Ab initio and molecular mechanics (MM3) calculations on alkyl- and arylboronic acids

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ABSTRACT: The boronic acid functional group has been incorporated into various biologically important compounds. In order to study this class of compounds better with molecular mechanics, five alkyl- and arylboronic acids were calculated using *ab initio* methods (Spartan) at the RHF/6–31G^{*} level. MM3 force field parameters were developed based on the theoretically calculated geometries, vibrational spectra, and torsional profiles. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: alkylboronic acids; arylboronic acids; ab initio; MM3; molecular mechanics; force field parameters

INTRODUCTION

A wide variety of boronic acid derivatives of divergent biologically important compounds have been synthesized as anti-metabolites for a possible two-pronged attack on cancer.^{1–3} In addition to inhibition of tumor growth, the use of boron-10 neutron capture therapy⁴ would be possible owing to the preferential localization of boron compounds in tumor tissue. Boronic acid analogs have been synthesized as transition state analogs for acyl transfer reactions⁵ and inhibitors of dihydoorotase.⁶ The boronic acid moiety has also been incorporated into amino acids and nucleosides as anti-tumor, anti-viral agents.⁷ In order to study these biologically important type of molecules by molecular mechanics methods (MM3), the necessary parameters had to be developed.

Molecular mechanics is a standard tool used to study molecular structures and their conformational energies. The MM3 force field^{8–10} has significantly advanced the accuracy of these calculations. MM3 can accurately handle many different functional groups, including alcohols and ethers,¹¹ amines,¹² aldehydes and ketones,¹³ carboxylic acids and esters,¹⁴ sulfides¹⁵ and sulfones¹⁶ phosphines.¹⁷ Force field parameters for alkylboronic acids have been developed for a generic force field¹⁸ in which reproducing the geometry was the main goal. In this work, however, highly accurate force field parameters for both alkyl-and arylboronic acids were derived by fitting the geometries, vibrational frequencies, and torsional profiles of five model molecules calculated using the RHF/6– $31G^*$ basis set.

COMPUTATIONAL METHODS

Owing to the lack of high-quality experimental data for boronic acid compounds in our training set, the force field parameterization was based almost entirely on *ab initio* calculations. Methyl-, ethyl-, propyl-, isopropyl-, and phenylboronic acids were calculated at the RHF/6–31G* level using Spartan 4.0 (Wavefunction, Irvine, CA, USA) (Fig. 1).

The *ab initio* structures were then fully optimized by MM3 with an initial parameter set using a full-matrix scheme to obtain both vibrational frequencies and lowenergy structures. The MM3 and RHF/6-31G* frequencies were compared, as also were other structural data including bond lengths and angles. The root mean square deviations (RMSDs) of vibrational frequencies, bond lengths, angles, etc., between all MM3 and RHF/6-31G* values were tabulated. Each parameter was then modified systematically in cycles to obtain the best correlation between the molecular mechanics and *ab initio* values by the Parameter Analysis Refinement Toolkit System (PARTS) program.¹⁹ The optimizations of bonded parameters and torsion curves by PARTS were repeated in turn in cycles until the change in RMSD between MM3 and *ab initio* values was smaller than a specifically defined threshold value.

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Isopropyl boronic acid

Phenyl boronic acid

Figure 1. Structures of alkyl-and arylboronic acids used in the training set



Figure 2. Relative conformations of the boronic acid hydroxyl groups and their energies





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Table	1.	MM3	parameter	set for	boronic	acid ^a
	••	1411413	parameter	500100	Solollic	acia

Bond stretching parameters		
Bond	$K_{\rm s}({ m mdyn}\ { m \AA}^{-1})$	<i>l</i> _r (Å)
1–26	3.9304	1.5612
6–26	3.9430	1.3638
2–26	2.3718	1.5038
Angle bending parameters		
Angle	$K (\mathrm{mdyn} \mathrm{\AA} \mathrm{rad}^{-2})$	θ (°)
1-26-6	0.4808	122.6377
6–26–6	0.7187	120.8639
1-1-26	0.6085	109.2459
5-1-26	0.4948	109.9322
21-6-26	0.5120	109.5659
2-26-6	0.6786	127.0404
2-2-26	0.6854	121.1796
Out-of-plane bending parar	neters	
Angle	$K_{\rm opb}$ (mdyn Å rad ⁻²)	
0-2-26	0.1082	
0–26–6	0.1082	
0-26-1	0.1082	
0-26-2	0.1082	
Torsion parameters		
Туре	V_1 (kcal mol ⁻¹)	V_2 (kcal mol ⁻¹)
1-1-26-6	0.0000	2.9168
1-1-1-26	-1.2376	0.7815
5-1-1-26	0.0000	0.0000
5-1-26-6	0.0000	0.0000
21-6-26-1	-1.4600	5.0964
21-6-26-6	-0.5197	4.5608
2-2-2-26	0.0000	11.6000
5-2-2-26	0.0000	11.6000
21-6-26-2	-1.6710	4.1751
2-2-26-6	0.0000	1.6702
Dipole moment		
Bond	Dipole moment (D)	
1–26	-0.6000	
1–26 2–26	-0.6000 -0.6000	

The atom type numbers have their usual meanings: 1 is saturated carbon; 2 is phenyl carbon; 5 is alkane or alkene hydrogen; 6 is alcohol oxygen; 21 is alcohol hydrogen; 26 is boron.

RESULTS AND DISCUSSION

Vibrational Spectra

The compounds included in this study were methyl-, ethyl-, propyl-, isopropyl- and phenylboronic acids. All the newly developed MM3 parameters are listed in Table 1. Owing to the lack of experimental data for alkyl- and arylboronic acid vibrational spectra, the vibrational spectra were obtained by ab initio molecular orbital calculation using Spartan 4.0. Since the Hartree-Fock method usually overestimates the experimental frequencies by about 10%, 20 the MM3 vibrational frequencies were compared with scaled *ab initio* values (90%). The RMS error for the vibrational spectra of all five training molecules ranges from 15 to 50 cm^{-1} (Table 2–6). For methylboronic acid, the frequency for methyl rotation is an imaginary frequency in MM3 calculation, owing to the pseudo-'sixfold'; symmetry of the methyl group rotation. This methyl group can be considered as a free rotor only controlled by non-bonded interactions between methyl hydrogen and hydroxyl hydrogen. The rotation barrier is

 V_3 (kcal mol⁻¹)

