RECEIVED

DEC 18 2001

Journal of Organic Chemistry

SI J011051X

Supporting information for

"Substituent Effects on the Acidity of Weak Acids. 1 Bicyclo[2.2.2]octane-1-carboxylic Acids and Bicyclo[1.1.1]pentane-1-carboxylic Acids

Kenneth B. Wiberg

Tables of calculated ΔHacid, bond dipoles, charge distributions, calculated energies and B3LYP/6-311+G* optimized geometries

Table S1. Gas-phase Acidities of 4-Substituted Bicyclo[2.2.2]octane-1-carboxylic acids, and C-X Bond Dipoles

X	ΔHacid		μx C-X[a]
	calc[b]	obs	
H	343.5	344.4	0.000
CH_3	343.1	343.4	0.153
NH_2	342.8		0.694
OH	340.6		1.490
F	338.8	338.8	2.797
H_3Si	341.1		1.226
SH	340.5		2.092
Cl	338.5	338.2	3.216
CF_3	337.5	337.9	3.529
HCO	337.5		3.271
CN	334.9	335.8	4.936
NO_2	334.8	335.6	5.292

a. Calculated dipole moments of substituted bicyclo[2.2.2]octanes, MP2/6-311++G**. The values are relative to that for CH.

b. MP2/6-311++G**//B3LYP/6-311+G*.

Table S2 Charge distribution for Bicyclo[2.2.2]octane-1-carboxylic acids

a. acids

X	ipso	ortho	meta	para	CO_2H	X
H	0.039	0.002	0.002	0.018	-0.075	0.006
Me	0.039	0.002	-0.003	0.045	-0.075	-0.009
NH_2	0.039	0.005	-0.003	0.095	-0.073	-0.068
OH	0.039	0.008	0.002	0.172	-0.070	-0.121
F	0.038	0.013	0.012	0.145	-0.066	-0.194
SiH_3	0.039	0.005	0.017	-0.024	-0.072	-0.012
SH	0.039	0.009	0.010	0.066	-0.067	-0.095
Cl	0.039	0.013	0.017	0.108	-0.064	-0.172
CF_3	0.039	0.014	0.009	0.025	-0.066	-0.066
CHO	0.039	0.011	0.011	0.032	-0.067	-0.071
CN	0.039	0.018	0.028	0.062	-0.066	-0.171
NO_2	0.039	0.019	0.021	0.100	-0.059	-0.201

b. carboxylate anions

H	0.027	-0.033	-0.045	0.012	-0.791	-0.017
Me	0.027	-0.031	-0.044	0.044	-0.790	-0.056
NH_2	0.027	-0.029	-0.044	0.092	-0.788	-0.144
HO	0.027	-0.026	-0.041	0.199	-0.785	-0.162
F	0.026	-0.021	-0.031	0.142	-0.782	-0.228
SiH_3	0.027	-0.026	-0.019	-0.024	-0.784	-0.085
SH	0.027	-0.023	-0.028	0.070	-0.781	-0.162
Cl	0.026	-0.019	-0.022	0.114	-0.778	-0.241
CF_3	0.026	-0.019	-0.031	0.023	-0.779	-0.118
CN	0.027	-0.017	-0.016	0.053	-0.774	-0.204
CHO	0.027	-0.022	-0.028	0.030	-0.782	-0.126
NO_2	0.026	-0.014	-0.017	0.100	-0.773	-0.259

Table S3. Comparison of Estimated and Observed Dipole Moments for 4-Substituted Bicyclo[2.2.2]octane-1-carboxylic Acids.

X	μ_x(C-X)	μ_x(acid)[a]	
		calc	obs
H	0.00	(-1.51)	-1.51
Me	0.15	-1.36	-1.46
NH_2	0.69	-0.82	-1.02
OH	1.49	-0.02	0.11
F	2.80	1.29	1.20
SiH_3	1.23	0.28	0.62
SH	2.09	0.58	0.45
Cl	3.22	1.71	1.49
CF_3	3.52	2.01	1.85
CHO	3.27	1.76	1.39
CN	4.94	3.43	3.47
NO_2	5.29	3.78	3.75

a. Component along the bridgehead-bridgehead axis.

Table. S4. Gas-phase Acidities of 3-Substituted Bicyclo[2.2.2]octane-1-carboxylic Acids.

X	ΔHacid	
	Calc	Obs
H	343.5	344.4
Me	343.5	
NH_2	343.1	
OH	339.5	
F	340.0	
SiH_3	341.3	
SH	340.3	
Cl	338.9	339.4
CF_3	337.6	
CHO	338.4	
CN	335.6	337.9
NO_2	335.7	

Table S5. Gas-phase Acidities of 3-Substituted Bicyclo[1.1.1]pentane-1-carboxylic Acids and C-X Bond Dipoles

X	ΔH_{acid}		μ_x, C-X[a]
	Calc[b]	Obs	
H	343.0	342.9	0.000
Me	343.5		-0.180
NH_2	342.0		0.040
HO	340.3		1.018
F	336.9		2.194
SiH_3	340.2		0.805
SH	338.4		1.885
Cl	336.1		2.565
CF_3	334.8		3.233
CHO	336.6		3.047
CN	332.6		4.668
NO_2	330.9		5.096

a. Calculated dipole moments of the substituted bicyclo[1.1.1]pentanes, MP2/6-311++G**.

b. MP2/6-311++G**//B3LYP/6-311+G*.

Table S6. Charge Distribution for Bicyclo[1.1.1]pentane-1-carboxylic Acids and Anions.

a. acids.

