Supporting Information

Conformational Equilibrium and Internal Rotation Potential Functions of the *Axial* and *Equatorial* Families of 1-Methylcyclohexanol

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1) Completion of Ref. [17].
2) MP2/6-311++G(d,p) geometries of the observed conformers.
3) Tables of transition frequencies.
4) Description of the structural relaxations taken into account in the flexible model calculations.

1) Completion of Reference [17].

M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.

2) MP2/6-311++G(d,p) geometries of the observed conformers.

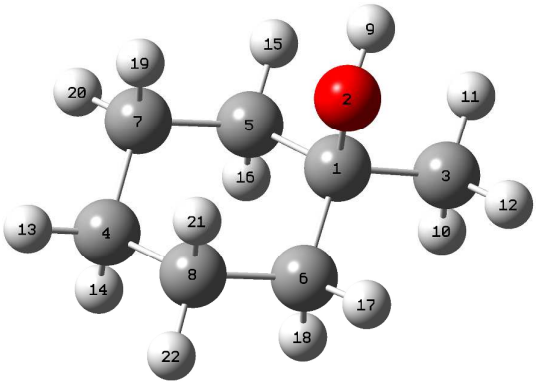
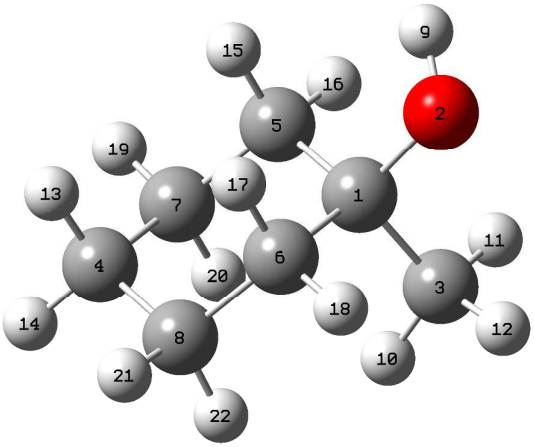
Axial	*Equatorial*
	

Table S1-a: Geometry of **conformer *Ag***.

Bond lengths/Å		Angles/°		Dihedral angle/°	
O2C1	1.4391				
C3C1	1.5252	C3C1O2	109.5		
C4C1	2.9705	C4C1O2	99.8	C4C1O2C3	178.6
C5C1	1.5341	C5C1O2	109.8	C5C1O2C3	-122.0
C6C1	1.5288	C6C1O2	105.1	C6C1O2C3	119.3
C7C5	1.5308	C7C5C1	112.3	C7C5C1O2	-61.3
C8C6	1.5309	C8C6C1	112.2	C8C6C1O2	64.1
H9O2	0.9638	H9O2C1	106.9	H9O2C1C3	59.0
H10C3	1.0950	H10C3C1	110.9	H10C3C1O2	177.7
H11C3	1.0972	H11C3C1	110.5	H11C3C1H10	119.7
H12C3	1.0943	H12C3C1	109.9	H12C3C1H10	-120.6
H13C4	1.0963	H13C4C1	152.2	H13C4C1O2	2.7
H14C4	1.0999	H14C4C1	100.8	H14C4C1O2	-177.2
H15C5	1.0997	H15C5C1	108.9	H15C5C1O2	61.6
H16C5	1.0991	H16C5C1	108.5	H16C5C1O2	177.4
H17C6	1.0966	H17C6C1	108.3	H17C6C1O2	-58.5
H18C6	1.0987	H18C6C1	108.1	H18C6C1O2	-174.9
H19C7	1.0963	H19C7C5	109.3	H19C7C5C1	64.4
H20C7	1.0964	H20C7C5	109.8	H20C7C5C1	-178.1
H21C8	1.0958	H21C8C6	109.1	H21C8C6C1	-64.5
H22C8	1.0964	H22C8C6	109.6	H22C8C6C1	178.1

Table S1-b: Geometry of **conformer *At***.

Bond lengths/Å		Angles/°		Dihedral angle/°	
O2C1	1.4384				
C3C1	1.5204	C3C1O2	104.6		
C4C1	2.9833	C4C1O2	105.5	C4C1O2C3	180.0
C5C1	1.5345	C5C1O2	110.1	C5C1O2C3	-119.2
C6C1	1.5345	C6C1O2	110.1	C6C1O2C3	119.2
C7C5	1.5325	C7C5C1	112.7	C7C5C1O2	-68.1
C8C6	1.5325	C8C6C1	112.7	C8C6C1O2	68.1
H9O2	0.9624	H9O2C1	107.7	H9O2C1C3	180.0
H10C3	1.0944	H10C3C1	110.5	H10C3C1O2	180.0
H11C3	1.0943	H11C3C1	109.9	H11C3C1H10	120.3
H12C3	1.0943	H12C3C1	109.9	H12C3C1H10	-120.3
H13C4	1.0962	H13C4C1	152.5	H13C4C1O2	0.0
H14C4	1.0991	H14C4C1	100.4	H14C4C1O2	180.0
H15C5	1.0964	H15C5C1	108.4	H15C5C1O2	54.8
H16C5	1.0989	H16C5C1	108.4	H16C5C1O2	171.3
H17C6	1.0964	H17C6C1	108.4	H17C6C1O2	-54.8
H18C6	1.0989	H18C6C1	108.4	H18C6C1O2	-171.3
H19C7	1.0998	H19C7C5	110.1	H19C7C5C1	65.7
H20C7	1.0959	H20C7C5	109.7	H20C7C5C1	-178.0
H21C8	1.0998	H21C8C6	110.1	H21C8C6C1	-65.7
H22C8	1.0959	H22C8C6	109.7	H22C8C6C1	178.0