0.0000

0.2011 0.0503

0.3250 -0.10520.3140 0.0000

0.0000

0.7787

0.0000

Bond length	Ab initio	MM3 (r _g)	Deviation	MM3 (r _e)	Deviation
B(1)—C(2)	1.585	1.582	-0.003	1.572	-0.013
B(1)—O(6)	1.354	1.357	0.003	1.348	-0.006
B(1)—O(7)	1.366	1.358	-0.008	1.350	-0.016
O(6)—H(8)	0.950	0.954	0.004	0.935	-0.015
O(7)—H(9)	0.950	0.953	0.003	0.935	-0.015
C—H	1.089	1.112	0.023	1.089	0.000
			RMSD = 0.016		RMSD = 0.012
Bond angle	Ab initio	MM3	Deviation		
C(2) - B(1) - O(6)	120.1	120.6	0.5		
C(2) - B(1) - O(7)	122.8	121.4	-1.4		
O(6) - B(1) - O(7)	117.2	118.1	0.9		
B(1)—O(6)—H(8)	112.1	111.3	-0.8		
B(1)—O(7)—H(9)	114.2	113.1	-1.1		
H(4) - C(2) - H(5)	106.6	108.1	1.5		
B—C—H	111.4	111.6	-0.5		
			RMSD = 0.8		
Vibrational mode	Ab initio	MM3	Deviation		
O _c —H str.	3732	3706	-26		
O _t —H str.	3697	3702	4		
asym C—H str.	2955	2979	24		
asym C—H str.	2905	2979	74		
sym C—H	2865	2883	18		
H–C–H bend	1463	1426	-37		
H—C—H bend	1458	1421	-36		
C—B str.	1378	1399	21		
asym B—O str.	1351	1316	-35		
C—B str.	1271	1245	-26		
$H - O_t - B$ bend, $B - O_c$ str.	1009	1045	35		
$H - O_c - B$ bend, $B - O_t$ str.	982	992	11		
B—O—O—C out-of-plane	906	906	0		
CH ₃ rock	850	872	22		
C—B str.	723	696	-26		
H—O _c out-of-plane	488	608	121		
H—O _t out-of-plane	594	558	-36		
O—B—O bend	422	437	15		
C—B—O bend	316	348	31		
B—O—O—C out-of-plane	427	319	-108		
CH ₃ torsion	37	-62	-99		
-			RMSD = 50		

Table 2. Structural data and vibrational modes of methylboronic acid

less than 0.2 kcal mol⁻¹. (1 kcal = 4.184 kJ). Since the parameters for van der Waals interaction between the alkyl hydrogen and the hydroxyl hydrogen were adjusted previously to fit alcohol compounds best, we did not alter these parameters. Also, it is not worthwhile to introduce a new atom type to fit the methyl group (free rotor) rotation profile. Another main source of difference between the *ab initio* and MM3 frequencies is the mode of C—B—O_c— H_c torsion. The deviation between *ab initio* and MM3 frequency is *ca* 110 cm⁻¹ for methyl-, ethyl-, propyl-, and isoprophylboronic acids. The higher frequency values calculated by MM3 can be attributed to the overestimated van der Walls interaction between hydro-xyl and alkyl hydrogen by MM3.

Torsional profiles

The two hydroxyls of boronic acid can be all-*trans*, all*cis* and mixed *trans*-*cis* relative to the B—C bond (Fig. 2). According to the *ab initio* results, the *cis*-*trans* conformation is the most stable. Both hydrogens are in the O—B—O plane. Most probably, the oxygen lone pairs have a resonance interaction with the empty p orbital of boron, which forces the hydrogen to be in the O—B—O plane. The energy for the *trans*-*trans* conformation is $3.22 \text{ kcal mol}^{-1}$ higher owing to the unfavorable steric interaction between the two hydroxyl hydrogens, while the energy for the *cis*-*cis* conformation is $3.15 \text{ kcal mol}^{-1}$ higher than that for the *trans*-*cis*

Table 3. Structural	data and	vibrational	modes of	ethylboronic acid

Bond length	Ab initio	MM3 (r _g)	Deviation	MM3 (r _e)	Deviation
C(1)—C(4)	1.533	1.529	-0.004	1.519	-0.014
B(2) - C(4)	1.585	1.583	-0.002	1.574	-0.011
B(2) - O(5)	1.363	1.359	-0.004	1.351	-0.013
B(2)—O(6)	1.356	1.359	0.003	1.350	-0.006
O(5)—H(9)	0.945	0.952	0.007	0.934	-0.012
O(6)—H(8)	0.948	0.954	0.006	0.935	-0.013
$C - H (CH_3)$	1.087	1.114	0.027	1.090	0.003
$C - H (CH_2)$	1.089	1.115	0.026	1.092	0.003
< <i>2</i> /			RMSD = 0.018		RMSD = 0.010
Bond angle	Ab initio	MM3	Deviation		
C(4)—B(2)—O(5)	124.3	124.0	-0.3		
C(4) - B(2) - O(6)	118.4	118.9	0.5		
O(5) - B(2) - O(6)	117.3	117.1	-0.2		
C(1) - C(4) - B(2)	116.4	116.4	0.1		
B(2) - O(5) - H(9)	114.4	114.5	0.0		
B(2) - O(6) - H(8)	112.1	111.3	-0.8		
C(1) - C(4) - H(3)	109.8	108.6	-1.2		
C(1) - C(4) - H(7)	109.8	108.6	-1.2		
H(3) - C(4) - H(7)	104.8	106.1	1.3		
C—C—H	111.6	111.5	-0.1		
			RMSD = 0.6		
Vibrational mode	Ab initio	MM3	Deviation		
O _c —H str.	3738	3728	-10		
O _t —H str.	3699	3702	3		
asym C—H str.	2915	2964	49		
CH_2 asym C—H str.	2934	2960	25		
CH ₂ asym C—H str.	2889	2916	26		
$CH_2 CH_3$ sym str.	2870	2874	4		
$CH_2 CH_3$ sym str.	2867	2859	-8		
H—C—C bend	1410	1486	76		
H—C—H bend	1491	1462	-29		
H—C—H bend	1488	1452	-36		
H—C—H bend	1443	1425	-18		
CH ₃ umbrella	1410	1381	-29		
B—O str.	1329	1325	-4		
B—O str.	1235	1231	-3		
CH ₂ twist	1250	1215	-36		
H—O _t —B bend	1005	1046	41		
CH ₃ twist	991	1011	21		
H—O _c —B bend	983	1003	20		
CH ₃ rock	1026	998	-28		
C—C str, H—O—B bend	938	950	13		
CH ₂ twist	752	787	35		
B—O str. B—C str.	693	670	-24		
H—O _c out-of-plane	492	592	101		
H—O _t out-of-plane	581	558	-23		
O—B—O bend	456	448	-9		
O—B—C bend	378	355	-23		
B—O—O—C out-of-plane	427	333	-94		
B—C—C bend	199	244	45		
CH ₃ torsion	225	230	5		
O_B_C_C torsion	35	92	56		
			RMSD = 38		

conformation owing to the loss of hydrogen bonding. In order to differentiate these two hydroxyls, the atoms of the hydroxyl that are *trans* to the B—C bond are called O_t , H_t , and the atoms of the hydroxyl that are *cis* are

called O_c and H_c (Fig. 2). The torsion curve of C—C— B—O for both alkyl- and arylboronic acids show twofold symmetry with a corresponding barrier of 2.93 kcal mol⁻¹ for ethyl- and 1.67 kcal mol⁻¹ for