X	ipso	ortho	para	CO_2H	X
H	0.034	0.010	0.018	-0.096	0.013
Me	0.032	0.003	0.051	-0.099	0.007
NH_2	0.032	0.003	0.097	-0.096	-0.043
OH	0.034	0.011	0.121	-0.090	-0.096
F	0.037	0.026	0.138	-0.079	-0.175
SiH_3	0.035	0.024	-0.026	-0.093	0.012
SH	0.035	0.026	0.055	-0.086	-0.079
Cl	0.038	0.036	0.092	-0.077	-0.160
CF_3	0.039	0.034	0.019	-0.076	-0.084
CN	0.039	0.046	0.057	-0.074	-0.160
CHO	0.038	0.029	0.034	-0.083	-0.073
NO_2	0.042	0.050	0.042	-0.067	-0.217

b. carboxylate anions

H	0.035	-0.051	-0.011	-0.846	-0.025
Me	0.034	-0.051	0.031	-0.845	-0.058
NH_2	0.034	-0.054	0.077	-0.839	-0.113
OH	0.035	-0.048	0.099	-0.830	-0.163

F	0.036	-0.032	0.113	-0.816	-0.237
SiH_3	0.037	-0.024	-0.042	-0.835	-0.089
SH	0.036	-0.024	0.043	-0.821	-0.183
Cl	0.031	-0.011	0.081	-0.799	-0.284
CF_3	0.040	-0.020	-0.001	-0.822	-0.153
CN	0.040	-0.007	0.035	-0.818	-0.233
CHO	0.039	-0.024	0.015	-0.823	-0.159
NO_2	0.042	-0.003	0.080	-0.803	-0.303

Table S7. Calculated Energies of 4-Substituted Bicyclo[2.2.2]octane-1-carboxylic acids

	acids			anions		
	B3LYP[a]	MP2[b]	Hcorr[c]	B3LYP	MP2	Hcorr
H	-501.98206	-500.56918	0.23172	-501.42982	-500.00945	0.21707
Me	-541.30633	-539.77273	0.26067	-540.75482	-539.21360	0.24594
NH_2	-557.34809	-555.80046	0.24986	-556.79827	-555.24207	0.23535
OH	-577.22343	-575.65389	0.23670	-576.67607	-575.09904	0.22220
F	-601.25996	-599.65632	0.22441	-600.71606	-599.10435	0.20992
SiH_3	-792.69283	-790.77345	0.24863	-792.14490	-790.21757	0.23400
SH	-900.19467	-898.24464	0.23241	-899.64962	-897.69003	0.21796
Cl	-961.61301	-959.63936	0.22361	-961.07098	-959.08815	0.20919
CF_3	-839.13729	-837.03781	0.23992	-838.59537	-836.48778	0.22538
CHO	-615.33347	-613.64936	0.24254	-614.78956	-613.09743	0.22600
CN	-594.24594	-592.60879	0.23204	-593.71052	-592.06324	0.21773
NO_2	-706.55066	-704.68549	0.23700	-706.01354	-704.13986	0.22255

a. B3LYP/6-311+G* geometry optimizations.

b. MP2/6-311++G** calculations using the B3LYP geometries.

c. This includes the zero-point energy and the change in enthalpy on going to 298 K.

Calculated gas phase ΔHacid, kcal/mol

	B3LYP	MP2
H	338.8	343.5
Me	338.3	343.1
NH_2	337.4	342.8
OH	335.9	340.6
F	333.7	338.8
SiH_3	336.2	341.1
SH	334.5	340.5
Cl	332.6	338.3
CF_3	332.4	337.5
CHO	332.4	337.5
CN	328.5	334.9
NO_2	329.5	334.8

Table S8. Calculated energies of 3-Substituted Bicyclo[2.2.2]ocatane-1-carboxylic acids[a]

	acids				anions		
	B3LYP[b]	MP2[c]	Hcorr[d]		B3LYP	MP2	Hcorr
H	-501.98206	-500.56918	0.23172	H	-501.42981	-500.00945	0.21707
Me, a	-541.30338		0.26008	Me, a	-540.75162		0.24635
Me,b	-541.30385	-539.76929	0.26093	Me,b	-540.75186	-539.20966	0.24631
NH_2,a	-557.34532		0.24929	NH_2,b	-556.79343		0.23560
NH_2,b	-557.34540	-555.79692	0.25024	NH_2,a	-556.79377	-555.23799	0.23568
OH,a	-577.21816		0.23705	OH,a	-576.67203		0.22261
OH,b	-577.21826	-575.64825	0.23703	OH,b	-576.67225	-575.09420	0.22164
F,a	-601.25608		0.22472	F,b	-600.71019		0.21017
F,b	-601.25624	-599.65235	0.22476	F,a	-600.71059	-599.09841	0.21022
SiH_3,a	-792.69318		0.24876	SiH_3,b	-792.14512		0.23414
SiH_3,b	-792.69324	-790.77315	0.24874	SiH_3,a	-792.14523	-790.21712	0.23417
SH,a	-900.19236		0.23251	SH,b	-899.64666		0.21810
SH,b	-900.19318	-898.24148	0.23251	SH,a	-899.64728	-897.68721	0.21813
Cl,a	-961.60964		0.22379	Cl,b	-961.06669		0.20931
Cl,b	-961.61001	-959.63483	0.22380	Cl,a	-961.06699	-959.08275	0.20935

