions, and orbital interaction. They conclude that the latter two terms only contribute tenths of kcal/mol to the difference in energy of the staggered and eclipsed conformations and that Pauli repulsion dominates. Weinhold disputes that conclusion in an adjoining rebuttal[6] and notes that Pophristic and Goodman's[2] formulation of hyperconjugation in terms of natural bond orbitals has a history going back to 1979[9] and was quantitatively established in 1991.[10] More recently, another group,[7] using ab initio valence bond theory, which formulates hyperconjugation in another way, 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 still is unresolved.

One reason that the steric model has gained wide acceptance is the success of molecular mechanics methods,[11] which predict sensible structures of many molecules. These methods use classical rather than quantum mechanics and treat a molecule as a collection of atoms whose energy can be expressed as a sum of quadratic terms assigned to stretching, bending, torsion, and interaction terms among them for bonded atoms. Longer range interactions are accounted for by additional terms for nonbonded atom pairs (van der Waals (vdW)) and electrostatic interactions. These methods account for staggered conformations in ethane and other hydrocarbons by vdW potentials between the nonbonded atoms, which are repulsive at short distances and weakly attractive at longer distances. It is this example that leads one author in the controversy[4] to complain about the steric hindrance model, "There are many examples of this kind where we ... actually believe what we have heard over and over again, even if it is incorrect."

The language and meaning of the approximations made by the various authors contribute to the ethane barrier controversy.[2−8] However, there is a distinguishing characteristic of the competing models that transcends language ambiguities. Both models depend on the distance separating the interacting orbitals/atoms, but only hyperconjugation depends strongly upon the symmetry and orientation of the orbitals. This symmetry distinction between the models suggests a way to evaluate and test them.

We raise the question about which model dominates at greater separations of the interacting groups because the models make different predictions that can be clearly tested by experiment. Consider separating the methyl groups of ethane in a structurally benign way with a cylindrically symmetrical spacer. 2-Butyne (dimethylacetylene, $CH_3-C{\equiv}C-CH_3$) does that. Though the barrier to internal rotation in ethane is 2900 cal/mol[1], it is only 16 cal/mol in dimethyl acetylene (actually $CH_3-C{\equiv}C-CD_3$).[12] The equilibrium conformation of dimethylacetylene is not known.[12,13] Rotational spectra reveal the barrier to internal rotation but not the structure at the energy minimum because the methyl groups are symmetric tops. In principle, the orientation of the methyl groups could be determined by destroying the methyl group symmetry by selective partial deuteration (e.g., $CH_2D-C{\equiv}C-CH_2D$) and analysis of its microwave spectrum. But the combination of tiny dipole moments (hence a very weak spectrum), broadening of the

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TABLE 1: Assignment and Fit of Rotational Transitions of 3-Hexyne

J''	K_p''	K_o''	←	J'	K_p'	K_o'	frequency (MHz)	diff (kHz)		
									A (MHz)	9410.841(12)[a]
1	1	1		0	0	0	10680.623	−2	B (MHz)	1407.9618(5)
2	1	2		1	0	1	13220.182	−1	C (MHz)	1269.7329(3)
3	1	3		2	0	2	15691.341	0	P_{cc} (u Å^2)	7.31
4	1	4		3	0	3	18096.356	1	Δ_J (kHz)	1.122(7)
5	1	5		4	0	4	20438.855	1	Δ_{JK} (kHz)	−26.7(12)
6	1	6		5	0	5	22723.83	−1	δ_J (kHz)	0.518(2)
6	0	6		5	1	5	8917.169	2	Φ_J (kHz)	−0.00028(5)
7	0	7		6	1	6	11923.728	0	Φ_{JK} (kHz)	0.030(2)
8	0	8		7	1	7	14959.419	−2	ϕ_1 (kHz)	−0.000048(14)
9	0	9		8	1	8	18014.313	2	no. of lines	21
10	0	10		9	1	9	21078.092	0	rmsd (kHz)	2.0
1	1	0		1	0	1	8141.162	3		
2	1	1		2	0	2	8281.256	2		
3	1	2		3	0	3	8494.683	−2		
4	1	3		4	0	4	8785.359	−2		
5	1	4		5	0	5	9158.421	2		
6	1	5		6	0	6	9620.121	−2		
7	1	6		7	0	7	10177.697	0		
8	1	7		8	0	8	10839.078	2		
9	1	8		9	0	9	11612.55	−1		
10	1	9		10	0	10	12506.315	0		

[a] Numbers in parentheses are one standard deviation in the last printed digit.