|--|

ond length					
	Ab initio	$MM3(R_g)$	Deviation	MM3 (<i>R</i> _e)	Deviation
(1) - C(4)	1 534	1 532	-0.002	1 522	-0.012
(1) $C(10)$	1.528	1.535	0.002	1.525	-0.003
(1) - C(10)	1.526	1.555	0.007	1.525	-0.003
2)-C(4)	1.585	1.583	-0.003	1.573	-0.012
2)—O(5)	1.364	1.359	-0.005	1.351	-0.013
(2)—O(6)	1.356	1.359	0.003	1.350	-0.006
5)_H(9)	0.945	0.952	0.007	0.934	-0.012
(5) $H(9)$	0.049	0.952	0.007	0.025	0.012
(6) - H(8)	0.948	0.954	0.006	0.935	-0.013
$-H(CH_2)$	1.090	1.115	0.026	1.091	0.002
$-H(CH_2)$	1.086	1.113	0.027	1.089	0.003
	11000		RMSD = 0.019	1.005	RMSD = 0.009
ond angle	Ab initio	MM3	Deviation		
4) - C(1) - C(10)	113.3	112.4	-0.9		
11) - C(1) - H(12)	106.3	107.1	0.7		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	100.5	107.1	0.7		
+) - D(2) - O(3)	124.4	124.1	-0.2		
4)-B(2)-O(6)	118.4	118.8	0.4		
5) - B(2) - O(6)	117.2	117.1	-0.1		
1) - C(4) - B(2)	116.7	116.6	_0.1		
D(2) = D(2)	110./	110.0	-0.1		
2)—U(5)—H(9)	114.4	114.5	0.1		
2)—O(6)—H(8)	112.1	111.3	-0.7		
1)-C(4)-H(3)	109.6	108.7	-1.0		
1) - C(A) - H(7)	100 6	108 7	_1.0		
1 - C(4) - H(7)	109.0	100.7	-1.0		
5)—C(4)—H(7)	104.8	106.2	1.4		
-C-H (CH ₂ , CH ₃)	108.7	109.0	0.3		
-СН	107 7	108.1	0.4		
- 	107.7	100.1	RMSD = 0.6		
brational mode	Ab initio	MM3	Deviation		
—H str.	3739	3730	-10		
—H str.	3699	3702	3		
H str	2036	2970	34		
-11 Su.	2024	2070	24		
I_3 asym C—H str.	2934	2968	34		
I ₂ asym C—H str.	2890	2920	30		
asym C—H str.	2866	2916	50		
n CH CH etr	2870	2880	1		
$\Pi CH_3, CH_2 SU.$	2019	2000	1		
n CH ₃ , CH ₂ str.	2859	2867	7		
n CH ₃ , CH ₂ str.	2859	2860	0		
L rock	1410	1520	109		
I truist	1490	1459	21		
	1480	1458	-21		
–C—H bend	1490	1453	-37		
–C—H bend	1476	1436	-40		
-C-H bend	1442	1425	_17		
	1410	1423	-1/		
	1410	1407	-4		
₃ umbrella, H—C—H bend					
I ₃ umbrella, H—C—H bend I ₃ umbrella, CH ₂ rock	1345	1353	8		
I_3 umbrella, H—C—H bend I_3 umbrella, CH ₂ rock –O str.	1345 1318	1353 1325	8 7		
¹³ umbrella, H—C—H bend ¹³ umbrella, CH ₂ rock –O str.	1345 1318 1307	1353 1325 1236	8 7 7		
¹³ umbrella, H—C—H bend ¹³ umbrella, CH ₂ rock –O str. ¹² twist	1345 1318 1307	1353 1325 1236	8 7 -72		
³ umbrella, H—C—H bend ³ umbrella, CH ₂ rock -O str. ² twist -O str.	1345 1318 1307 1213	1353 1325 1236 1234	8 7 -72 21		
H_3 umbrella, H—C—H bend H_3 umbrella, CH ₂ rock -O str. H_2 twist -O str. H_2 twist H_3 twist	1345 1318 1307 1213 1307	1353 1325 1236 1234 1224	8 7 -72 21 -83		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock -O str. $_{2}$ twist -O str. $_{2}$ twist -C str.	1345 1318 1307 1213 1307 1072	1353 1325 1236 1234 1224 1053	8 7 -72 21 -83 -19		
I_3 umbrella, H—C—H bend I_3 umbrella, CH ₂ rock –O str. I_2 twist –O str. I_2 twist –C str. O R band	1345 1318 1307 1213 1307 1072	1353 1325 1236 1234 1224 1053			
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock -O str. $_{2}$ twist -O str. $_{2}$ twist -C str. -O _t —B bend	1345 1318 1307 1213 1307 1072 1008	1353 1325 1236 1234 1224 1053 1043	$ \begin{array}{r} 8 \\ 7 \\ -72 \\ 21 \\ -83 \\ -19 \\ 35 \\ \end{array} $		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock -O str. $_{2}$ twist -O str. $_{2}$ twist -C str. $_{2}$ cwist -C str. $_{3}$ wag	1345 1318 1307 1213 1307 1072 1008 1021	1353 1325 1236 1234 1224 1053 1043 1026	8 7 -72 21 -83 -19 35 5		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock -O str. $_{2}$ twist -O str. $_{2}$ twist -C str. -C str. -O _t —B bend $_{3}$ wag $_{3}$, CH ₂ wag	1345 1318 1307 1213 1307 1072 1008 1021 1008	1353 1325 1236 1234 1224 1053 1043 1026 998	$ \begin{array}{r} 8 \\ 7 \\ -72 \\ 21 \\ -83 \\ -19 \\ 35 \\ 5 \\ -10 \\ \end{array} $		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock -O str. $_{2}$ twist -O str. $_{2}$ twist -C str. $_{3}$ wag $_{3}$, CH ₂ wag -O = B bend	1345 1318 1307 1213 1307 1072 1008 1021 1008 977	1353 1325 1236 1234 1224 1053 1043 1026 998 973	$ \begin{array}{r} 8 \\ 7 \\ -72 \\ 21 \\ -83 \\ -19 \\ 35 \\ 5 \\ -10 \\ -4 \\ \end{array} $		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock –O str. $_{2}$ twist –O str. $_{2}$ twist –C str. $_{2}$ twist $_{3}$ wag $_{3}$, CH ₂ wag $_{3}$, CH ₂ wag $_{3}$ CH ₂ bend $_{4}$ C for bend	1345 1318 1307 1213 1307 1072 1008 1021 1008 977 977	1353 1325 1236 1234 1224 1053 1043 1026 998 973 802	$ \begin{array}{r} 8 \\ 7 \\ -72 \\ 21 \\ -83 \\ -19 \\ 35 \\ 5 \\ -10 \\ -4 \\ 14 \end{array} $		
³ umbrella, H—C—H bend ³ umbrella, CH ₂ rock -O str. ² twist -O str. ² twist -C str. $-O_t$ —B bend ³ wag ³ , CH ₂ wag $-O_c$ —B bend -C —C bend	1345 1318 1307 1213 1307 1072 1008 1021 1008 977 879	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 893	$ \begin{array}{r} 8 \\ 7 \\ -72 \\ 21 \\ -83 \\ -19 \\ 35 \\ 5 \\ -10 \\ -4 \\ 14 \\ 25 \\ \end{array} $		
³ umbrella, H—C—H bend ³ umbrella, CH ₂ rock -O str. ² twist -O str. ² twist -C str. $-O_t$ —B bend ³ wag ³ , CH ₂ wag $-O_c$ —B bend $-O_c$ —B bend -C—C bend ² wag	1345 1318 1307 1213 1307 1072 1008 1021 1008 977 879 836	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870	$ \begin{array}{r} 8 \\ 7 \\ -72 \\ 21 \\ -83 \\ -19 \\ 35 \\ 5 \\ -10 \\ -4 \\ 14 \\ 35 \\ \end{array} $		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock –O str. $_{2}$ twist –O str. $_{2}$ twist –C str. $_{2}$ twist $_{3}$ cH ₂ wag $_{3}$, CH ₂ wag $_{2}$ wag	1345 1318 1307 1213 1307 1072 1008 1021 1008 977 879 836 714	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870 765	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ \end{array} $		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock –O str. $_{2}$ twist –O str. $_{2}$ twist –C str. $_{2}$ twist $_{3}$ wag $_{3}$, CH ₂ wag $_{2}$ wag $_{2}$ wag $_{2}$ wag $_{2}$ wag $_{2}$ wag $_{2}$ costr	$1345 \\ 1318 \\ 1307 \\ 1213 \\ 1307 \\ 1072 \\ 1008 \\ 1021 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734$	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870 765 707	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ \end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock -O str. I ₂ twist -O str. I ₂ twist -C str. -O _t —B bend I ₃ wag I ₃ , CH ₂ wag -O _c —B bend -C—C bend I ₂ wag I ₂ wag -C str. -O _t —B bend -C—C bend I ₂ wag -C str.	$\begin{array}{c} 1345\\ 1318\\ 1307\\ 1213\\ 1307\\ 1072\\ 1008\\ 1021\\ 1008\\ 977\\ 879\\ 836\\ 714\\ 734\\ 401\end{array}$	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870 765 707	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 10\\ \end{array} $		