Table S1-c: Geometry of **conformer *Et***.

Bond lengths/Å		Angles/°		Dihedral angle/°	
O2C1	1.4367				
C3C1	1.5234	C3C1O2	104.1		
C4C1	2.9855	C4C1O2	147.4	C4C1O2C3	180.0
C5C1	1.5331	C5C1O2	109.6	C5C1O2C3	-119.8
C6C1	1.5331	C6C1O2	109.6	C6C1O2C3	119.8
C7C5	1.5331	C7C5C1	112.9	C7C5C1O2	-174.3
C8C6	1.5331	C8C6C1	112.9	C8C6C1O2	174.3
H9O2	0.9638	H9O2C1	107.0	H9O2C1C3	180.0
H10C3	1.0923	H10C3C1	111.9	H10C3C1O2	180.0
H11C3	1.0942	H11C3C1	109.5	H11C3C1H10	120.6
H12C3	1.0942	H12C3C1	109.5	H12C3C1H10	-120.6
H13C4	1.0993	H13C4C1	101.0	H13C4C1O2	0.0
H14C4	1.0962	H14C4C1	152.0	H14C4C1O2	180.0
H15C5	1.1011	H15C5C1	107.9	H15C5C1O2	-54.4
H16C5	1.0965	H16C5C1	108.8	H16C5C1O2	61.4
H17C6	1.1011	H17C6C1	107.9	H17C6C1O2	54.4
H18C6	1.0965	H18C6C1	108.8	H18C6C1O2	-61.4
H19C7	1.0962	H19C7C5	109.6	H19C7C5C1	177.5
H20C7	1.0974	H20C7C5	109.9	H20C7C5C1	-65.8
H21C8	1.0962	H21C8C6	109.6	H21C8C6C1	-177.5
H22C8	1.0974	H22C8C6	109.9	H22C8C6C1	65.8

Table S1-d: Geometry of **conformer *Eg***.

Bond lengths/Å		Angles/°		Dihedral angle/°	
O2C1	1.4371				
C3C1	1.5283	C3C1O2	108.8		
C4C1	2.9799	C4C1O2	142.8	C4C1O2C3	175.8
C5C1	1.5331	C5C1O2	109.5	C5C1O2C3	-122.4
C6C1	1.5281	C6C1O2	104.9	C6C1O2C3	119.8
C7C5	1.5328	C7C5C1	112.9	C7C5C1O2	-169.0
C8C6	1.5323	C8C6C1	112.6	C8C6C1O2	171.6
H9O2	0.9641	H9O2C1	107.0	H9O2C1C3	60.2
H10C3	1.0932	H10C3C1	112.3	H10C3C1O2	177.6
H11C3	1.0971	H11C3C1	110.0	H11C3C1H10	120.0
H12C3	1.0942	H12C3C1	109.5	H12C3C1H10	-120.9
H13C4	1.0989	H13C4C1	100.9	H13C4C1O2	4.2
H14C4	1.0963	H14C4C1	152.1	H14C4C1O2	-175.5
H15C5	1.0979	H15C5C1	107.3	H15C5C1O2	-48.5
H16C5	1.0994	H16C5C1	109.2	H16C5C1O2	67.4
H17C6	1.0978	H17C6C1	107.3	H17C6C1O2	51.2
H18C6	1.0965	H18C6C1	108.9	H18C6C1O2	-64.6
H19C7	1.0962	H19C7C5	109.6	H19C7C5C1	177.4
H20C7	1.0975	H20C7C5	110.2	H20C7C5C1	-65.7
H21C8	1.0960	H21C8C6	109.4	H21C8C6C1	-177.5
H22C8	1.0977	H22C8C6	110.2	H22C8C6C1	65.8

3) Tables of transitions frequencies.

Table S2-a: Experimental transition frequencies of 1MCH: **parent species, conformer *Ag***.

