Supporting information for

More complex, less complicated? Explicit solvation of hydroxyl groups for the analysis of VCD spectra

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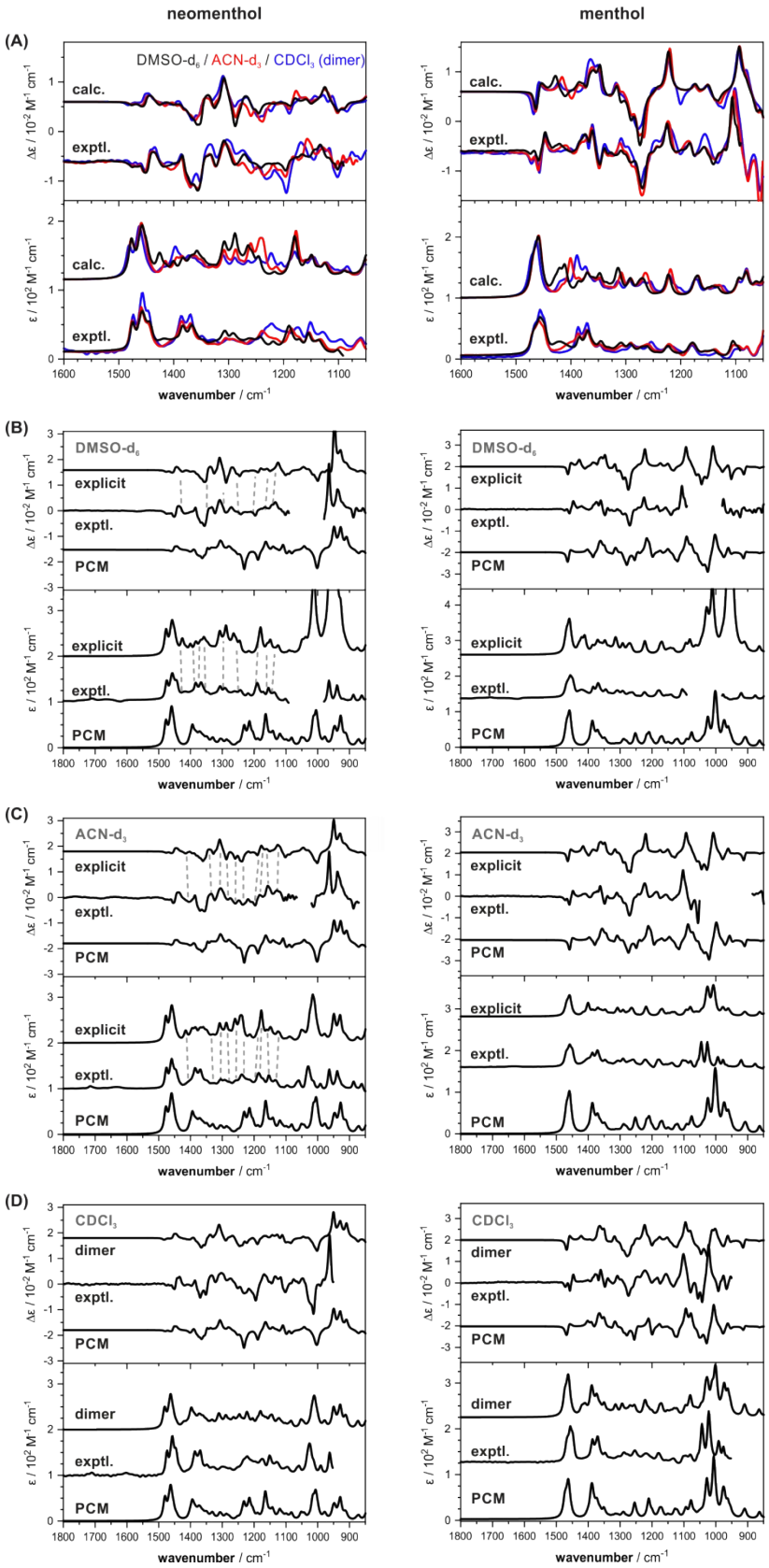


Figure S1. Experimental and calculated spectra of neomenthol (left) and menthol (right). Panel A shows an overlay of experimental and computed spectra to highlight similarities.