Is umbrella, H—C—H bend I ₃ umbrella, CH ₂ rock –O str. I ₂ twist –O str. I ₂ twist –C str. –O _t —B bend I ₃ wag I ₃ , CH ₂ wag –O _c —B bend –C—C bend I ₂ wag I ₂ wag –C, str. –O _c out-of-plane	1345 1318 1307 1213 1307 1072 1008 1021 1008 977 879 836 714 734 491	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870 765 707 592	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ \end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock –O str. I ₂ twist –O str. I ₂ twist –C str. –O _t —B bend Is wag Is, CH ₂ wag –O _c —B bend –C—C bend I ₂ wag I ₂ wag –C str. –O _t cout-of-plane –O _t out-of-plane	$1345 \\ 1318 \\ 1307 \\ 1213 \\ 1307 \\ 1072 \\ 1008 \\ 1021 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734 \\ 491 \\ 582 \\ $	$ \begin{array}{r} 1353 \\ 1325 \\ 1236 \\ 1234 \\ 1024 \\ 1053 \\ 1043 \\ 1026 \\ 998 \\ 973 \\ 893 \\ 870 \\ 765 \\ 707 \\ 592 \\ 558 \\ \end{array} $	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ \end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock -O str. -O str. I ₂ twist -C str. $-O_t$ —B bend Is wag Is, CH ₂ wag $-O_c$ —B bend $-O_c$ —B bend $-C_c$ bend Iz wag Iz wag Iz wag -C str. $-O_c$ out-of-plane $-O_c$ bend $-O_c$ obend $-O_c$ obend $-O_c$ obend $-O_c$ out-of-plane $-O_c$ bend $-O_c$ bend $-O_c$ out-of-plane $-O_c$ bend $-O_c$	$1345 \\ 1318 \\ 1307 \\ 1213 \\ 1307 \\ 1072 \\ 1008 \\ 1021 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734 \\ 491 \\ 582 \\ 476 \\ $	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870 765 707 592 558 473	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock –O str. I ₂ twist –O str. I ₂ twist –C str. –O _t —B bend Is wag Is, CH ₂ wag –O _c —B bend –C—C bend I ₂ wag –C str. –O _c out-of-plane –O _t out-of-plane –B—O bend B—C bend	$1345 \\ 1318 \\ 1307 \\ 1213 \\ 1307 \\ 1072 \\ 1008 \\ 1021 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734 \\ 491 \\ 582 \\ 476 \\ 271 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734 \\ 977 \\ 879 \\ 879 \\ 836 \\ 714 \\ 734 \\ 977 \\ 879 \\ 879 \\ 879 \\ 870 \\ $	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870 765 707 592 558 473	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ 14\\ \end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock –O str. I ₂ twist –O str. I ₂ twist –C str. –O _t —B bend Is wag Is, CH ₂ wag –O _c —B bend –C—C bend I ₂ wag I ₂ wag –C str. –O _c out-of-plane –O _t out-of-plane –O _t obend –B—O bend –B—C bend	$1345 \\ 1318 \\ 1307 \\ 1213 \\ 1307 \\ 1072 \\ 1008 \\ 1021 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734 \\ 491 \\ 582 \\ 476 \\ 371 \\ $	$ \begin{array}{r} 1353 \\ 1325 \\ 1236 \\ 1234 \\ 1224 \\ 1053 \\ 1043 \\ 1026 \\ 998 \\ 973 \\ 893 \\ 870 \\ 765 \\ 707 \\ 592 \\ 558 \\ 473 \\ 357 \\ \end{array} $	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ \end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock -O str. I ₂ twist -O str. I ₂ twist -C str. -O _t —B bend Is wag Is, CH ₂ wag -O _c —B bend -C—C bend I ₂ wag I ₂ wag -C str. -O _c out-of-plane -O _c out-of-plane -O _c bend -B—O bend -B—O bend -B—C bend -B—O bend -B—O bend -B—C bend	$1345 \\ 1318 \\ 1307 \\ 1213 \\ 1307 \\ 1072 \\ 1008 \\ 1021 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734 \\ 491 \\ 582 \\ 476 \\ 371 \\ 432 \\ $	$ \begin{array}{r} 1353 \\ 1325 \\ 1236 \\ 1234 \\ 1024 \\ 1053 \\ 1043 \\ 1026 \\ 998 \\ 973 \\ 893 \\ 870 \\ 765 \\ 707 \\ 592 \\ 558 \\ 473 \\ 357 \\ 335 \\ \end{array} $	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ -97\\ \end{array} $		
Is umbrella, H—C—H bend I ₃ umbrella, CH ₂ rock –O str. I ₂ twist –C str. –O _t —B bend I ₃ wag I ₃ , CH ₂ wag –O _c —B bend –C—C bend I ₂ wag –C—C bend I ₂ wag –C str. –O _c out-of-plane –O _t out-of-plane –B—O bend –B—C bend –B—C bend –C—C bend –C—C bend –C—C bend –C—C bend –B—C bend –C—C bend –C—C bend –B—C bend –C—C bend	$1345 \\ 1318 \\ 1307 \\ 1213 \\ 1307 \\ 1072 \\ 1008 \\ 1021 \\ 1008 \\ 977 \\ 879 \\ 836 \\ 714 \\ 734 \\ 491 \\ 582 \\ 476 \\ 371 \\ 432 \\ 307 \\ $	$ \begin{array}{r} 1353 \\ 1325 \\ 1236 \\ 1234 \\ 1224 \\ 1053 \\ 1043 \\ 1026 \\ 998 \\ 973 \\ 893 \\ 870 \\ 765 \\ 707 \\ 592 \\ 558 \\ 473 \\ 357 \\ 335 \\ 310 \\ \end{array} $	$ \begin{array}{c} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ -97\\ 3\end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock –O str. I ₂ twist –O str. I ₂ twist –C str. –O _t —B bend Is wag Is, CH ₂ wag –O _c —B bend –C—C bend I ₂ wag -C _c str. –O _c out-of-plane –O _t out-of-plane –O _t out-of-plane –B—O bend –B—C bend –B—C bend –O _c —C bend –C—C, C—C—C bend Is wag -C—C, C—C—C bend Is wag -C—C bend -C—C bend -	$\begin{array}{c} 1345\\ 1318\\ 1307\\ 1213\\ 1307\\ 1072\\ 1008\\ 1021\\ 1008\\ 977\\ 879\\ 836\\ 714\\ 734\\ 491\\ 582\\ 476\\ 371\\ 432\\ 307\\ 228\end{array}$	1353 1325 1236 1234 1224 1053 1043 1026 998 973 893 870 765 707 592 558 473 357 335 310	$ \begin{array}{c} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ -97\\ 3\\ 6\end{array} $		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock –O str. $_{2}$ twist –O str. $_{2}$ twist –C str. $-O_{t}$ —B bend $_{3}$ wag $_{3}$, CH ₂ wag $-O_{c}$ —B bend -C—C bend $_{2}$ wag $_{2}$ wag $_{2}$ wag $_{2}$ wag -C str. $-O_{c}$ out-of-plane $-O_{c}$ out-of-plane $-O_{c}$ bend -B—C bend -D—C bend -D—C bend -B—C bend -D—C bend -B—C bend -D—C bend -D—	$\begin{array}{c} 1345\\ 1318\\ 1307\\ 1213\\ 1307\\ 1072\\ 1008\\ 1021\\ 1008\\ 977\\ 879\\ 836\\ 714\\ 734\\ 491\\ 582\\ 476\\ 371\\ 432\\ 307\\ 238\\ 307\\ 238\\ \end{array}$	$ \begin{array}{r} 1353 \\ 1325 \\ 1236 \\ 1234 \\ 1053 \\ 1043 \\ 1026 \\ 998 \\ 973 \\ 893 \\ 870 \\ 765 \\ 707 \\ 592 \\ 558 \\ 473 \\ 357 \\ 335 \\ 310 \\ 232 \\ 75 75 70 7 7 7 7 7 $	$ \begin{array}{r} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ -97\\ 3\\ -6\\ 6\end{array} $		
Is umbrella, H—C—H bend Is umbrella, CH ₂ rock -O str. I ₂ twist -O str. I ₂ twist -C str. -O _t —B bend Is wag Is, CH ₂ wag -O _c —B bend -C—C bend Iz wag I ₂ wag I ₂ wag -C—C bend I ₂ wag -C str. -O _c out-of-plane -O _t out-of-plane -O _t out-of-plane -B—O bend -B—O bend -B—C bend -B—C bend -C—C bend -C—C bend -C—C bend -C—C bend -B—C bend -B—C bend -B—C bend -B—C bend -B—C bend -B—C bend -C—C bend -C—C, C—C—C bend Is torsion -C—C, C—C—C bend	$\begin{array}{c} 1345\\ 1318\\ 1307\\ 1213\\ 1307\\ 1072\\ 1008\\ 1021\\ 1008\\ 977\\ 879\\ 836\\ 714\\ 734\\ 491\\ 582\\ 476\\ 371\\ 432\\ 307\\ 238\\ 146\\ \end{array}$	$ \begin{array}{r} 1353 \\ 1325 \\ 1236 \\ 1234 \\ 1224 \\ 1053 \\ 1043 \\ 1026 \\ 998 \\ 973 \\ 893 \\ 870 \\ 765 \\ 707 \\ 592 \\ 558 \\ 473 \\ 357 \\ 335 \\ 310 \\ 232 \\ 179 \\ \end{array} $	$ \begin{array}{c} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ -97\\ 3\\ -6\\ 32\\ \end{array} $		
I_3 umbrella, H—C—H bend I_3 umbrella, CH ₂ rock –O str. I_2 twist –O str. I_2 twist –O str. I_2 twist –C str. $-O_t$ —B bend I_3 wag I_3 , CH ₂ wag $-O_c$ —B bend -C—C bend I_2 wag I_2 wag I_2 wag I_2 wag I_2 wag -C str. $-O_c$ out-of-plane $-O_t$ out-of-plane $-O_t$ out-of-plane $-O_t$ out-of-plane $-D_t$ bend -B—C bend -D—C bend -B—C bend -C—C bend I_3 torsion -C—C, C—C—C bend I_3 torsion -C—C torsion	$\begin{array}{c} 1345\\ 1318\\ 1307\\ 1213\\ 1307\\ 1072\\ 1008\\ 1021\\ 1008\\ 977\\ 879\\ 836\\ 714\\ 734\\ 491\\ 582\\ 476\\ 371\\ 432\\ 307\\ 238\\ 146\\ 94 \end{array}$	$\begin{array}{c} 1353\\ 1325\\ 1236\\ 1234\\ 1224\\ 1053\\ 1043\\ 1026\\ 998\\ 973\\ 893\\ 870\\ 765\\ 707\\ 765\\ 707\\ 592\\ 558\\ 473\\ 357\\ 335\\ 310\\ 232\\ 179\\ 110\\ \end{array}$	$ \begin{array}{c} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ -97\\ 3\\ -6\\ 32\\ 16\end{array} $		
$_{3}$ umbrella, H—C—H bend $_{3}$ umbrella, CH ₂ rock -O str. $_{2}$ twist -O str. $_{2}$ twist -C str. $-O_{t}$ —B bend $_{3}$ wag $_{3}$, CH ₂ wag $-O_{c}$ —B bend -C—C bend $_{2}$ wag $_{2}$ wag $_{2}$ wag $_{2}$ wag $_{2}$ wag $_{2}$ wag -C str. $-O_{c}$ out-of-plane $-O_{t}$ out-of-plane $-O_{t}$ out-of-plane -B—O bend -B—C bend -B—C bend -B—C bend -C—C comtof-plane -C—C, C—C—C bend $_{3}$ torsion -C—C, C—C bend -C—C torsion -C—C torsion	$\begin{array}{c} 1345\\ 1318\\ 1307\\ 1213\\ 1307\\ 1072\\ 1008\\ 1021\\ 1008\\ 977\\ 879\\ 836\\ 714\\ 734\\ 491\\ 582\\ 476\\ 371\\ 432\\ 307\\ 238\\ 146\\ 94\\ 46\end{array}$	1353 1325 1236 1234 1024 1053 1043 1026 998 973 893 870 765 707 592 558 473 357 335 310 232 179 110 87	$ \begin{array}{c} 8\\ 7\\ -72\\ 21\\ -83\\ -19\\ 35\\ 5\\ -10\\ -4\\ 14\\ 35\\ 51\\ -27\\ 101\\ -24\\ -3\\ -14\\ -97\\ 3\\ -6\\ 32\\ 16\\ 41\\ \end{array} $		

