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AB *INITIO* AND MOLECULAR MECHANICS (MM3) CALCULATIONS ON PROPARGYL ALCOHOL AND DERIVATIVES

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Ab initio calculations at both the Hartree–Fock and Møller–Plesset (MP2) levels of theory utilizing various basis sets were carried out on propargyl alcohol and its derivatives. The results of these calculations were used in conjunction with available experimental data in the formulation of an MM3 force field for these compounds. The energetic data obtained via the _ab initio_ calculations were modeled well within the MM3 formalism, and are in agreement with the experimental results to within 1 kcal mol^{-1}. For those structural parameters which were the focus of this study, the calculated results agreed well with existing experimental and _ab initio_ data. The vibrational frequencies are also in good agreement with only small deviations in a few modes of methyl propargyl ether and propargyl fluoride.

INTRODUCTION

With the increasing knowledge of receptor–protein structures (provided by x-ray crystallography and nuclear magnetic resonance spectroscopy) and the availability of both fast computers and efficient algorithms, the investigation of receptor–substrate interactions may be carried out through the use of theoretical models. To facilitate useful predictions, establishment of a model of molecular properties is necessary. Since small molecules have a limited number of intramolecular interactions whereas biomolecules are affected by a plethora of them, small molecule interactions are easier to describe than large molecule interactions. Furthermore, for small molecules, the inclusion of solvent interactions in the model is not critical if one assumes that the molecules bind to the receptor in their desolvated forms. Biomolecules are more likely to be forced into a specific conformation owing to the influence of the surrounding solvent. Unfortunately, this influence cannot be reproduced adequately by many of the models available today.

In order to investigate the binding of steriods to receptors, a study was undertaken to establish an MM3 (94) force field[1] for these molecules. As steroids in general do not show rare structural features such as triple bonds nor contain rare atoms such as magnesium, silicon or transition metals, many of them could be described with the parameters already established in the MM3 force field. To describe the steroids bearing a propargyl alcohol or related group at the C-17 position, it was necessary to formulate parameters that allow for an accurate description of this functional group. In order to develop these parameters, model structures were selected which contained the functional group of interest, propargyl alcohol and its derivatives. Through both experimental data and *ab initio* results, an accurate model of these compounds was established using the MM3 force field.

METHODOLOGY

The model structures chosen consisted of propargyl alcohol, but-2-yn-1-ol, 2-methylbut-3-yn-2-ol, methyl propargyl ether, 2-methylbut-3-yn-2-ol acetate and propargyl fluoride. These structures were chosen for various reasons, including ease of computation, availability of experimental data and homology to the steric environment of the steroids.

The *ab initio* results in this study were obtained via the Gaussian 92 suite of programs[2] on an IBM RS/6000 cluster. Optimizations were carried out at the restricted Hartree–Fock (HF) level of theory with the standard 6–31G** basis set for all of the model compounds. For propargyl alcohol and propargyl fluoride, optimizations were also carried out with electron correlation at the Møller–Plesset (MP2) level with the inclusion of diffuse functions for carbon, oxygen and hydrogen in the 6–31G** basis set (6–31++G**). For the molecular mechanics calculations, the MM3 (94) force field was

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used, and the parameters formulated in this study are included in this release of the program. All molecular mechanics calculations herein used this program and were carried out on a Silicon Graphics 4D/310GTX computer.

The general strategy for the MM3 parameterization is as follows: (1) determine the missing MM3 parameters (bond stretching, angle bending, torsional, etc.) for the model compounds, (2) obtain the necessary data (experimental and/or *ab initio*) to determine these parameters and (3) optimize the parameters to reproduce accurately the *ab initio* or experimental data. Since experimental data on the rotational barriers and structures of these compounds are sparse, *ab initio* methods were undertaken in an attempt to supplement these missing experimental numbers. The final parameterization of the force field was carried out to fit energetic and geometrical information obtained through the experimental and *ab initio* studies.

The *ab initio* study began with the determination of the torsional profiles about certain dihedrals within these compounds. To accomplish this, a reaction coordinate method was used in which the torsion under examination was rotated from 0 to 180° in increments of 15°. These resulting profiles were later used in the determination of torsional parameters for MM3. Once these *ab initio* rotational profiles had been characterized, minima were located by choosing conformations near valleys in the potential energy surface, then any geometrical constraints were released and the geometries were allowed to fully optimize.

RESULTS AND DISCUSSION

Ab initio

Energetics

The initial torsional profile calculation focused on the hydroxyl group of propargyl alcohol. A reaction coordinate method was used as mentioned previously with the coordinate being the C_{sp}—C_{sp3}—O—H torsion. The result of this calculation from 0 to 180°, in 15° increments, is shown in Figure 1.

Hirota[3] was the first to investigate this torsional barrier through the interpretation of microwave results and found that the minimum energy conformation has a C_{sp}—C_{sp3}—O—H torsion angle of $59 \pm 3°$. It should also be mentioned that Hirota calculated the barrier to this rotation to be $0{\cdot}26 \pm 0{\cdot}03$ kcal (1 kcal = 4·184 kJ) at the 0° conformation and $1{\cdot}70 \pm 0{\cdot}57$ kcal at the 120° conformation. The results of RHF/6–31G** and MP2/6–31++G** agree well with Hirota's results, finding minima at 56·8 and 53·7° at the respective levels of theory. The estimated barriers at the appropriate level are somewhat different than Hirota's results. At both the HF and MP2 levels of theory, the barrier at 0° is *ca* 1·15 kcal mol^{-1}, about 1 kcal mol^{-1} greater than the reported results by Hirota. As for the 120° conformer, one observes the same pattern: the HF and MP2 results show a barrier of *ca* 2·75 kcal mol^{-1}, differing from Hirota's result by about 1 kcal mol^{-1}. These results, nevertheless, are still in reasonable agreement with the experimental data since we have shown that *ab initio* barriers derived from torsional profiles tend to be in error by approximately 1 kcal mol^{-1}.[4]

For the purpose of comparison, the methyl propargyl ether rotational profile is also interesting. The results of the reaction coordinate method involving the C_s—C_{sp3}—O—C_{sp3} torsion from 0 to 180°, in 15° increments, is illustrated in Figure 2. Marstokk Møllendal[5] published an excellent microwave study of this molecule in which they found the dihedral angle C_{sp}—C_{sp3}—O—C_{sp3} to be $68 \pm 2°$. Another study of the microwave spectrum of methyl propargyl ether was reported by Hayashi *et al.*[6]. They reported the C_{sp}—C_{sp3}—O—C_{sp3} dihedral to measure 67·5°. The results of the HF calculations in this study with a dihedral angle of 69.0° are in excellent agreement with these microwave data.

