

# MOLECULAR MECHANICS CALCULATIONS (MM3) ON NITRILES AND ALKYNES

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The MM3 force field has been extended to include the nitriles and alkynes. Structures, heats of formation, dipole moments and conformational equilibria for aliphatic nitriles and alkynes compounds are fitted to within experimental error. The vibrational spectra for aliphatic nitriles and alkynes were studied, and the experimental values were fitted to an rms error of about  $30\text{ cm}^{-1}$ . Previous MM2 studies of nitriles and alkynes left unresolved the length of the  $\text{C}_{\text{sp}}-\text{C}_{\text{sp}^3}$  bonds in isopropyl nitrile, 3-methylbutyne, and *tert*-butylacetylene. In each of these compounds, previous MM2 results disagree with experiment. The present MM3 studies and quantum mechanical calculations (MP2/6–31G\*\* and B3LYP/6–31G\*) confirmed the previous MM2 results.

## INTRODUCTION

Applications of molecular mechanics to the determination of structures, conformational energies and vibrational spectra have become extensive in recent years, and the widely used MM2 force field is gradually being replaced by MM3.<sup>1</sup> The predictive value of the force field for systems as varied as the alkanes, alkenes, ethers, carbonyls, and many other functional groups has been established. Here, we are concerned in extending the MM3 force field to nitriles and alkynes. Previous force field applications to alkynes include MM2 studies of structures and conformations;<sup>2</sup> studies of heats of hydrogenation and implications of changes of the triple bond in the chain;<sup>3</sup> and studies of cyclooctyne with the specific investigation of torsional barriers for the non-linear acetylenes.<sup>4</sup> Earlier force field calculations on the nitriles included the MM2,<sup>5</sup> UFF<sup>6</sup> and Urey–Bradley<sup>7</sup> approaches. This paper will deal with all these issues, including improvements in the calculated structures, heats of formation and torsional barriers of nitriles and alkynes, as well as a detailed vibrational spectra study.

The sparse experimental data available on smaller aliphatic and some cyclic nitriles consist primarily of electron diffraction studies<sup>8</sup> and microwave spectra.<sup>9–15</sup> The vibrational infrared and Raman spectra<sup>16–17</sup> of the

simple mononitriles focused on both molecular structures and thermodynamic properties which are readily compared with the heat of formation data.<sup>18–22</sup> Previous MM2 work on nitriles<sup>5</sup> discussed structural and  $\Delta H_f^\circ$  results, but here, with the development of MM3 parameters, we also focus on assignments of vibrational spectral frequencies and intensities. Force fields which attempt to satisfy both experimental data and vibrational spectra illustrate the coupled effect of various sections of the potential surface and present an interesting challenge. We attempt here to obtain optimum parameters which match vibrational details at the surface minima, coupled to accurate structural details which depend on the location of these minima on the surface. In this paper, we compare the structural results in MM3 and MM2 and how well the MM3 vibrational spectra compare with experiment. The MM3 force field<sup>1</sup> has both improved torsion–stretch terms and a softened van der Waals potential relative to MM2, which yield more accurate energies and structures in addition to reasonable vibrational spectra.

The alkynes have been the object of intense experimental and theoretical scrutiny. The diverse chemical properties of the alkynes combined with physical properties such as bond strength are still a subject of refinement, both experimentally and computationally. In

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recent years, the preparation of polymeric network allotropes of carbon has become the subject of much interest.<sup>23</sup> The key step in preparing such networks may be the synthesis of monomeric precursors with a high C:H ratio. Both cyclic and acyclic acetylenic precursors are obvious possibilities in this respect. Many acyclic alkynes have been synthesized and characterized. However, cyclic alkynes still remain a challenge. Cyclooctyne is one of the few cyclic compounds for which we have significant laboratory gas-phase data,<sup>24-26</sup> and it allows a study of a strained C≡C bond. The ring is small enough to exhibit a large strain energy, yet the compound is stable enough to study experimentally. However, an early MM2 study disagreed with the experimental structure of cyclooctyne, mainly regarding the torsional angle around the triple bond.<sup>2-4</sup>

Experimental structures of some simple alkynes and nitriles remain problems. For example, the experimental bond lengths between an sp-hybridized carbon and a secondary (or tertiary) carbon atom (≡C—C—) are significantly longer than MM2 values.<sup>2-5</sup> These experimental structural problems were addressed in the present study with the help of quantum mechanical calculations.<sup>27</sup>

## RESULTS AND DISCUSSION

### Structures of nitriles and alkynes

The initial parameters for the nitriles and alkynes were based on the previous MM2 values.<sup>2-5</sup> The parameters were adjusted to fit the vibrational frequencies obtained from experiment and are presented in Table 1. The calculated structural data are summarized in Table 2. The MM3 results in Table 3 show highly accurate moments of inertia for simple nitriles and alkynes, with an average deviation below 1%, much of which deviation results from the experimental moments of inertia being determined from  $r_z$  bond lengths, while MM3 bond lengths are  $r_g$ . Table 5 gives the dipole moments of some alkynes and nitriles. Since these MM3 structures remain essentially the same as those from MM2, these calculations need not be discussed further for the most part. However, we would like to call attention to the systematic discrepancy between theory and experiment concerning the  $C_{sp}-C_{sp^3}$  distances for four molecules, namely isopropyl nitrile, *tert*-butyl cyanide, 3-methylbutyne and *tert*-butylacetylene (Table 4). These experimental C—C distances are much longer than those given by MP2 and MM3. We noticed this problem in our previous MM2 studies of nitriles and alkynes.<sup>2-5</sup> The nature of the experiments was such that these bond lengths contained large uncertainties because of correlated parameters. At the time of our earlier work, we were not able to establish how much of the error was in the experimental values and how much was in the MM2 values. In the present study we calculated the structures

of these molecules at the *ab initio* MP2/6-31G\*\* level, hoping that these reasonably high-level *ab initio* calculations could clear up the ambiguities in the experimental structures. The MP2 results agree well with MM2 and MM3 structures, indicating that the experimental structures are indeed inaccurate.