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Lahlo 5 Structural	data ar	nd vibrational	modes of	ISONTONV	Inoronic	acid
Table J. Structural	uata ai		i moues oi	isopiopy	1001011IC	aciu

Bond length	Ab initio	MM3 (r _g)	Deviation	MM3 (r _e)	Deviation
B(1)—O(2)	1.357	1.359	0.002	1.350	-0.007
B(1)—O(4)	1.363	1.360	-0.003	1.351	-0.012
B(1) - C(6)	1.585	1.588	0.003	1.578	-0.007
D(2) - H(3)	0.948	0.954	0.006	0.935	-0.013
(4) - H(5)	0.945	0.952	0.007	0.934	-0.012
C(6) - C(7)	1.540	1.534	-0.005	1.525	-0.015
C(6) - C(9)	1.540	1.534	-0.001	1.524	_0.013
$\Gamma(0) = C(9)$ $\Gamma(6) = U(10)$	1.001	1.119	0.027	1.024	-0.011
$\frac{1}{100}$	1.091	1.110	0.027	1.092	0.001
$-H(CH_3)$	1.087	1.114	0.027	1.090	0.005
			RMSD = 0.012		RMSD = 0.009
ond angle	Ab initio	MM3	Deviation		
(2) - B(1) - O(4)	117.0	116.7	-0.3		
(2) - B(1) - C(6)	118.4	120.1	1.7		
(4) - B(1) - C(6)	124.5	123.1	-1.4		
(1) - O(2) - H(3)	112.1	111.4	-0.8		
(1) - O(4) - H(5)	114.5	114.4	-0.1		
(1) - C(6) - C(7)	110.8	111.4	0.6		
(1) - C(6) - C(9)	114.2	113.7	-0.4		
(1) - C(6) - H(10)	105.8	106.1	0.3		
(7) - C(6) - C(9)	110.9	110.9	0.0		
(7) - C(6) - H(10)	107.0	107.1	0.1		
(9) - C(6) - H(10)	107.8	107.1	_0.6		
-C - H (CB CH - U)	111.0	111 8	0.0		
-C - H	111.2	107.2	0.0		
I—C—n	107.5	107.5	RMSD = 0.6		
/ibrational mode	Ab initio	MM3	Deviation		
) —H str	3741	3730	11		
-H etr	3698	3703	1		
H asym C Hetr	2006	2068	63		
\square asym C \square str	2000	2064	8		
$H_3 asym C H atr$	2930	2904	0 27		
H_3 asym $C_{}H$ su.	2927	2903	57		
H_3 asym C—H str.	2917	2962	45		
H C—H str.	2849	2900	51		
H ₃ sym str.	2859	2873	14		
H ₃ sym str.	2872	2870	-2		
	1494	1478	-17		
—C—H bend		1467	-15		
—C—H bend —C—H bend	1482	1107			
—C—H bend —C—H bend —C—H bend	1482 1494	1461	-33		
—C—H bend —C—H bend —C—H bend —C—H bend	1482 1494 1482	1461 1453	$-33 \\ -29$		
CH bend CH bend CH bend H ₂ twist	1482 1494 1482 1476	1461 1453 1437	$-33 \\ -29 \\ -39$		
$CH bend$ $CH bend$ $CH bend$ $H_3 twist$ $H_2 twist$	1482 1494 1482 1476 1491	1461 1453 1437 1431	-33 -29 -39 -60		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₄ umbrella BC str	1482 1494 1482 1476 1491 1415	1461 1453 1437 1431 1383	$-33 \\ -29 \\ -39 \\ -60 \\ -32$		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock	1482 1494 1482 1476 1491 1415 1309	1461 1453 1437 1431 1383 1354	-33 -29 -39 -60 -32 45		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str.	1482 1494 1482 1476 1491 1415 1309 1200	1461 1453 1437 1431 1383 1354	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ 17 \\ \end{array} $		
CH bend CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. O str.	1482 1494 1482 1476 1491 1415 1309 1309	1461 1453 1437 1431 1383 1354 1292	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 17 \\ 17 \\ 17 \\ 17 \\ 17 \\ 17 \\ $		
CH bend CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag	1482 1494 1482 1476 1491 1415 1309 1309 1234	1461 1453 1437 1431 1383 1354 1292 1252	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 2 \end{array} $		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str.	1482 1494 1482 1476 1491 1415 1309 1309 1234 1074	1461 1453 1437 1431 1383 1354 1292 1252 1077	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ 22 \\ \end{array} $		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock	1482 1494 1482 1476 1491 1415 1309 1309 1234 1074 1164	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ -5$		
$\begin{array}{c}CH \text{ bend} \\CH \text{ bend} \\CH \text{ bend} \\ +-GH \text{ bend} \\ +_3 \text{ twist} \\ +_3 \text{ twist} \\ +_3 \text{ umbrella, B}C \text{ str.} \\ + \text{ trock} \\O \text{ str.} \\ + \text{ wag} \\C \text{ str.} \\ +_3 \text{ rock} \\O_tB \text{ bend} \\ \end{array}$	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006$	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072 1042	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ \end{array} $		
CH bend CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock O ₁ B bend H ₃ rock	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026$	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072 1042 1027	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ \end{array} $		
$\begin{array}{c}CH \text{ bend} \\CH \text{ bend} \\CH \text{ bend} \\ +_3 \text{ twist} \\ +_3 \text{ twist} \\ +_3 \text{ umbrella, B}C \text{ str.} \\ + \text{ rock} \\O \text{ str.} \\ + \text{ wag} \\C \text{ str.} \\ + H_3 \text{ rock} \\O_tB \text{ bend} \\ +_3 \text{ rock} \\O_cB \text{ bend} \\O_cB \text{ bend} \\ \end{array}$	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976$	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072 1072 1042 1027 975	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ \end{array} $		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock O _c B bend H ₃ rock O _c B bend H ₃ twist	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906$	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072 1042 1027 975 961	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ \end{array} $		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock O _c B bend H ₃ twist H ₃ twist H ₃ wag	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 1006 \\ 951 \\ 1006$	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072 1042 1027 975 961 936	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ \end{array} $		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock O _t B bend H ₃ rock O _t B bend H ₃ twist H ₃ wag C str. C str.	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863$	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072 1042 1027 975 961 936 857	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ \end{array} $		
CH bend CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock O _c B bend H ₃ twist H ₃ twist H ₃ twist O _c C str. O str. 	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694$	1461 1453 1437 1431 1383 1354 1292 1252 1077 1072 1042 1027 975 961 936 857 654	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ \end{array} $		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock O _c B bend H ₃ twist H ₃ wag C str. O str. 	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 $	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 975 \\ 967 \\ 1000 \\ 1$	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ \end{array} $		
CH bend CH bend CH bend A_3 twist A_3 twist A_3 twist A_3 twist A_3 twist A_3 twist A_3 umbrella, BC str. H rock O str. H wag C str. A_3 rock O _t	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 540$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 1000 \\ $	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ \end{array} $		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H ₃ rock O _c B bend H ₃ rock O _c B bend H ₃ twist H ₃ wag C str. O str. O str. O c out-of-plane O _t out-of-plane O _t bend	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 549 \\ 494 \\ 549 \\ 549 \\ 544$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 451 \\ 1072 \\ 1$	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ 22 \\ \end{array} $		