As shown in Figure 2, the barrier at the 120° conformation is of the same magnitude as the barrier observed in the case of propargyl alcohol (*ca* 2·75 kcal mol^{-1}). At the 0° conformation, the barrier is *ca* 4·50 kcal mol^{-1}, 3·4 kcal mol^{-1} higher than the barrier observed in propargyl alcohol. This barrier implies a significant 'steric' repulsion between the CH_3 group of the ether with the electron density associated with the $C_{sp}{\equiv}C_{sp}$ triple bond. These results could lead to two hypotheses: (1) a true steric energy increase of 3·4 kcal mol^{-1} results upon substitution of a CH_3 group for the H of propargyl alcohol, or (2) a weak hydrogen bond is formed between the hydrogen of the hydroxyl group and the electron density of the $C_{sp}{\equiv}C_{sp}$ triple bond in propargyl alcohol, causing the energy to be lower at the 0° conformer. The last point seems unlikely since the inclusion of diffuse functions and electron correlation show no change in this barrier.

Torsional profiles for the remaining structures (but-2-yn-1-ol, 2-methylbut-3-yn-2-ol, and 2-methylbut-3-yn–2-ol acetate) at the RHF/6–31G** level are illustrated in Figures 3–5. The results are as expected and similar to the torsional profiles of propargyl alcohol and methyl propargyl ether. For but-2-yn-1-ol (Figure 3), the profile is nearly identical to the propargyl alcohol barrier because these compounds are very similar sterically. The 2-methylbut-3-yn-2-ol profile differs from that of propargyl alcohol at the 120° conformation (Figure 4). This energy increase can be attributed to the steric repulsion between the hydroxyl group and the two methyl groups present in 2-methylbut-3-yn-2-ol. Finally, for 2-methylbut-3-yn-2-ol acetate, one observes a rotational profile similar to that for methyl propargyl ether. The energy increase at 0° is primarily due to steric

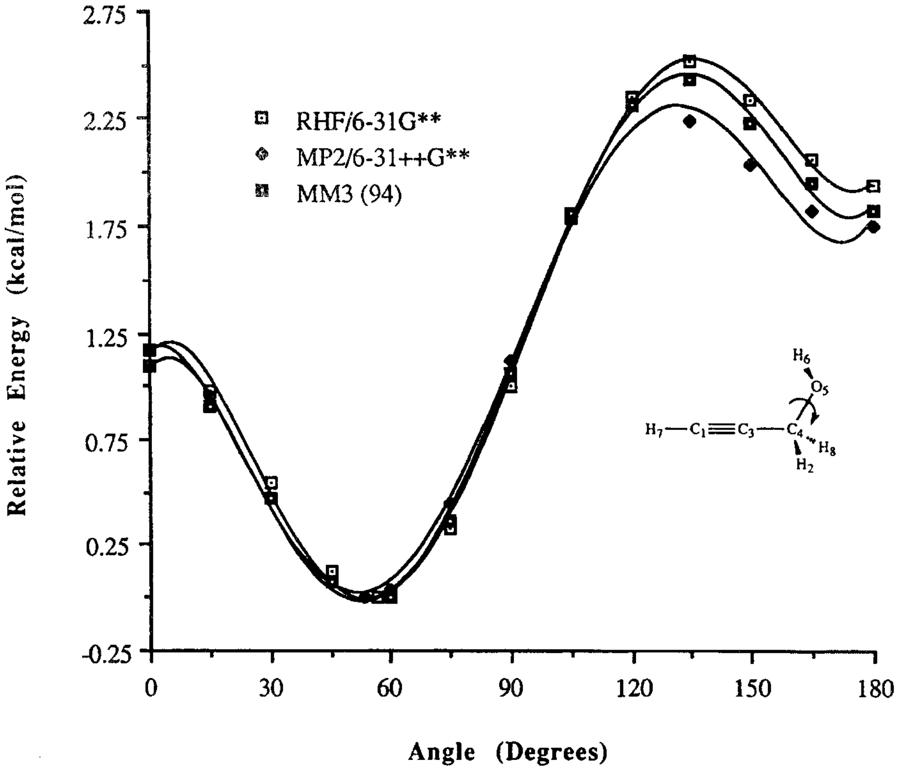


Figure 1. *Ab initio* and MM3 (94) rotational profiles for propargyl alcohol

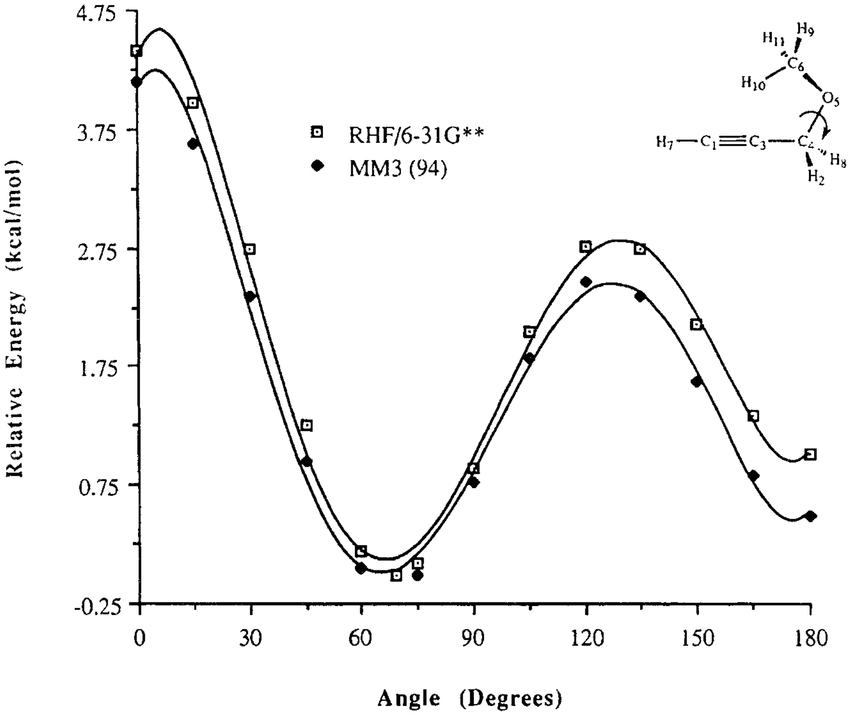


Figure 2. *Ab initio* and MM3 (94) rotational profiles for methyl propargyl ether