CF_3,a	-839.13546		0.24025	CF_3,b	-838.59314		0.22561
CF_3,b	-839.13587	-837.03444	0.24025	CF_3,a	-838.59350	-836.48414	0.22557
CHO,a	-615.33152		0.24258	CHO,a	-614.78832		0.22806
CHO,b	-615.33167	-613.64662	0.24260	CHO,b	-614.78863	-613.09513	0.22805
CN,a	-594.24759		0.23225	CN,b	-593.70828		0.21773
CN	-594.24759	-592.60736	0.23227	CN,a	-593.70886	-592.06036	0.21775
NO_2,a	-706.54960		0.23722	NO_2,a	-706.01040		0.22280
NO_2,b	-706.54971	-704.68358	0.23718	NO_2,b	-706.01056	-704.13560	0.22175

a. The acids designated by "a" have the substituent oriented toward the carboxylic carbonyl, whereas those designated by "b" have the substituent oriented toward the carboxylic OH. The designation for the anions refer to the acid from which they are derived.

b. B3LYP/6-311+G* geometry optimizations.

c. MP2/6-311++G** calculations using the B3LYP geometries.

d. This includes the zero-point energy and the change in enthalpy on going to 298 K.

Calculated gas phase ΔHacid, kcal/mol

	B3LYP	MP2
H	338.8	343.5
Me, a	339.1	
Me,b	338.7	343.5
NH_2,a	339.2	
NH_2,b	338.5	343.1
OH,a	335.1	
OH,b	334.5	339.5
F,a	334.9	-
F,b	334.8	340.0
SiH_3,a	336.2	
SiH_3,b	336.2	341.3
SH,a	334.9	
SH,b	335.0	340.3
Cl,a	333.1	
Cl,b	333.2	338.9
CF_3,a	332.6	
CF_3,b	332.6	337.6

CHO,a	333.3	
CHO,b	333.1	338.4
CN,a	330.8	
CN,b	330.4	335.6
NO_2,a	330.8	
NO_2,b	330.1	335.7

Table S9. Calculated energies of 3-Substituted bicyclo[1.1.1]pentane-1-carboxylic acids

	acids			anions		
	B3LYP[a]	MP2[b]	Hcorr[c]	B3LYP	MP2	Hcorr
H	-383.92990	-382.88910	0.13941	-383.37910	-382.33057	0.12511
Me	-423.25901	-422.09355	0.16845	-422.70735	-421.53426	0.15416
NH_2	-439.30082	-438.12182	0.15760	-438.75107	-437.56412	0.14254
OH	-459.17424	-457.97482	0.14453	-458.62766	-457.42078	0.13039
F	-483.20693	-481.97441	0.13232	-482.66668	-481.42574	0.11810
SiH_3	-674.64699	-673.09592	0.15660	-674.10141	-672.54206	0.14247
SH	-782.14611	-780.56385	0.14015	-781.60426	-780.01292	0.12605
Cl	-843.56166	-841.95706	0.13124	-843.02518	-841.40972	0.11713
CF_3	-721.08671	-719.35456	0.14772	-720.54976	-718.80931	0.13364
CHO	-497.28274	-495.96697	0.15043	-496.74343	-495.41876	0.13630
CN	-476.19820	-474.92743	0.13992	-475.66508	-474.38580	0.12590
NO_2	-588.49626	-586.99986	0.14465	-587.96653	-586.46086	0.13051

a. B3LYP/6-311+G* geometry optimizations.

b. MP2/6-311++G** calculations using the B3LYP geometries

c. This includes the zero-point energy and the change in enthalpy on going to 298 K.

Calculated gas phase ΔHacid, kcal/mol

	B3LYP	MP2
H	338.2	343.0
Me	338.7	343.5
NH_2	337.0	342.0
OH	335.6	340.3
F	331.6	336.9
SiH_3	335.0	340.2
SH	332.7	338.4
Cl	329.3	336.1
CF_3	329.6	334.8
CHO	331.1	336.6
CN	327.2	332.6
NO_2	325.0	330.9

Table S10. Calculated geometries for Bicyclooctanecarboxylic acids

Bicyclo222octanecarboxylic acid, C1, B3LYP/6-311+G* = -501.98206

Zpe = 138.65

0 1			
C	-0.804214	-1.226311	-1.624009
C	-0.059540	-0.000348	-2.180492
C	0.064147	0.000833	0.426008
C	-0.667067	-1.274660	-0.075453
H	-1.859416	-1.178643	-1.912841
H	-0.402663	-2.140767	-2.071511
H	-1.645086	-1.348075	0.403681
H	-0.098004	-2.156481	0.236378
C	-0.712661	1.278547	-1.628478
H	-0.165051	2.154993	-1.989896
H	-1.733564	1.372589	-2.012011
C	-0.721316	1.244299	-0.073522
H	-0.267378	2.151752	0.336904
H	-1.741439	1.203912	0.313746
C	1.485495	0.031387	-0.172373
H	1.989309	0.947201	0.147710
H	2.072824	-0.791804	0.240364
C	1.408122	-0.053281	-1.722380
H	1.970443	0.766944	-2.179704
H	1.870067	-0.979110	-2.080851
C	0.134358	0.000034	1.941631
O	-1.098728	-0.000399	2.516573
H	-0.967180	-0.001446	3.477559
O	1.139165	-0.000068	2.610843