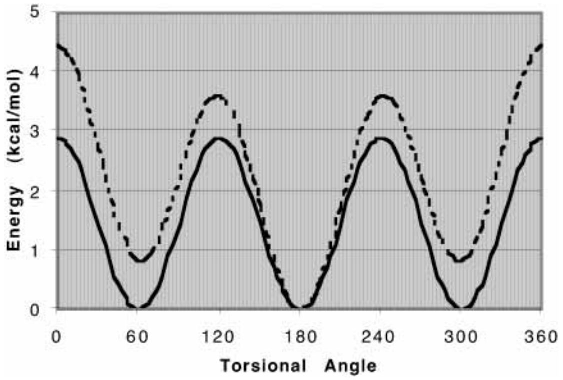

Figure 1. Torsional potential functions of ethane (solid line) and butane (dashed).

transitions due to deuterium quadrupole coupling, and the likelihood of tunneling perturbations from multiple torsional minima make that experiment impractical.

A corollary of the staggered structure of ethane is the staggered structure of butane, which has two stable conformations, trans and gauche.[14] Figure 1 shows the torsional potential functions of butane[14] and ethane. The torsional potentials are very similar and the added methyl−methyl interaction in butane makes only a modest change. From the similarity of the potential curves, we conclude that the origins of the ethane and butane barriers derive from the same principles. Consider the extended analogue of butane, 3-hexyne, $CH_3-CH_2-C\equiv C-CH_2-CH_3$, where the two ethyl groups are separated by a $C\equiv C$ spacer. Because ethyl groups are asymmetric, their relative orientation can be determined from the compound's rotational constants. If the hyperconjugation model were to apply to 3-hexyne, as it does to butane and ethane, then the stable conformations would remain staggered and appear as gauche and trans species. Consider the steric model's predictions. In butane, the shortest nonbonded distances between H atoms in one ethyl group and atoms in the other are 2.6 Å, smaller than the sums of their vdW radii, 3.3 Å, and the resulting repulsions are minimized in staggered conformations. In 3-hexyne, on the other hand, the nonbonded distances between atoms of the ethyl groups are increased by about 2.7 Å and are all greater than the sums of the atoms' vdW radii. In this regime, the steric interactions become weakly attractive and the stable conformation of the ethyl groups in 3-hexyne would not be gauche or trans but syn-eclipsed, C_{2v} symmetry. See Figure 2.

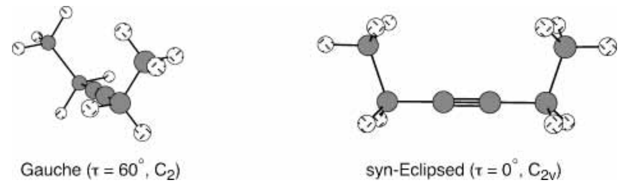

Figure 2. Possible conformations of 3-hexyne.

Although hydrocarbons are not normally considered polar molecules, in conformations without a center of symmetry, they have dipole moments adequately large to produce easily observable microwave spectra. For example, propane[15] and the gauche conformer of butane[16] have dipole moments of 0.09 D, amply large for this study. In this paper, the microwave rotational spectrum of 3-hexyne is observed and assigned and its equilibrium structure reported.

II. Experimental Section

3-Hexyne was purchased from Aldrich Chemical Co. A proton NMR spectrum revealed no significant impurities. An evacuated 4 L bulb was filled with 18 Torr of sample and then to 4 atm with first run Ne (~75% Ne, ~25% He). The sample constituted 0.6% of the gas mixture. The gas mixture was flowed into the pulsed-jet Fourier transform microwave[17,18] spectrometer at 5 Hz. Five microwave pulses were applied per gas pulse and the carrier gas pressure was 1 atm. Rotational spectra were observed between 8 and 23 GHz. Strong lines observed at 15 691.341 and 18 096.356 MHz were close to predicted frequencies of the $3_{13}-2_{02}$ and $4_{14}-3_{03}$ transitions. That suggested the presence of the $2_{12}-1_{01}$ transition near 13.2 GHz. A strong line was observed at 13220.182 MHz. Those three transitions form a coherent assignment that predicts frequencies of the other measured transitions.