$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	0^+		0^-	
	ν/MHz	$\Delta\nu$/kHz	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions				
2(1,1)-1(1,0)	6733.2074	1.4		
3(0,3)-2(0,2)	9639.9369	0.4	9639.4747	-0.6
3(1,3)-2(1,2)	9380.0903	0.1	9379.5581	-0.7
3(1,2)-2(1,1)	10081.3649	0.9	10081.2458	-1.9
3(2,2)-2(2,1)	9748.1327	6.0		
3(2,1)-2(2,0)	9856.3270	-3.2		
4(0,4)-3(0,3)	12741.2906	-0.7	12740.5417	2.0
4(1,4)-3(1,3)	12478.9253	1.2	12478.1808	-0.6
4(1,3)-3(1,2)	13404.4632	0.7	13404.2518	0.4
4(2,3)-3(2,2)	12975.8936	-0.8	12975.4864	-3.1
4(2,2)-3(2,1)	13231.9825	-2.3		
4(3,1)-3(3,0)	13059.3900	-6.8		
4(3,2)-3(3,1)	13047.1648	2.0		
5(0,5)-4(0,4)	15781.3355	-0.4	15780.2660	-0.1
5(1,5)-4(1,4)	15559.2211	1.5	15558.2484	1.4
5(1,4)-4(1,3)	16689.4504	1.9	16689.0839	1.5
5(2,3)-4(2,2)	16649.9524	1.5		
5(2,4)-4(2,3)	16185.4266	-0.7	16184.8813	-0.6
5(3,2)-4(3,1)	16364.2200	-3.7		
5(3,3)-4(3,2)	16322.2491	-0.3		
5(4,1)-4(4,0)	16309.2044	0.5		
5(4,2)-4(4,1)	16308.1940	-1.4		
μ_c-transitions				
2(1,1)-1(0,1)	8333.4877	0.4	8332.9977	-1.2
2(2,0)-1(1,0)	10858.3825	2.1	10856.6570	0.9
2(2,1)-1(1,1)	11065.1585	0.8	11063.5297	-2.5
3(1,2)-2(0,2)	11943.7568	1.5	11943.3986	3.9
3(2,1)-2(1,1)	13981.5057	1.2	13979.7113	-0.4
3(2,2)-2(1,2)	14548.9625	-4.9	14547.3858	-11.3
3(3,0)-2(2,0)	17154.1868	3.5	17151.3841	0.6
3(3,1)-2(2,1)	17179.7969	4.0	17177.0261	-3.3
3(0,3)-2(1,1)	7777.5428	-2.0	7777.3344	6.1
3(3,0)-3(2,2)	7433.7172	-7.0	7431.2596	9.5
3(3,1)-3(2,1)	7295.7943	-0.8	7293.1187	-0.2
4(1,3)-3(0,3)	15708.2840	2.3		
4(2,2)-3(1,2)	17132.1255	0.2	17130.3918	2.7
4(2,3)-3(1,3)	18144.7697	-1.9	18143.3328	5.0
4(3,2)-4(2,2)	7110.9735	0.4	7108.0763	0.2
4(4,1)-4(3,1)	10322.6253	-2.0	10319.0064	-3.9
4(0,4)-3(1,2)	10437.4709	-1.2	10436.6183	-2.0
4(3,1)-4(2,3)	7517.2249	-1.7	7514.9096	4.5
4(4,0)-4(3,2)	10337.0418	-4.3		
5(4,2)-5(3,2)	10266.5993	0.3		
5(5,1)-5(4,1)	13289.4622	-0.8		
5(3,2)-5(2,4)	7696.0246	1.6	7694.0100	-2.1
5(4,1)-5(3,3)	10324.0021	1.5		
5(5,0)-5(4,2)	13290.608	1.1		
6(4,3)-6(3,3)	10149.9467	3.8		
6(5,2)-6(4,2)	13261.8342	0.0		
6(4,2)-6(3,4)	10319.627	-1.7		
6(5,1)-6(4,3)	13267.539	1.3		

Table S2-b: Experimental transition frequencies of 1MCH: **parent species, conformer *At***.

$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions		
3(0,3)-2(0,2)	9575.2478	-1.8
3(1,2)-2(1,1)	10006.0277	-1.5
3(1,3)-2(1,2)	9317.5823	-0.6
3(2,1)-2(2,0)	9781.4832	-1.3
3(2,2)-2(2,1)	9678.3642	-1.2
4(0,4)-3(0,3)	12659.5894	-0.7
4(1,3)-3(1,2)	13305.9712	-3.1
4(1,4)-3(1,3)	12396.8041	-1.9
4(2,2)-3(2,1)	13128.7026	-3.3
4(2,3)-3(2,2)	12883.9280	-0.7
4(3,1)-3(3,0)	12963.2052	-0.5
4(3,2)-3(3,1)	12951.9173	2.7
5(0,5)-4(0,4)	15683.6557	-1.2
5(1,4)-4(1,3)	16569.9267	-8.2
5(1,5)-4(1,4)	15458.1558	1.5
5(2,3)-4(2,2)	16518.1452	-5.4
5(2,4)-4(2,3)	16072.1209	-5.3
5(3,2)-4(3,1)	16241.6678	-0.4
5(3,3)-4(3,2)	16202.8780	-2.5
5(4,1)-4(4,0)	16189.9186	4.1
5(4,2)-4(4,1)	16189.0164	3.8
6(1,6)-5(1,5)	18502.2599	6.5
μ_c-transitions		
2(1,1)-1(0,1)	8299.0116	0.0
2(2,0)-1(1,0)	10868.2935	0.2
2(2,1)-1(1,1)	11072.0750	-0.3
3(1,2)-2(0,2)	11879.1316	7.6
3(2,1)-2(1,1)	13967.4211	7.3
3(2,2)-2(1,2)	14528.3080	1.6
3(3,0)-2(2,0)	17177.4871	0.0
3(3,1)-2(2,1)	17201.9194	-2.3
4(1,3)-3(0,3)	15609.8513	2.6
4(2,2)-3(1,2)	17090.0928	2.3
4(2,3)-3(1,3)	18094.6562	4.0
5(4,1)-5(3,3)	10455.7482	-3.4
5(4,2)-5(3,2)	10402.7563	-2.9
6(4,2)-6(3,4)	10450.1771	0.3
6(4,3)-6(3,3)	10293.3148	0.0