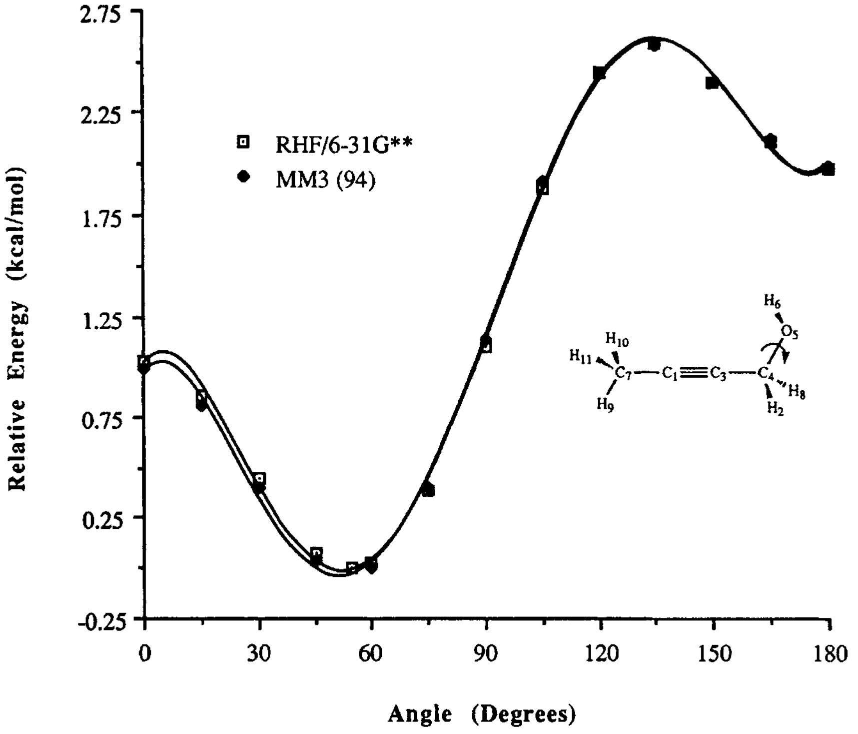


Figure 3. *Ab initio* and MM3 (94) rotational profiles for but-2-yn-1-ol

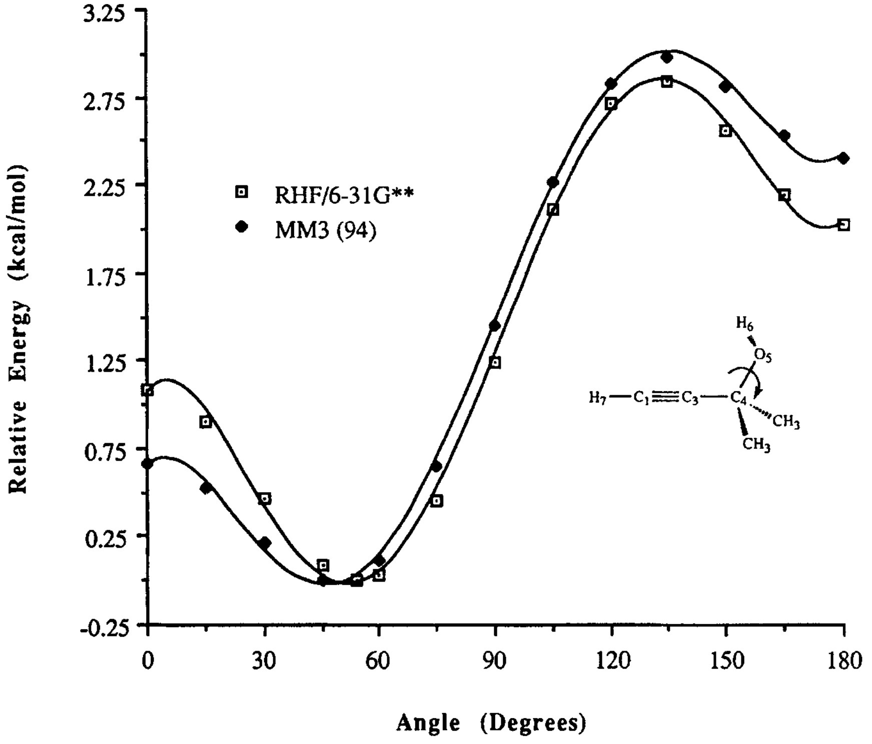


Figure 4. *Ab initio* and MM3 (94) rotational profiles for 2-methylbut-3-yn-2-ol

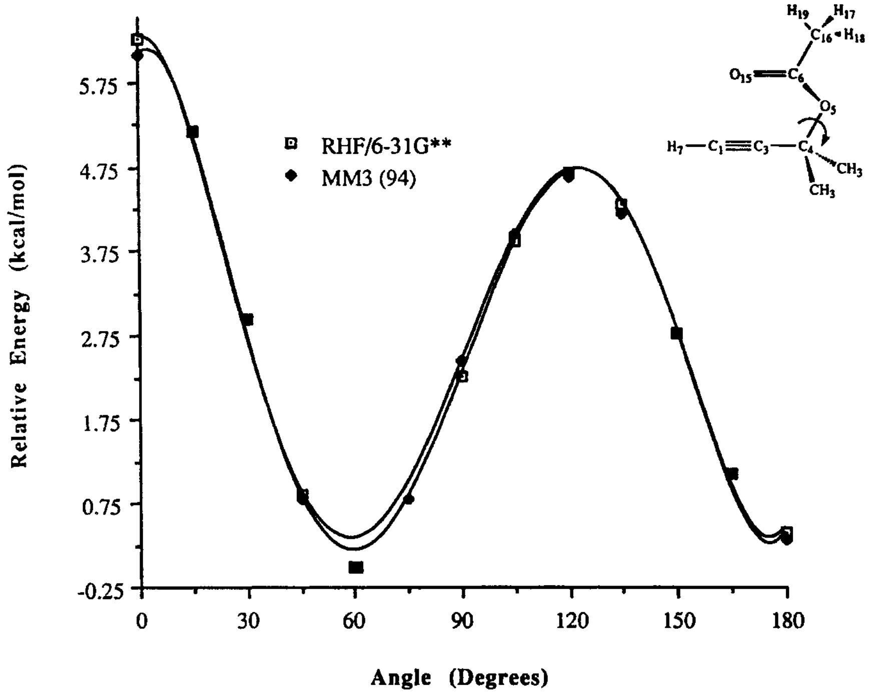


Figure 5. *Ab initio* and MM3 (94) rotational profiles for 2-methylbut-3-yn-2-ol Acetate

interaction of the acetate group with the $C_{sp}{\equiv}C_{sp}$ triple bond, while an increase in the barrier at 120° is due to the interaction of the acetate group with the two methyl groups.

Structure

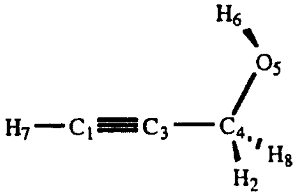
The results (unscaled) of the optimization of each of the structures examined are shown in Tables 1–6 at the corresponding levels of theory. Comparison with experimental values were made when these results were available.

For propargyl alcohol, numerous investigations involving both spectra and quantum mechanical calculations are known. Table 1 reports the results of a low-level HF calculation on propargyl alcohol with the STO-3G basis set[7] and a comparison with the RHF/6–31G** and MP2/6-31++G** results obtained in this study. Interestingly, there is a small difference in structure when higher levels of theory are used. The most significant difference in the geometry is observed in the C(4)—O(5)—H(6) bending angle, which is approximately 3.0° higher with the inclusion of electron correlation in the calculation. This result also supports the hypothesis that hydrogen bonding between the triple bond and the hydrogen of the hydroxyl group is insignificant. A larger repulsion is observed in the correlated results which should favor the formation of a hydrogen bond.

Table 2 illustrates the resulting HF geometry for methyl propargyl ether, as compared with the microwave results of Marstokk and Møllendal[5] and Hayashi *et al.*[6] The results are in good agreement with the microwave data, particularly with those derived by Marstokk and Møllendal. The most significant disagreement appears to be in the O(5)—C(4)—H(8) bending angle, which is calculated too small by the *ab initio* method. Owing to the asymmetry of the molecule (point group C_1), a difference is predicted between the O(5)—C(4)—H(2) and O(5)—C(4)—H(8) bending angles, but the deviation between these (4.2°) is unexpected.

