Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A rotational spectroscopic and *ab initio* study of *cis* and *trans* (-)-carveol: Further insights into conformational dynamics in monoterpenes and monoterpenoids

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Electronic Supplementary Information

Contents:

Conformations of Cyclohexene

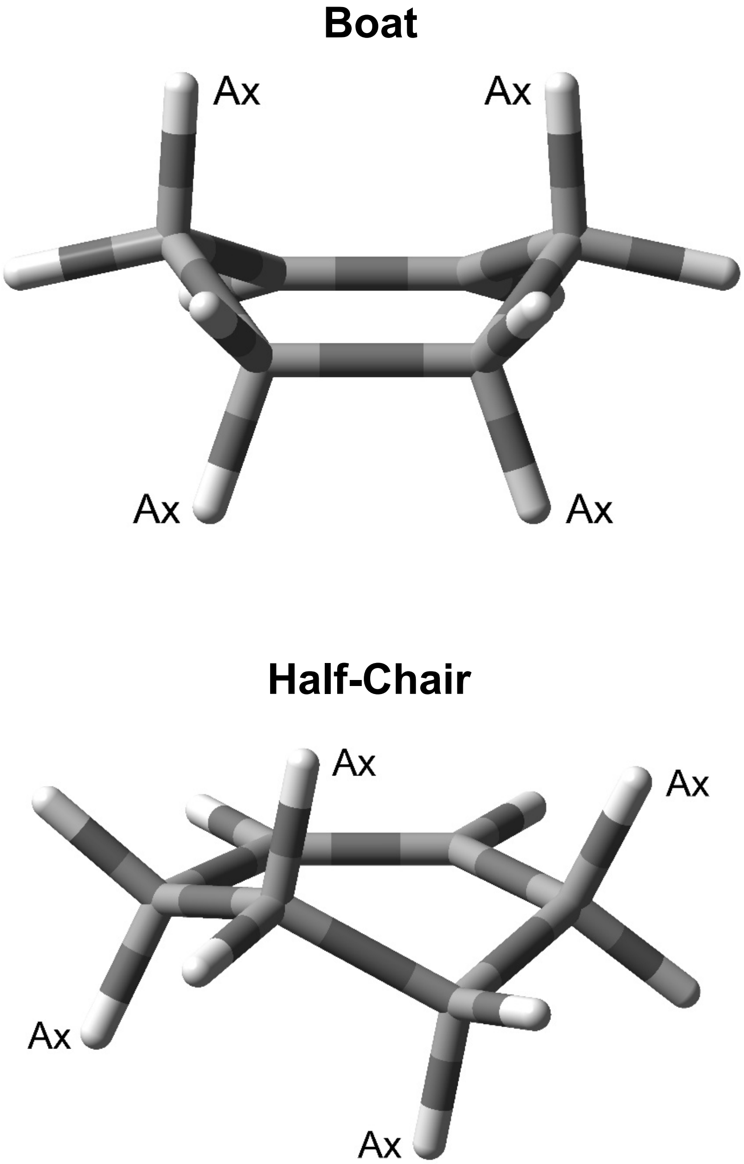
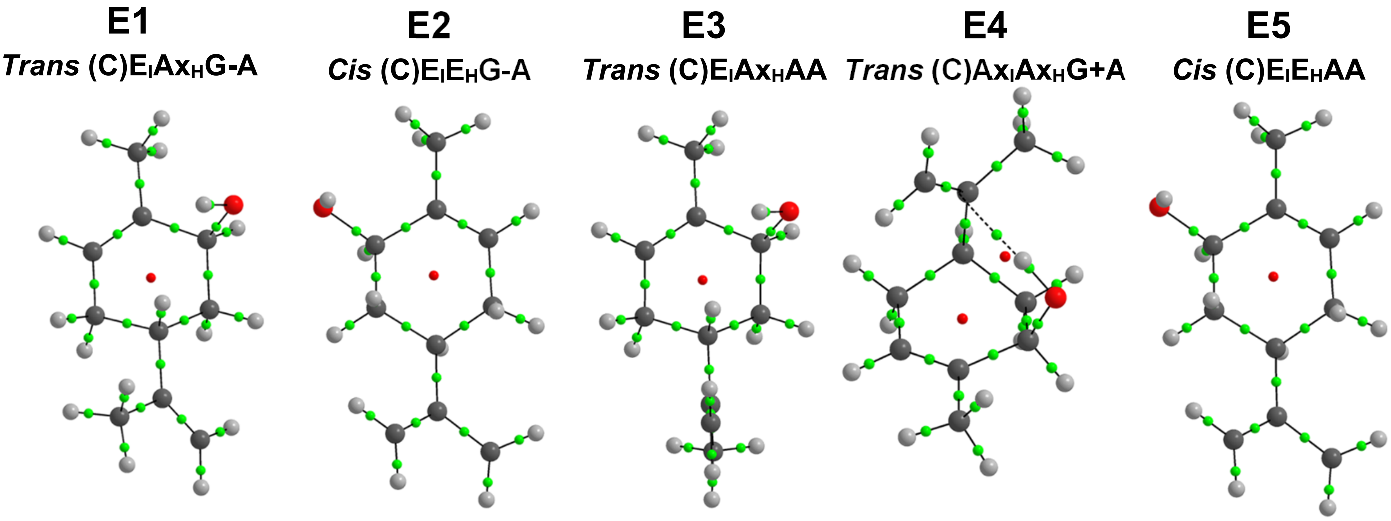


Figure S1. Boat and half-chair conformations of cyclohexene. Hydrogens in the axial position are labelled Ax.