Table S2-c: Experimental transition frequencies of 1MCH: **parent species, conformer *Et***.

$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions		
3(0,3)-2(0,2)	9496.1799	-1.3
3(1,2)-2(1,1)	9885.3397	-0.4
3(1,3)-2(1,2)	9255.8619	-0.8
3(2,1)-2(2,0)	9673.3904	1.2
3(2,2)-2(2,1)	9584.7843	0.5
4(0,4)-3(0,3)	12568.0918	-1.1
4(1,3)-3(1,2)	13150.3699	-4.5
4(1,4)-3(1,3)	12318.1146	-0.2
4(2,2)-3(2,1)	12973.6251	0.3
4(2,3)-3(2,2)	12762.0952	-2.2
4(3,1)-3(3,0)	12829.6958	0.4
4(3,2)-3(3,1)	12820.6265	7.1
5(0,5)-4(0,4)	15585.0230	0.3
5(1,4)-4(1,3)	16385.0558	-5.9
5(1,5)-4(1,4)	15364.6495	1.4
6(0,6)-5(0,5)	18564.8681	1.5
6(1,6)-5(1,5)	18395.7430	3.7
5(2,3)-4(2,2)	16313.4171	-3.3
5(2,4)-4(2,3)	15924.5007	-5.0
5(3,2)-4(3,1)	16068.7244	2.3
5(3,3)-4(3,2)	16037.4702	-0.3
5(4,1)-4(4,0)	16025.3811	-1.6
μ_c-transitions		
2(1,1)-1(0,1)	8169.8206	4.9
2(2,0)-1(1,0)	10700.6237	-1.2
2(2,1)-1(1,1)	10888.3941	5.5
3(1,2)-2(0,2)	11687.8687	4.0
3(2,1)-2(1,1)	13773.8184	-1.0
3(2,2)-2(1,2)	14293.6412	-4.4
3(3,0)-2(2,0)	16899.4232	-1.8
3(3,1)-2(2,1)	16920.4700	-0.9
4(1,3)-3(0,3)	15342.0609	3.0
4(2,2)-3(1,2)	16862.1056	1.5
4(2,3)-3(1,3)	17799.8813	1.0
5(1,4)-4(2,2)	12673.3330	1.0

Table S2-d: Experimental transition frequencies of 1MCH: **parent species, conformer *Eg***.