III. Results and Discussion

In 3-hexyne, the possible conformations of the ethyl groups range from antiperiplanar (trans, dihedral angle $\tau = 180°$, C_{2h}

symmetry), through intermediate dihedral angle values (gauche, $0 < \tau < 180°$, C_2 symmetry), to synperiplanar (syn-eclipsed, $\tau = 0°$, C_{2v} symmetry). The trans conformer is nonpolar, would not interact with microwave radiation, and would not be observable. Any other conformation will have a permanent dipole and should have an observable microwave spectrum. For obtuse values of τ, $\sim 100° < \tau < 180°$, the C_2 axis (axis of dipole moment) and *c* principal axis are collinear and *c*-type spectra are allowed. For smaller values of τ, *b*-type spectra are allowed. If a gauche conformer with a dihedral angle value of τ is observed, then, by symmetry, there will also be a conformer with dihedral angle $-\tau$; i.e., the torsional potential function would have a double minimum. If the torsional barriers are comparable to the 16 cal/mol value in 2-butyne, the rotational spectrum is expected to be strongly perturbed by tunneling splittings.[19] If the molecule has a single torsional minimum at $\tau = 0°$, C_{2v} symmetry, a straightforward pure rotational b-type spectrum would be observed. The out-of-plane second moment calculated from the rotational constants provides an independent measure of τ.

As the gas expands in the pulsed jet, conformers initially present at room temperature will relax to the global minimum energy structure if the potential barriers separating them are below ca. 1 kcal/mol.[20] 3-Hexyne's torsional barriers are expected to be much smaller so conformational relaxation will occur. At 2 K, the Boltzmann factor kT is 4 cal/mol, which suggests that only other less stable conformers with relative energies below about 10 cal/mol above the ground state could be observed.

The spectral assignment and derived constants are shown in Table 1. From the fact that 3-hexyne has an observable rotational spectrum, we conclude that the compound has a permanent dipole moment so that the conformation is not trans, C_{2h}. The transitions are clean and sharp and display no tunneling perturbations.[19] That observation requires that the torsional potential have a single global minimum. Because the $\tau = 180°$ minimum has been excluded, the structure must be synperiplanar, $\tau = 0°$. This is consistent with the b-type selection rules of the observed transitions. The 21 observed lines are well fit by three rotational constants and six centrifugal distortion constants of a conventional Hamiltonian[21] to a standard deviation of 0.002 MHz, about the experimental uncertainty. Finally, the dihedral angle can be determined from the second moment, P_{cc}, where $P_{cc} = (I_a + I_b - I_c)/2$. For a heavy-atom-planar structure, the only contributions to P_{cc} come from the four out-of-plane H-atom pairs of the methylene and methyl groups. Contributions to P_{cc} from one methyl or methylene group range from 1.43 u Å^2 for acetyl cyanide (CH_3COCN)[22] to 1.82 u Å^2 for *p*-anisaldehyde[23] ($CH_3OC_6H_4CHO$) both with heavy-atom-planar structures. Thus, C_{2v} 3-hexyne, with its four methylene/methyl groups, is expected to have a P_{cc} value in the range 5.7−7.3 u Å^2, with larger values occurring in less rigid molecules. P_{cc} for 3-hexyne is 7.31 u Å^2, consistent with a heavy-atom-planar C_{2v} structure. For a $\tau = 60°$ gauche conformation, P_{cc} of 3-hexyne would have a value of about 13.2 u Å^2.

IV. Summary

The microwave rotational spectrum clearly demonstrates that 3-hexyne has a heavy-atom-planar structure of C_{2v} symmetry. This structure is eclipsed. We have shown that although butane has a staggered structure, its extended analogue, 3-hexyne, is eclipsed. The conclusion is that steric interactions dominate in this extended analogue of ethane and butane.