H	-0.110306	-0.000330	-3.274453

Bicyclo222octanecarboxylate, C1, B3LYP/6-311+G* = -501.42981
Zpe = 129.61

-1 1

C	-0.798604	-1.213672	-1.612164
C	-0.020826	-0.000066	-2.153275
C	0.035667	-0.000143	0.478896
C	-0.693020	-1.253509	-0.058867
H	-1.846902	-1.145323	-1.932273
H	-0.402093	-2.134954	-2.058726
H	-1.677122	-1.305720	0.411242
H	-0.145087	-2.146194	0.265822
C	-0.672224	1.286462	-1.614071
H	-0.106492	2.156618	-1.972666
H	-1.684343	1.388780	-2.027528
C	-0.707027	1.245975	-0.057212
H	-0.244242	2.146588	0.362037
H	-1.731013	1.221963	0.321932
C	1.465422	0.009268	-0.094672
H	1.976067	0.915836	0.241779
H	2.029979	-0.819748	0.338187
C	1.433109	-0.073596	-1.650287
H	2.018728	0.738895	-2.100631
H	1.889113	-1.008263	-2.003397
C	0.002617	-0.000839	2.058979
O	-1.149605	-0.000444	2.558469
O	1.111246	-0.000587	2.644327
H	-0.040409	0.000490	-3.252099

4-Trifluoromethylbicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -839.13729, Zpe = 141.65

0 1

C	-0.844985	-1.165521	-0.486269
C	0.006774	0.000753	-1.040249
C	0.066793	-0.001942	1.575428
C	-0.631780	-1.281871	1.046211
H	-1.897993	-0.982999	-0.714147
H	-0.572995	-2.101050	-0.979982
H	-1.586447	-1.427086	1.553890
H	-0.009831	-2.150377	1.284072
C	-0.561170	1.329990	-0.490161
H	0.113258	2.147717	-0.755509
H	-1.524225	1.552376	-0.955469
C	-0.719432	1.228114	1.050202
H	-0.351236	2.140378	1.528226
H	-1.770312	1.130828	1.330305
C	1.496857	0.047851	1.004686
H	1.950671	1.010396	1.255141
H	2.116580	-0.711664	1.484204
C	1.458570	-0.163091	-0.531183
H	2.116870	0.550824	-1.031258
H	1.820755	-1.160203	-0.793693
C	0.099550	-0.000725	3.092695
O	-1.147827	0.000391	3.631917
H	-1.047441	0.003022	4.596791
O	1.088638	0.002079	3.783461
C	-0.024718	0.000784	-2.561969

F	0.648873	1.051772	-3.091552
F	0.532329	-1.118022	-3.088318
F	-1.288192	0.067586	-3.051456

4-trifluoromethylbicyclo[2.2.2]octane-1-carboxylate,
B3LYP/6-311+G* = -838.59537, Zpe = 132.61

-1 1

C	-0.938613	-1.102703	-0.461234
C	0.002594	-0.000599	-1.006421
C	0.035534	-0.011044	1.631656
C	-0.752528	-1.216365	1.077698
H	-1.972493	-0.843614	-0.711387
H	-0.725822	-2.056195	-0.955200
H	-1.715989	-1.264204	1.587487
H	-0.214881	-2.138505	1.327435
C	-0.477502	1.364849	-0.457508
H	0.249969	2.134903	-0.733290
H	-1.424848	1.644612	-0.929769
C	-0.630914	1.271411	1.087432
H	-0.177857	2.147616	1.562209
H	-1.682285	1.268180	1.383416
C	1.464131	-0.075116	1.065501
H	1.996614	0.842015	1.331724
H	2.011799	-0.884938	1.551016
C	1.434364	-0.270104	-0.477518
H	2.147299	0.397333	-0.972480
H	1.724216	-1.290918	-0.747540
C	-0.011126	-0.001282	3.211142
O	-1.168254	0.006618	3.696300

O	1.093519	0.009107	3.801479
C	-0.008421	0.003835	-2.523520
F	0.749131	1.001802	-3.060373
F	0.470510	-1.152044	-3.064042
F	-1.255525	0.165867	-3.048832

4-Chlorobicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -961.61301, Zpe = 132.79

0 1

C	-0.717656	-1.253013	-0.997949
C	-0.003654	-0.000002	-1.513567
C	0.064557	-0.000044	1.075651
C	-0.683066	-1.258236	0.559247
H	-1.746803	-1.260796	-1.364373
H	-0.229117	-2.141670	-1.403788
H	-1.694364	-1.274978	0.968558
H	-0.178454	-2.156513	0.926921
C	-0.714978	1.254508	-0.997927
H	-0.223678	2.142129	-1.402730
H	-1.743719	1.265219	-1.365372
C	-0.681977	1.258698	0.559310
H	-0.177462	2.156602	0.928041
H	-1.693708	1.275567	0.967566
C	1.497272	-0.000696	0.506890
H	2.037714	0.871438	0.880818
H	2.037362	-0.872619	0.881794
C	1.455206	-0.001579	-1.048900
H	1.965854	0.874298	-1.455854
H	1.963526	-0.879306	-1.454808

C	0.104651	-0.000014	2.593629
O	-1.139207	0.000037	3.140757
H	-1.032082	0.000193	4.104897
O	1.097708	0.000097	3.278752
Cl	-0.051482	0.000096	-3.352121

4-Chlorobicyclo[2.2.2]octanecarboxylate,
B3LYP/6-311+G* = -961.07098, Zpe = 123.84

-1 1

C	-0.721749	-1.252296	-0.970552
C	0.000802	-0.000002	-1.467566
C	0.035390	-0.000021	1.132384
C	-0.695365	-1.248248	0.590610
H	-1.747101	-1.253077	-1.353706
H	-0.229447	-2.140193	-1.379210
H	-1.705772	-1.261527	1.002695
H	-0.192559	-2.147721	0.961558
C	-0.720708	1.252885	-0.970537
H	-0.227083	2.140378	-1.378493
H	-1.745782	1.255018	-1.354416
C	-0.695432	1.248182	0.590645
H	-0.193259	2.147698	0.962330
H	-1.706140	1.260901	1.002014
C	1.468478	0.000036	0.571570
H	2.004517	0.870542	0.955641
H	2.004915	-0.869878	0.956397
C	1.453747	-0.000622	-0.990324
H	1.966138	0.877062	-1.397117
H	1.965070	-0.879284	-1.396362