Experimental methods have difficulties in dealing with gas-phase molecular structures for large molecules. For example, microwave spectroscopy allows one to determine only three structural parameters per molecule. For *tert*-butylacetylene, if the hydrogen positions and  $C_{3v}$  symmetry are assumed, one still has four parameters to evaluate and only three pieces of data. Often isotopically substituted molecules are used to increase the available data ( $r_s$  structures). However, the accuracy is then severely limited by the use of the harmonic approximation. One such example is the structure of isopropyl cyanide.<sup>9</sup> Even though 1.501 Å is the C—CN distance that fits the experimental rotational constants best, 1.481 Å fits the experimental data nearly as well. However, as can be seen in Table 4, both MP2 and MM3 results strongly support 1.481 Å as the best value for the C—CN distance in isopropyl cyanide. Both Nugent *et al.*<sup>9a</sup> and Durig and Li<sup>13a</sup> acknowledge experimental uncertainty in their results. In *tert*-butyl cyanide the authors acknowledge that the C—C≡ bond is '0.02–0.04 Å longer than the normal value.' It should be noted from Table 3 that our MM3 moments of inertia are consistent with experimental data on the isopropyl and *tert*-butyl cyanides.

The structural and thermodynamic data available on the alkynes are not as limited as those for the nitriles. The structures on which we shall focus here have been determined by electron diffraction and microwave methods for acetylene,<sup>28</sup> propyne,<sup>29</sup> 1-butyne,<sup>30</sup> 1-pentyne,<sup>31</sup> 3-methyl-1-butyne,<sup>32</sup> 3,3-dimethyl-1-butyne,<sup>33</sup> cyclooctyne,<sup>34</sup> and 1,5-cyclooctadiyne.<sup>35</sup> Beginning with the stretching and bending force parameters available from MM2<sup>2</sup>, we were able to modify and improve the structural parameters to the values presented in Table 1.

The  $C_{sp}-C_{sp^3}$  and  $C_{sp}-H$  bonds, with bond moments of  $-1.64$  and  $-0.92$ , respectively, result in a net dipole moment of  $0.72$  D for a primary acetylene, with the negative end from  $C_{sp^3}$  towards the sp carbons. As can be seen in Table 5, this fits the dipole moments of simple acetylenes and matches experiment with an rms of  $0.06$  D (maximum deviation  $-0.12$  D). We have not included the induced dipoles,<sup>36</sup> and this in part explains the deviation from experiment of up to  $0.12$  D for the alkyne dipole moments.

The stereochemical demands of a strained and bent triple bond are the theoretically most challenging aspect of cycloalkyne conformations. Cyclooctyne shows a strain energy in the heat of hydrogenation (in acetic acid solution) of  $69$  kcal ( $1$  kcal =  $4.184$  kJ).<sup>37</sup> This strained triple bond was also investigated using the

Table 1. Optimized MM3 parameters for Nitriles and Alkynes

Torsional parameters <sup>b</sup> (kcal mol <sup>-1</sup> )					
Atom type <sup>a</sup>	V <sub>1</sub>	V <sub>2</sub>	V <sub>3</sub>		
4-1-1-5	0.00	0.00	0.56		
4-1-2-2	-1.90	0.00	0.00		
124-4-4-124	0.04	0.00	0.00		
Bending parameters					
Atom type	K <sub>b</sub> (mdyn Å rad <sup>-2</sup> )	θ(o)(type I) <sup>c</sup>	θ(o)(type II)		
1-1-4	0.96	108.80	109.70		
1-1-4	0.96	110.00 (type III)			
1-4-10	0.335	180.00			
2-1-4	0.57	110.20 (type III)			
4-1-5	0.68	108.80 (type III)			
1-4-4	0.38	180.00			
4-4-124	0.25	180.00			
Stretching parameters					
Atom type	K <sub>s</sub> (mdyn Å <sup>-1</sup> )	l <sub>0</sub> (Å)	Bond moment (D)		
1-4	5.50	1.470	1.64		
4-10	17.33	1.158	2.50		
4-4	15.25	1.210	0.00		
4-124	5.97	1.080	-0.92		
Heat parameters <sup>d</sup> (kcal mol <sup>-1</sup> )					
C≡N	C—C≡(N)	NC—Me	NC— <i>iso</i>	NC— <i>tert</i>	
30.1003	-1.4683	3.5480	-2.2270	-4.4220	
C≡C	C—C≡(C)	≡C—Me	≡C— <i>iso</i>	≡C— <i>tert</i>	≡C—H
59.7633	-1.4683	0.1483	-0.9867	-5.39	-4.59
Strainless heat parameters <sup>e</sup> (kcal mol <sup>-1</sup> )					
C≡N	C—C≡(N)	NC—Me	NC— <i>iso</i>	NC— <i>tert</i>	
28.5300	-0.87	3.4800	-2.0400	3.9900	
C≡C	C—C≡(C)	≡C—Me	≡C— <i>iso</i>	≡C— <i>tert</i>	≡C—H
58.7917	0.2983	0.1867	-2.6083	-5.03	-3.46
Van der Waals parameters					
Atom type	r (Å)	ε (kcal mol <sup>-1</sup> )			
4	1.94	0.056			
10	1.93	0.043			
124	1.62	0.020			

<sup>a</sup> Atom type: 1 = C<sub>sp3</sub>; 4 = C<sub>sp</sub>; 10 = nitrogen (nitrile); 124 = hydrogen connected to C<sub>sp</sub>.