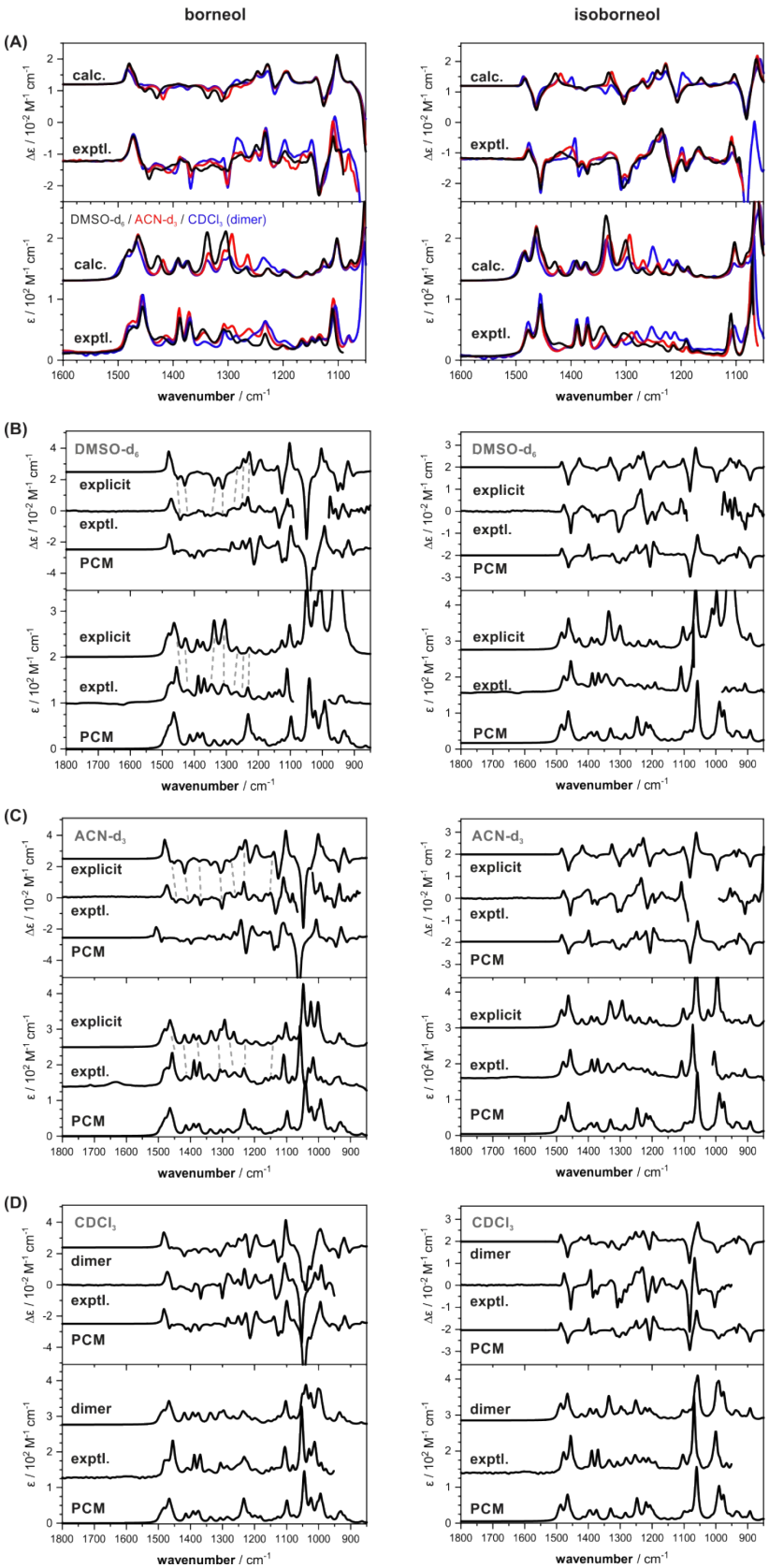


Figure S2. Experimental and calculated spectra of borneol (left) and isoborneol (right). Panel A shows an overlay of experimental and computed spectra to highlight similarities.

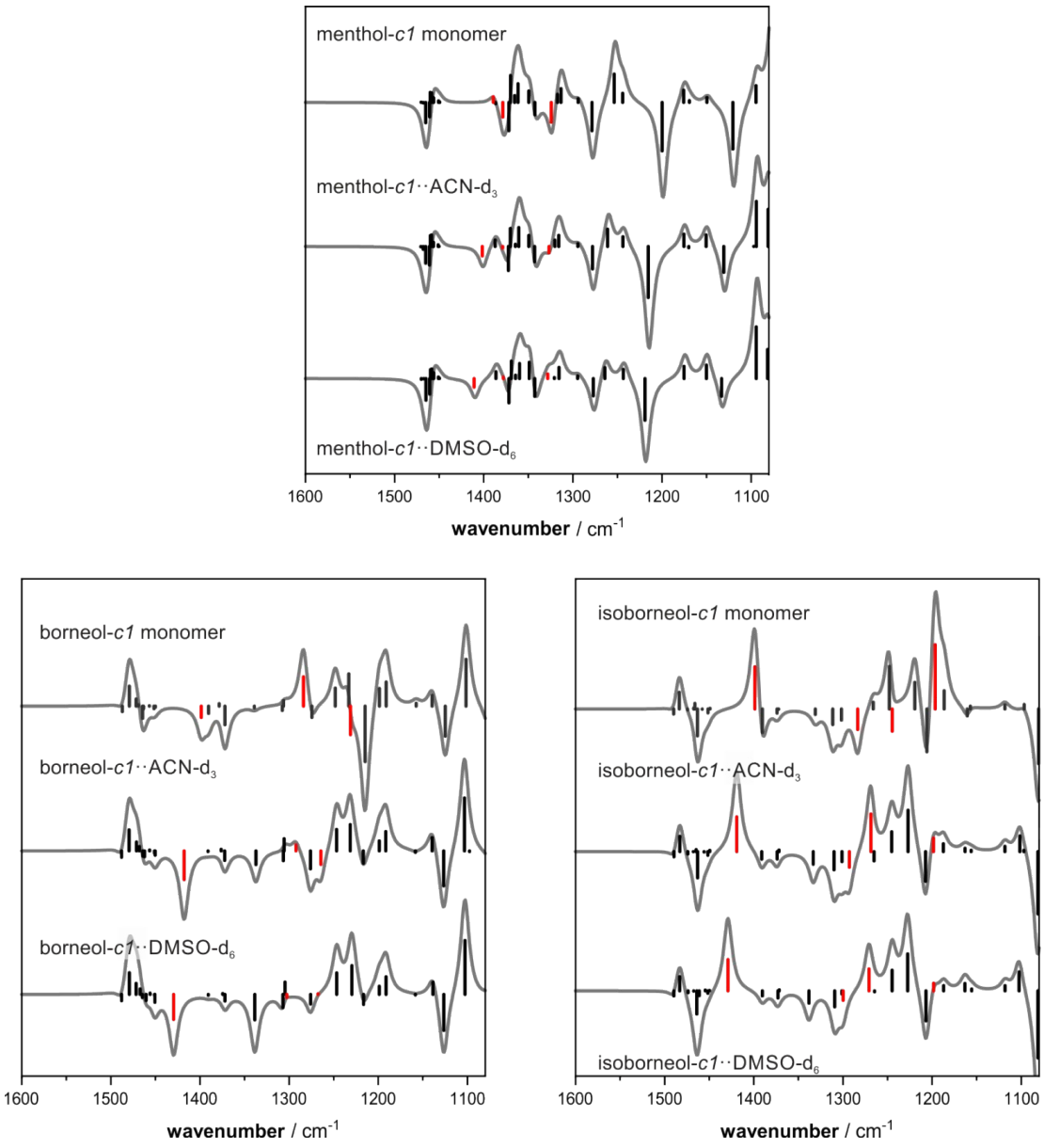


Figure S3. Line spectra of the conformer *c1* of menthol, borneol and isoborneol.