$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	0^+		0^-	
	ν/MHz	$\Delta\nu$/kHz	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions				
2(1,1)-1(1,0)	6627.0223	1.7		
3(0,3)-2(0,2)	9530.2200	-8.6	9532.4519	1.9
3(1,2)-2(1,1)	9925.0500	-1.4	9927.3933	3.0
3(1,3)-2(1,2)	9289.0800	-10.2	9291.2558	-0.6
3(2,1)-2(2,0)	9713.2472	10.3	9715.5466	1.7
3(2,2)-2(2,1)	9621.7170	-3.7		
4(0,4)-3(0,3)	12610.8416	1.9	12613.7823	0.4
4(1,3)-3(1,2)	13202.2130	0.6	13205.3263	-2.8
4(1,4)-3(1,3)	12361.7143	1.2	12364.5972	-3.3
4(2,2)-3(2,1)	13028.7987	0.6	13031.9020	2.4
4(2,3)-3(2,2)	12810.7454	-1.0	12813.8022	3.0
4(3,1)-3(3,0)	12880.7225	0.2		
4(3,2)-3(3,1)	12871.1233	-0.2		
5(0,5)-4(0,4)	15635.8115	1.6	15639.4672	1.3
5(1,4)-4(1,3)	16447.8196	-1.2	16451.7116	-3.7
5(1,5)-4(1,4)	15418.2341	4.5	15421.8398	0.8
5(2,3)-4(2,2)	16384.0357	-1.9	16387.9465	1.6
5(2,4)-4(2,3)	15984.3669	-1.0	15988.1901	-2.0
5(3,2)-4(3,1)	16133.8098	-1.8	16137.7388	-1.5
5(3,3)-4(3,2)	16100.7820	-3.8	16104.7148	2.5
5(4,1)-4(4,0)	16088.5855	-0.7		
6(1,6)-5(1,5)	18459.0285	8.1	18463.3533	-1.2
μ_c-transitions				
2(1,1)-1(0,1)	8179.4048	-0.6	8181.3420	-1.5
2(2,0)-1(1,0)	10669.9303	0.6	10672.4594	2.7
2(2,1)-1(1,1)	10859.1232	0.1	10861.7011	-0.9
3(0,3)-2(1,1)	7741.9941	2.5		
3(1,2)-2(0,2)	11713.2889	0.5	11716.0748	-0.9
3(2,1)-2(1,1)	13756.1479	1.9	13759.4202	-0.8
3(2,2)-2(1,2)	14278.8751	2.4		
3(3,0)-2(2,0)	16844.4718	-1.3	16848.4830	-0.6
3(3,1)-2(2,1)	16866.1943	2.5	16870.2069	-1.0
4(1,3)-3(0,3)	15385.2738	1.5	15388.9526	-2.2
4(2,2)-3(1,2)	16859.8907	-1.9	16863.9315	1.1
4(2,3)-3(1,3)	17800.5314	2.4	17804.8385	2.6
5(0,5)-4(1,3)	12861.3746	-2.8		
5(4,1)-5(3,3)	10072.8805	-5.4		
5(4,2)-5(3,2)	10027.8144	-6.8		
6(1,5)-5(2,3)	16054.9410	-3.8		
6(4,2)-6(3,4)	10066.2199	1.8		
6(4,3)-6(3,3)	9932.6056	5.5		

Table S2-e: Experimental transition frequencies of 1MCH: **OD species, conformer *Ag***.

*A*g				
$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	0^+		0^-	
	ν/MHz	$\Delta\nu$/kHz	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions				
3(0,3)-2(0,2)	9522.3825	0.9	9522.7337	5.7
3(1,2)-2(1,1)	9927.4870	-1.4	9927.9653	-4.0
3(1,3)-2(1,2)	9277.6809	0.6	9278.0285	1.9
3(2,2)-2(2,1)	9617.8459	-3.6	9618.2584	-4.4
4(0,4)-3(0,3)	12596.5509	1.4	12597.1380	-0.2
4(1,3)-3(1,2)	13203.8746	-0.7	13204.7679	-1.1
4(1,4)-3(1,3)	12345.4688	2.1	12346.2284	2.2
4(2,2)-3(2,1)	13032.0613	0.6	13032.1052	-0.4
4(2,3)-3(2,2)	12804.6085	-3.2	12805.0065	-4.2
5(0,5)-4(0,4)	15613.7981	-1.7	15614.7489	4.9
5(1,4)-4(1,3)	16447.0105	6.5	16448.5473	-2.4
5(1,5)-4(1,4)	15396.5483	-1.2	15398.1624	-1.8
5(2,3)-4(2,2)	16390.7703	-0.6	16389.8181	1.8
5(2,4)-4(2,3)	15975.1478	0.0	15975.5101	-2.8
μ_c-transitions				
2(1,1)-1(0,1)	8182.8553	5.65	8182.8553	-3.5
2(2,0)-1(1,0)	10663.0927	0.61	10662.4903	-3.0
2(2,1)-1(1,1)	10855.8768	7.07	10855.3512	6.3
3(1,2)-2(0,2)	11722.7430	-2.99	11723.0575	7.3
3(3,0)-2(2,0)	16835.2209	-1.35	16834.3177	-1.4
3(3,1)-2(2,1)	16857.9108	-2.86	16856.9744	-2.3

Table S2-f: Experimental transition frequencies of 1MCH: **OD species, conformer *At***.