<sup>b</sup> Torsional parameters of 1-4-4-1, V<sub>1</sub> = 0.0124 × Δθ<sub>1</sub>Δθ<sub>2</sub>; 1-1-4-4, V<sub>1</sub> = 0.0297 × Δθ; set text for explanation

<sup>c</sup> For the bend angle, A—B—C, type I refers to the angle with two hydrogen atoms connected to the atom B, type II refers to the angle with one hydrogen atom connected to the atom B and type III refers to the angle with no hydrogen atom connected to the atom B, apart from the hydrogens that may be represented by A and C.

<sup>d</sup> In a nitrile, C<sub>sp3</sub>—C<sub>sp</sub> and C≡N always occur as one of each. However, an alkyne may have 0, 1, or 2 C<sub>sp3</sub>—C<sub>sp</sub> bonds. Hence in the nitriles one parameter is enough and in the alkynes more parameters are needed.

Table 2. Selected structural parameters of nitriles and alkynes<sup>a</sup>

Nitriles					
Acetonitrile	<i>r</i> (MM3)	Exp. ( <i>r</i> <sub>e</sub> ) <sup>8,9,15</sup>	<i>θ</i>	MM3	Exp.
C—C	1.470	1.468	CCH	110.0	109.7
C≡N	1.158	1.159	HCH	108.9	108.9
C—H	1.108	1.095			
Propionitrile	<i>r</i> (MM3)	Exp. ( <i>r</i> <sub>0</sub> ) <sup>11</sup>	<i>θ</i>	MM3	Exp.
C≡N	1.158	1.157	C—C—C	110.5	110.3
C—C (nit.)	1.473	1.474	C—C—H (nit)	109.3	—
C—C	1.533	1.548	C—C—H	110.0	—
C—H (nit.)	1.113	1.091	H—C—H (nit.)	107.3	109.2
C—H	1.110		C—C—H (far)	111.5	—
Isopropyl nitrile	<i>r</i> (MM3)	Exp ( <i>r</i> <sub>0</sub> ) <sup>13</sup>	<i>θ</i>	MM3	Exp.
C—C (nit.)	1.476	1.501	C—C—H (nit.)	108.1	
C—C	1.536	1.530	C—C—C (nit.)	109.8	113.8
C—H	1.112	1.092	C—C—H	111.5	
C≡N	1.158		H—C—H	107.3	
2,2-Dimethylpropanenitrile ( <i>tert</i> -butyl cyanide)	<i>r</i> (MM3)	Exp. ( <i>r</i> <sub>0</sub> ) <sup>9</sup>	<i>θ</i>	MM3	Exp.
C—C (nit.)	1.478	1.495	C—C—C (nit.)	108.6	—
C—C	1.538	1.536	C—C—C	110.4	110.5
C—H	1.112	1.156	C—C—H	111.7	—
C≡N	1.158		H—C—H	107.2	—
Alkynes					
Acetylene <sup>b</sup>	<i>r</i> (MM3)	Exp. ( <i>r</i> <sub>0</sub> ) <sup>35</sup>	<i>θ</i>	MM3	Exp.
C≡C	1.211	1.209		180.0	
C—H	1.081	1.059			
Methylacetylene (propyne)	<i>r</i> (MM3)	Exp. ( <i>r</i> <sub>0</sub> ) <sup>29</sup>	<i>θ</i>	MM3	Exp.
C≡C	1.211	1.207	C—C—H	110.0	110.8
C—H (acet)	1.081	1.056	H—C—H	109.0	108.1
C—C (acet)	1.4712	1.460			
C—H	1.1097	1.097			
Dimethylacetylene (2-butyne staggered)	<i>r</i> (MM3)	Exp. ( <i>r</i> <sub>e</sub> ) <sup>50</sup>	<i>θ</i>	MM3	Exp.
C≡C	1.2119	1.213	C—C—H	110.0	110.7
C—C (acet)	1.4716	1.467	H—C—H	109.0	108.9
C—H	1.1097	1.115			
3-Methyl-1-butyne	<i>r</i> (MM3)	Exp. ( <i>r</i> <sub>0</sub> ) <sup>32</sup>	<i>θ</i>	MM3	Exp.
C—C≡	1.477	1.495	C—C—C≡	109.7	109.6
C—C	1.536	1.527	C—C—C	111.1	112.9
C≡C	1.211		C—C—H	111.6	—

(continued)

Table 2. *Continued*

1-Pentyne, <i>trans</i> and <i>gauche</i>	$r$		Exp. ( $r_0$ ) <sup>31</sup>	$\theta$	(MM3)		Exp.	
	<i>trans</i>	<i>gauche</i>			<i>trans</i>	<i>gauche</i>	<i>trans</i>	<i>gauche</i>
C <sub>1</sub> ≡C <sub>2</sub>	1.2113	1.2113	1.207	C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	110.59	111.41	311.4	111.7
C <sub>1</sub> —H	1.0813	1.0813	1.056	C <sub>3</sub> C <sub>4</sub> C <sub>5</sub>	112.20	113.10	114.5	115.6
C <sub>2</sub> —C <sub>3</sub>	1.4742	1.4742	1.460					
C <sub>3</sub> —C <sub>4</sub>	1.5353	1.5362						
C <sub>3</sub> —H	1.1144	1.1113	1.096					
C <sub>4</sub> —C <sub>5</sub>	1.5341	1.5347	1.526					
<i>tert</i> -Butylacetylene	$r$	(MM3)	Exp. ( $r_a$ ) <sup>28</sup>					
C≡C	1.211	1.210						
≡C—C	1.480	1.498						
C—C	1.5327	1.529						
C—H	1.112	1.10						

<sup>a</sup> Bond lengths in Å and angles in degrees

<sup>b</sup> Standard MM3 bond lengths are  $r_s$  values. MM3 will also calculate  $r_0$  values, and these were used to reproduce the experimental values: C≡C  $r_0$  = 1.120 Å and C—H  $r_0$  = 1.057 Å for acetylene

Table 3. Experimental and MM3 moments of inertia of nitriles and alkynes (au).