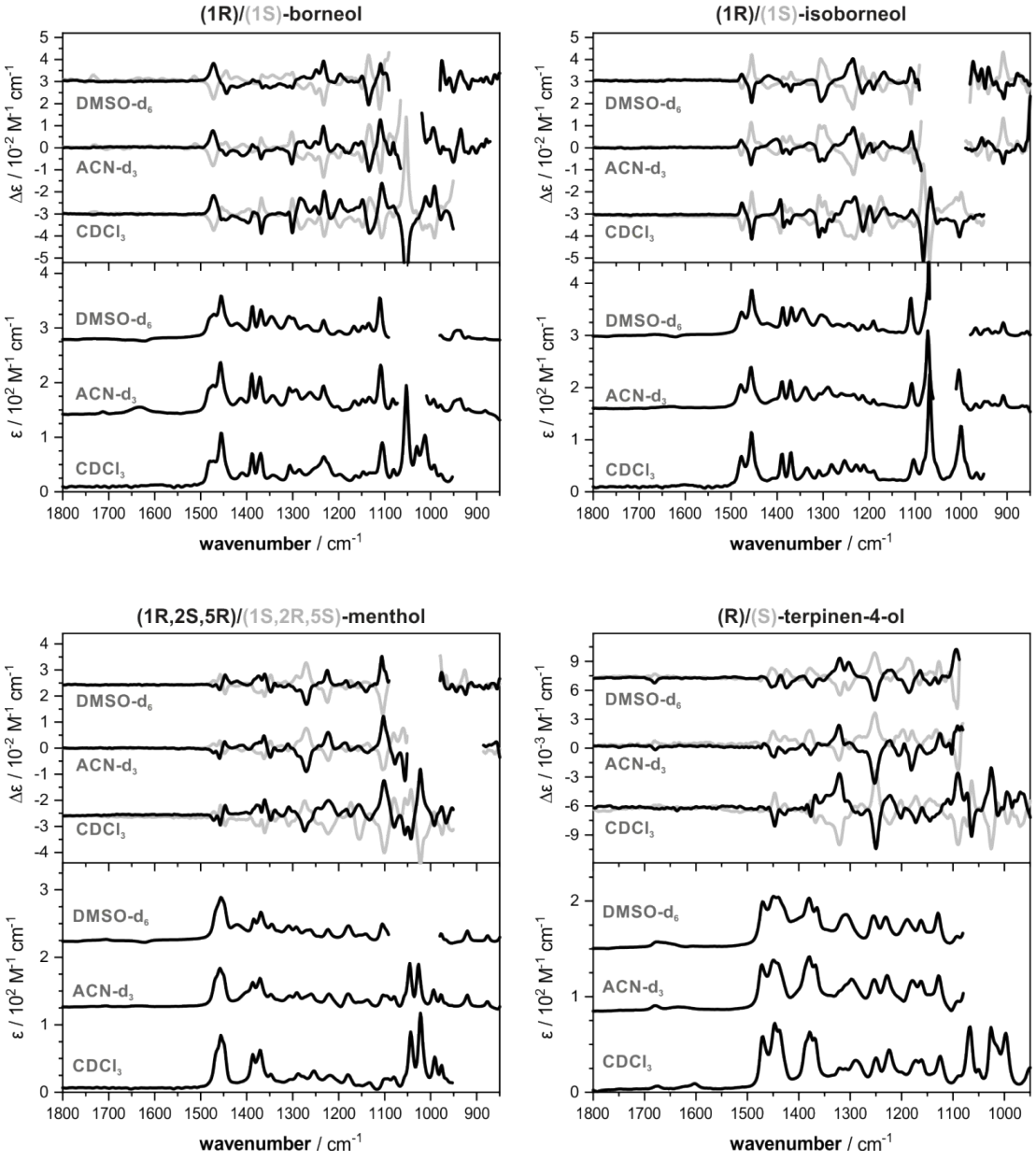


Figure S4. Experimental spectra of the enantiomers of borneol, isoborneol, menthol and terpinen-4-ol. The enantiomers of the other alcohols were not available.

2. Conformational analysis of neomenthol

Table S4. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **neomenthol** solvated with the IEFPCM of **DMSO**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]	**α_{OH}** [deg]	**α_{iPr}** [deg]
neomenthol-c1	0.00	0.00	36.5	40.8	179.8	176.0
neomenthol-c2	0.19	0.33	26.5	23.3	-60.6	177.4
neomenthol-c3	0.31	0.29	21.5	25.1	62.6	176.7
neomenthol-c4	1.24	1.53	4.5	3.1	178.6	-78.7
neomenthol-c5	1.56	1.75	2.6	2.1	64.7	-78.4
neomenthol-c6	1.56	1.80	2.6	2.0	-71.1	-82.0
neomenthol-c7	1.57	1.90	2.6	1.7	176.6	55.4
neomenthol-c8	1.83	2.14	1.7	1.1	58.1	56.1
neomenthol-c9	1.90	2.28	1.5	0.9	-60.9	62.9

[a] referenced to E_{ZPC} = -468.211562 hartree and G_{298K} = -468.249376 hartree.

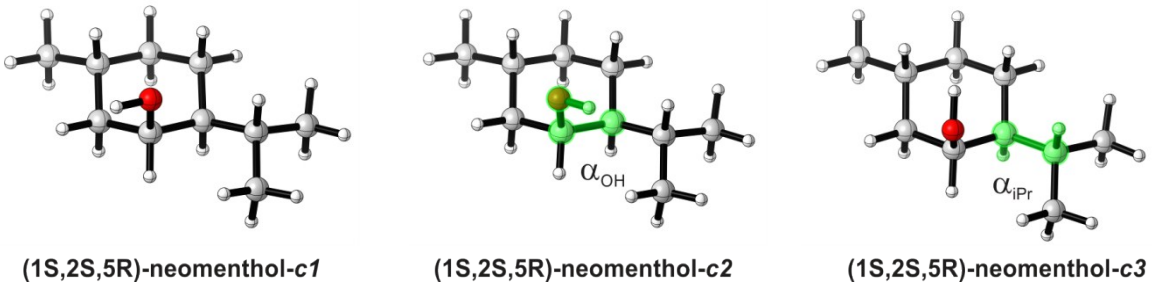


Figure S5. Conformers of (1S,2S,5R)-neomenthol and torsional angle definition.

Table S5. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **neomenthol explicitly solvated** with one molecule of **DMSO-d_6** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
neomenthol-c1··(DMSO-d_6)^A	0.00	0.00	33.1	53.0
neomenthol-c1··(DMSO-d_6)^T	0.21	0.33	23.3	30.2
neomenthol-c2··(DMSO-d_6)^A	0.58	1.19	12.5	7.1
neomenthol-c2··(DMSO-d_6)^T	0.77	1.82	9.0	2.4
neomenthol-c3··(DMSO-d_6)^A	1.25	2.06	4.0	1.6
neomenthol-c4··(DMSO-d_6)^A	1.35	2.27	3.4	1.1
neomenthol-c4··(DMSO-d_6)^T	1.54	2.87	2.5	0.4
neomenthol-c3··(DMSO-d_6)^T	1.55	2.57	2.4	0.7
neomenthol-c6··(DMSO-d_6)^A	1.68	2.76	2.0	0.5
neomenthol-c7··(DMSO-d_6)^A	1.69	2.74	1.9	0.5
neomenthol-c9··(DMSO-d_6)^A	1.76	2.84	1.7	0.4
neomenthol-c7··(DMSO-d_6)^T	1.82	2.43	1.5	0.9
neomenthol-c6··(DMSO-d_6)^T	1.87	3.06	1.4	0.3
neomenthol-c9··(DMSO-d_6)^T	1.88	2.47	1.4	0.8
neomenthol-c5··(DMSO-d_6)^A	2.64	3.76	0.4	0.1
neomenthol-c5··(DMSO-d_6)^T	2.87	4.42	0.3	0.0
neomenthol-c8··(DMSO-d_6)^A	2.97	4.37	0.2	0.0
neomenthol-c8··(DMSO-d_6)^T	3.15	4.60	0.2	0.0