Table 3 shows the results of the RHF/6–31G** calculation on propargyl fluoride and a comparison with RHF/6–31G*[8], NMR[9] and microwave[10] results. As expected, excellent agreement is found between the RHF/6–31G* and RHF/6–31G** results since the addition of p-functions on hydrogen atoms should have little effect for this structure. Good agreement is also observed between these results and those obtained by the microwave method. The largest deviation is observed in the H(2)—C(4)—H(6) bending angle, which may be due to the influence of the fluorine over these light atoms. Agreement with the NMR results is less, but still reasonable.

Table 1. *Ab initio* and MM3 (94) geometries for propargyl alcohol[a]



	RHF/STO-3G[7]	RHF/6–31G**	MP2/6–31++G**	MM3 (94)
Bond				
C(1)—H(7)	1·065	1·057	1·064	1·0836
C(1)—C(3)	1·171	1·187	1·223	1·2137
C(3)—C(4)	1·492	1·477	1·468	1·4721
C(4)—H(2)	1·099	1·087	1·094	1·1171
C(4)—H(8)	1·099	1·082	1·088	1·1088
C(4)—O(5)	1·445	1·396	1·431	1·4254
O(5)—H(6)	0·989	0·943	0·967	0·9489
Angle				
H(7)—C(1)—C(3)	180[b]	179·59	179·02	179·709
C(1)—C(3)—C(4)	180[b]	179·02	177·90	174·285
C(3)—C(4)—H(2)	108·8	108·71	109·39	110·162
C(3)—C(4)—H(8)	108·8	109·30	110·28	109·861
C(3)—C(4)—O(5)	114·1	113·13	112·72	109·792
C(4)—O(5)—H(6)	104·7	109·65	107·89	108·776
H(2)—C(4)—H(8)		107·49	108·08	107·792
O(5)—C(4)—H(2)		111·39	110·89	109·901
O(5)—C(4)—H(8)		106·64	105·33	109·302
Dihedral angle				
H(7)—C(1)—C(3)—C(4)[c]		168·0	156·6	180·0
C(l)—C(3)—C(4)—O(5)[c]		−74·3	−59·3	−68·2
C(l)—C(3)—C(4)—H(2)[c]		50·0	69·9	53·0
C(l)—C(3)—C(4)—H(8)[c]		167·1	−171·3	171·6
C(3)—C(4)—O(5)—H(6)		56·8	53·7	55·2
H(6)—O(5)—C(4)—H(2)		−66·0	−69·4	−66·1
H(6)—O(5)—C(4)—H(8)		177·0	173·9	175·8

[a] Bond lengths are given in Å and angles in degrees.
[b] Value was kept constant during the geometry optimization.
[c] Not very meaningful (torsion angle including a triple bond).

Tables 4–6 show the results of RHF/6–31G** optimizations on the remaining propargyl alcohol derivatives. Owing to the lack of available experimental or other *ab initio* data, comparison with these structural results could not be made.