Quantum theory of atoms-in-molecules (QTAIM) results



E1 ***Trans*** **(C)E$_{\mathrm{I}}$Ax$_{\mathrm{H}}$G-A**

E2 ***Cis*** (C)E$_{\mathrm{I}}$E$_{\mathrm{H}}$G-A

E3 ***Trans*** **(C)E$_{\mathrm{I}}$Ax$_{\mathrm{H}}$AA**

E4 ***Trans*** (C)Ax$_{\mathrm{I}}$**Ax$_{\mathrm{H}}$G+A**

E5 ***Cis*** **(C)E$_{\mathrm{I}}$E$_{\mathrm{H}}$AA**

Figure S2. Graphical representations of QTAIM results of the five experimentally assigned conformers.

Theoretical Conformers

Table S1. Theoretical results for *trans* (-)-carveol conformers obtained from the 2D PES scan and CREST searches

(V)W$_I$X$_H$YZ[a]	**ΔE$_0$ / kJ mol^{-1} df-MP2**	**ΔE$_0$ / kJ mol^{-1} B3LYP-D3(BJ)**	**A / MHz**[d]	**B / MHz**[d]	**C / MHz**[d]	**μ$_a$ / D**[d]	**μ$_b$ / D**[d]	**μ$_c$ / D**[d]
(C)E$_I$Ax$_H$AA[b]	**0.0**	**0.0**	**2134.81**	**663.21**	**597.58**	**0.5**	**1.6**	**0.1**
(C)E$_I$Ax$_H$G-A[c]	**0.8**	**1.0**	**2145.20**	**665.47**	**584.85**	**-0.5**	**-1.7**	**0.0**
(C)E$_I$Ax$_H$G+A	1.0	1.3	2122.44	697.78	570.25	0.3	1.1	0.4
(C)E$_I$Ax$_H$AG+	1.6	2.9	2136.89	666.86	598.25	0.3	0.1	1.6
(C)E$_I$Ax$_H$G-G+	1.9	3.3	2143.46	668.36	587.64	0.2	0.4	0.7
(C)E$_I$Ax$_H$AG-	2.8	3.9	2129.35	668.19	600.10	1.3	1.2	0.7
(C)E$_I$Ax$_H$G+G+[c]	3.2	4.3	2120.71	701.17	571.90	-0.2	0.7	1.1
(C)E$_I$Ax$_H$G-G-	3.2	4.5	2137.99	669.85	588.75	1.3	1.2	0.3
(C)E$_I$Ax$_H$G+G-	3.7	4.6	2116.63	703.47	572.92	1.4	0.6	0.2
(C)Ax$_I$E$_H$G+A	2.9	6.1	1627.21	843.77	725.21	0.6	0.7	1.3
(C)Ax$_I$E$_H$G+G+	4.1	8.1	1657.93	834.27	717.12	1.5	0.8	0.1
(C)Ax$_I$E$_H$G+G-	4.6	8.2	1638.70	841.88	720.61	0.2	0.5	0.8
(C)Ax$_I$E$_H$AA	10.5	12.1	1728.38	798.12	721.15	0.3	1.0	1.2
(C)Ax$_I$E$_H$G-A	10.7	13.4	1668.29	819.18	721.91	1.0	1.4	1.2
(C)Ax$_I$E$_H$AG+	10.8	13.7	1741.26	797.49	717.59	0.9	0.3	0.3
(C)Ax$_I$E$_H$AG-	12.5	14.7	1735.08	798.15	717.65	0.3	1.2	0.9
(C)Ax$_I$E$_H$G-G-	12.9	15.9	1678.18	817.35	714.82	0.4	1.0	0.9
(B)Ax$_I$Ax$_H$AG-	21.8	24.0	1901.97	753.84	659.03	1.3	1.4	0.1
(B)E$_I$E$_H$AG+	22.9	24.9	2120.28	667.19	583.32	1.0	0.5	0.7
(B)E$_I$E$_H$AA	24.3	25.0	2099.87	667.65	582.76	0.3	0.7	0.7
(B)E$_I$E$_H$AG-	24.2	25.6	2105.32	665.24	582.16	0.7	0.8	1.3
(B)E$_I$E$_H$G+A	26.3	26.9	2076.87	668.65	558.24	0.5	0.3	1.4
(B)Ax$_I$Ax$_H$G-G-	27.0	30.2	1863.48	756.31	684.64	0.6	1.0	0.4

[a] Nomenclature describing the conformation of each conformer. The letter in parentheses describes whether the conformer is in the half-chair (C) or boat (B) conformation. The following *WXYZ* letters describe the axial or equatorial position of the isopropenyl group, the axial or equatorial position of the hydroxyl group, the conformation of the isopropenyl group (A or G- or G+), and the conformation of the hydroxyl group(A or G- or G+), respectively. A, G-, and G+ are antiperiplanar, gauche -, and gauche + conformations, respectively. [b] Conformers highlighted in bold were experimentally identified. [c] Conformers identified from the 2D PES scan. [d] The rotational constants and dipole moment components reported were calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Table S2. Theoretical results for *cis* (-)-carveol conformers obtained from the 2D PES scan and CREST searches