C	-0.009548	-0.000048	2.714056
O	-1.166468	0.000020	3.199537
O	1.095237	0.000036	3.302909
Cl	-0.018667	0.000025	-3.341330

4-Cyanobicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -594.24594, Zpe = 137.97

0 1

C	-1.285455	-0.663771	-1.072418
C	0.003401	-0.001511	-1.642078
C	0.037259	-0.059806	0.971760
C	-1.064798	-0.998655	0.423441
H	-2.119305	0.033518	-1.193390
H	-1.538587	-1.560566	-1.639931
H	-1.993580	-0.887978	0.983903
H	-0.746017	-2.039589	0.546689
C	0.115468	1.434056	-1.055199
H	1.144450	1.785467	-1.182713
H	-0.524736	2.134399	-1.593983
C	-0.271713	1.373997	0.437970
H	0.272991	2.134878	1.000707
H	-1.337681	1.579640	0.575682
C	1.394057	-0.512135	0.381678
H	2.133081	0.276943	0.536874
H	1.768420	-1.390001	0.910894
C	1.223750	-0.812066	-1.127564
H	2.126465	-0.549540	-1.684313
H	1.045816	-1.876905	-1.307025
C	0.105892	-0.000726	2.484096

O	-1.120744	0.038955	3.064177
H	-0.985896	0.127707	4.021056
O	1.119729	0.058774	3.135683
C	-0.037727	0.042556	-3.101261
N	-0.079728	0.091223	-4.253698

4-cyanobicyclo[2.2.2]octane-1-carboxylate,
B3LYP/6-311+G* = -593.71052, Zpe = 128.89

-1 1

C	-0.812853	-1.207095	-1.066319
C	-0.001444	-0.000385	-1.610773
C	0.035170	-0.001355	1.024288
C	-0.694145	-1.248995	0.482888
H	-1.855454	-1.102463	-1.385984
H	-0.438232	-2.128820	-1.523786
H	-1.677683	-1.302398	0.952689
H	-0.146039	-2.144766	0.795589
C	-0.635738	1.308371	-1.067202
H	-0.035915	2.157864	-1.411401
H	-1.632319	1.434310	-1.503734
C	-0.697487	1.245973	0.485218
H	-0.243980	2.144686	0.915920
H	-1.729329	1.218328	0.840440
C	1.467464	0.002892	0.463654
H	1.974117	0.915487	0.787332
H	2.030064	-0.819692	0.909147
C	1.457976	-0.103477	-1.087778
H	2.060433	0.686561	-1.548614
H	1.882799	-1.054594	-1.427129

C	-0.009516	-0.000885	2.606054
O	-1.166257	0.000659	3.090746
O	1.095931	0.000273	3.193653
C	-0.016001	0.000755	-3.074004
N	-0.026631	0.001893	-4.230259

4-Fluorobicyclo[2.2.2]octanecarboxylic acid, C1

B3LYP/6-311+G* = -601.25996, Zpe = 133.59

0 1

C	-0.787035	-1.217143	-1.321643
C	-0.023887	-0.000053	-1.839727
C	0.065060	0.000188	0.740622
C	-0.662537	-1.273532	0.227842
H	-1.832924	-1.143506	-1.632449
H	-0.379222	-2.119071	-1.784946
H	-1.645542	-1.350055	0.694591
H	-0.096614	-2.157479	0.536849
C	-0.672168	1.283188	-1.324756
H	-0.101104	2.142150	-1.687558
H	-1.678647	1.369784	-1.742289
C	-0.710979	1.245797	0.229865
H	-0.265353	2.153365	0.646987
H	-1.738848	1.205463	0.594427
C	1.494119	0.028014	0.158713
H	1.994074	0.946366	0.475271
H	2.078423	-0.792394	0.579187
C	1.433742	-0.066772	-1.391742
H	1.990062	0.748283	-1.861818
H	1.874846	-1.000694	-1.751105

C	0.116929	-0.000315	2.257843
O	-1.122990	-0.000320	2.814536
H	-1.008198	-0.000534	3.777788
O	1.114779	0.000042	2.936122
F	-0.071637	0.000479	-3.252477

4-Fluorobicyclo[2.2.2]octanecarboxylate,
B3LYP/6-311+G* = -600.71606, Zpe = 124.59

-1 1

C	-0.725746	-1.248637	-1.304696
C	-0.007129	0.000003	-1.804009
C	0.035984	-0.000014	0.794906
C	-0.697176	-1.249691	0.255043
H	-1.751302	-1.245773	-1.690778
H	-0.231737	-2.133311	-1.721523
H	-1.705451	-1.263520	0.672125
H	-0.193241	-2.148584	0.625909
C	-0.724659	1.249265	-1.304684
H	-0.229291	2.133531	-1.720773
H	-1.749924	1.247780	-1.691536
C	-0.697234	1.249645	0.255079
H	-0.193953	2.148578	0.626714
H	-1.705827	1.262895	0.671417
C	1.468752	0.000036	0.229077
H	2.005936	0.869868	0.613002
H	2.006337	-0.869192	0.613778
C	1.442885	-0.000639	-1.331200
H	1.949676	0.877973	-1.746269
H	1.948611	-0.880246	-1.745468