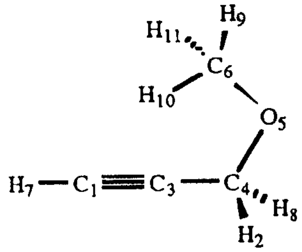
MM3 (94)

For many of the energetic and structural features of these compounds, MM3 parameters for acetylene and its derivatives are already established, and thus those parameters were not variable in this investigation. The parameters optimized in this study are illustrated in Table 7 and are those parameters which optimally reproduce the available experimental and *ab initio* data.

Energetics

The construction of an MM3 force field that accurately models these propargyl alcohol derivatives focused primarily on the rotational barriers illustrated in Figures 1–5. The torsional terms characterizing the rotational potential of a triple bond such as the C_{sp}—C_{sp}—C_{sp3}—O (4–4–1–6) torsion were established with Fourier terms of zero, yielding a barrier of essentially 0 kcal mol^{-1}. These terms were selected since torsions involving two essentially collinear bonds

Table 2. *Ab initio*, MM3 (94) and microwave geometries for methyl propargyl ether[a]



	RHF/6-31G**	MM3 (94)	Microwave[5]	Microwave[6]
Bond				
C(1)—H(7)	1·057	1·0816	1·055[b]	1·056[b]
C(1)—C(3)	1·187	1·2119	1·205[b]	1·206[b]
C(3)—C(4)	1·479	1·4736	1·459[b]	1·459[b]
C(4)—H(2)	1·089	1·1154	1·093[c]	1·101[d]
C(4)—H(8)	1·082	1·1081	1·093[c]	1·101[d]
C(4)—O(5)	1·390	1·4161	1·410[c]	1·410
O(5)—C(6)	1·398	1·4187	1·410[c]	1·410
Angle				
H(7)—C(1)—C(3)	179·74	179·972	180·0[b]	180[de]
C(1)—C(3)—C(4)	179·43	179·073	180·0[b]	180[de]
C(3)—C(4)—H(2)	108·70	110·148	109·5[c]	108·73[d]
C(3)—C(4)—H(8)	108·91	109·123	109·5[c]	108·73[d]
C(3)—C(4)—O(5)	113·68	111·383	112	112·48[f]
C(4)—O(5)—C(6)	115·11	112·870	111·8[c]	113·50[f]
H(2)—C(4)—H(8)	107·80	107·106		107·22[d]
O(5)—C(4)—H(2)	110·88	110·288	109·5[c]	109·82[d]
O(5)—C(4)—H(8)	106·68	108·677	109·5[c]	109·82[d]
Dihedral angle				
H(7)—C(1)—C(3)—C(4)[g]	-64·4	0·0		
C(1)—C(3)—C(4)—O(5)[g]	-178·0	-68·5		
C(1)—C(3)—C(4)—H(2)[g]	-54·0	-54·2		
C(1)—C(3)—C(4)—H(8)[g]	63·2	171·5		
C(3)—C(4)—O(5)—C(6)	69·0	64·5	68	67·5[f]
H(2)—C(4)—O(5)—C(6)	-53·8	-58·2		
H(8)—C(4)—O(5)—C(6)	-171·0	-175·3		
C(4)—O(5)—C(6)—H(9)	58·6	54·2		

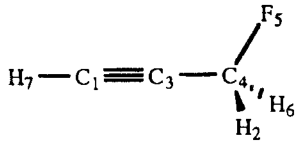
[a] Bond lengths are given in Å and angles in degrees.
[b] Taken from propyne.
[c] Taken from dimethyl ether.
[d] Taken from *trans*—ethyl methyl ether.
[e] Assumed.
[f] Adjusted.
[g] Not very meaningful (torsion angle including a triple bond).

are somewhat arbitrary. The remaining torsional parameters were established through a fit to the *ab initio* rotational profiles. The results of MM3 (94) torsion profile calculations with the optimized parameters in Table 7 are illustrated in Figures 1–5. In all cases, the agreement between the *ab initio* and the MM3 (94) profiles is fairly good. The only difference of any significance is in the case of 2-methylbut-3-yn-2-ol, in which the barrier at the 0° conformation is *ca* 0·5 kcal mol^{-1} lower than the HF barrier. This deviation is acceptable, however, since *ab initio* barriers calculated in this manner at this level of theory may be uncertain by *ca* 1 kcal mol^{-1}.[4]

Structure

The majority of the structural features of the compounds studied were established with the investigation

Table 3. *Ab initio*, MM3 (94), microwave and NMR geometries for propargyl fluoride[a]



	RHF/6-31G**[8]	RHF/6-31G**	MM3 (94)	NMR[9]	Microwave[10]
Bond					
H(7)—C(1)	1·057	1·057	1·0811	1·045(1)	1·056
C(1)—C(3)	1·186	1·186	1·2111	1·196(1)	1·206
C(3)—C(4)	1·469	1·468	1·4713	1·463(3)	1·454
C(4)—H(2)	1·081	1·082	1·1077	1·096	1·096
C(4)—H(6)	1·081	1·082	1·1071	1·096	1·096
C(4)—F(5)	1·364	1·364	1·3919	1·337(2)	1·393
Angle					
H(7)—C(1)—C(3)	179·9	179·99	179·718		179·6
C(1)—C(3)—C(4)	179·8	179·22	179·980		178·9
C(3)—C(4)—H(2)	110·2	110·10	109·702	109·77(2)	110·6
C(3)—C(4)—H(6)	110·2	110·10	109·702	109·77(2)	110·6
C(3)—C(4)—F(5)	110·8	110·85	110·925	109·47(3)	111·0
F(5)—C(4)—H(2)		108·37	109·333		
F(5)—C(4)—H(6)		108·37	109·333		
H(2)—C(4)—H(6)	109·0	108·98	107·787	112·01(5)	109·3

[a] Bond lengths are given in Å and angles in degrees.

of acetylene and its derivatives. Consequently, only a few features were the focus of this structural study. In addition to the torsional parameters previously mentioned, three bending parameters, C_{sp}—C_{sp3}—F (4–1–11), C_{sp}—C_{sp3}—O (4–1–6), and C_{sp}—$C_{sp}3$—O_{ester} (4–1–75) were optimized to reproduce the experimental and *ab initio* structures. The results of an MM3 (94) calculation of these model structures, using the optimized parameters in Table 7, are given in Tables 1–6. These results are compared with the *ab initio* results from this study and experimental data where available.