(V)W$_I$X$_H$YZ[a]	**ΔE$_0$ / kJ mol^{-1} df-MP2**	**ΔE$_0$ / kJ mol^{-1} B3LYP-D3(BJ)**	**A / MHz**	**A / MHz[d]**	**B / MHz[d]**	**C / MHz[d]**	**μ$_a$ / D[d]**	**μ$_b$ / D[d]**
(C)Ax$_I$Ax$_H$G+A[b]	**0.0**	**0.0**	**1689.73**	**902.97**	**802.91**	**0.7**	**1.5**	**0.6**
(C)E$_I$E$_H$AA[b]	**6.8**	**4.3**	**2130.68**	**647.17**	**568.57**	**0.7**	**0.9**	**1.1**
(C)E$_I$E$_H$G-A[b]	**7.5**	**5.1**	**2161.15**	**662.04**	**541.75**	**0.8**	**1.3**	**0.6**
(C)E$_I$E$_H$AG-	7.1	5.8	2148.98	646.6	568.35	0.9	0.5	0.5
(C)E$_I$E$_H$G+A[c]	8.7	6.0	2103.62	661.45	552.70	0.6	-0.9	-0.2
(C)E$_I$E$_H$AG+	8.4	6.4	2134.10	650.22	569.49	0.8	0.9	0.6
(C)E$_I$E$_H$G-G-	8.0	6.7	2182.58	660.73	541.74	1.1	0.0	1.1
(C)E$_I$E$_H$G-G+	9.5	7.6	2165.73	664.22	542.67	0.5	1.4	1.2
(C)E$_I$E$_H$G+G-[c]	10.0	8.4	2123.10	661.23	551.51	1.0	0.8	1.0
(C)E$_I$E$_H$G+G+	11.1	9.0	2108.52	665.09	551.98	0.7	0.4	1.5
(C)Ax$_I$Ax$_H$G-A	12.7	12.5	1534.19	948.05	804.45	1.1	1.8	0.5
(C)Ax$_I$Ax$_H$G+G-	15.3	15.6	1609.81	923.35	805.76	0.1	0.6	1.8
(C)Ax$_I$Ax$_H$AG-	17.0	15.8	1716.23	863.42	791.20	0.4	0.1	1.5
(C)Ax$_I$Ax$_H$AG+	20.6	18.3	1719.58	855.58	781.92	2.0	0.8	0.2
(B)E$_I$Ax$_H$AG+	25.2	24.3	2165.58	700.65	641.62	1.7	0.6	0.2
(B)Ax$_I$E$_H$AG-	24.8	25.0	1931.74	721.83	641.64	0.4	0.6	0.7
(B)Ax$_I$E$_H$AA	26.9	25.8	1916.68	721.32	639.50	0.6	0.9	0.7
(B)Ax$_I$E$_H$AG+	26.7	26.3	1912.30	726.96	645.28	1.0	1.1	0.9
(B)Ax$_I$E$_H$G+A	30.1	29.5	1813.47	749.67	629.05	0.9	0.2	0.4

[a] Nomenclature describing the conformation of each conformer (see footnote, Table S13). [b] Conformers in bold were experimentally identified. [c] Conformers identified from the 2D PES scan. [d] The rotational constants and dipole moment components reported were calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Experimental Assignment to Theoretical Results Comparison

Table S3. *cis* (-)-carveol experiment vs. theory comparison. [a]RMS difference between experiment and theory (B3LYP-D3(BJ)/def2-TZVP level).

	E2	**(C)E_IE_HG-A**	**E4**	**(C)Ax_IAx_HG+A**
A / MHz	2150.22733(47)	2161.15	1664.60349(57)	1689.73
B	660.47853(13)	662.04	907.27707(25)	902.97
C	541.08651(15)	541.75	805.36654(24)	802.91
|μ|	$\mu_b > \mu_a > \mu_c$	μ_a=0.8, μ_b=1.3, μ_c=0.6	$\mu_b > \mu_a > \mu_c$	μ_a=0.7, μ_b=1.5, μ_c=0.6
[a]σ / MHz	-	11.1	-	25.6
	E5	**(C)E_IE_H AA**		
A / MHz	2120.28916(69)	2130.68		
B	645.66680(28)	647.17		
C	567.21505(28)	568.57		
|μ|	$\mu_c > \mu_a \simeq \mu_b$	μ_a=0.7, μ_b=0.9, μ_c=1.1		
[a]σ / MHz	-	10.6		

Table S4. *trans* (-)-carveol experiment vs. theory comparison. [a]RMS difference between experiment and theory (B3LYP-D3(BJ)/def2-TZVP level).

	E1	**(C)E_IAx_HG-A**	**E3**	**(C)E_IAx_HAA**
A / MHz	2130.99910(81)	2145.20	2122.02820(73)	2143.81
B	665.16017(26)	665.47	662.63495(17)	663.21
C	583.88177(25)	584.85	596.35973(18)	597.58
|μ|	$\mu_b > \mu_a$	μ_a=0.5, μ_b=1.7, μ_c=0.0	$\mu_b > \mu_a >> \mu_c$	μ_a=0.5, μ_b=1.6, μ_c=0.1
[a]σ / MHz	-	14.2	-	21.8