[a] referenced to E_{ZPC} = -1021.456372 hartree and G_{298K} = -1021.510299 hartree.

neomenthol-*c1*··(DMSO-d_6)^T neomenthol-*c1*··(DMSO-d_6)^A

Figure S6. Structures of the DMSO-solvated conformer *c1* of neomenthol. The difference between the two structures is the relative orientation of the DMSO molecule: Methyl groups are pointing towards (T) or away (A) from the molecule.

Table S6. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **neomenthol** solvated with the IEFPCM of **acetonitrile**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
neomenthol-c1	0.00	0.00	36.5	40.7
neomenthol-c2	0.19	0.33	26.5	23.2
neomenthol-c3	0.31	0.28	21.5	25.3
neomenthol-c4	1.24	1.53	4.5	3.1
neomenthol-c5	1.56	1.75	2.6	2.1
neomenthol-c6	1.56	1.79	2.6	2.0
neomenthol-c7	1.57	1.90	2.6	1.6
neomenthol-c8	1.83	2.14	1.7	1.1
neomenthol-c9	1.90	2.29	1.5	0.9

[a)] referenced to E_{ZPC} = -468.211497 hartree and G_{298K} = -468.249312 hartree.

Table S7. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **neomenthol explicitly solvated** with one molecule of **acetonitrile-d_3** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
neomenthol-c1··(ACN-d_3)	0.00	0.00	50.9	57.2
neomenthol-c2··(ACN-d_3)	0.53	0.70	20.7	17.7
neomenthol-c3··(ACN-d_3)	1.00	1.34	9.3	6.0
neomenthol-c4··(ACN-d_3)	1.20	1.09	6.7	9.0
neomenthol-c9··(ACN-d_3)	1.57	1.66	3.6	3.5
neomenthol-c7··(ACN-d_3)	1.58	1.90	3.5	2.3
neomenthol-c6··(ACN-d_3)	1.59	1.66	3.5	3.5
neomenthol-c5··(ACN-d_3)	2.26	2.74	1.1	0.6
neomenthol-c8··(ACN-d_3)	2.57	3.21	0.7	0.3

[a)] referenced to E_{ZPC} = -600.986709 hartree and G_{298K} = -601.037189 hartree.

Table S8. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **neomenthol** solvated with the IEFPCM of **chloroform**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
neomenthol-c1	0.00	0.00	36.8	39.1
neomenthol-c2	0.20	0.32	26.5	22.9
neomenthol-c3	0.34	0.21	20.7	27.6
neomenthol-c4	1.19	1.50	4.9	3.1
neomenthol-c7	1.53	1.88	2.8	1.6
neomenthol-c6	1.56	1.77	2.6	2.0
neomenthol-c5	1.58	1.76	2.5	2.0
neomenthol-c8	1.85	2.16	1.6	1.0
neomenthol-c9	1.92	2.31	1.4	0.8

[a)] referenced to E_{ZPC} = -468.210028 hartree and G_{298K} = -468.247834 hartree.

Table S9. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the **dimers of neomenthol** solvated with the IEFPCM of **chloroform**. Only dimers build based on the three lowest energy conformers are considered.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
neomenthol-(c1··c3)	0.00	0.07	31.0	24.4
neomenthol-(c1··c2)	0.26	0.00	19.9	27.5
neomenthol-(c1··c1)	0.47	0.50	14.0	11.9
neomenthol-(c2··c2)	0.55	0.22	12.3	19.1
neomenthol-(c2··c3)	0.70	0.55	9.4	10.9
neomenthol-(c3··c3)	1.00	1.55	5.8	2.0
neomenthol-(c2··c1)	1.30	1.47	3.4	2.3
neomenthol-(c2··c3)	1.42	1.79	2.8	1.3
neomenthol-(c3··c3)	1.86	2.23	1.3	0.6

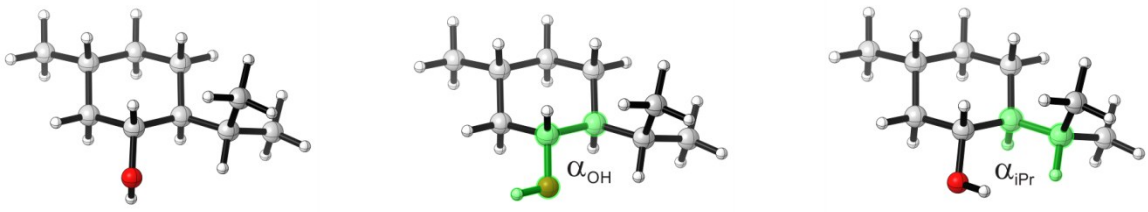
[a)] referenced to E_{ZPC} = -936.424386 hartree and G_{298K} = -936.484766 hartree.

3. Conformational analysis of menthol

Table S10. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **menthol** solvated with the IEFPCM of **DMSO**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]	**α_{OH}** [deg]	**α_{iPr}** [deg]
menthol-c1	0.00	0.00	32.8	35.1	-64.2	-67.4
menthol-c2	0.04	0.08	30.8	30.9	-178.1	-65.9
menthol-c3	0.15	0.18	25.6	25.8	68.2	-65.7
menthol-c4	1.22	1.38	4.2	3.4	-62.3	79.1
menthol-c5	1.25	1.52	4.0	2.7	-178.7	79.9
menthol-c6	1.79	1.96	1.6	1.3	71.3	80.4
menthol-c7	2.66	2.86	0.4	0.3	-179.8	-150.4
menthol-c8	2.71	2.84	0.3	0.3	-69.3	-152.3
menthol-c9	2.97	3.05	0.2	0.2	64.1	158.9

[a] referenced to E_{ZPC} = -468.213208 hartree and G_{298K} = -468.25096 hartree.



(1R,2S,5R)-menthol-*c1* **(1R,2S,5R)-menthol-*c2*** **(1R,2S,5R)-menthol-*c3***

Figure S7. Conformers of (1R,2S,5R)- menthol and torsional angle definition.