$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	$F' \leftarrow F''$	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions			
3(0,3)-2(0,2)	4-3	9524.3705	-0.4
3(0,3)-2(0,2)	3-2	9524.3594	-6.4
3(0,3)-2(0,2)	2-1	9524.3848	1.5
3(1,2)-2(1,1)	4-3	9914.7413	4.4
3(1,2)-2(1,1)	3-2	9914.7583	6.4
3(1,2)-2(1,1)	2-1	9914.7413	-2.3
3(1,3)-2(1,2)	4-3	9284.6214	2.0
3(1,3)-2(1,2)	3-2	9284.6317	-0.7
3(1,3)-2(1,2)	2-1	9284.6214	7.0
3(2,1)-2(2,0)	4-3	9703.7058	-0.7
3(2,1)-2(2,0)	3-2	9703.7672	-2.6
3(2,1)-2(2,0)	2-1	9703.6706	-3.2
3(2,2)-2(2,1)	4-3	9614.0364	2.9
3(2,2)-2(2,1)	3-2	9614.0845	-5.1
3(2,2)-2(2,1)	2-1	9614.0040	1.6
4(0,4)-3(0,3)	5-4	12604.7519	-3.2
4(0,4)-3(0,3)	4-3	12604.7519	4.1
4(0,4)-3(0,3)	3-2	12604.7519	-9.3
4(1,3)-3(1,2)	5-4	13189.1578	5.2
4(1,3)-3(1,2)	4-3	13189.1578	0.4
4(1,3)-3(1,2)	3-2	13189.1578	-0.4
4(1,4)-3(1,3)	5-4	12356.2086	1.9
4(1,4)-3(1,3)	4-3	12356.2086	-2.3
4(1,4)-3(1,3)	3-2	12356.2086	1.9
4(2,2)-3(2,1)	5-4	13014.7597	2.2
4(2,2)-3(2,1)	4-3	13014.7900	1.2
4(2,2)-3(2,1)	3-2	13014.7597	9.1
4(2,3)-3(2,2)	5-4	12800.8788	-6.5
4(2,3)-3(2,2)	4-3	12800.9080	0.1
4(2,3)-3(2,2)	3-2	12800.8788	-0.7
5(0,5)-4(0,4)	6-5	15630.0539	4.2
5(0,5)-4(0,4)	5-4	15630.0370	-5.0
5(0,5)-4(0,4)	4-3	15630.0539	0.6
5(1,4)-4(1,3)	6-5	16432.7518	-1.5
5(1,4)-4(1,3)	5-4	16432.7518	-1.6
5(1,4)-4(1,3)	4-3	16432.7518	-5.7
5(1,5)-4(1,4)	6-5	15411.9520	5.3
5(1,5)-4(1,4)	5-4	15411.9520	4.4
5(1,5)-4(1,4)	4-3	15411.9520	4.7
5(2,3)-4(2,2)	6-5	16365.2670	-2.2
5(2,3)-4(2,2)	5-4	16365.2855	-2.8
5(2,3)-4(2,2)	4-3	16365.2670	-0.7
5(2,4)-4(2,3)	6-5	15972.6417	-2.9
5(2,4)-4(2,3)	5-4	15972.6585	3.3
5(2,4)-4(2,3)	4-3	15972.6417	-2.0
μ_c-transitions			
2(2,0)-1(1,0)	3-2	10675.0530	1.1
2(2,0)-1(1,0)	2-1	10674.9892	-9.5
2(2,1)-1(1,1)	3-2	10862.7542	2.5
2(2,1)-1(1,1)	2-1	10862.7542	4.4
3(3,0)-2(2,0)	4-3	16853.1760	-2.1
3(3,0)-2(2,0)	3-2	16853.1520	-6.4
3(3,0)-2(2,0)	2-1	16853.1760	1.6
3(3,1)-2(2,1)	4-3	16874.4691	1.0
3(3,1)-2(2,1)	3-2	16874.4549	2.0
3(3,1)-2(2,1)	2-1	16874.4691	7.2
3(1,2)-2(0,2)	4-3	11702.8001	5.4
3(1,2)-2(0,2)	3-2	11702.8113	-5.2
3(1,2)-2(0,2)	2-1	11702.8001	2.5
4(2,2)-3(1,2)	5-4	16858.8694	5.9
4(2,2)-3(1,2)	4-3	16858.8418	8.2
4(2,2)-3(1,2)	3-2	16858.8694	-8.6

Table S2-g: Experimental transition frequencies of 1MCH: **OD species, conformer *Et***.