The most significant difference in the bond lengths occurs in the calculation of the H—C_{sp} bond. For most of the compounds studied, the difference in the MM3-calculated bond lengths and those obtained by both experimental and *ab initio* methods is *ca* 0·025 Å. Since the deviation is consistent throughout the results, the error appears to be systematic and may make necessary a re-evaluation of the bonding parameter involved.

The angle bending results are also in good agreement with the available structural data. The C_{sp}—C_{sp3}—F (4–1–11) parameter was optimized to reproduce the structural data for propargyl fluoride, which show very good correspondence with the *ab initio* and microwave results. The C_{sp}—C_{sp3}—O_{ester} (4–1–75) parameter was also well established by modeling 2-methylbut-3-yn-2-ol acetate. The C_{sp}—C_{sp3}—O (4–1–6) bending parameter was more difficult to model since all of the remaining compounds contained this particular bending angle. As a result, compromises in the MM3 structures had to be made in order to create a force field that could model this bending angle well. The results, however, are still good and show deviations of *ca* 1.5° on average.

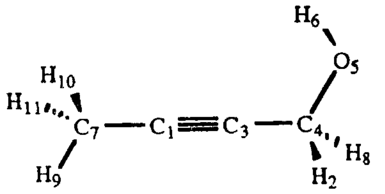
Vibrational frequencies

After the structures and energies had been characterized in the MM3 (94) force field, the vibrational frequencies were fitted to the available experimental data. The results of these calculations with the optimized parameter set are given in Tables 8–10. The vibrational comparisons were only made for propargyl alcohol, methyl propargyl ether and propargyl fluoride, since these were the only complete experimental frequency data sets.

The first propargyl alcohol spectrum was reported by Gredy[11] in 1934. The first assignment of normal modes to the reported frequencies was carried out by Nyquist and Potts[12] in 1960. Hirakawa and Tsuboi[13] later established a few more normal modes through the examination of their spectra. The O—H stretching frequency of Hirakawa and Tsuboi was later reassigned by Visser and van der Maas[14] in 1985. Nyquist[15], however, in 1971 made a complete normal mode analysis of the vibrational spectra of propargyl alcohol.

In the MM3 (94) parameterization of these vibra-

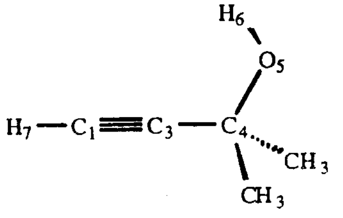
Table 4. *Ab initio* and MM3 (94) geometries for But-2-yn-1-ol[a]



	RHF/6-31G**	MM3 (94)
Bond		
C(1)—C(7)	1·468	1·4714
C(l)—C(3)	1·188	1·2117
C(3)—C(4)	1·476	1·4717
C(4)—H(2)	1·088	1·1079
C(4)—H(8)	1·082	1·1165
C(4)—O(5)	1·398	1·4252
O(5)—H(6)	0·943	0·9480
Angle		
C(7)—C(1)—C(3)	179·43	179·793
C(l)—C(3)—C(4)	178·97	179·916
C(3)—C(4)—H(2)	108·91	110·111
C(3)—C(4)—H(8)	109·54	109·895
C(3)—C(4)—O(5)	113·24	109·766
C(4)—O(5)—H(6)	109·41	108·651
H(2)—C(4)—H(8)	107·38	107·811
O(5)—C(4)—H(2)	111·15	109·927
O(5)—C(4)—H(8)	106·43	109·302
Dihedral angle		
H(9)—C(7)—C(1)—C(3)[b]	53·8	15·2
C(7)—C(1)—C(3)—C(4)[b]	-176·6	111·3
C(l)—C(3)—C(4)—O(5)[b]	-60·5	-14·0
C(l)—C(3)—C(4)—H(2)[b]	63·7	107·1
C(1)—C(3)—C(4)—H(8)[b]	-179·1	-134·3
C(3)—C(4)—O(5)—H(6)	54·7	54·0
H(6)—O(5)—C(4)—H(2)	-68·2	-67·3
H(6)—O(5)—C(4)—H(8)	175·2	174·6

[a] Bond lengths are given in Å and angles in degrees.
[b] Not very meaningful (torsion angle including a triple bond).

Table 5. *Ab initio* and MM3 (94) geometries for 2-methylbut-3-yn-2-ol[a]



	RHF/6-31G**	MM3 (94)
Bond		
C(1)—H(7)	1·057	1·0812
C(1)—C(3)	1·188	1·2113
C(3)—C(4)	1·488	1·4763
C(4)—C(2)	1·531	1·5299
C(4)—C(8)	1·527	1·5290
C(4)—O(5)	1·408	1·4293
O(5)—H(6)	0·944	0·9478
Angle		
H(7)—C(1)—C(3)	179·56	179·755
C(l)—C(3)—C(4)	179·05	179·781
C(3)—C(4)—C(2)	109·58	109·814
C(3)—C(4)—C(8)	110·09	109·438
C(3)—C(4)—O(5)	109·94	109·159
O(5)—C(4)—C(2)	110·07	109·214
O(5)—C(4)—C(8)	105·77	108·102
C(2)—C(4)—C(8)	111·32	111·074
C(4)—O(5)—H(6)	109·80	108·896
Dihedral angle		
H(7)—C(1)—C(3)—C(4)[b]	168·9	0·0
C(1)—C(3)—C(4)—C(2)[b]	47·9	42·6
C(1)—C(3)—C(4)—C(8)[b]	107·7	164·8
C(l)—C(3)—C(4)—O(5)[b]	-73·2	-77·1
C(3)—C(4)—O(5)—H(6)	54·3	48·3
H(6)—O(5)—C(4)—C(2)	-66·5	-71·8
H(6)—O(5)—C(4)—C(8)	173·2	167·3
O(5)—C(4)—C(2)—H(9)	61·5	60·7
O(5)—C(4)—C(8)—H(12)	-59·4	-59·4

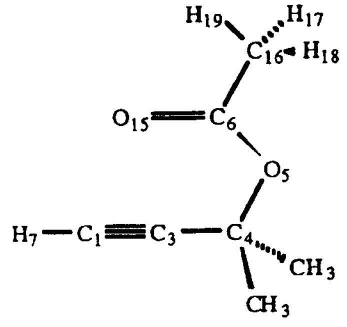
[a] Bond lengths are given in Å and angles in degrees.
[b] Not very meaningful (torsion angle including a triple bond).

tional frequencies, the focus was primarily on the results of Nyquist in 1971, since a complete normal-mode analysis was carried out. The results of the MM3 (94) calculation are given in Table 8 with the appropriate experimental results.