Rotational Transition Frequencies for Experimental Conformers

Table S5. Measured frequencies of assigned rotational transitions of E1 (*trans*-(C)E_IAx_HG-A). $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
2	1	1	2	0	2	1631.675	-0.006
3	1	2	3	0	3	1764.614	0.002
4	1	3	4	0	4	1952.887	0.000
5	1	4	5	0	5	2204.981	0.001
3	0	3	2	1	2	2346.164	0.000
2	1	2	1	1	1	2416.811	0.006
2	0	2	1	0	1	2494.804	0.008
6	1	5	6	0	6	2529.681	0.001
2	1	1	1	1	0	2579.352	-0.009
1	1	1	0	0	0	2714.878	-0.003
7	1	6	7	0	7	2934.370	0.000
8	1	7	8	0	8	3423.118	0.001
3	1	3	2	1	2	3623.192	-0.001
4	0	4	3	1	3	3686.583	-0.002
3	0	3	2	0	2	3734.010	-0.002
8	2	6	8	1	7	3774.661	-0.001
9	2	7	9	1	8	3783.763	0.000
6	1	5	5	2	4	3785.213	0.001
7	2	5	7	1	6	3823.863	0.000
10	2	8	10	1	9	3863.485	-0.003
3	1	2	2	1	1	3866.940	-0.003
2	1	2	1	0	1	3882.640	-0.005
6	2	4	6	1	5	3916.833	-0.001
9	1	8	9	0	9	3995.163	0.003
11	2	9	11	1	10	4024.091	0.002
5	2	3	5	1	4	4037.288	0.000
4	2	2	4	1	3	4168.361	0.004
3	2	1	3	1	2	4294.100	0.006
4	1	4	3	1	3	4827.292	0.016
4	2	3	4	1	4	4931.601	-0.004
4	0	4	3	0	3	4963.610	-0.003
4	2	3	3	2	2	4993.604	0.001
3	1	3	2	0	2	5011.037	-0.004
4	2	2	3	2	1	5026.150	-0.001
5	0	5	4	1	4	5040.334	-0.003
5	2	4	5	1	5	5141.022	-0.004
4	1	3	3	1	2	5151.885	-0.003
7	1	6	6	2	5	5285.000	-0.002

6	2	5	6	1	6	5394.134	-0.002
7	2	6	7	1	7	5691.275	0.004
5	1	5	4	1	4	6028.473	-0.001
8	2	7	8	1	8	6032.377	0.005
4	1	4	3	0	3	6104.303	-0.002
5	0	5	4	0	4	6181.028	-0.001
5	2	4	4	2	3	6237.902	0.008
5	2	3	4	2	2	6302.048	-0.005
6	0	6	5	1	5	6396.557	-0.001
9	2	8	9	1	9	6416.839	-0.006
5	1	4	4	1	3	6433.123	0.002
5	1	5	4	0	4	7169.170	0.004

Table S6. Measured frequencies of assigned rotational transitions of E2 (*cis*-(C)E_IE_HG-A). $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
3	1	2	3	0	3	1937.482	-0.007
3	0	3	2	1	2	2200.031	0.002
4	1	3	4	0	4	2229.290	-0.001
2	1	2	1	1	1	2283.738	-0.001
2	0	2	1	0	1	2396.243	0.004
2	1	1	1	1	0	2522.515	-0.006
5	1	4	5	0	5	2626.324	0.002
1	1	1	0	0	0	2691.315	0.000
4	0	4	3	1	2	2801.182	-0.012
1	1	0	0	0	0	2810.703	-0.003
6	1	5	6	0	6	3141.613	0.003
3	1	3	2	1	2	3421.421	0.002
6	2	5	6	1	5	3457.246	-0.002
4	0	4	3	1	3	3517.296	0.002
3	0	3	2	0	2	3577.281	0.002
5	0	5	4	1	3	3647.137	0.002
6	1	5	5	2	4	3721.199	-0.004
2	1	2	1	0	1	3773.489	0.001
3	1	2	2	1	1	3779.345	0.001
7	1	6	7	0	7	3781.031	0.005
5	2	4	5	1	4	3784.068	0.000
7	2	5	7	1	6	3871.972	-0.002
6	2	4	6	1	5	3909.605	-0.001
8	2	6	8	1	7	3928.528	-0.002
5	2	3	5	1	4	4017.288	0.001

4	2	3	4	1	3	4065.000	-0.010
9	2	7	9	1	8	4098.867	-0.002
2	1	1	1	0	1	4131.663	0.000
4	2	2	4	1	3	4166.894	0.005
13	3	11	14	1	14	4263.195	0.000
3	2	2	3	1	2	4294.591	-0.008
3	2	1	3	1	2	4328.925	0.018
10	2	8	10	1	9	4398.601	0.002
8	1	7	8	0	8	4539.926	0.004
4	1	4	3	1	3	4554.412	0.001
4	0	4	3	0	3	4738.686	0.003
3	1	3	2	0	2	4798.671	0.003
4	2	3	3	2	2	4800.901	0.006
4	3	2	3	3	1	4819.325	-0.002
5	0	5	4	1	4	4839.305	-0.003
4	2	2	3	2	1	4868.463	-0.003
3	2	2	3	1	3	5010.693	-0.005
4	1	3	3	1	2	5030.486	0.001
3	2	1	3	1	3	5045.021	0.014
4	2	3	4	1	4	5257.164	-0.019
7	1	6	6	2	5	5265.129	-0.012
4	2	2	4	1	4	5359.070	0.009
9	1	8	9	0	9	5402.710	0.003
3	1	2	2	0	2	5514.771	0.003
5	2	4	5	1	5	5567.999	0.000
5	1	5	4	1	4	5681.699	0.001
4	1	4	3	0	3	5775.804	0.004
5	0	5	4	0	4	5876.425	-0.001
6	2	5	6	1	6	5943.780	0.002
5	2	4	4	2	3	5992.520	0.005
5	3	3	4	3	2	6029.002	-0.002
5	3	2	4	3	1	6034.201	-0.001
5	2	3	4	2	2	6123.855	0.000
6	0	6	5	1	5	6147.589	-0.003
5	1	4	4	1	3	6273.458	0.002
7	2	6	7	1	7	6384.278	-0.009
5	1	5	4	0	4	6718.821	0.005
6	1	6	5	1	5	6802.672	0.001
6	0	6	5	0	5	6989.986	0.003
6	2	4	5	2	3	7397.591	0.000
3	2	2	2	1	1	8073.927	-0.015
7	0	7	6	0	6	8082.981	0.009