μ_a-transitions				μ_c-transitions			
$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	$F' \leftarrow F''$	ν/MHz	$\Delta\nu$/kHz	$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	$F' \leftarrow F''$	ν/MHz	$\Delta\nu$/kHz
3(0,3)-2(0,2)	4-3	9349.7743	1.1	2(1,1)-1(0,1)	3-2	8011.8064	1.8
3(0,3)-2(0,2)	3-2	9349.7556	-4.4	2(2,0)-1(1,0)	2-1	10535.2857	4.6
3(0,3)-2(0,2)	2-1	9349.7743	7.3	2(2,0)-1(1,0)	3-2	10535.3076	2.4
3(1,2)-2(1,1)	4-3	9697.6609	1.9	2(2,1)-1(1,1)	3-2	10707.1805	-1.8
3(1,2)-2(1,1)	3-2	9697.6461	0.1	2(2,1)-1(1,1)	2-1	10707.2611	-0.8
3(1,2)-2(1,1)	2-1	9697.6609	-10.2	3(3,0)-2(2,0)	4-3	16632.8313	2.7
3(1,3)-2(1,2)	4-3	9126.6107	0.7	3(3,0)-2(2,0)	3-2	16632.8313	-5.8
3(1,3)-2(1,2)	3-2	9126.5907	-2.3	3(3,0)-2(2,0)	2-1	16632.8313	-5.2
3(1,3)-2(1,2)	2-1	9126.5907	-8.4				
3(2,1)-2(2,0)	4-3	9498.1670	-0.0				
3(2,1)-2(2,0)	3-2	9498.1357	2.2				
3(2,1)-2(2,0)	2-1	9498.1890	-0.6				
3(2,2)-2(2,1)	4-3	9423.9708	-1.9				
3(2,2)-2(2,1)	3-2	9423.9348	7.1				
3(2,2)-2(2,1)	2-1	9424.0036	5.9				
4(0,4)-3(0,3)	5-4	12386.9405	0.3				
4(0,4)-3(0,3)	4-3	12386.9189	-6.1				
4(0,4)-3(0,3)	3-2	12386.9405	2.5				
4(1,3)-3(1,2)	5-4	12905.3491	-0.2				
4(1,3)-3(1,2)	4-3	12905.3397	-0.9				
4(1,3)-3(1,2)	3-2	12905.3491	-4.6				
4(1,4)-3(1,3)	5-4	12149.3667	0.6				
4(1,4)-3(1,3)	4-3	12149.3568	1.0				
4(1,4)-3(1,3)	3-2	12149.3568	-2.8				
4(2,2)-3(2,1)	5-4	12728.8626	0.3				
4(2,2)-3(2,1)	4-3	12728.8626	7.1				
4(2,2)-3(2,1)	3-2	12728.8626	-3.2				
4(2,3)-3(2,2)	5-4	12550.5885	4.2				
4(2,3)-3(2,2)	4-3	12550.5627	-0.6				
4(2,3)-3(2,2)	3-2	12550.5885	-1.2				
4(3,1)-3(3,0)	5-4	12606.6975	8.9				
4(3,1)-3(3,0)	4-3	12606.6494	-2.0				
4(3,1)-3(3,0)	3-2	12606.6975	-6.3				
4(3,2)-3(3,1)	5-4	12599.7169	7.9				
4(3,2)-3(3,1)	4-3	12599.6685	-2.2				
4(3,2)-3(3,1)	3-2	12599.7169	-7.6				
5(0,5)-4(0,4)	6-5	15374.8491	3.2				
5(0,5)-4(0,4)	5-4	15374.8277	-2.6				
5(0,5)-4(0,4)	4-3	15374.8491	4.4				
5(1,4)-4(1,3)	6-5	16088.1973	-0.6				
5(1,4)-4(1,3)	5-4	16088.1886	-0.8				
5(1,4)-4(1,3)	4-3	16088.1973	-3.2				
5(1,5)-4(1,4)	6-5	15158.5932	2.3				
5(1,5)-4(1,4)	5-4	15158.5851	2.1				
5(1,5)-4(1,4)	4-3	15158.5851	-1.6				
5(2,3)-4(2,2)	6-5	15995.9898	4.2				
5(2,3)-4(2,2)	5-4	15995.9898	2.5				
5(2,3)-4(2,2)	4-3	15995.9898	3.9				
5(2,4)-4(2,3)	6-5	15664.7331	2.3				
5(2,4)-4(2,3)	5-4	15664.7169	-1.0				
5(2,4)-4(2,3)	4-3	15664.7331	0.7				
5(3,2)-4(3,1)	6-5	15784.0603	0.2				
5(3,2)-4(3,1)	5-4	15784.0439	0.5				
5(3,2)-4(3,1)	4-3	15784.0603	-4.5				
5(3,3)-4(3,2)	6-5	15759.9657	0.8				
5(3,3)-4(3,2)	5-4	15759.9480	2.2				
5(3,3)-4(3,2)	4-3	15759.9657	-4.4				

Table S2-h: Experimental transition frequencies of 1MCH: **OD species, conformer *Eg***