C	-0.004542	-0.000040	2.376550
O	-1.159922	0.000007	2.866367
O	1.101640	0.000018	2.963564
F	-0.025597	0.000026	-3.238049

4-formylbicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -615.33347, Zpe = 144.16

0 1

C	-0.896235	-0.978490	-1.117608
C	0.083471	0.108241	-1.585440
C	0.061599	-0.009902	1.029618
C	-0.791413	-1.156551	0.421353
H	-1.912335	-0.697349	-1.408324
H	-0.684097	-1.916357	-1.635413
H	-1.782348	-1.163232	0.878555
H	-0.323987	-2.114910	0.669256
C	-0.350650	1.471840	-0.989323
H	0.399329	2.232055	-1.231081
H	-1.287558	1.799298	-1.450010
C	-0.525975	1.342409	0.548212
H	-0.024420	2.169581	1.059512
H	-1.580468	1.396610	0.824851
C	1.505773	-0.133538	0.505835
H	2.087804	0.726414	0.848149
H	1.983624	-1.013169	0.940644
C	1.499089	-0.219203	-1.043478
H	2.235146	0.471007	-1.468427
H	1.784779	-1.221311	-1.377660
C	0.043118	-0.084109	2.545276

O	-1.205620	0.089795	3.052604
H	-1.137667	0.027626	4.018269
O	0.996228	-0.272805	3.260999
C	0.149561	0.228030	-3.091050
H	0.823844	1.035730	-3.457630
O	-0.447067	-0.460035	-3.882486

4-Formylbicyclo[2.2.2]octanecarboxylate,
B3LYP/6-311+G* = -614.78956, Zpe = 135.15

-1 1

C	-1.003727	-1.126494	-0.962447
C	-0.130212	0.015511	-1.553086
C	0.047948	-0.011779	1.081595
C	-0.755651	-1.225313	0.569446
H	-2.060133	-0.921591	-1.177972
H	-0.761570	-2.072028	-1.462666
H	-1.695882	-1.274979	1.121202
H	-0.201971	-2.142178	0.801556
C	-0.649961	1.354081	-0.960737
H	0.004992	2.165054	-1.300390
H	-1.649707	1.574851	-1.356747
C	-0.672022	1.264013	0.591891
H	-0.186010	2.144325	1.024985
H	-1.694673	1.252600	0.975420
C	1.442828	-0.051031	0.431293
H	1.987121	0.857726	0.702552
H	2.017697	-0.873911	0.861235
C	1.329291	-0.191794	-1.115761
H	1.971245	0.527620	-1.634503

H	1.661623	-1.181343	-1.450183
C	0.088347	-0.012286	2.661920
O	-1.040891	-0.039815	3.209954
O	1.221974	0.026904	3.192252
C	-0.320422	0.040775	-3.043766
H	-1.385072	0.162527	-3.358991
O	0.535646	-0.056187	-3.895652

4-Aminobicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -557.34809, Zpe = 149.26

0 1

C	-0.807887	-1.201528	-1.298941
C	-0.032184	0.000479	-1.867394
C	0.067976	-0.000718	0.760018
C	-0.656740	-1.273054	0.244348
H	-1.857320	-1.107096	-1.590612
H	-0.439479	-2.123664	-1.762328
H	-1.631655	-1.363201	0.726329
H	-0.078133	-2.154565	0.538648
C	-0.658764	1.288596	-1.303443
H	-0.074042	2.150734	-1.645320
H	-1.660915	1.404837	-1.723579
C	-0.706340	1.243352	0.247712
H	-0.268200	2.150065	0.675909
H	-1.736950	1.197206	0.605048
C	1.495337	0.027138	0.179813
H	1.990255	0.952259	0.486740
H	2.084400	-0.784509	0.611883
C	1.429100	-0.084797	-1.366767

H	2.016744	0.710985	-1.837299
H	1.864342	-1.031442	-1.707084
C	0.116852	-0.000825	2.276602
O	-1.123903	0.001921	2.833401
H	-1.007181	0.002427	3.796333
O	1.112694	-0.001605	2.959006
N	-0.167759	0.003957	-3.327443
H	0.318743	0.802328	-3.727569
H	0.259281	-0.828456	-3.725945

4-Aminobicyclo[2.2.2]octanecarboxylate, C1,
B3LYP/6-311+G* = -556.79827, Zpe = 140.23

-1 1

C	-0.825399	-1.188130	-1.281513
C	-0.022644	0.001801	-1.834405
C	0.037066	-0.003901	0.813453
C	-0.718509	-1.236769	0.269694
H	-1.864851	-1.087054	-1.613165
H	-0.447367	-2.116092	-1.733732
H	-1.704575	-1.268275	0.736659
H	-0.192750	-2.143674	0.590642
C	-0.639363	1.297557	-1.280852
H	-0.049423	2.152313	-1.641999
H	-1.642956	1.414732	-1.704489
C	-0.671782	1.259184	0.274648
H	-0.186715	2.148392	0.691972
H	-1.696970	1.262402	0.650458
C	1.466694	-0.029015	0.244537
H	2.001196	0.862524	0.582683

H	2.009863	-0.874198	0.673081
C	1.427610	-0.106153	-1.309124
H	2.027089	0.695555	-1.762997
H	1.858465	-1.050702	-1.670724
C	0.000122	-0.001524	2.394403
O	-1.153029	0.004271	2.889966
O	1.108065	-0.001405	2.980654
N	-0.116916	0.008579	-3.308225
H	0.417993	0.794078	-3.674640
H	0.326349	-0.831275	-3.676182