Molecule	$I_{xx}$		$I_{yy}$		$I_{zz}$	
	Exp.	MM3	Exp.	MM3	Exp.	MM3
Acetonitrile		3.279	54.87	55.492 (1.1%)	54.87	55.492 (1.1%)
Propionitrile	18.500	18.543 (0.2%)	107.224	107.564 (0.3%)	119.348	119.643 (0.3%)
Isopropyl cyanide	63.64	63.827 (0.1%)	127.363	128.365 (0.8%)	174.207	174.653 (0.2%)
<i>tert</i> -Butyl cyanide		112.581	183.809	184.952 (0.6%)	183.809	184.952 (0.6%)
Acetylene		0.0	14.32	14.531 (1.5%)	14.320	14.531 (1.5%)
Propyne		3.289	59.146	59.856 (1.2%)	59.146	59.856 (1.2%)
Dimethylacetylene	6.599	6.578 (-0.3%)	152.243	152.191 (-0.03%)	152.243	152.191 (-0.03%)
1-Pentyne ( <i>gauche</i> )	50.939	51.473 (1.1%)	159.285	160.976 (1.1%)	191.864	193.201 (0.7%)
1-Pentyne ( <i>trans</i> )	21.653	22.098 (2.1%)	226.568	227.782 (0.5%)	238.793	240.178 (0.6%)
<i>tert</i> -Butylacetylene		112.593	188.379	189.318 (0.5%)	188.379	189.318 (0.5%)

Table 4. Experimental and theoretical  $\equiv\text{C}-\text{C}$  bond distances for several alkynes and nitriles ( $\text{\AA}$ )

	Acetonitrile	Isopropylnitrile	<i>tert</i> -Butyl cyanide	Propyne	3-Methylbutyne	<i>tert</i> -Butylacetylene
Exp.	1.468	1.501 (1.481)	1.499 (1.478)	1.460	1.495	1.498 (1.496)
MP2	1.462 <sup>a</sup>	1.470 <sup>a</sup>	1.473 <sup>b</sup>		1.467 <sup>a</sup>	1.470 <sup>b</sup>
MM3	1.470	1.476	1.478	1.472	1.477	1.480

<sup>a</sup> Basis set: 6-31G\*\*.<sup>b</sup> Basis set: 6-31G\*.

Table 5. Heats of formation and dipole moments of nitriles and alkynes

Molecule	$\Delta H_f^\circ$ (kcal mol <sup>-1</sup> )		Dipole moment (D)	
	Exp.	MM3	Exp.	MM3
Acetonitrile	20.9	20.9	3.92	4.14
Propionitrile	12.32	12.74	4.05	4.14
Fluoroacetonitrile			2.92	3.87
Diffluoroacetonitrile			2.32	3.30
Butyl cyanide	8.12	7.76		
Isopropyl cyanide			4.29	4.14
<i>tert</i> -butyl cyanide	-0.6	-0.6	3.95	4.14
Pentyl cyanide	2.51	2.73		
Heptyl cyanide	-7.41	-7.37		
Octyl cyanide	-12.07	-12.40		
Cyclohexyl cyanide	1.15	1.33		
Acetylene	54.34	54.31	0.00	0.00
Propyne	44.32	44.38	0.75	0.72
1-Butyne	39.49	39.58		
2-Butyne	34.69	34.66	3.95	0.00
4-Octyne	12.59	14.9		
3-Methyl-1-butyne	32.6	34.07	0.72	0.72
1-Pentyne	34.51	34.41	<i>t</i> : 0.84 <i>g</i> : 0.77	<i>t</i> : 0.72 <i>g</i> : 0.72
Cyclooctyne	45-50	50.58		
Cyclononyne	30.17	35.34		
Cyclodecyne	19.62	22.16		

MM3 force field, which has torsional terms similar to those in MM2 to deal with the non-linearity about the triple bond,<sup>4</sup> accompanied with a new MM3 acetylenic parameter set.

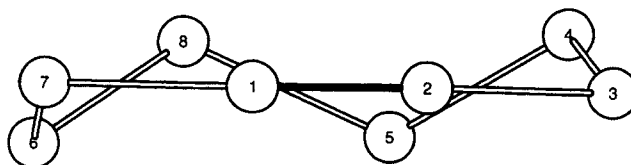
Two parameters received special attention, namely  $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}}-\text{C}_{\text{sp}}-\text{C}_{\text{sp}^3}$  (1-4-4-1) and  $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}}-\text{C}_{\text{sp}}-\text{C}_{\text{sp}^3}$  (1-1-4-4). As in previous MM2 work,<sup>4</sup> we attempted to fit the torsional potential about each of these bonds when, as in the case of cycloalkynes, there is significant deviation from linearity. The torsional potential depends strongly on, and increases with, increasing values of the angles away from linearity. The change from the linear conformation denoted by the angle  $\theta$  may be symmetric or asymmetric. For the torsion of  $\text{C}-\text{C}\equiv\text{C}-\text{C}$ , the  $V_1$  term which best describes the system is given by

$$V_1 = 0.0124 \times \Delta\theta_1 \times \Delta\theta_2$$

which slightly differs from the MM2:  $V_1 = \text{constant} \times (\Delta\theta_{\text{ave}}^2)$  and  $\Delta\theta_{\text{ave}} = \frac{1}{2}(\Delta\theta_1 + \Delta\theta_2)$ . The new MM3 potential fits *ab initio* data better than the MM2 potential. For the torsion of  $\text{C}-\text{C}-\text{C}\equiv\text{C}$ , the  $V_1$  correction is the same as the MM2 value,<sup>4</sup> with  $V_1 = 0.0297 \times \Delta\theta$ .