Table S7. Measured frequencies of assigned rotational transitions of E3 (*trans*-(C)$\mathrm{E_IAx_HAA}$). $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
3	1	2	3	0	3	1700.973	0.002
4	1	3	4	0	4	1850.887	0.000
5	1	4	5	0	5	2049.833	-0.005
6	1	5	6	0	6	2304.358	-0.003
3	0	3	2	1	2	2372.853	0.002
2	1	2	1	1	1	2451.700	-0.013
2	0	2	1	0	1	2515.790	0.007
2	1	1	1	1	0	2584.262	-0.003
7	1	6	7	0	7	2620.680	0.002
1	1	1	0	0	0	2718.384	-0.003
8	1	7	8	0	8	3003.552	0.000
7	1	7	6	2	4	3215.682	0.005
9	1	8	9	0	9	3455.148	0.003
3	1	3	2	1	2	3676.212	0.001
4	0	4	3	1	3	3710.697	0.001
9	2	7	9	1	8	3739.774	-0.002
6	1	5	5	2	4	3743.832	0.004
10	2	8	10	1	9	3752.670	-0.001
3	0	3	2	0	2	3768.172	-0.001
8	2	6	8	1	7	3775.767	-0.002
3	2	2	2	2	1	3776.976	-0.004
9	6	4	10	5	5	3795.814	0.000
11	2	9	11	1	10	3823.440	-0.001
7	2	5	7	1	6	3850.160	-0.002
3	1	2	2	1	1	3874.992	-0.001
2	1	2	1	0	1	3911.101	-0.003
6	2	4	6	1	5	3951.169	-0.002
12	2	10	12	1	11	3959.686	0.000
10	1	9	10	0	10	3974.222	0.000
5	2	3	5	1	4	4066.327	0.000
13	2	11	13	1	12	4167.774	0.004
4	2	2	4	1	3	4183.382	0.007
3	2	1	3	1	2	4291.183	0.008
2	2	0	2	1	1	4380.366	-0.012
14	2	12	14	1	13	4452.758	-0.001
11	1	10	11	0	11	4555.928	-0.001
3	2	2	3	1	3	4677.773	0.004
12	3	10	11	4	7	4733.513	-0.001
4	2	3	4	1	4	4812.879	-0.002
4	1	4	3	1	3	4899.146	0.002
5	2	4	5	1	5	4982.843	-0.005

4	0	4	3	0	3	5014.058	0.001
4	2	3	3	2	2	5034.255	-0.001
4	2	2	3	2	1	5056.174	0.000
5	2	3	5	1	5	5059.196	0.012
5	0	5	4	1	4	5063.114	0.002
3	1	3	2	0	2	5071.531	-0.002
4	1	3	3	1	2	5163.972	-0.001
6	2	5	6	1	6	5188.147	-0.005
7	1	6	6	2	5	5212.787	-0.005
7	2	6	7	1	7	5429.159	-0.004
3	1	2	2	0	2	5469.161	0.017
8	2	7	8	1	8	5706.025	-0.006
9	2	8	9	1	9	6018.614	0.001
5	1	5	4	1	4	6120.096	0.003
4	1	4	3	0	3	6202.504	-0.001
7	2	6	7	0	7	6203.713	0.018
5	0	5	4	0	4	6251.558	-0.001
5	2	4	4	2	3	6290.065	0.005
5	4	1	4	4	0	6299.855	-0.009
5	2	3	4	2	2	6333.462	0.000
6	0	6	5	1	5	6422.315	0.001
5	1	4	4	1	3	6450.508	-0.002
2	2	0	1	1	1	7030.909	-0.010
5	1	5	4	0	4	7308.541	0.000
7	0	7	6	1	6	7780.267	0.001

Table S8. Measured frequencies of assigned rotational transitions of E4 (*cis*-(C)Ax$_{\mathrm{I}}$Ax$_{\mathrm{H}}$G+A). Δν^{a} is the difference between observed and calculated frequencies.

J'	K$_{a}$'	K$_{c}$'	J''	K$_{a}$''	K$_{c}$''	ν$_{\mathrm{Exp}}$/ MHz	Δν^{a}/ MHz
5	2	3	5	1	4	2016.688	-0.009
6	2	4	6	1	5	2030.329	0.012
4	2	2	4	1	3	2073.946	-0.002
7	2	5	7	1	6	2137.889	-0.005
3	2	1	3	1	2	2172.911	-0.005
2	2	0	2	1	1	2281.592	0.011
6	1	5	6	0	6	2289.559	0.012
8	2	6	8	1	7	2356.802	0.000
1	1	1	0	0	0	2469.961	-0.008
1	1	0	0	0	0	2571.881	0.001
2	2	1	2	1	2	2577.707	0.002
2	0	2	1	1	1	2658.354	0.004
3	2	2	3	1	3	2736.311	-0.010
7	1	6	7	0	7	2864.999	0.003