%chk=/scratch/bcacid

%mem=8000000

freq=raman rb3lyp/6-311+g(d) geom=allcheck guess=tcheck

Hydroxybicyclo[2.2.2]octanecarboxylic acid, conf 2, B3LYP/6-311+G* opt

0 1

C	-0.716973	1.254890	1.314812
C	-0.014898	0.000000	1.859669
C	0.064421	0.000000	-0.749427
C	-0.689362	1.258020	-0.239334
H	-1.751015	1.278605	1.678958
H	-0.219630	2.138600	1.723161
H	-1.700016	1.267788	-0.651108
H	-0.189572	2.156476	-0.613611
C	-0.728396	-1.248428	1.314672
H	-0.247610	-2.136589	1.732944
H	-1.766473	-1.255549	1.668140
C	-0.684488	-1.260876	-0.239055

H	-0.172609	-2.157046	-0.602474
H	-1.690622	-1.282435	-0.661238
C	1.493491	0.002763	-0.170113
H	2.039762	-0.863576	-0.549592
H	2.031485	0.878815	-0.539270
C	1.439401	-0.006670	1.381472
H	1.937619	-0.888783	1.792379
H	1.949481	0.863320	1.803380
C	0.113382	0.000000	-2.266649
O	-1.128082	-0.000133	-2.822630
H	-1.012483	0.000000	-3.785723
O	1.108972	0.000238	-2.948408
O	0.021067	-0.000103	3.288587
H	-0.883438	0.002866	3.627376

4-hydroxybicyclo[2.2.2]octanecarboxylate, C1,
B3LYP/6-311+G* = -576.67607, Zpe = 132.01

-1 1

C	-0.712917	1.248536	1.294477
C	0.007047	0.000057	1.825287
C	0.036267	0.000012	-0.803493
C	-0.695249	1.249216	-0.262714
H	-1.744392	1.254423	1.676725
H	-0.221670	2.135877	1.709452
H	-1.704941	1.262129	-0.677209
H	-0.193302	2.147839	-0.637732
C	-0.713412	-1.248150	1.294570
H	-0.222455	-2.135721	1.709406
H	-1.744868	-1.253690	1.676949

C	-0.695890	-1.248810	-0.262628
H	-0.194432	-2.147692	-0.637671
H	-1.705612	-1.261188	-0.677060
C	1.468901	-0.000326	-0.238624
H	2.004820	-0.869650	-0.626388
H	2.005263	0.868688	-0.626448
C	1.451034	-0.000295	1.319770
H	1.962107	-0.877814	1.731989
H	1.962541	0.876998	1.731966
C	-0.010847	-0.000042	-2.384584
O	-1.168360	-0.000001	-2.870647
O	1.092350	-0.000105	-2.977991
O	0.056223	0.000123	3.268922
H	-0.854371	-0.001512	3.591394

4-Mercaptobicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -900.19467, Zpe = 137.95

0 1

C	-0.717113	1.255371	0.980602
C	0.000236	0.008634	1.529737
C	0.065739	-0.002241	-1.084778
C	-0.590328	1.306046	-0.569411
H	-1.765927	1.229104	1.286846
H	-0.286571	2.156317	1.426771
H	-1.569350	1.436852	-1.033567
H	0.022524	2.158522	-0.878711
C	-0.708423	-1.249802	0.991546
H	-0.170762	-2.139086	1.332009
H	-1.717882	-1.313548	1.407434

C	-0.766067	-1.202427	-0.561715
H	-0.376299	-2.132821	-0.985271
H	-1.795905	-1.107299	-0.910795
C	1.494469	-0.099777	-0.516161
H	1.943222	-1.045305	-0.830936
H	2.116116	0.686895	-0.948241
C	1.457456	0.005478	1.034608
H	1.997242	-0.825161	1.494786
H	1.954461	0.921630	1.369802
C	0.102837	-0.006631	-2.602276
O	-1.141659	0.035409	-3.147709
H	-1.035179	0.031691	-4.111870
O	1.093295	-0.041272	-3.290741
S	-0.098811	-0.071764	3.378546
H	0.619361	1.049425	3.619707

4-Mercaptobicyclo[2.2.2]octanecarboxylate,
B3LYP/6-311+G* = -899.64962, Zpe = 128.97

-1 1

C	-0.732463	1.247799	0.957247
C	0.002948	0.005839	1.490963
C	0.036149	-0.000190	-1.138901
C	-0.634326	1.281082	-0.597431
H	-1.774340	1.214987	1.292889
H	-0.293970	2.150393	1.399406
H	-1.620806	1.374760	-1.055206
H	-0.052544	2.150826	-0.923561
C	-0.706865	-1.255959	0.964860
H	-0.170990	-2.143191	1.320564

H	-1.717631	-1.309950	1.385500
C	-0.750753	-1.211271	-0.592923
H	-0.328838	-2.132544	-1.008426
H	-1.777178	-1.147594	-0.959086
C	1.467194	-0.066737	-0.577948
H	1.939437	-0.993250	-0.914436
H	2.061129	0.740356	-1.011642
C	1.454468	0.015306	0.978987
H	2.001154	-0.819414	1.429447
H	1.948387	0.931003	1.328278
C	-0.010745	-0.000982	-2.719740
O	-1.167012	0.039006	-3.205480
O	1.092814	-0.040883	-3.311199
S	-0.063133	-0.072191	3.354679
H	0.636252	1.064369	3.584148

4-Methylbicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -541.30633, Zpe = 155.96