The methyl propargyl ether spectrum was also investigated, since this molecule has been the subject of many vibrational studies. The first spectral data (17 Raman frequencies) were published by Gredy[11] in 1934. In 1974, three studies were published. Seth-Paul *et al.*[16] assigned vibrational frequencies to the normal modes. Although originally assuming C_s symmetry and interpreting the experimental data accordingly, Seth-Paul *et al.* came to the conclusion that methyl propargyl ether shows C_1 symmetry. Charles *et al.*[17] investigated the vibrational spectrum and calculated the height of the torsion barrier. Bjørseth and Gustavsen[18] recorded infrared spectra for methyl propargyl ether in all three states. Furthermore, they investigated the Raman spectra of the liquid ether and one deuterated species and assigned the frequencies and calculated force constants. The results of the MM3 (94) calculation of the vibrational spectrum are given in Table 9 along with the experimental data previously described. The results illustrated in Table 9 are in good agreement with the available experimental data, with the largest deviation being 40 cm^{-1} in the CH_2 twisting mode.

Two vibrational analyses of propargyl fluoride have

Table 6. *Ab initio* and MM3 (94) geometries for 2-methylbut-3-yn-2-ol acetate[a]



	RHF/6-31G**	MM3 (94)
Bond		
C(1)—H(7)	1·057	1·0811
C(1)—C(3)	1·186	1·2112
C(3)—C(4)	1·480	1·4780
C(4)—C(2)	1·530	1·5299
C(4)—C(8)	1·529	1·5293
C(4)—O(5)	1·435	1·4474
O(5)—C(6)	1·331	1·3607
C(6)—O(15)	1·186	1·2141
C(6)—C(16)	1·505	1·4920
Angle		
H(7)—C(1)—C(3)	179·05	179·444
C(1)—C(3)—C(4)	177·08	179·657
C(3)—C(4)—O(5)	110·43	109·491
C(3)—C(4)—C(2)	111·32	110·447
C(3)—C(4)—C(8)	109·25	108·386
C(4)—O(5)—C(6)	122·36	119·218
O(5)—C(4)—C(2)	111·16	111·695
O(5)—C(4)—C(8)	103·55	106·483
O(5)—C(6)—O(15)	124·69	123·835
O(5)—C(6)—C(16)	110·53	111·254
O(15)—C(6)—C(16)	124·78	124·910
Dihedral angle		
H(7)—C(1)—C(3)—C(4)[b]	160·8	0·0
C(1)—C(3)—C(4)—O(5)[b]	140·5	143·1
C(1)—C(3)—C(4)—C(2)[b]	-95·5	-93·1
C(1)—C(3)—C(4)—C(8)[b]	27·2	27·1
C(3)—C(4)—O(5)—C(6)	60·4	59·6
C(4)—O(5)—C(6)—O(15)	3·0	0·1
C(4)—O(5)—C(6)—C(16)	-177·0	-179·8

[a] Bond lengths are given in Å and angles in degrees.
[b] Not very meaningful (torsion angle including a triple bond).

been reported. The first was carried out by Nyquist and Potts[12] in 1960 in conjunction with their study of methyl propargyl ether. In 1963, Evans and Nyquist[19] re-evaluated the vibrational bands of this molecule and carried out a complete normal-mode analysis. These experimental and MM3 (94) results are given in Table 10.

Comparing the vibrational frequencies reported by Evans and Nyquist and the results of the MM3 (94) calculation, one finds a good agreement (deviation less than 30 cm^{-1}) for most of the invariant frequencies. Disagreements include CH$_2$ rocking and CCH bending. For CH$_2$ rocking, the experimental value of 1018 cm^{-1}

Table 7. MM3 (94) parameter set for propargyl alcohol and its derivatives

Torsions				V_1^a	V_2	V_3
4	1	6	21	0·150	−0·750	0·708
4	1	6	1	0·100	−1·000	0·900
4	1	75	3	−2·100	−0·100	1·800
4	4	1	6	0·000	0·000	0·000
4	4	1	11	0·000	0·000	0·000
4	4	1	75	0·000	0·000	0·000
Bond angles					K_θ[b]	θ_0[c]
4		1	11		1·280	110·70
4		1	6		0·900	109·00
4		1	75		0·800	107·50

[a] The units of the Fourier torsional terms (V_1, V_2, and V_3) are kcal mol^{-1}.

[b] K_θ is expressed in mdyn Å rad^{-2}.

[c] θ_0 is in degrees.

Table 8. Experimental and MM3 (94) vibrational frequencies for propargyl alcohol[a,b]

Experimental				
Ref. 13	Ref. 11	Ref. 15	Ref. 12	MM3 (94)
3620 OH str[c]		3663 OH str		3678·2 OH str
		3331 CH str	3316 CH str	3310·7 CH str
	2940	2940 CH_2 as str		2971·3CH_2 as str
		2930 CH_2 s str		2875·7CH_2 s str
	2905			
	2118	2138 C≡C str	2120 C≡C str	2124·3 C≡C str
				1549·9 CH_2 wag
	1455	1470 CH_2 bnd		1424·0 CH_2 sciss
	1358	1390 CH_2 wag		
				1314·1 CH_2 tw
		1289 OH bnd		1282·3 COH bnd
	1233	1217 CH_2 tw		
1034 CO str	1026	1046 CO str		1094·6 CO str
		967 CH_2 rck		952·5 CH_2 rck
911 C—C str	916	907 C—C str	902 C—C str	933·6 C—C str
		648 CH bnd	650 CH bnd	725·2 CCH bnd
		628 CH bnd	629 CH bnd	661·5 CCH bnd
552 CCO i df	558	550 CCO bnd		496·3 CCO bnd
308 CCC o df	315	305 CCC bnd		376·4 CCC bnd
217 CCC i df	222	240 CCC bnd		326·3 CCC bnd
		192 OH tors		254·6 OH tors

[a] Frequencies are given in wavenumbers (cm^{-1}).