4	2	3	4	1	4	2950.278	-0.005
10	3	7	10	2	8	3060.033	-0.002
11	3	8	11	2	9	3084.392	0.007
9	3	6	9	2	7	3139.571	0.004
10	2	8	10	1	9	3164.716	-0.008
5	2	4	5	1	5	3220.237	-0.001
8	3	5	8	2	6	3292.438	0.005
2	1	2	1	1	1	3323.375	0.000
2	0	2	1	0	1	3415.672	-0.003
7	3	4	7	2	5	3481.753	0.012
8	1	7	8	0	8	3507.554	0.007
2	1	1	1	1	0	3527.194	-0.001
6	2	5	6	1	6	3545.503	-0.001
6	3	3	6	2	4	3670.095	0.009
5	3	2	5	2	3	3827.359	-0.001
4	1	4	3	2	1	3845.298	-0.002
14	12	2	13	13	1	3872.386	0.000
7	2	6	7	1	7	3923.606	-0.005
4	3	1	4	2	2	3937.414	0.003
3	3	0	3	2	1	4000.217	0.013
3	3	1	3	2	2	4047.127	0.007
2	1	2	1	0	1	4080.692	-0.009
3	0	3	2	1	1	4129.293	0.008
9	1	8	9	0	9	4186.411	-0.002
6	3	4	6	2	5	4202.431	-0.001
7	3	5	7	2	6	4324.653	-0.007
8	2	7	8	1	8	4350.167	-0.014
2	1	1	1	0	1	4386.431	-0.002
3	0	3	2	1	2	4435.019	0.003
8	3	6	8	2	7	4494.709	-0.004
6	1	5	5	3	2	4644.371	0.009
9	3	7	9	2	8	4717.608	-0.002
4	1	3	3	2	1	4860.441	0.006
4	1	3	3	2	2	4907.940	0.018
3	1	3	2	1	2	4979.308	-0.002
10	3	8	10	2	9	4996.010	-0.005
3	0	3	2	0	2	5100.036	-0.005
3	2	2	2	2	1	5137.932	0.005
3	2	1	2	2	0	5175.806	0.000
5	1	5	4	2	2	5182.793	-0.013
3	1	2	2	1	1	5284.469	-0.002
4	0	4	3	1	2	5604.021	0.001
3	1	3	2	0	2	5644.327	-0.009
17	3	14	17	3	15	5699.508	0.002
2	2	1	1	1	0	5799.159	-0.010

2	2	0	1	1	0	5808.782	0.005
2	2	1	1	1	1	5901.094	0.015
2	2	0	1	1	1	5910.694	0.007
10	1	9	9	4	6	6045.148	-0.002
4	0	4	3	1	3	6214.916	0.004
3	1	2	2	0	2	6255.231	0.003
4	1	4	3	1	3	6629.104	-0.003
4	0	4	3	0	3	6759.207	0.001
4	2	3	3	2	2	6843.070	0.001
4	1	3	3	1	2	7033.336	-0.015
4	1	4	3	0	3	7173.398	-0.004
3	2	2	2	1	1	7409.886	-0.014
5	0	5	4	1	4	7978.150	0.003
3	2	1	2	1	2	7763.123	0.004

Table S9. Measured frequencies of assigned rotational transitions of E5 (*cis*-(C)E_IE_HAA). $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
2	1	1	2	0	2	1633.941	-0.011
5	1	4	5	0	5	2181.871	0.006
3	0	3	2	1	2	2227.987	0.005
2	1	2	1	1	1	2348.208	-0.002
2	0	2	1	0	1	2423.333	-0.005
6	1	5	6	0	6	2491.230	0.000
2	1	1	1	1	0	2504.512	-0.004
1	1	1	0	0	0	2687.796	-0.007
1	1	0	0	0	0	2765.953	-0.004
7	1	6	7	0	7	2876.654	0.001
9	2	8	9	1	8	2912.952	-0.003
4	0	4	3	1	2	3061.422	-0.002
8	2	7	8	1	7	3214.211	0.002
8	1	7	8	0	8	3342.539	0.003
6	1	5	5	2	3	3414.923	-0.002
7	2	6	7	1	6	3493.714	-0.008
6	1	5	5	2	4	3519.172	0.013
3	1	3	2	1	2	3520.459	0.000
4	0	4	3	1	3	3530.271	0.002
3	0	3	2	0	2	3627.473	-0.002
6	2	5	6	1	5	3746.311	-0.005
3	1	2	2	1	1	3754.842	-0.002
9	2	7	9	1	8	3795.267	0.006
8	2	6	8	1	7	3798.423	0.000
2	1	2	1	0	1	3822.826	-0.006

7	2	5	7	1	6	3855.238	-0.002
10	2	8	10	1	9	3857.756	0.005
9	1	8	9	0	9	3889.008	-0.010
6	2	4	6	1	5	3951.698	-0.004
5	2	4	5	1	4	3968.074	-0.010
11	2	9	11	1	10	3995.925	-0.007
2	1	1	1	0	1	4057.286	-0.004
5	0	5	4	1	3	4065.397	-0.003
5	2	3	5	1	4	4072.328	0.010
4	2	3	4	1	3	4156.162	-0.010
4	2	2	4	1	3	4201.243	-0.001
3	2	1	3	1	2	4323.661	0.007
2	2	1	2	1	1	4423.871	0.008
2	2	1	2	1	2	4658.326	0.004
4	1	4	3	1	3	4690.578	-0.003
7	1	6	6	2	4	4769.672	0.001
3	2	1	3	1	3	4792.507	0.007
4	0	4	3	0	3	4822.745	-0.001
5	0	5	4	1	4	4846.417	-0.002
4	2	3	3	2	2	4850.372	0.006
4	3	2	3	3	1	4858.549	-0.004
4	3	1	3	3	0	4859.008	0.016
4	2	2	3	2	1	4880.338	-0.007
3	1	3	2	0	2	4919.947	-0.004
4	2	3	4	1	4	4937.185	-0.007
7	1	6	6	2	5	4975.046	-0.012
4	2	2	4	1	4	4982.265	0.001
4	1	3	3	1	2	5002.753	-0.002
5	2	4	5	1	5	5138.328	-0.008
5	2	3	5	1	5	5242.566	-0.003
6	2	5	6	1	6	5381.407	-0.005
3	1	2	2	0	2	5388.793	-0.004
6	2	4	6	1	6	5586.798	-0.001
7	2	6	7	1	7	5666.768	-0.010
7	0	7	6	1	5	5844.710	-0.011
5	1	5	4	1	4	5858.031	-0.002
4	1	4	3	0	3	5983.052	-0.005
5	0	5	4	0	4	6006.728	-0.003
5	2	4	4	2	3	6059.179	0.003
5	4	2	4	4	1	6072.620	0.012
5	2	3	4	2	2	6118.335	-0.003
6	0	6	5	1	5	6166.264	0.000
5	1	4	4	1	3	6247.261	-0.004
9	2	8	9	1	9	6363.936	0.009
4	1	3	3	0	3	6764.074	-0.003