Table S11. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **menthol explicitly solvated** with one molecule of **DMSO-d_6** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
menthol-c2··(DMSO-d_6)^A	0.00	0.18	24.93	21.06
menthol-c2··(DMSO-d_6)^T	0.19	0.00	18.18	28.70
menthol-c1··(DMSO-d_6)^A	0.37	0.50	13.34	12.24
menthol-c3··(DMSO-d_6)^A	0.37	0.50	13.34	12.33
menthol-c3··(DMSO-d_6)^T	0.39	0.31	12.94	17.10
menthol-c1··(DMSO-d_6)^T	0.55	0.98	9.88	5.45
menthol-c5··(DMSO-d_6)^A	1.34	1.86	2.59	1.24
menthol-c5··(DMSO-d_6)^T	1.59	2.25	1.70	0.65
menthol-c4··(DMSO-d_6)^A	1.80	2.65	1.19	0.33
menthol-c4··(DMSO-d_6)^T	1.99	2.49	0.87	0.43
menthol-c7··(DMSO-d_6)^A	2.63	4.07	0.29	0.03
menthol-c7··(DMSO-d_6)^T	2.67	3.07	0.27	0.16
menthol-c8··(DMSO-d_6)^A	3.07	3.47	0.14	0.08
menthol-c9··(DMSO-d_6)^A	3.08	3.29	0.14	0.11
menthol-c9··(DMSO-d_6)^T	3.23	3.71	0.11	0.05
menthol-c8··(DMSO-d_6)^T	3.39	4.24	0.08	0.02

[a)] referenced to E_{ZPC} = -1021.458018 hartree and G_{298K} = -1021.510874 hartree.

Table S12. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **menthol** solvated with the IEFPCM of **acetonitrile**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
menthol-c1	0.00	0.00	32.7	34.9
menthol-c2	0.03	0.07	31.0	31.1
menthol-c3	0.15	0.18	25.6	25.8
menthol-c4	1.22	1.37	4.2	3.4
menthol-c5	1.24	1.50	4.0	2.8
menthol-c6	1.79	1.95	1.6	1.3
menthol-c7	2.65	2.85	0.4	0.3
menthol-c8	2.71	2.83	0.3	0.3
menthol-c9	2.97	3.04	0.2	0.2

[a)] referenced to E_{ZPC} = -468.213136 hartree and G_{298K} = -468.250881 hartree.

Table S13. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **menthol explicitly solvated** with one molecule of **acetonitrile-d_3** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
menthol-c2··(ACN-d_3)	0.00	0.00	39.2	44.0
menthol-c3··(ACN-d_3)	0.20	0.33	27.9	25.2
menthol-c1··(ACN-d_3)	0.27	0.43	24.7	21.4
menthol-c5··(ACN-d_3)	1.26	1.19	4.7	5.9
menthol-c4··(ACN-d_3)	1.63	1.72	2.5	2.4
menthol-c7··(ACN-d_3)	2.64	2.90	0.5	0.3
menthol-c8··(ACN-d_3)	2.89	2.79	0.3	0.4
menthol-c9··(ACN-d_3)	2.95	2.83	0.3	0.4

[a] referenced to E_{ZPC} = -600.986709 hartree and G_{298K} = -601.037189 hartree.

Table S14. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **menthol** solvated with the IEFPCM of **chloroform**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
menthol-c2	0.00	0.00	33.6	35.9
menthol-c1	0.03	0.06	31.7	32.4
menthol-c3	0.22	0.28	23.0	22.4
menthol-c5	1.16	1.39	4.7	3.4
menthol-c4	1.21	1.40	4.4	3.4
menthol-c6	1.83	1.93	1.5	1.4
menthol-c7	2.58	2.79	0.4	0.3
menthol-c8	2.61	2.40	0.4	0.6
menthol-c9	2.97	3.04	0.2	0.2

[a] referenced to E_{ZPC} = -468.211550 hartree and G_{298K} = -468.249284 hartree.

Table S15. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the **dimers of menthol** solvated with the IEFPCM of **chloroform**. Only dimers build based on the three lowest energy conformers are considered.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
menthol-(c2··c1)	0.00	0.40	25.1	12.2
menthol-(c1··c1)	0.29	0.07	15.3	21.3
menthol-(c3··c1)	0.36	0.00	13.6	23.9
menthol-(c2··c3)	0.40	0.91	12.7	5.1
menthol-(c2··c2)	0.43	0.30	12.1	14.3
menthol-(c3··c2)	0.61	0.49	8.9	10.4
menthol-(c1··c2)	0.81	0.56	6.4	9.3
menthol-(c1··c3)	0.87	1.15	5.7	3.4
menthol-(c3··c3)	0.90	1.58	5.5	1.6

[a] referenced to E_{ZPC} = -936.428049 hartree and G_{298K} = -936.488877 hartree.

4. Conformational analysis of borneol

Table S16. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations of the conformers of **borneol** solvated with in the IEFPCM of **DMSO**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
borneol-c1 (gauche -)	0.00	0.00	44.5	42.4
borneol-c2 (trans)	0.23	0.15	30.1	32.9
borneol-c3 (gauche +)	0.33	0.32	25.5	24.7

[a] referenced to E_{ZPC} = -467.002864 hartree and G_{298K} = -467.037716 hartree.

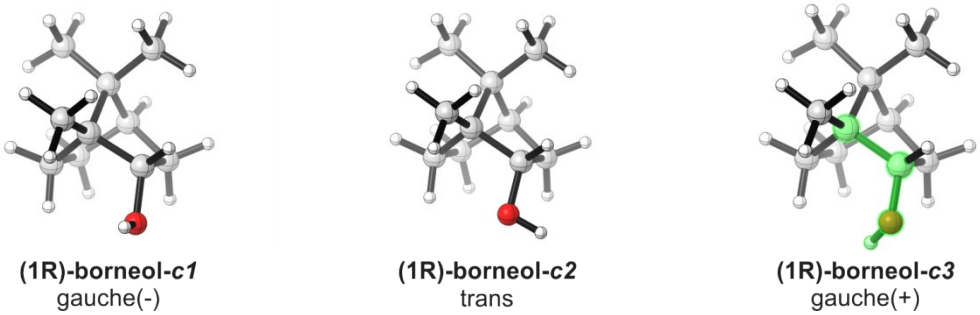


Figure S8. Conformers of (1R,2S)-borneol. The torsional angle C_Q-C*-O-H, which is used to differentiate the conformers, is highlighted for borneol-c3.