Experimentally, the molecular structure of cyclooctyne<sup>24-26</sup> has been investigated using electron diffraction (ED) and NMR coupling constants. The resulting data are interpreted as indicating a highly distorted dihedral angle about  $\text{C}-\text{C}\equiv\text{C}-\text{C}$  equal to 40-46°, and a bent (tight)  $\text{C}-\text{C}\equiv\text{C}$  angle of 154.5° (see Table 6). However, MM3 results show only a 3.6° dihedral twist, and a correspondingly more open angle (159.9°). In interpreting the radial distribution function from the electron diffraction study of cyclooctyne,<sup>24</sup> one major assumption made (see Table 6) was that the  $\text{sp}^3-\text{sp}^3$  bonds are all of the same length. In an MM3

Table 6. Experimental and theoretical structure of cyclooctyne



Parameter	Exp.	MM3	<i>Ab initio</i> <sup>a</sup>	
			MP2	B3LYP
<i>Bond lengths</i> (Å)				
C <sub>1</sub> ≡C <sub>2</sub>	1.228	1.212	1.226	1.211
C <sub>2</sub> C <sub>3</sub>	1.457	1.469	1.461	1.461
C <sub>3</sub> C <sub>4</sub>	1.534	1.548	1.544	1.556
C <sub>4</sub> C <sub>5</sub>	1.565	1.561	1.543	1.552
C <sub>5</sub> C <sub>6</sub>	1.565	1.572	1.556	1.565
C <sub>8</sub> ⋯C <sub>3</sub>	3.866	3.866	3.927	3.913
<i>Valence angles</i> (°)				
C≡C—C	154.5	159.9	157.5	157.6
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	108.3	106.0	106.7	107.1
C <sub>3</sub> C <sub>4</sub> C <sub>5</sub>	115.3	114.5	114.2	115.7
C <sub>4</sub> C <sub>5</sub> C <sub>6</sub>	118.9	117.0	117.3	118.3
<i>Dihedral angles</i> (°)				
C—C≡C—C	-40.2(10.4)	3.6	9.0	4.0
C≡C—C—C	-39.1(5.3)	-13.5	-20.9	-18.0
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub> C <sub>5</sub>	50.7(10)	39.1	46.7	46.5
C <sub>3</sub> C <sub>4</sub> C <sub>5</sub> C <sub>6</sub>	-87.1(5)	-87.4	-89.9	-88.0
C <sub>4</sub> C <sub>5</sub> C <sub>6</sub> C <sub>7</sub>	105.0(10)	117.7	113.1	108.1

<sup>a</sup>Basis set: 6-31G\*.

calculation, these are each explicitly determined. The calculated and experimental results differ most significantly in the torsional angle about the triple bond. One may also note that MM3 gives a shorter acetylenic bond, and generally smaller C—C—C angles. To resolve the large difference between the experimental and the MM3 (MM2) values for the torsional angle of cyclooctyne, we optimized the molecular structure at both the MP2/6-31G\* and B3LYP/6-31G\* levels (Table 6). The quantum mechanical results indicate a 4–9° torsional angle, strongly supporting the MM3 structure of cyclooctyne. Our quantum mechanical and MM3 calculations also indicate that there is no local minimum with a torsion angle of greater than 10°.

When MM3 calculation was carried out at a 40° dihedral angle, all accompanying bond lengths were more relaxed (C<sub>3</sub>⋯C<sub>8</sub>), with bond angles still smaller than those that Traetteberg *et al.*<sup>24</sup> found. One should note that the results of early ED work by Haase and Krebs<sup>26</sup> are actually in better agreement with our results. In that work, the C≡C—C angle was 158.5° and there

is a 0° dihedral angle about C—C≡C—C (however, Traetteberg *et al.*<sup>24</sup> pointed out that Haase and Krebs's model was not optimized). In addition to the agreement with the quantum mechanical structural results, our MM3 vibrational frequency for the C≡C stretch also agrees with the experimental stretching frequencies.<sup>24</sup> Experimental values (gas phase) for cyclooctyne and dimethylacetylene are 2206 and 2240 cm<sup>-1</sup>, respectively, while the corresponding MM3 values are 2242 and 2267 cm<sup>-1</sup>. The deformation of the cyclooctyne system thus weakens the triple bond, and lowers the stretching frequency by 34 cm<sup>-1</sup> (experiment) and 25 cm<sup>-1</sup> (MM3).

### Heats of formation

The heats of formation of nitriles and alkynes calculated with MM3 are in excellent agreement with experimental values (standard deviation 0.24 kcal mol<sup>-1</sup>). The same ten parameters as used in MM2 to fit heats of formation were used here. Table 1

also contains strain factors, defined as

$$E(\text{steric energy}) + \sum H(\text{bonds, structure}) \\ - \sum H(\text{bonds, structure, strainless})$$

with acetylene assigned zero parameters. Strain energies may be calculated in the usual way.<sup>1</sup> Strainless group increments were also optimized for the group of compounds as shown in Table 1. Strain energies which we shall tabulate for the cycloalkynes will include the inherent strain just described, augmented with torsional and conformational energy.<sup>38</sup>

In older work, the recommended value for the heat of formation ( $H_f^\circ$ ) of methyl cyanide was 21.0 kcal mol<sup>-1</sup>.<sup>20-22</sup> Recently, this value was reported to be 15.5 kcal mol<sup>-1</sup>.<sup>39</sup> We chose the former value in parameterizing the heats of formation. A common difficulty, when several experimental values are presented for the  $\Delta H_f^\circ$  of the nitriles, is resolved by matching the data to group additivity rules. This is true for propyl cyanide,<sup>40</sup> isopropyl cyanide,<sup>40,41</sup> and *n*-butyl and *tert*-butyl cyanide. Most of the measurements on longer alkyl cyanides<sup>43,44</sup> were reported by Stridh *et al.*,<sup>42</sup> and MM3 results match their results closely.