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References and Notes

(1) Pitzer, K. S. *Discuss. Faraday Soc*. **1951**, *10*, 66. Hirota, E.; Endo, Y.; Saito, S.; Duncan, J. L. *J. Mol. Spectrosc*. **1981**, *89*, 285. Weis, S.; Leroi, G. E. *J. Chem. Phys*. **1968**, *48*, 962. Moazzen-Ahmadi, N.; Gush, H. P.; Halpern, M.; Jagannath, H.; Leung, A. *J. Chem. Phys*. **1987**, *88*, 563. Fernandez-Sanchez, J. M.; Valdenebro, A. G.; Montero, S. *J. Chem. Phys*. **1989**, *91*, 3327. Fantoni, R.; van Helvoort, K.; Knippers, J.; Reuss, W. *Chem. Phys*. **1987**, *110*, 1.

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

(3) Weinhold, F. *Nature* **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) Pauling, L. C. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. Sovers, O. J.; Kern, C. W.; Pitzer, R. M.; Karplus, M. *J. Chem. Phys.* **1968**, *49*, 2592.

(9) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1979**, *101*, 1700.

(10) Reed, A. E.; Weinhold, F. *Isr. J. Chem.* **1991**, *31*, 277.

(11) Examples of widely used molecular mechanics methods: (MM4) Allinger, N. L.; Chien, K.; Lii, J.-H. *J. Comput. Chem.* **1996**, *17*, 642. (AMBER94) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M., Jr.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179. (OPLS-AA) MacDonald, N. A.; Jorgensen, W. L. *J. Phys. Chem. B* **1998**, *102*, 8049. (MMFF94) Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490. Nonbonded interactions are explicitly discussed in Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 520. (CHARMM22) MacKerrell, A. D., Jr.; Bashford, D.; Bellott, M.; Dunbrack, R. L., Jr.; Evanseck, J. D.; Field, M. J.; Fischer, S.; Gao, J.; Guo, H.; Ha, S.; Joseph-McCarthy, D.; Kuchnir, L.; Kuczera, K.; Lau, F. T. K.; Mattos, C.; Michnik, S.; Ngo, T.; Nguyen, D. T.; Prodhom, B.; Reiher, W. E., III.; Roux, B.; Schlenkrich, M.; Smith, J. C.; Stote, R.; Straub, J.; Watanabe, M.; Wiorkiewicz-Kuczera, J.; Yin, D.; Karplus, M. *J. Phys. Chem. B* **1998**, *102*, 3586.

(12) Nakagawa, J.; Imachi, M.; Hayashi, M. *J. Mol. Struct.* **1984**, *112*, 201.

(13) The low *T* crystal structure of 2-butyne requires a molecular center of inversion, therefore, staggered (Ibberson, R. M.; Prager, M. *Acta Crystallogr., Sect. B: Struct. Sci.* **1995**, *51*, 71), but that conformation is believed to be crystallographically imposed (Kirstein, O.; Prager, M.; Johnson, M. R.; Parker, S. F. *J. Chem. Phys.* **2002**, *117*, 1313).

(14) 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.

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

(16) Hüttner, W.; Majer, W.; Kästle, H. *Mol. Phys.* **1989**, *67*, 131.

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

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

(19) Tunneling perturbations of the rotational spectrum are clearly evident in the case of benzyl fluoride, which has a reduced internal rotation constant value similar to 3-hexyne. The 2-fold torsional barrier in benzyl fluoride is 166(2) cal mol^{-1}, a barrier much higher than that expected for 3-hexyne. Bohn, R. K.; Sorenson, S. A.; True, N. S.; Brupbacher, T.; Gerry, M. C. L.; Jäger, W. *J. Mol. Spectrosc.* **1997**, *184*, 167.

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

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

(22) Scappini, V.; Dreizler, H. *Z. Naturforsch. A* **1976**, *31*, 840.

(23) Liu, X.-Z.; Bohn, R. K.; Sorenson, S.; True, N. S. *J. Mol. Struct.* **1991**, *243*, 325. Table 3 displays many examples of P_{cc} values of methylene/methyl groups.