Table S17. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations of the conformers of **borneol explicitly solvated** with one molecule of **DMSO-d_6** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
borneol-c1··(DMSO-d_6)^T	0.19	0.20	21.2	22.6
borneol-c1··(DMSO-d_6)^A	0.00	0.24	29.2	21.0
borneol-c2··(DMSO-d_6)^T	0.25	0.00	19.1	31.7
borneol-c2··(DMSO-d_6)^A	0.15	0.23	22.7	21.6
borneol-c3··(DMSO-d_6)^T	1.29	3.45	3.3	0.1
borneol-c3··(DMSO-d_6)^A	1.11	1.39	4.5	3.0

[a] referenced to E_{ZPC} = -1020.247645 hartree and G_{298K} = -1020.298426 hartree.

Table S18. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations of the conformers of **borneol** solvated with the IEFPCM of **acetonitrile**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
borneol-c1	0.00	0.00	44.3	42.1
borneol-c2	0.23	0.14	30.3	33.2
borneol-c3	0.33	0.31	25.4	24.7

[a] referenced to E_{ZPC} = -467.002793 hartree and G_{298K} = -467.037641 hartree.

Table S19. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations of the conformers of **borneol explicitly solvated** with one molecule of **acetonitrile-d_3** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
borneol-c1··(ACN-d_3)	0.00	0.63	47.1	22.1
borneol-c2··(ACN-d_3)	0.07	0.00	41.8	63.9
borneol-c3··(ACN-d_3)	0.86	0.90	11.1	13.9

[a] referenced to E_{ZPC} = -599.778254 hartree and G_{298K} = -599.826429 hartree.

Table S20. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations of the conformers of **borneol** solvated with in the IEFPCM of **chloroform**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
borneol-c1	0.00	0.00	43.3	39.2
borneol-c2	0.16	0.03	33.2	37.2
borneol-c3	0.36	0.30	23.5	23.6

[a] referenced to E_{ZPC} = -467.001217 hartree and G_{298K} = -467.036017 hartree.

Table S21. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations of the **dimers of borneol** solvated with in the IEFPCM of **chloroform**.

conformer (D··A)	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
borneol-(c1··c1)	0.17	0.14	18.4	21.4
borneol-(c1··c2)	0.59	0.71	9.0	8.2
borneol-(c1··c3)	0.23	0.53	16.6	11.0
borneol-(c2··c1)	0.00	0.00	24.3	27.0
borneol-(c2··c2)	0.77	0.67	6.7	8.7
borneol-(c2··c3)	0.25	0.27	16.1	17.2
borneol-(c3··c1)	1.15	1.80	3.5	1.3
borneol-(c3··c2)	1.78	2.48	1.2	0.4
borneol-(c3··c3)	1.02	1.02	4.3	4.8

[a)] referenced to E_{ZPC} = -934.006835 hartree and G_{298K} = -934.062585 hartree.

5. Conformational analysis of isoborneol

Table S22. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **isoborneol** solvated with in the IEFPCM of **DMSO**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
isoborneol-c1 (gauche +)	0.00	0.00	69.0	68.1
isoborneol-c2 (trans)	0.69	0.62	21.6	23.8
isoborneol-c3 (gauche -)	1.18	1.26	9.3	8.1

[a] referenced to E_{ZPC} = -467.002486 hartree and G_{298K} = -467.037312 hartree.

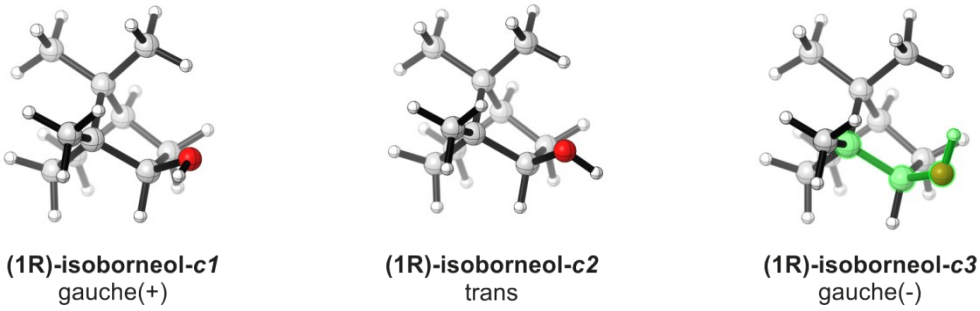


Figure S9. Conformers of (1R,2R)-isoborneol. The torsional angle C_Q-C*-O-H, which is used to differentiate the conformers, is highlighted for isoborneol-c3.

Table S23. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **isoborneol explicitly solvated** with one molecule of **DMSO-d_6** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
isoborneol-c1··(DMSO-d_6)^T	0.00	0.00	64.9	37.5
isoborneol-c1··(DMSO-d_6)^A	1.14	0.40	9.4	19.2
isoborneol-c2··(DMSO-d_6)^T	0.70	0.47	20.1	16.9
isoborneol-c2··(DMSO-d_6)^A	1.86	0.33	2.8	21.4
isoborneol-c3··(DMSO-d_6)^T	1.87	1.18	2.8	5.1
isoborneol-c3··(DMSO-d_6)^A	4.11	5.09	0.1	0.0

[a] referenced to E_{ZPC} = -1020.003261 hartree and G_{298K} = -1020.051375 hartree.

Table S24. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **isoborneol** solvated with in the IEFPCM of **acetonitrile**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
isoborneol-c1	0.00	0.00	69.1	68.3
isoborneol-c2	0.69	0.63	21.6	23.7
isoborneol-c3	1.19	1.26	9.3	8.0

[a] referenced to E_{ZPC} = -467.002423 hartree and G_{298K} = -467.037248 hartree.

Table S25. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **isoborneol explicitly solvated** with one molecule of **acetonitrile-d_3** and implicitly by its IEFPCM.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
isoborneol-c1··(ACN-d_3)	0.00	0.20	52.9	32.7
isoborneol-c2··(ACN-d_3)	0.47	0.00	24.0	46.2
isoborneol-c3··(ACN-d_3)	0.49	0.46	23.2	21.1

[a] referenced to E_{ZPC} = -599.777611 hartree and G_{298K} = -599.824916 hartree.

Table S26. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the conformers of **isoborneol** solvated with in the IEFPCM of **chloroform**.

conformer	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
isoborneol-c1	0.00	0.00	70.3	69.3
isoborneol-c2	0.70	0.65	21.4	23.2
isoborneol-c3	1.27	1.32	8.3	7.5

[a] referenced to E_{ZPC} = -467.000972 hartree and G_{298K} = -467.035766 hartree.