All of the  $H_f^\circ$  values are listed in Table 5. Frequently, when no experimental  $H_f^\circ$  are available, Benson's additivity rules<sup>20</sup> become useful in these calculations. Table 5 also contains MM3 heats of formation of the alkynes with the C<sub>sp</sub>-H value arbitrarily picked to be -4.590 kcal mol<sup>-1</sup> (as for other C-H bonds, since it is a number that must be fixed arbitrarily) and the C<sub>sp</sub>-C<sub>sp</sub> values arrived at by least-squares fitting for the six simple alkynes. MM3 results for the simple alkynes match the experimental data<sup>3</sup> with an rms deviation of 0.06.

Results for some cyclic acetylenes are also presented in Table 5. Heat of formation data are not available from heats of combustion for cyclooctyne, -nonyne or -decyne. By using the heat of hydrogenation data,<sup>3</sup> for cyclic alkynes in hexane solution, we calculated the heats of formation for these compounds. The molecular mechanics results for cyclodecyne and 4-octyne agree nicely with this experimental approximation (Table 5), as expected. The heat of formation of cyclooctyne can be readily calculated from its heat of hydrogenation in solution.<sup>37,44</sup> Since the available experimental heat of hydrogenation was determined in acetic acid solvent, an estimated correction of 1.0 kcal is added to allow approximately for the effect of hydrogen bonding of the solvent to the acetylene. Therefore, if we add the gas-phase heat of formation of the cycloalkane to the heat of hydrogenation of cyclooctyne, and correcting for the solvent effect:

$$69.0(\text{sol}) + [-29.73(\text{g})] + 1 = 40.94 \\ \Delta H_{\text{H}_2} \text{ cyclooctyne} \quad \Delta H_f^\circ \text{ cyclooctane} \quad \text{solvent correction}$$

The heat of hydrogenation of cyclooctyne is believed

to be 10% too low, since only 90% of the H<sub>2</sub> was absorbed. Cyclooctyne is suspected to undergo partial polymerization in the calorimeter, and the directly determined experimental value is therefore 'thought to be in error of at least 4-6 kcal mol<sup>-1</sup>.'<sup>37</sup> If one assumes, then, that 10% polymerization had occurred, the value for the heat of hydrogenation is raised from 69.0 to 76.67 kcal. We therefore estimate the experimental  $H_f^\circ$  of cyclooctyne to be 47.94 kcal mol<sup>-1</sup>. This compares reasonably with the MM3 value of 50.00 kcal mol<sup>-1</sup>. A factor which may also contribute to the heat of formation discrepancies for cyclic systems involves the increase in the 1-4-4 bending parameter (0.380, Table 1, relative to the 0.2 MM2 value). This parameter was nearly doubled in MM3 in order to obtain adequate vibrational spectra for simple and cyclic alkynes. As may be seen in Tables 2, 3 and 5, the MM3 structural and the  $H_f^\circ$  values are satisfactory for simple alkynes. As mentioned earlier, structure and spectra focus on the potential surface minima whereas the gross features of the surface relate to energies, both conformational differences and heats of formation.

### Vibrational spectra

Nitriles and acetylenes exhibit similar spectra, as they possess similar geometries, and belong to similar symmetry point groups. They differ mainly in the positions of the C≡N and C≡C bands and also the H-C≡C stretching and bending bands, which of course are not found in the nitriles. The overall vibrational spectral results for the various alkynes show consistency and agreement with experiment to within 30 wavenumbers (rms), which is the limit of accuracy for MM3 with alkanes. MM3 vibrational data for acetylene are presented in Table 7. The bands at 3285 ( $\Sigma_u$ ) and 584 ( $\Pi_u$ ) cm<sup>-1</sup> are calculated by MM3 to be intense (strong) bands in the infrared, which agrees with the medium to strong intensities measured experimentally.<sup>45</sup>

The experimental vibrational spectra of the aliphatic nitriles/alkynes are compared with the calculated MM3 values in Tables 8-10.

In comparing nitriles and acetylenes, examples of pairs of analogs include acetonitrile and methylacetylene (Table 8) and propionitrile and 1-butyne. We shall focus

Table 7. Experimental and MM3 vibrational frequencies (cm<sup>-1</sup>) of acetylene

Type of mode	Experimental	MM3	Difference
$\Sigma_g^+$ CH stretch	3372.8	3364	-9
$\Sigma_g^+$ CC stretch	1974.3	1944	-30
$\Sigma_u^+$ CH stretch	3281.9	3285	3
$\Pi_u$ CH bend	730.3	717	-13
$\Pi_g$ CH bend	612.8	584	29



on comparisons (Table 9) for propionitrile and 1-butyne.<sup>30</sup> There are common difficulties in the assignments of the bending motions of C—C—C and C—C≡N or C—C≡C, as they appear in the same region of the spectrum and overlap. The experimental C—C≡N and C—C≡C bending frequencies fall within 7–20 cm<sup>-1</sup> of one another. To match these data, MM3 results need to average the coupling of the

bending and torsion assignments of the C—H IR stretching bands (from 2958 to 2851 cm<sup>-1</sup>).<sup>28–31</sup> Band intensity information resolves this experimentally. The overlapping bands, resonance interactions and torsion–bending problems are similarly clarified with the use of the MM3 calculated band intensities.