$\begin{array}{c}CH \ \text{bend} \\CH \ \text{bend} \\CH \ \text{bend} \\CH \ \text{bend} \\ +_3 \ \text{twist} \\ +_3 \ \text{twist} \\ +_3 \ \text{twist} \\ +_3 \ \text{umbrella, B}C \ \text{str.} \\ + \ \text{rock} \\O \ \text{str.} \\ + \ \text{wag} \\C \ \text{str.} \\ +_3 \ \text{rock} \\ -O_cB \ \text{bend} \\ +_3 \ \text{rock} \\ -O_cB \ \text{bend} \\ +_3 \ \text{twist} \\C \ \text{str.} \\O \ \text{str.} \\ -O \ \text{out-of-plane} \\O_t \ \text{out-of-plane} \\B \ \text{obend} \\B \ $	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 540 \\ 540$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 122 \\ 1022 \\ 1022 \\ 1023 \\ 10$	$ \begin{array}{r} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 10 \end{array} $		
$\begin{array}{c}CH \ \text{bend} \\CH \ \text{bend} \\CH \ \text{bend} \\ +-CH \ \text{bend} \\ +-GH \ \text{bend} \\ +-GH \ \text{bend} \\ +-GH \ \text{bend} \\ +-GH \ \text{bend} \\ +-GG \ \text{str.} \\ +-GG \ \text{str.} \\ +-GB \ \text{bend} \\ +-GB \ \text{bend} \\ +-GB \ \text{bend} \\ +-GB \ \text{bend} \\ +-GG \ \text{str.} \\ +-G \ \text{str.} \\ +-G \ \text{str.} \\ +-G \ \text{str.} \\G \ \text{out-of-plane} \\G - \ \text{out-of-plane} \\G - \ \text{obend} \\GC \ \text{bend} \\ +-GC \ \text{bend} \\GC \ \text{bend} \\GC \ \text{bend} \\GG \ \text{bend} \\$	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 414 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 414 \\ 1006 \\ 10$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 1433 \\ 1453 \\ 14$	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \end{array}$		
$\begin{array}{c}CH \ \text{bend} \\CH \ \text{bend} \\CH \ \text{bend} \\ +-CH \ \text{bend} \\ +_3 \ \text{twist} \\ +_3 \ \text{twist} \\ +_3 \ \text{twist} \\ +_3 \ \text{umbrella, B}C \ \text{str.} \\ + \ \text{rock} \\O \ \text{str.} \\ + \ \text{wag} \\C \ \text{str.} \\ + \ \text{ock} \\O_tB \ \text{bend} \\ +_3 \ \text{rock} \\O_cB \ \text{bend} \\ +_3 \ \text{twist} \\ +_3 \ \text{wag} \\C \ \text{str.} \\O \ \text{str.} \\O \ \text{str.} \\O \ \text{str.} \\O \ \text{str.} \\O_c \ \text{out-of-plane} \\O_t \ \text{out-of-plane} \\BO \ \text{bend} \\CC \ \text{bend} \\BC \ \text{bend} \\C \ \text{bend} \\C \ \text{bend} \\$	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 414 \\ 321 \\ 1000 $	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 351 \\ 1400 \\ 140$	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \\ 30 \end{array}$		
$\begin{array}{c}CH \ \text{bend} \\CH \ \text{bend} \\CH \ \text{bend} \\ +-CH \ \text{bend} \\ +_3 \ \text{twist} \\ +_3 \ \text{twist} \\ +_3 \ \text{umbrella, B}C \ \text{str.} \\ + \ \text{rock} \\O \ \text{str.} \\ + \ \text{wag} \\C \ \text{str.} \\ + \ \text{dstr.} \$	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 414 \\ 321$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 351 \\ 349$	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \\ 30 \\ 28 \end{array}$		
$\begin{array}{c}CH \text{ bend} \\CH \text{ bend} \\CH \text{ bend} \\ +-CH \text{ bend} \\ +_3 \text{ twist} \\ +_3 \text{ twist} \\ +_3 \text{ umbrella, B}C \text{ str.} \\ + \text{ rock} \\O \text{ str.} \\ + \text{ wag} \\C \text{ str.} \\ +_3 \text{ rock} \\O_cB \text{ bend} \\ +_3 \text{ rock} \\O_cB \text{ bend} \\ +_3 \text{ twist} \\ +_3 \text{ wag} \\C \text{ str.} \\O \text{ str.} \\O \text{ str.} \\O \text{ str.} \\O \text{ cout-of-plane} \\O_t \text{ out-of-plane} \\BO \text{ bend} \\CC \text{ bend} \\BC \text{ bend} \\CC bend$	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 414 \\ 321 \\ 321 \\ 321 \\ 276 \\ 1482 \\ 1$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 351 \\ 349 \\ 283 \\ 1437 \\ 1453 \\ 1457 \\ 1453 \\ 1457 $	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -11 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \\ 30 \\ 28 \\ 7 \end{array}$		
$\begin{array}{c}CH \ bend \\CH \ bend \\C \ str. \\ +$	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 512 \\ 211 \\ 321$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 351 \\ 349 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 283 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 1451 \\ 285 \\ 237 \\ 285 \\ $	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \\ 30 \\ 28 \\ 7 \\ 3 \end{array}$		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H wag C str. H ₃ rock O _c B bend H ₃ rock O _c B bend H ₃ twist H ₃ wag C str. O str. O str. O str. O str. O str. O tot-of-plane O bend C bend C bend C bend C bend C bend C bend 	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 414 \\ 321 \\ 321 \\ 321 \\ 321 \\ 276 \\ 234 \\ 208 \\ 148 \\ 208 \\ 148 \\ 208 \\ 148 \\ 208 \\ 148 \\ 208 \\ 148 \\ 208$	$1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 351 \\ 349 \\ 283 \\ 237 \\ 199 \\ 199 \\ 1437 \\ 1437 \\ 149 \\ 1438 \\ 149 \\ 149 \\ 149 \\ 140 \\ 1$	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \\ 30 \\ 28 \\ 7 \\ 3 \\ -8 \end{array}$		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. H wag C str. H ₃ rock O _c B bend H ₃ rock O _c B bend H ₃ twist H ₃ wag C str. O bend CC bend CC bend DC out-of-plane 	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 414 \\ 321 \\ 321 \\ 321 \\ 276 \\ 234 \\ 208 \\ 208$	$ \begin{array}{r} 1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 351 \\ 349 \\ 283 \\ 237 \\ 199 \\ 102 \end{array} $	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \\ 30 \\ 28 \\ 7 \\ 3 \\ -8 \\ 41 \end{array}$		
CH bend CH bend CH bend H ₃ twist H ₃ twist H ₃ umbrella, BC str. H rock O str. H wag C str. Hy rock O _c B bend H ₃ rock O _c B bend H ₃ rock O _c B bend H ₃ twist H ₃ wag C str. O str. O str. O c out-of-plane D _c out-of-plane D _c out-of-plane D _c bend C bend C bend C bend C bend C-C bend C bend 	$1482 \\ 1494 \\ 1482 \\ 1476 \\ 1491 \\ 1415 \\ 1309 \\ 1234 \\ 1074 \\ 1164 \\ 1006 \\ 1026 \\ 976 \\ 906 \\ 951 \\ 863 \\ 694 \\ 494 \\ 549 \\ 494 \\ 549 \\ 494 \\ 414 \\ 321 \\ 321 \\ 276 \\ 234 \\ 208 \\ 234 \\ 208 \\ 234 \\ 21 \\ 321 \\ 321 \\ 331 \\$	$ \begin{array}{r} 1461 \\ 1453 \\ 1437 \\ 1431 \\ 1383 \\ 1354 \\ 1292 \\ 1252 \\ 1077 \\ 1072 \\ 1042 \\ 1027 \\ 975 \\ 961 \\ 936 \\ 857 \\ 654 \\ 597 \\ 556 \\ 471 \\ 433 \\ 351 \\ 349 \\ 283 \\ 237 \\ 199 \\ 193 \\ 193 \\ 193 \\ 193 \\ 193 \\ 193 \\ 193 \\ 193 \\ 193 \\ 193 \\ 102 $	$\begin{array}{c} -33 \\ -29 \\ -39 \\ -60 \\ -32 \\ 45 \\ -17 \\ 17 \\ 3 \\ -92 \\ 36 \\ 1 \\ -1 \\ 55 \\ -15 \\ -6 \\ -40 \\ 103 \\ 6 \\ -23 \\ 19 \\ 30 \\ 28 \\ 7 \\ 3 \\ -8 \\ -41 \\ 22 \end{array}$		