Table S27. Relative zero-point corrected and Gibbs Free Energies, ΔE_{ZPC} and ΔG_{298K}, and the corresponding Boltzmann populations for the **dimers of isoborneol** solvated with in the IEFPCM of **chloroform**.

Conformer (D··A)	**ΔE_{ZPC}** [kcal mol^{-1}]	**ΔG_{298K}** [kcal mol^{-1}]	**pop-ΔE_{ZPC}** [%]	**pop-ΔG_{298K}** [%]
isoborneol-(c1··c1)	0.04	0.24	32.5	20.9
isoborneol-(c1··c2)	1.35	2.05	3.6	1.0
isoborneol-(c1··c3)	0.96	0.58	6.9	11.9
isoborneol-(c2··c1)	0.63	0.44	12.0	15.1
isoborneol-(c2··c2)	1.92	1.50	1.4	2.5
isoborneol-(c2··c3)	1.47	0.97	2.9	6.1
isoborneol-(c3··c1)	0.00	0.00	34.9	31.6
isoborneol-(c3··c2)	1.52	1.67	2.7	1.9
isoborneol-(c3··c3)	1.43	0.74	3.1	9.0

[a] referenced to E_{ZPC} = -934.00639 hartree and G_{298K} = -934.061331 hartree.

6. Cartesian coordinates of selected structure

neomenthol-*c1*

C	0.05406900	-1.30985000	0.51687600
C	-0.71893000	-0.22479300	-0.25688700
C	0.02908800	1.11734600	-0.18002500
C	1.49459900	0.98499200	-0.60589300
C	2.26499400	-0.09295000	0.16557400
C	1.51501500	-1.42597500	0.06730000
H	-0.70632100	-0.50217900	-1.32075700
H	0.01789400	-1.08042400	1.58736800
H	-0.43394600	-2.27767000	0.38941500
H	1.51656700	0.74962300	-1.67746700
H	1.98765000	1.95818300	-0.49649600
H	2.28762400	0.20074900	1.22170500
H	1.54751200	-1.77516800	-0.97345000
H	2.02772200	-2.18673500	0.66513900
H	-0.45460700	1.83279900	-0.85274600
C	3.70939400	-0.20974500	-0.32478400
H	4.24104400	0.74089500	-0.22655800
H	4.26081900	-0.96178600	0.24632900
H	3.74229700	-0.50210300	-1.37930300
C	-2.20676500	-0.12464000	0.16749800
H	-2.22847200	0.08011700	1.24328800
C	-2.94869900	1.01865400	-0.53997000
H	-4.00408100	1.01831100	-0.25555300
H	-2.54147200	1.99786700	-0.28519400
H	-2.90120700	0.90471300	-1.62818700
C	-2.96031800	-1.44121700	-0.07670700
H	-2.55361000	-2.27167400	0.50160900
H	-4.01203800	-1.33453700	0.20120300
H	-2.92500200	-1.72010900	-1.13526400
O	-0.08168200	1.61537600	1.16992400
H	0.39040300	2.45518600	1.21763500

neomenthol-*c2*

C	-0.05832100	1.30955400	0.50326100
C	0.71279900	0.21873200	-0.26235600
C	-0.03833600	-1.12706500	-0.16654200
C	-1.49976800	-1.00051100	-0.59028600
C	-2.26958000	0.08772200	0.16839400
C	-1.52011800	1.41977400	0.05494700
H	0.70137600	0.48431500	-1.32949000
H	-0.02127500	1.08745400	1.57562900
H	0.42787500	2.27714700	0.36861000
H	-1.52139400	-0.77436500	-1.66299700
H	-1.98683800	-1.97236700	-0.46346100
H	-2.29532000	-0.19354500	1.22751600

H	-1.55407100	1.75825900	-0.98927300
H	-2.03164700	2.18678900	0.64569700
H	0.44101100	-1.85413800	-0.82940400
C	-3.71262500	0.19869500	-0.32736100
H	-4.24492800	-0.75027900	-0.21764200
H	-4.26522200	0.95869600	0.23193500
H	-3.74234100	0.47670100	-1.38590400
C	2.20299500	0.12075100	0.15743100
H	2.23726500	-0.09748800	1.23321800
C	2.95427900	-1.00075500	-0.57803900
H	4.00817900	-1.00228100	-0.29000100
H	2.55918200	-1.99511800	-0.36097900
H	2.90695700	-0.85512900	-1.66191000
C	2.95012000	1.44620000	-0.05630600
H	2.54434100	2.25801100	0.54784500
H	4.00405100	1.33508600	0.21026600
H	2.90415000	1.75205200	-1.10661700
O	-0.03481300	-1.66331500	1.17416500
H	0.87848000	-1.81186500	1.44478600

neomenthol-*c3*

C	-0.05475600	1.30884800	0.50273100
C	0.72020800	0.21706900	-0.26092600
C	-0.03045600	-1.12882200	-0.16557400
C	-1.49385400	-0.99905500	-0.60076500
C	-2.26641300	0.08736100	0.15901300
C	-1.51642300	1.42031200	0.05300700
H	0.70373000	0.48721000	-1.32669700
H	-0.01658600	1.10174900	1.58068600
H	0.43304200	2.27563800	0.37067700
H	-1.51203400	-0.76294600	-1.67183300
H	-1.98276000	-1.97085900	-0.48259300
H	-2.30565400	-0.19287100	1.22109100
H	-1.54697500	1.76006900	-0.99036300
H	-2.02937400	2.18558300	0.64422400
H	0.45264900	-1.85598900	-0.81832700
C	-3.70979500	0.19895900	-0.33581100
H	-4.24076900	-0.75072900	-0.22846800
H	-4.26225100	0.95766500	0.22501800
H	-3.73747000	0.47906100	-1.39353700
C	2.20783100	0.12175600	0.16222400
H	2.23207200	-0.08901000	1.23728100
C	2.95129800	-1.01657300	-0.55184200
H	4.00830700	-1.01161300	-0.27396900
H	2.55121200	-1.99863200	-0.29694900
H	2.89609700	-0.90044500	-1.63943100
C	2.95830500	1.44135100	-0.07496900
H	2.55116300	2.26763200	0.50903500
H	4.01036800	1.33465600	0.20139200

H	2.92160600	1.72664700	-1.13166700
O	0.07672300	-1.72607200	1.14392600
H	-0.33582400	-1.14147100	1.79049700

neomenthol-*c1*··(ACN-d_3)