0 1

C	-0.810479	-1.196259	-1.287873
C	-0.022114	0.000340	-1.863532
C	0.065702	-0.001385	0.772226
C	-0.656177	-1.274054	0.255459
H	-1.866483	-1.096269	-1.562425
H	-0.459395	-2.123825	-1.752039
H	-1.628511	-1.370901	0.741764
H	-0.072040	-2.154463	0.542610
C	-0.637041	1.295862	-1.290790
H	-0.034438	2.151195	-1.615416

H	-1.636312	1.446586	-1.712836
C	-0.711606	1.239927	0.259189
H	-0.287977	2.147846	0.699786
H	-1.746890	1.182272	0.602011
C	1.492104	0.030917	0.190322
H	1.978253	0.964451	0.486477
H	2.088498	-0.769723	0.632913
C	1.432467	-0.100995	-1.354734
H	2.041443	0.676344	-1.828152
H	1.856324	-1.058919	-1.676123
C	0.114111	-0.000661	2.288432
O	-1.127315	0.000195	2.845110
H	-1.010095	0.002285	3.807952
O	1.109084	0.001405	2.972171
C	-0.071231	0.002845	-3.391597
H	-1.102929	0.037141	-3.756948
H	0.454900	0.869838	-3.804425
H	0.397087	-0.895888	-3.806003

4-Methylbicyclo[2.2.2]octanecarboxyate,
B3LYP/6-311+G* = -540.75482, Zpe = 146.78

-1 1

C	-0.788737	-1.207350	-1.269868
C	-0.006828	-0.000094	-1.832647
C	0.035838	-0.000771	0.825638
C	-0.692366	-1.249465	0.282064
H	-1.835377	-1.135454	-1.596144
H	-0.394539	-2.131107	-1.714698
H	-1.679926	-1.299550	0.744905

H	-0.149939	-2.144981	0.607808
C	-0.653577	1.284742	-1.270668
H	-0.081601	2.152862	-1.625674
H	-1.662747	1.393613	-1.690911
C	-0.699192	1.245106	0.283952
H	-0.237244	2.145355	0.704531
H	-1.726186	1.224784	0.654913
C	1.466041	0.004442	0.257757
H	1.978822	0.909477	0.594776
H	2.026926	-0.826205	0.692045
C	1.440062	-0.079200	-1.296142
H	2.033647	0.729664	-1.743768
H	1.893804	-1.016435	-1.646751
C	-0.005770	-0.000723	2.405907
O	-1.160825	-0.000156	2.898373
O	1.099764	0.000497	2.996742
C	-0.026201	0.001483	-3.362431
H	-1.052033	0.035163	-3.748666
H	0.508172	0.869718	-3.766589
H	0.451091	-0.898652	-3.768073

4-Nitrobicyclo[2.2.2]octanecarboxylic acid,
B3LYP/6-311+G* = -706.55066. Zpe = 140.39

0 1

C	-0.134111	1.434429	0.783833
C	-0.029477	-0.009277	1.302423
C	0.056260	-0.030447	-1.284186
C	0.057115	1.428770	-0.757866
H	-1.112529	1.843010	1.052908

H	0.619616	2.052673	1.271399
H	-0.735525	1.999755	-1.242992
H	1.003980	1.906358	-1.026420
C	-1.201135	-0.840843	0.775928
H	-1.087071	-1.878909	1.093740
H	-2.137505	-0.486255	1.209314
C	-1.232215	-0.729243	-0.775171
H	-1.317098	-1.723265	-1.222794
H	-2.104101	-0.161921	-1.105682
C	1.281404	-0.766398	-0.705820
H	1.244037	-1.817491	-1.001391
H	2.196519	-0.361718	-1.141437
C	1.303203	-0.627380	0.840963
H	1.442239	-1.601862	1.316820
H	2.124761	0.009457	1.172993
C	0.099907	-0.048006	-2.801966
O	-0.979315	0.566769	-3.351487
H	-0.885923	0.514353	-4.315686
O	0.966277	-0.540197	-3.481473
N	-0.024931	0.020165	2.837743
O	0.837767	0.701485	3.373299
O	-0.860052	-0.641178	3.435437

4-Nitrobicyclo[2.2.2]octanecarboxylate,

B3LYP/6-311+G* = -706.01354, Zpe = 131.43

-1 1

C	-0.155901	1.438078	0.757035
C	-0.030997	-0.008539	1.267462
C	0.031061	-0.015277	-1.339162

C	0.014938	1.426660	-0.789962
H	-1.137808	1.830706	1.045427
H	0.596528	2.061409	1.243869
H	-0.793552	1.972662	-1.278189
H	0.949797	1.925687	-1.067845
C	-1.201431	-0.844909	0.747118
H	-1.080355	-1.881704	1.072926
H	-2.136119	-0.490155	1.189646
C	-1.227454	-0.734124	-0.807639
H	-1.291539	-1.731897	-1.252902
H	-2.107231	-0.185681	-1.149547
C	1.265846	-0.733353	-0.766232
H	1.244635	-1.781497	-1.073987
H	2.169132	-0.311504	-1.210316
C	1.304255	-0.612916	0.786509
H	1.451748	-1.589928	1.260539
H	2.121292	0.030121	1.123220
C	0.005197	0.007555	-2.920184
O	-0.984910	0.599064	-3.412506
O	0.957102	-0.562734	-3.499887
N	-0.006075	0.010139	2.805305
O	0.852387	0.697543	3.347989
O	-0.821716	-0.666153	3.420699

4-silylbiccyclo[2.2.2]octylcarboxylic acid,
B3LYP/6-311G* = -792.69283, Zpe = 147.70

0 1

C	-0.802839	-1.199529	-0.956015
C	-0.003294	-0.001137	-1.525953