The commonality is further extended to the Fermi resonance with overtones in the C—H stretch region of

Table 8. Experimental and theoretical vibrational frequencies (cm<sup>-1</sup>) of acetonitrile and propyne

Mode	Symmetry	Acetonitrile			Propyne		
		Exp.	MM3	Diff.	Exp.	MM3	Diff.
≡C—H stretch.	A <sub>1</sub>				3329	3324	-5
CH <sub>3</sub> stretch.	E	3009	3020	11	2994	3004	10
CH <sub>3</sub> stretch.	A <sub>1</sub>	2954	2919	-35	2926	2903	-23
N(C)≡C stretch.	A <sub>1</sub>	2267	2251	-16	2124	2128	4
CH <sub>3</sub> def.	E	1448	1419	-29	1448	1416	-32
CH <sub>3</sub> def.	A <sub>1</sub>	1385	1381	-4	1382	1377	-5
CH <sub>3</sub> rock.	E	1041	1032	-9	1041	1031	-10
C—C stretch.	A <sub>1</sub>	920	907	-13	926	906	-20
C≡C—H bend.	E				643	646	3
N(C)≡C—C bend.	E	362	374	12	336	318	-18

Table 9. Experimental and theoretical vibrational frequencies (cm<sup>-1</sup>) of propionitrile and 1-butyne

Type of mode	Propionitrile			1-Butyne		
	Exp.	MM3	Diff.	Exp.	MM3	Diff.
C—H stretch.				3332	3324	-8
CH <sub>3</sub> stretch.	3001	2977	-24	2991	2974	-17
CH <sub>3</sub> stretch.	3001	2974	-27	2988	2974	-14
CH <sub>3</sub> stretch.	2955	2972	17	2945	2959	14
CH <sub>3</sub> stretch.	2900	2924	24	2939	2909	-30
CH <sub>3</sub> stretch.	2849	2880	31	2925	2879	-46
C≡N, C≡C stretch.	2252	2251	-1	2116	2127	11
H <sub>3</sub> C def.	1465	1474	8	1470	1469	-1
H <sub>3</sub> C def.	1465	1462	-3	1462	1461	-1
H <sub>2</sub> C scissor.	1433	1456	23	1446	1456	12
H <sub>3</sub> C def.	1382	1433	51	1385	1431	46
H <sub>2</sub> C wag.	1324	1370	46	1322	1368	46
H <sub>2</sub> C twist.	165	1239	-26	1262	1237	-25
C—C≡ stretch.	1077	1047	-30	1090	1046	-44
C—C stretch.	1008	1035	-32	1070	1034	-36
H <sub>3</sub> C rock.	1022	990	-32	1007	989	-18
H <sub>2</sub> C rock.	837	849	12	840	850	10
H <sub>2</sub> C rock.	786	839	53	782	839	57
C—C—H bend.				634	656	22
C—C—H bend.				630	645	15
CCC def.	530	505	-25	507	470	-37
C—C≡N, C—C≡C bend.	371	348	-23	344	313–31	
C—C≡N, C—C≡C bend.	220	235	15	208	221	13
Torsion	—	221			196	

Table 10. Experimental and theoretical vibrational frequencies ( $\text{cm}^{-1}$ ) of dimethylacetylene ( $D_{3h}$ )

Type of mode	Symmetry	Exp.	MM3	Diff.
CH stretch.	$A_1'$	2916	2904	-12
$\text{C}\equiv\text{C}$		2240	2267	27
$\text{CH}_3$ twist.-rock.	$A_1''$	1380	1363	-17
$\text{C}-\text{C}$ stretch.		725	699	-26
Free internal rotation	$A_1''$	0	0	
$\text{CH}_3$ stretch.	$A_2''$	2915	2903	-12
$\text{CH}_3$ def.		1382	1422	40
$\text{C}-\text{C}$ stretch.		1152	1102	-50
CH stretch.	$E'$	2973	3004	31
$\text{CH}_3$ twist.		1456	1416	-40
$\text{C}-\text{C}\equiv\text{C}$ torsion bend.		213	165	-24
CH stretch.	$E''$	2966	3004	8
$\text{CH}_3$ def.		1448	1416	-32
$\text{CH}_3$ twist., rock.		1029	1023	-7
$\text{C}-\text{C}\equiv\text{C}-\text{C}$ bend.		371	448	77

1-butyne and propionitrile. The experimental  $\text{CH}_2$  rock for butyne is a weak band at  $1090\text{ cm}^{-1}$  whereas it is  $1022\text{ cm}^{-1}$  for propionitrile (Table 9). The  $\text{C}-\text{C}\equiv\text{N}$  bend is more difficult, as some experimentalists<sup>17,18,46</sup> assign the fundamental at  $236\text{ cm}^{-1}$  and the overtone at  $471\text{ cm}^{-1}$ , whereas others<sup>17,18</sup> assume it to be at  $358\text{ cm}^{-1}$ . As is seen in Table 9 for propionitrile, we chose to average these values. Other general bands which are difficult to assign are the  $\text{CH}_3$  torsion bands that are calculated (MM3) at  $221\text{ cm}^{-1}$  and are observed experimentally<sup>14,17,18</sup> as an intense Raman band at  $220\text{ cm}^{-1}$ . 1-Butyne's methyl torsion band has not been observed, but was determined to be at  $225\text{ cm}^{-1}$  from the barrier to internal rotation as determined from microwave spectra.<sup>13</sup>

Table 8 shows the MM3 and experimental spectra of methyl cyanide,<sup>16</sup>  $C_{3v}$  point group. There are four totally symmetric  $A_1$  modes and four pairs of degenerate ( $E$ ) modes. All modes are both IR and Raman active. Some of the bands, known as hot bands ( $\nu_1 + \nu_g - \nu_g$ ), are measured from the shoulder rather than the center of the band, and therefore the calculated  $\text{CH}_3$  symmetric stretch deviates from experiment by more than  $30\text{ cm}^{-1}$ . The  $\text{CH}_3$  symmetric deformation couples to the  $\text{C}-\text{C}$  stretch ( $\nu_3, \nu_4$ ) due to Fermi resonance, and here MM3 results are fairly accurate in matching these complex bands. The large deviation in  $\nu_6$  is due to the symmetric overlapping methyl deformation  $\nu_3$ , and we observe that experimental ambiguity in these bands is high. The MM3 intensity of  $\nu_6$ , however, deviates from experiment, as we find it to be weak whereas the experimental antisymmetric deformation is observed to be intense.<sup>16</sup> It

is not surprising to observe these differences in a complex spectrum.