C	-2.26267000	0.65351100	-0.77308900
C	-1.73036000	-0.39010400	0.22747800
C	-0.22547600	-0.17132100	0.46882000
C	0.07976900	1.27580800	0.87714700
C	-0.44842400	2.31732300	-0.11609100
C	-1.94681300	2.09161700	-0.34648800
H	-2.21413500	-0.19785100	1.19620900
H	-1.82431900	0.46004900	-1.75819000
H	-3.34302300	0.54668100	-0.88647600
H	-0.36985300	1.45562000	1.86234700
H	1.16185400	1.38796400	1.00584100
H	0.06384200	2.15827700	-1.07232100
H	-2.48677300	2.32102200	0.58208800
H	-2.31791200	2.79291200	-1.10142400
H	0.09786000	-0.82382900	1.28721100
C	-0.14897400	3.74307900	0.35099000
H	0.92483300	3.89961600	0.48731400
H	-0.50478700	4.48024600	-0.37435100
H	-0.63964500	3.95313400	1.30697300
C	-2.08294200	-1.84509600	-0.17384700
H	-1.65900200	-2.02258700	-1.16797700
C	-1.48017200	-2.88471500	0.78220800
H	-1.79780700	-3.89115000	0.49732800
H	-0.38963500	-2.87128700	0.77524300
H	-1.81431700	-2.71333200	1.81111100
C	-3.60137600	-2.06388600	-0.26194800
H	-4.07257700	-1.43928200	-1.02184500
H	-3.82220700	-3.10469000	-0.51274600
H	-4.08322600	-1.84604300	0.69728300
O	0.48655000	-0.54140200	-0.72270300
H	1.43844400	-0.53030300	-0.52901600
C	4.57832800	-0.71336200	-0.17983400
N	3.43380900	-0.64676600	-0.26473100
C	6.02608100	-0.79671400	-0.07361600
H(Iso=2)	6.35605900	-1.80901100	-0.30865900
H(Iso=2)	6.48814700	-0.09876800	-0.77238200
H(Iso=2)	6.33728700	-0.54565600	0.94079400

neomenthol-*c1*··(DMSO-d_6)^{A}

C	-3.01340200	0.10061100	-0.81425100
C	-2.19634600	-0.71099000	0.20912800
C	-0.86079500	-0.00098900	0.50114000
C	-1.07683200	1.46027100	0.91835900
C	-1.88888900	2.27207800	-0.09718500

C	-3.21477000	1.55759600	-0.38209200
H	-2.75064600	-0.69985400	1.15903400
H	-2.50139600	0.07414300	-1.78240200
H	-3.99041300	-0.36205600	-0.96610000
H	-1.59608500	1.46909700	1.88573000
H	-0.10079600	1.92856300	1.08533100
H	-1.31822700	2.30245500	-1.03278500
H	-3.83350500	1.58387000	0.52510600
H	-3.77286800	2.09995100	-1.15281300
H	-0.36663800	-0.51345300	1.33423600
C	-2.10415500	3.71152600	0.37423100
H	-1.15139100	4.21917500	0.54953100
H	-2.66088500	4.29210800	-0.36689300
H	-2.67118200	3.73613900	1.31056600
C	-2.02533700	-2.19665900	-0.19751700
H	-1.53182700	-2.21384800	-1.17506000
C	-1.14107600	-2.97986200	0.78371700
H	-1.09202300	-4.03264800	0.49330000
H	-0.11917700	-2.60012600	0.81374600
H	-1.54791500	-2.93763100	1.79979900
C	-3.37736500	-2.91332900	-0.33789300
H	-4.00516700	-2.47757700	-1.11611900
H	-3.22623700	-3.96570700	-0.59227400
H	-3.93704700	-2.87836800	0.60304400
O	-0.02436400	-0.09576000	-0.65932800
H	0.87966600	0.18963600	-0.41502600
C	4.68974800	-0.29634800	1.31492500
H(Iso=2)	4.06214800	-0.63490000	2.13716800
H(Iso=2)	5.54345100	-0.96349800	1.19729100
H(Iso=2)	5.00962400	0.73343500	1.46992500
C	4.88289500	0.30526200	-1.35650800
H(Iso=2)	5.73201900	-0.37482000	-1.41999200
H(Iso=2)	4.38371400	0.37005900	-2.32147600
H(Iso=2)	5.19011600	1.29187000	-1.01166900
O	2.59037200	0.68052200	-0.02635000
S	3.67516100	-0.38557000	-0.18888100

neomenthol-*c1*··(DMSO-d$_6$)^T

C	2.79365600	0.09381400	0.95582400
C	2.12087000	-0.71372000	-0.17038300
C	0.83595800	-0.00203600	-0.63423600
C	1.10630700	1.45995700	-1.01539800
C	1.77626000	2.26875400	0.10132900
C	3.05143900	1.55217800	0.55957500
H	2.79625700	-0.69825900	-1.03828000
H	2.15601700	0.06369800	1.84602000
H	3.74145000	-0.36982100	1.23566600
H	1.75009100	1.47024100	-1.90471100
H	0.16161100	1.92937200	-1.31016100

H	1.08594200	2.29856600	0.95254900
H	3.78645500	1.58085000	-0.25618900
H	3.50113900	2.09161500	1.40005000
H	0.45494700	-0.51219400	-1.52594500
C	2.05415000	3.70877600	-0.33439800
H	1.13390000	4.21798100	-0.63444200
H	2.50751000	4.28731200	0.47557200
H	2.74122900	3.73444100	-1.18652200
C	1.89886300	-2.20139900	0.20313300
H	1.27670200	-2.22385000	1.10420400
C	1.15890700	-2.98150900	-0.89327000
H	1.07320400	-4.03576200	-0.61702100
H	0.14977300	-2.60376900	-1.06156300
H	1.70093000	-2.93363700	-1.84385200
C	3.22056600	-2.91681000	0.52365100
H	3.73482900	-2.48458700	1.38292000
H	3.03835800	-3.97082500	0.74925600
H	3.90383900	-2.87571900	-0.33148400
O	-0.14629200	-0.09854700	0.40653900
H	-1.00676300	0.19839200	0.04854200
C	-4.19562000	0.57027200	1.51608100
H(Iso=2)	-4.19844200	1.65161400	1.63983600
H(Iso=2)	-5.14563900	0.15371100	1.85036100
H(Iso=2)	-3.35811200	0.12115500	2.04852000
C	-3.94016800	-1.56663000	-0.18726900
H(Iso=2)	-4.89499900	-1.93742600	0.18491800
H(Iso=2)	-3.77494800	-1.91705200	-1.20433400
H(Iso=2)	-3.11942500	-1.86439900	0.46394300
O	-2.62330100	0.72788200	-0.65451000
S	-4.02039100	0.24773700	-0.26449500