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Table 6. Structural data and vibrational modes of phenylboronic acid
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Bond length	Ab initio	$MM3 (r_{a})$	Deviation	$MM3 (r_{a})$	Deviation
B(1) C(2)	1 576	1 577	0.000	1 565	0.011
B(1) = C(2) B(1) = O(13)	1.370	1.377	0.000	1.303	-0.011
P(1) = O(13)	1.303	1.302	-0.001	1.555	-0.010
C(2) = C(4)	1.330	1.502	0.000	1.333	-0.005
C(2) = C(4)	1.394	1.402	0.008	1.394	0.000
O(13) = H(16)	0.045	0.052	0.003	0.034	-0.003
O(13) - H(15)	0.945	0.952	0.007	0.934	-0.011
$C_{}C_{-$	1 386	1 395	0.000	1 390	0.004
СН	1.500	1.575	0.010	1.080	0.004
C—II	1.070	1.105	RMSD = 0.017	1.000	RMSD = 0.004
Bond angle	Ab initio	MM3	Deviation		
C(2)—B(1)—O(13)	124.2	124.2	0.1		
C(2) = B(1) = O(14)	118.6	121.5	2.9		
O(13) - B(1) - O(14)	117.2	114.3	-3.0		
B(1) - C(2) - C(4)	122.7	122.0	-0.7		
B(1) - C(2) - C(5)	119.7	119.2	-0.5		
B(1) - O(13) - H(16)	115.5	113.7	-1.8		
B(1) - O(14) - H(15)	112.1	111.4	-0.7		
C(4) = C(2) = C(5)	117.6	118.8	1.2		
C(2) = C(5) = C(6)	121 3	120.7	_0.5		
C(2) = C(3) = C(3)	121.5	120.7	_11		
$C_{}C_{-$	110 0	119.7	_0 2		
С_С_Н	12.2	120.0	_0.2		
C−C−II	120.1	120.0	RMSD = 0.7		
Vibrational mode	Ab initio	MM3	Deviation		
O _c —H str.	3748	3730	-18		
O _t —H str.	3705	3701	-4		
asym C—H str.	2994	3066	71		
asym C—H str.	3055	3057	2		
asym C—H str.	3044	3051	8		
asym C—H str.	3032	3045	13		
asym C—H str.	3020	3040	21		
aromatic C-C str.	1628	1663	35		
aromatic C—C str.	1628	1659	31		
aromatic C—C str.	1598	1618	20		
sym aromatic C—C—H	1505	1509	4		
asym aromatic C—C—	1444	1451	7		
asym aromatic C—C—	1349	1368	19		
B_O str	1317	1300	-16		
B_O str	1325	1271	-54		
asym aromatic C-C-	1100	1271	25		
sym aromatic C—C—H	1181	1209	23		
aromatic C—H out of plane	1021	1008	27		
H_O_B herd	1021	1090	10		
asym aromatic C	1095	10/1	-22		
H O B band	1005	1041	-24		
aromatic C Hout of plana	999 004	1030	22		
aromatic C — C band	990	1028	33 40		
U O P hand	1010	907	-49		
$\Pi - U_c - D$ Utild	950	938	-12		
sym aromatic C—H out-of-plane	945	927	-18		
sym aromatic C—C str	950	914	-35		
aromatic C—H out-of-plane	86/	//1	-96		
sym aromatic C—H out-of-plane	//0	0/2	-99		
aromatic C—C—C bend	/00	663	-3/		
aromatic C—C—C bend	611	603	-8		
$H - O_t$, $C - H$ out-of-plane	540	589	49		
$H - O_t$, aromatic C - H	540	577	37		
U—B—O bend	512	533	20		
H—O _c out-of-plane	450	483	33		
H—O _c , aromatic C—H	450	449	-1		
O—B—C bend	397	416	19		
$C \cap O \cup U \to C $	399	366	-33		
aromatic C—C—C—H out-or-plane			77		
B—O—O—C out-of-plane	416	339	= / /		
B—O—O—C out-of-plane B—C str.	416 316	339 322	-// 6		
aromatic C—C—H out-of-plane B—O—O—C out-of-plane B—C str. O—B—C bend	416 316 168	339 322 222	-77 6 54		
aromatic C—C—H out-of-plane B—O—O—C out-of-plane B—C str. O—B—C bend out-of-plane bend	416 316 168 134	339 322 222 149	6 54 15		
aromatic C—C—H out-of-plane B—O—O—C out-of-plane B—C str. O—B—C bend out-of-plane bend O—B—C—C torsion	416 316 168 134 12	339 322 222 149 34	6 54 15 21		