Table 9 shows our MM3 results for propionitrile,  $C_s$  point group, with nine atoms and 21 degrees of vibrational freedom which are divided among  $A'$  and  $A''$  bands. All bands should appear in both the IR and the Raman spectra.<sup>17,18</sup> The experimental  $\text{CH}_3$  stretch ( $\nu_1, A'$ ) at  $3008\text{ cm}^{-1}$  couples with  $\nu_4$  ( $A''$ ) and thus the MM3 deviation of  $24\text{ cm}^{-1}$  is understood.

The  $\text{C}-\text{N}$  stretch is unambiguous both experimentally and from MM3 values, and the agreement is good. Experimental coupling of the  $\text{CH}_2$  wagging motion is observed, and as a result, the MM3 results do deviate significantly. MM3 matches the  $\text{CH}_2$  rocking motion in the  $780-790\text{ cm}^{-1}$  region, and we find the band to be of high intensity as in the observed IR spectrum. The  $\text{C}-\text{C}\equiv\text{N}$  out-of-plane bending is matched nicely by averaging the bands. MM3 results show the torsion to appear at  $221\text{ cm}^{-1}$ . An estimate of the barrier height for internal rotation for  $993\text{ cm}^{-1}$  yields  $5.2\text{ kcal}$ .<sup>17</sup> Surprisingly, this barrier is larger than in ethane and may be due to the large propionitrile dipole. However, it is possible that this barrier is estimated too high. Table 9 presents the propionitrile spectra with the resonance interactions and overlapping bands discussed above and yields a fairly consistent rms value of roughly  $30\text{ cm}^{-1}$ .

The MM3 agreement with the IR and Raman spectra of propyne is adequate. The high  $C_{3v}$  molecular symmetry reduces the spectrum to  $A'$  and  $E'$  symmetries, each consisting of five bands.<sup>47-49</sup> The  $1382\text{ cm}^{-1}$  in the spectra of propyne is unique for a  $\text{CH}_3$  group attached to an sp carbon. Typically, as in 1-butyne, the  $\text{CH}_2$

adjacent to the acetylinic carbon gives a band in 1320–1340  $\text{cm}^{-1}$  region. In dimethylacetylene, we expect a similar band in the 1380  $\text{cm}^{-1}$  region. MM3 results show good accuracy in both propyne ( $-5 \text{ cm}^{-1}$  deviation) and dimethyl acetylene  $C_s$  ( $-17 \text{ cm}^{-1}$  deviation). Because these molecules are highly symmetric, like acetylene, we are unable to compare MM3 IR band intensities directly, as most modes are observed in the Raman spectra.

Spectroscopic interest in dimethylacetylene centers on the internal rotation of one methyl group relative to the other. Earlier heat capacity studies indicated that the restricting potential is less than 0.500  $\text{kcal mol}^{-1}$ .<sup>48</sup> The symmetry modes involving the free internal rotations are  $A_1''$  and  $E'$  (Raman active). We find the  $A_1''$  to yield no contribution to internal rotation whereas the  $E'$  165  $\text{cm}^{-1}$  torsion mode contributes 0.46  $\text{kcal mol}^{-1}$ , in excellent agreement with experiment.  $\text{CH}_3$  wagging frequencies are expected to lie close together, since the methyl groups are separated by the triple bond. Unlike ethane, where the methyl groups interact strongly and split to 827 and 1170  $\text{cm}^{-1}$ .<sup>49</sup> we agree with experimental data and find a  $\text{CH}_3$  twist-rocking mode at 1023  $\text{cm}^{-1}$ . The symmetric  $A_1'$ , C—C stretching frequency is found to lie below 1000  $\text{cm}^{-1}$ , as anticipated experimentally, while the antisymmetric  $A_1''$  lies somewhat above. This is a subtle mass effect due to the shifting in symmetry and MM3 calculates this closely. A larger MM3 deviation in the spectrum of dimethylacetylene involves the  $A_2''$  C—C stretch, which may arise from a binary combination near 2270  $\text{cm}^{-1}$ , due to cross terms (arising from  $A_2'' \times A_2''$ ,  $E' \times E'$  and  $E'' \times E''$ ). This band, to quote experimentalists,<sup>36b</sup> 'will show the impossibility of finding a reasonable assignment. We have assumed an overtone to be responsible for resonance splitting.'

### CONCLUSIONS

The MM3 force field has been extended to include nitriles and alkynes. Structures, heats of formation, dipole moments and conformational equilibria for aliphatic nitriles and alkynes compounds are fitted to within experimental error. The vibrational spectra for aliphatic nitriles were studied, and the experimental values were fitted to an rms of about 30  $\text{cm}^{-1}$ , which is the approximate limit of accuracy imposed by the alkane force field. Previous MM2 studies of nitriles and alkynes left two questions unresolved. One was the torsional angle along the triple bond in cyclooctyne and the other was the length of the  $C_{sp}-C_{sp^3}$  bond in isopropyl nitrile, 3-methylbutyne and *tert*-butylacetylene. In both cases, previous MM2 results disagreed significantly with experiments. The present MM3 studies confirmed the previous MM2 results. Furthermore, our quantum mechanical calculations are also consistent with the molecular mechanical results

and indicate that the torsional angle along the triple bond in cyclooctyne is only  $4^\circ$ , and that there is no bond-lengthening effect in isopropyl nitrile, 3-methylbutyne and *tert*-butylacetylene. Thus the quantum mechanical calculations (MP2/6-31G\* and B3LYP/6-31G\*) and MM3 results suggest that the experimental structures of these molecules are simply inaccurate with respect to these points.

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