2	2	1	1	1	0	6928.396	0.017
2	2	1	1	1	1	7006.545	0.013
5	1	5	4	0	4	7018.342	-0.002
6	1	6	5	1	5	7022.397	-0.001
6	0	6	5	0	5	7177.882	0.004
6	2	5	5	2	4	7265.477	0.002
7	0	7	6	1	6	7479.826	0.009
6	1	5	5	1	4	7487.235	-0.008
6	1	6	5	0	5	8034.003	-0.008
3	2	1	2	1	1	8078.508	0.009
7	1	7	6	0	6	9039.560	0.013

Theoretical Geometries for the Experimental Conformers

Table S10. Atom positions for conformer E1 (*trans*-(C)E$_{I}$Ax$_{H}$G-A), optimized at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Atom	X	Y	Z
O	1.69981	1.57166	-1.11818
C	1.43380	0.97094	0.16237
C	1.96711	-0.44068	0.20308
C	1.13711	-1.48320	0.22806
C	-0.36026	-1.39097	0.22097
C	-0.87342	0.00211	-0.18452
C	-0.04310	1.05835	0.53753
C	-2.93847	0.98917	0.83378
C	-2.36993	0.11794	0.00439
C	-3.20307	-0.83457	-0.80980
C	3.46008	-0.58386	0.19216
H	1.38580	0.96490	-1.79819
H	2.00817	1.58748	0.85869
H	1.55579	-2.48512	0.26274
H	-0.74794	-1.63668	1.21824
H	-0.76157	-2.15498	-0.44881
H	-0.68971	0.10883	-1.26335
H	-0.39572	2.06295	0.30189
H	-0.13895	0.91886	1.61890
H	-2.36499	1.68167	1.43331
H	-4.01534	1.03676	0.93823
H	-3.04071	-1.87083	-0.50273
H	-2.94049	-0.77523	-1.87033
H	-4.26571	-0.61784	-0.70716
H	3.76340	-1.62966	0.14115
H	3.89791	-0.14339	1.09335
H	3.89254	-0.05245	-0.65863

Table S11. Atom positions for conformer E2 (*cis*-(C)E$_{I}$E$_{H}$G-A), optimized at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Atom	X	Y	Z
O	-2.30029	1.81432	0.01854
C	-1.40879	0.77951	0.44972
C	-1.87757	-0.58954	0.00394
C	-1.01288	-1.49979	-0.44347
C	0.47336	-1.30841	-0.52465
C	0.95303	-0.09292	0.29081
C	0.02015	1.08077	0.01228

C	2.87421	1.27709	-0.55035
C	2.42182	0.18410	0.05858
C	3.36609	-0.87416	0.56009
C	-3.34621	-0.86760	0.13493
H	-2.26167	1.85548	-0.94458
H	-1.47285	0.82806	1.54246
H	-1.39088	-2.46907	-0.75600
H	0.96845	-2.21820	-0.17681
H	0.78205	-1.18242	-1.57008
H	0.84256	-0.36023	1.35066
H	0.36180	1.98671	0.51396
H	0.01314	1.28965	-1.06381
H	2.21689	2.05316	-0.91663
H	3.93519	1.43176	-0.70241
H	4.40497	-0.57694	0.42164
H	3.21571	-1.82392	0.04050
H	3.20190	-1.06833	1.62420
H	-3.94038	-0.17778	-0.46645
H	-3.67303	-0.72839	1.17004
H	-3.58082	-1.88847	-0.16615

Table S12. Atom positions for conformer E3 (*trans*-(C)E_IAx$_H$AA), optimized at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Atom	X	Y	Z
O	1.66799	-1.90467	0.40956
C	1.37532	-0.85144	-0.52548
C	1.96219	0.45654	-0.04886
C	1.17775	1.45028	0.36966
C	-0.32151	1.40152	0.41397
C	-0.86691	-0.02878	0.29771
C	-0.11818	-0.75371	-0.82517
C	-3.14626	-0.51181	1.12395
C	-2.36953	-0.06526	0.14019
C	-2.95072	0.41510	-1.16060
C	3.45950	0.54785	-0.05910
H	1.40793	-1.60028	1.28645
H	1.89606	-1.16347	-1.43467
H	1.63939	2.37610	0.70138
H	-0.68072	1.85571	1.34148
H	-0.72323	2.02432	-0.39420
H	-0.63579	-0.54128	1.23757
H	-0.51274	-1.76111	-0.96827
H	-0.24911	-0.20942	-1.76519