[b] Abbreviations: as asymmetric; s, symmetric; i, in-plane; o, out-of-plane; bnd, bending; rck, rocking; sciss, scissoring; df, deformation; str, stretching; tors, torsion; tw twisting; wag, wagging.

[c] From Ref. 14.

Table 9. Experimental and MM3 (94) vibrational frequencies for methyl propargyl ether[a,b]

Ref. 11	Ref 17	Ref. 18	Ref. 16	MM3 (94)
	3331$\equiv$C–H	3329	3329 CH str	3325·4 CH str
3002	3004 CH_3 as str	3003	3005 CH3 as str	2994·4 CH_3 as str
			3005 CH_3 as str	
2951	2958 CH_3 as str	2958	2956 CH_2 as str	2970·2 CH_2 as str
	2927 CH_2 as str	2927	2931 CH_2 as str	2937·4 CH_3 as str
	2890 CH_3 s str	2890		2882·5 CH_2 s str
2828	2855 CH_2 s str	2829	2828 CH_3 s str	2853·2 CH_3 s str
2118	2127$C\equiv C$ str	2125	2116 $C\equiv C$ str	2129·2 $C\equiv C$ str
				1565·2 CH_2 wag
				1492·3 CH_3 s df
	1465 CH_3 as df		1463 CH_3 as df	1467·2 CH_3 as df
	1458 CH_3 as df	1460	1463 CH_2 bnd	
	1452 CH_3 s df	1451	1451 CH_3 as df	
1447	1449 CH_2 df	1437		1443·9 CH_2 sciss
				1428·1 CH_3 as df
		1385	1384 CH_3 s df	
1362	1354 CH_2 wag	1361	1362 CH_2 wag	
1282	1285 CH_2 tw	1282	1282 CH_2 tw	1325·3 CH_2 tw
	1194 CH_3 rck	1194	1194 CH_3 i rck	1185·1 COC as df
	1157 CH_3 rck	1158	1161 CH_3 o rck	
1101	1120 COC as str	1116	1118 COC a str	1112·0 CH_3 rck
				1098·9 CH_3 rck
1005	1011 CH_2 rck	1010	1009 CH_2 rck	987·3 CH_2 rck
945	938 COC s str	938	937 COC s str	918·4 COC s str
894	900 C—C str	899	899 C—C str	875·3 C—C str
841				
	670 $C\equiv CH$ df	666	666 CH o bnd	706·0 CCH bnd
	641 $C\equiv CH$ df		633 CH i bnd	619·7 CH bnd
572	572 CCO df	578	571 CCO i bnd	
516		517	516 COC o bnd	513·6 COC bnd
	380 COC df	381	388 COC i bnd	377·1 COC s bnd
324	317 $C\equiv CC$ df	318	317 CCC o bnd	277·0 CCH bnd
236	227 $C\equiv CC$ df	236	236 CH_3 tors	189·6 CH_3 tors
178	190 CH_3O tors	178	178 CCC i bnd	
	127 CH_3O tors	105		110·2 CH_3O tors

[a] Frequencies are given in wavenumbers (cm^{-1}).

[b] For abbreviations, see Table 8.

is consistent with assignments for methyl propargyl ether and the MM3 result for methyl propargyl ether. For propargyl alcohol and methyl propargyl ether, the experimental CH_2 rocking frequency is reported at 967 and 1010 cm^{-1}, respectively. The data are consistent with the MM3 calculation. The results for propargyl fluoride appear to be questionable. It appears that the CCH bending frequency is calculated to be too high with too much splitting. For propargyl alcohol and methyl propargyl ether, on the other hand, it appears that the frequency is calculated to be too low. The large splitting, however, remains unchanged.

CONCLUSIONS

Ab initio calculations at the Hartree–Fock and second-order Møller–Plesset levels of theory utilizing various basis sets were carried out on propargyl alcohol and its derivatives in order to supplement experimental data. The results of these calculations and experiment were used in the formulation of an MM3 force field for these compounds. Torsional profiles, energetic differences between conformers, geometry and vibrational frequencies were calculated and compared with experimental data when possible. The energy and structure resulting from the *ab initio* calculations are in excellent agreement with many of the experimental data, particularly in the cases of propargyl alcohol and methyl propargyl ether.

The concentration of the MM3 formulation was on the rotational profiles of the C_{sp}—$C_{sp}3$—O—H ($C_{sp}3$) portions of the molecules. The resulting parameterization of these torsions shows excellent agreement with the calculated *ab initio* torsional profiles. MM3 structural investigations focused principally on three bending angles which involved the C_{sp}—$C_{sp}3$—O (F)

Table 10. Experimental and MM3 (94) vibrational frequencies for propargyl fluoride[a,b]

Experimental		
Ref. 12	Ref. 19	MM3 (94)
3322 CH str	3338 ≡CH str	3327·1 ≡CH str
	2972 CH_2 str	2996·6 CH_2 str
	2955 CH_2 str	2943·0 CH_2 s str
2148 C≡C str	2150 C≡C str	2131·7 C≡C str
	1465 CH_2 bnd	1489·8 CH_2 wag
	1381 CH_2 wag	1414·7 CH_2 sciss
	1242 CH_2 tw	1241·5 CH_2 tw
1045	1039 CF str	1062·3 CF str
	1018 CH_2 rck	896·0 CH_2 rck
	940 C—C str	948·1 C—C str
674 ≡CH bnd	675 CH bnd	732·2 CCH bnd
636 ≡CH bnd	635 CH bnd	666·1 CCH bnd
	539 skel bnd	520·3 CCF bnd
	310 skel bnd	312·5 CCH bnd
	211 skel bnd	232·5 CCC bnd

[a] Frequencies are given in wavenumbers (cm^{-1}).
[b] For abbreviations, see Table 8.

bending. Parameter optimization was carried out in an attempt to reproduce available structural data, both experimental and *ab initio*, and known vibrational data. All of the resulting parameters were found to reproduce the available structural and vibrational data well.

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