phenylboronic acid. The torsion profile of C—C—B—O of ethylboronic acid showed some disagreement between MM3 and *ab initio* calculations when the *cis*-hydroxyl is rotated toward the methyl group (Fig. 3). This is caused by the overestimation of the van der Waals interaction between hydroxyl hydrogen and methyl hydrogen by MM3. Owing to the symmetrical nature of the phenyl group, this is not a problem for the C—C—B—O profile in phenylboronic acid. In the case of methylboronic acid, there is an imperfect sixfold symmetry (twofold in boron oxygen, threefold in methyl), so the torsion energy dose not depend on the V_1 , V_2 or V_3 terms. The other torsional curves including C—C—C—B, H—C—C—B and H—O—B—C agree very well between *ab initio* and MM3 calculations.

Structural data

The ab initio and MM3 geometries for methyl-, ethyl-, propyl-, isopropyl- and phenylboronic acids given in Tables 2-6. The structures of five training molecules and their atom numbering are shown in Fig. 1. The agreement between MM3 and the RHF/6-31G* calculations is consistently good. For bond length calculations, MM3 calculates rg values as default whereas the ab initio method calculates $r_{\rm e}$ values. Because of anharmonicity, in all normal cases $r_{\rm e}$ is shorter than $r_{\rm g}$. The difference is very large in the case of hydrogen, which has a very small mass and lies high up in the potential well, so the r_g value will be larger than r_e by about 0.02–0.03 Å.²¹ For atoms heavier than hydrogen, the differences are very small in most cases. Both MM3 $r_{\rm g}$ and MM3 $r_{\rm e}$ values are listed in Tables 2-6. The bond angles calculated by MM3 and the ab initio method are generally in good agreement. For methylboronic acid, the H-C-H bond angle next to the $H_{\rm c}$ hydroxyl is slightly larger (1.5°) in MM3 than in the corresponding ab initio structure (Table 2, Fig. 1). This may also be caused by the overestimation of the van der Waals interaction between the hydroxyl hydrogen and methyl hydrogen by MM3. For ethyl- and propyl boronic acids, the H-C-H bond angle for CH₂ that is next to boron is slightly larger (1.3°; Tables 3 and 4, Fig. 1) in MM3. At the same time, the MM3 C-C-H bond angle for the same CH₂ group is smaller (1°; Tables 3 and 4, Fig. 1). This may be traced to the equilibrium C—C—H and H—C—H bond angles which were parameterized previously for alkanes where the C-C-C bond angle that centered around the CH₂ group is about 110°. In alkylboronic acids, the C-C-B bond angle that centered around the CH₂ group is about 116°. Therefore, the increase in the C-C-B bond angle caused a decrease in two C-C-H bond angles and an increase in the H-C-H bond angle. For phenylboronic acid, the largest discrepancies between the ab initio and MM3 methods are the O—B—O and O_c—B—C bond angles. The O—B—O bond angle calculated by MM3 is about 3° smaller than that in the *ab initio* structure, and the O_c---

B—C bond angle in the MM3 structure is about 3° larger than that in the *ab initio* structure (Table 6, Fig. 1). This disagreement may be attributed to a favorable interaction between the lone pair of O_c and the *ortho* aromatic hydrogen. Obviously this interaction is not reflected in the MM3 structure.

CONCLUSION

A new set of MM3 force field parameters has been developed to model the structures and vibrational spectra of alkyl- and arylboronic acids. The close agreement between the MM3 and *ab initio* calculations will enable researchers to carry out quantitative molecular modeling studies of this biologically important class of compounds with high accuracy.

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