H	-2.72746	-0.87125	2.05621
H	-4.22508	-0.53642	1.03102
H	-2.62540	1.43102	-1.39787
H	-2.63176	-0.21886	-1.99180
H	-4.03954	0.40738	-1.12882
H	3.80788	1.48524	0.37478
H	3.84504	0.47904	-1.08114
H	3.90074	-0.28105	0.49897

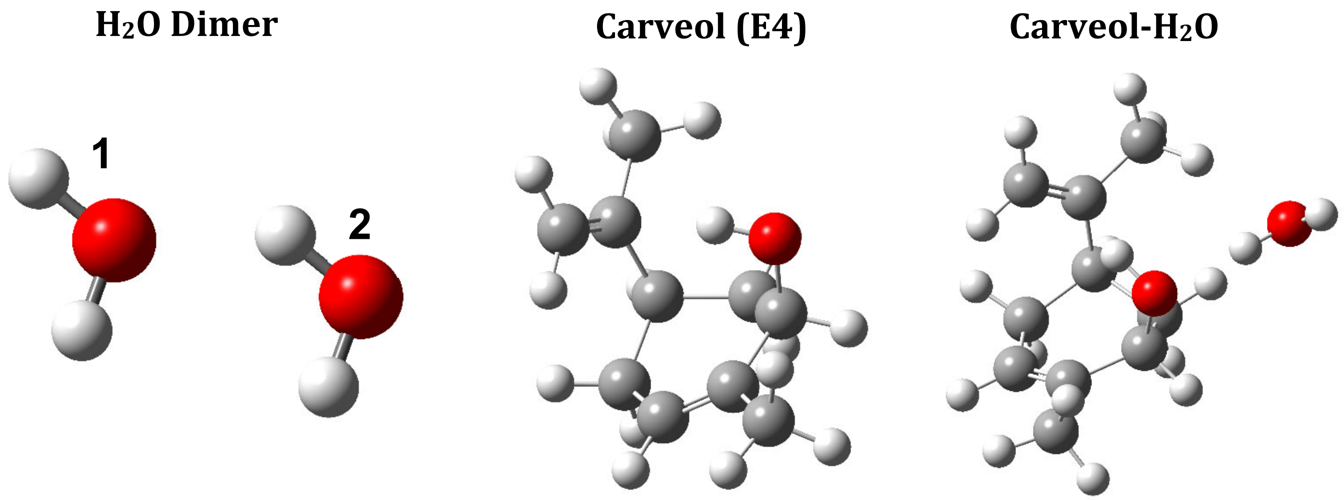
Table S13. Atom positions for conformer E4 (*cis*-(C)Ax$_{I}$Ax$_{H}$G+A), optimized at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Atom	X	Y	Z
O	-0.46503	-1.91295	0.33530
C	-0.93961	-0.96054	-0.62865
C	-1.74692	0.12772	0.04341
C	-1.29786	1.38031	0.10502
C	0.01086	1.85123	-0.46318
C	0.98158	0.71043	-0.78300
C	0.18952	-0.40409	-1.49422
C	1.53097	0.51237	1.66785
C	1.78038	0.18900	0.39939
C	2.91409	-0.73488	0.04659
C	-3.05006	-0.30339	0.64598
H	0.07708	-1.42652	0.97107
H	-1.60855	-1.54522	-1.26644
H	-1.91184	2.13377	0.59046
H	-0.18465	2.41140	-1.38577
H	0.47678	2.56698	0.21803
H	1.72249	1.08621	-1.49720
H	-0.24439	0.01755	-2.40565
H	0.83634	-1.22687	-1.79836
H	0.71530	1.16230	1.95152
H	2.14605	0.12606	2.47128
H	2.54389	-1.66172	-0.39710
H	3.50244	-0.99426	0.92590
H	3.57761	-0.27140	-0.68896
H	-3.54200	0.51697	1.16899
H	-2.89285	-1.12378	1.34996
H	-3.73118	-0.67677	-0.12530

Table S14. Atom positions for conformer E5 (*cis*-(C)$E_{I}E_{H}$AA), optimized at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Atom	X	Y	Z
O	2.17369	-1.88703	-0.05963
C	1.35471	-0.82016	0.43252
C	1.89044	0.53705	0.02465
C	1.07239	1.51374	-0.36899
C	-0.42421	1.41208	-0.42459
C	-0.94927	0.20652	0.37045
C	-0.09997	-1.01983	0.02354
C	-3.29201	0.22730	1.15841
C	-2.43073	-0.01757	0.17413
C	-2.89225	-0.52352	-1.16438
C	3.37543	0.72495	0.13169
H	2.12138	-1.88032	-1.02295
H	1.44226	-0.91320	1.52068
H	1.50213	2.47048	-0.65182
H	-0.87135	2.32971	-0.03241
H	-0.75003	1.34781	-1.46933
H	-0.79182	0.42819	1.43082
H	-0.49046	-1.91866	0.50388
H	-0.13119	-1.19097	-1.05828
H	-2.95818	0.58032	2.12667
H	-4.35795	0.08325	1.03094
H	-2.49695	-1.52266	-1.36505
H	-2.54958	0.11948	-1.97894
H	-3.97936	-0.57609	-1.20937
H	3.66226	1.74208	-0.13485
H	3.91631	0.02758	-0.51005
H	3.71586	0.52579	1.15253

Molecular Systems for Hydrogen Bond NBO Analyses



H_2O Dimer

Carveol (E4)

Carveol-H_2O

Figure S3. Three hydrogen bond containing systems used for the NBO analyses