$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	0^+		0^-	
	ν/MHz	$\Delta\nu$/kHz	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions				
3(0,3)-2(0,2)	9323.5089	-0.6	9324.0654	-0.7
3(1,2)-2(1,1)	9698.4878	-3.3	9699.1617	-2.8
3(1,3)-2(1,2)	9088.2783	0.8	9088.8270	0.8
3(2,2)-2(2,1)	9406.6607	0.7	9407.3284	2.3
4(0,4)-3(0,3)	12343.0562	-1.1	12343.7625	-2.0
4(1,3)-3(1,2)	12903.2311	0.8	12904.1159	-0.4
4(1,4)-3(1,3)	12096.0153	3.6	12096.7429	3.4
4(2,2)-3(2,1)	12724.7986	-2.6	12725.8264	1.6
4(2,3)-3(2,2)	12525.6934	-1.6	12526.6398	-8.3
4(3,1)-3(3,0)	12588.8616	-7.9	12589.9297	2.7
4(3,2)-3(3,1)	12580.6366	0.3	12581.6876	0.2
5(0,5)-4(0,4)	15309.5120	2.1	15310.3712	3.2
5(1,4)-4(1,3)	16079.7426	2.6	16080.8274	4.5
5(1,5)-4(1,4)	15088.8246	1.1	15089.7371	4.0
5(2,3)-4(2,2)	15998.4100	-5.9	15999.7473	1.2
5(2,4)-4(2,3)	15630.7444	3.8	15632.0945	1.7
5(3,2)-4(3,1)	15765.3889	0.4	15766.7150	-6.2
5(3,3)-4(3,2)	15737.0056	-2.7	15738.3203	-1.1
6(1,6)-5(1,5)	18066.8487	-0.1	18067.9481	-4.6
μ_c-transitions				
2(2,0)-1(1,0)	10593.4172	2.3	10592.9365	1.4
2(2,1)-1(1,1)	10776.1186	-1.4	10775.6718	1.3
3(1,2)-2(0,2)	11493.1437	5.2	11493.5954	-8.1
3(2,1)-2(1,1)	13608.2613	0.2	13608.0416	1.9
3(3,0)-2(2,0)	16737.9192	-1.1	16737.0889	0.1
3(3,1)-2(2,1)	16757.6959	-5.0	16756.8779	-2.4
4(1,3)-3(0,3)	15072.8624	3.1	15073.6598	6.1
4(2,2)-3(1,2)	16634.5726	1.5	16634.7002	0.2
4(2,3)-3(1,3)	17552.9444	4.2	17553.1928	-0.5

4) Description of the structural relaxations taken into account in the flexible model calculations.

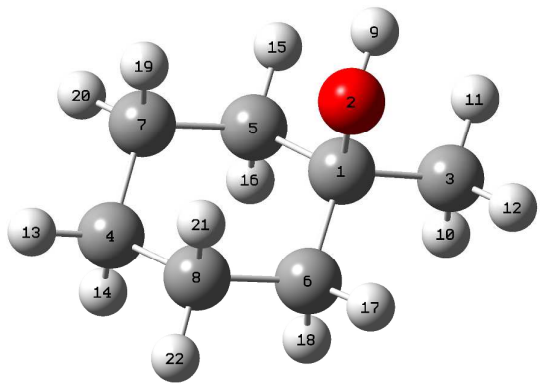
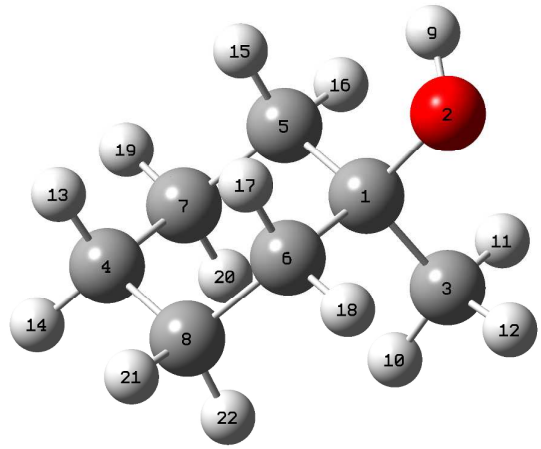
Axial	*Equatorial*
	

Table S3: Structural relaxations of of the other parameters upon internal rotation of the hydroxyl group. τ (≡ H9O2-C1C3) is the parameter describing the internal rotation of the OH group. τ = 0 corresponds to the B_2 barrier between the two gauche forms.

Axial species	*Equatorial* species
H10C3-C1O2/° = 180.0-2.3·sinτ	C4C1O2 = 141.8+2.8·(1.-cosτ)
C4C1O2 = 98.4+3.0·(1.-cosτ)	C4C1-O2C3 = 180.-2.5·sinτ
C5C1O2 = 107.3+2.6·sinτ	C5C1O2 = 107.3+2.6·sinτ
C6C1O2 = 107.3-2.6·sinτ	C6C1O2 = 107.3-2.6·sinτ
C8C6-C1O2 = 61.0+4.0·(1.-cosτ)	C8C6-C1O2 = 169.0+2.6·(1.-cosτ)
C7C5-C1O2 = -61.-4.·(1.-cosτ)	C7C5-C1O2 = -169.0-2.6·(1.-cosτ)
C3C1O2 = 110.1-3.0·(1.-cosτ)	C3C1O2 = 109.6+-2.3·(1.-cosτ)
C4C1 = 2.9673+0.008·(1.-cosτ)	H10C3-C1O2 = 180.+2.3·sinτ
H16C5-C1O2 = 178.1-3.5·(1.-cosτ)	H16C5-C1O2 = 66.8-2.7·(1.-cosτ)
H18C6-C1O2 = -178.1+3.5·(1.-cosτ)	H18C6-C1O2 = -66.8+2.7·(1.-cosτ)
H15C5-C1O2 = 61.4-3.5·(1.-cosτ)	H15C5-C1O2 = -48.5-2.7·(1.-cosτ)
H17C6-C1O2 = -61.4+3.5·(1.-cosτ)	H17C6-C1O2 = 48.5+2.7·(1.-cosτ)