Electronic supplementary information

Low-temperature heat capacity and pseudorotation in 2-methyltetrahydrofuran

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Contents

Table S1 Raw experimental molar heat capacity of 2-MTHF in the crystal and liquid states (Molar mass = 86.132 g·mol^{-1}, p^o = 101.3 kPa)

T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ /(J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})
Crystal		42.62	35.569	63.25	50.292	84.34 [b]	61.820 [b]
7.52	0.83264	43.46	36.286	63.30	50.333	84.89 [b]	62.219 [b]
7.67	0.88411	44.27	36.987	63.65	50.462	85.44 [b]	62.451 [b]
9.92	1.8872	45.06	37.656	63.80	50.565	85.98 [b]	62.775 [b]
10.62	2.3824	45.83	38.224	64.05	50.705	86.52 [b]	63.082 [b]
11.51	3.0011	46.59	38.787	64.29	50.876	87.06 [b]	63.261 [b]
12.43	3.7666	47.32	39.349	64.78	51.071	87.60 [b]	63.589 [b]
12.75	4.0348	48.04	39.915	65.27	51.298	88.13 [b]	63.909 [b]
13.72	4.9383	48.75	40.425	65.75	51.536	88.66	64.210
14.77	5.9598	49.45	40.917	66.23	51.772	89.19	64.526
15.66	6.8720	50.13	41.400	66.70	52.096	89.71	64.705
16.44	7.7170	50.80	41.887	67.17	52.427	79.25[a]	58.997[a]
17.15	8.5047	51.45	42.403	67.64	52.646	80.06	59.464
17.79	9.2327	52.10	42.880	68.10	52.825	80.87	59.969
18.39	9.9026	52.73	43.433	68.56	53.085	81.68	60.361
18.95	10.563	53.36	43.968	69.02	53.393	82.49[b]	60.821 [b]
19.47	11.191	53.52	44.068	69.47	53.625	83.30 [b]	61.294 [b]
19.97	11.775	54.00	44.416	69.92	53.825	84.11 [b]	61.701 [b]
20.17	12.024	54.49	44.840	70.47	54.117	84.92 [b]	62.154 [b]
21.48	13.552	54.97	45.227	71.13	54.419	85.73 [b]	62.555 [b]
21.60	13.680	55.44	45.486	71.79	54.838	86.54 [b]	63.043 [b]
23.52	15.926	55.91	45.912	72.44	55.230	87.35 [b]	63.488 [b]
24.07	16.564	56.37	46.240	73.08	55.508	88.16 [b]	63.883 [b]
25.26	18.007	56.83	46.575	73.72	55.928	88.97	64.321
26.12	18.989	57.28	46.872	74.35	56.249	89.78	64.732
27.91	20.981	57.73	47.199	74.97	56.628	90.59	65.158
29.51	22.809	58.18	47.378	75.59	56.959	91.40	65.592
30.98	24.437	58.62	47.635	76.21	57.348	92.21	66.094
32.33	25.905	59.06	47.948	76.82	57.697	93.03	66.522
33.60	27.225	59.49	48.101	77.42	58.044	93.84	66.874
34.79	28.475	59.92	48.307	78.02	58.464	94.65	67.308
35.91	29.511	60.35	48.493	78.62	58.782	95.46	67.780
36.99	30.528	60.78	48.859	79.21	59.047	96.27	68.204
38.02	31.473	61.20	49.105	79.79	59.395	97.08	68.652
39.00	32.354	61.71	49.405	80.37	59.711	97.90	69.054
39.96	33.240	62.03	49.581	80.95	60.005	98.71	69.507
40.87	34.040	62.29	49.725	81.52	60.392	99.52	69.911
41.76	34.837	62.80	50.125	82.66[b]	61.043 [b]	100.33	70.333

Table S1 (continued)

T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ /(J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})
101.15	70.754	131.86[c]	89.322[c]	172.17	131.78	202.09	134.04
101.95	71.182	132.66[c]	91.398[c]	172.98	131.74	203.31	134.11
102.76	71.655	133.46[c]	93.599[c]	173.79	131.77	204.54	134.22
103.57	72.048	134.27	95.102	174.61	131.83	205.76	134.43
104.38	72.511	136.10	122.64	175.42	131.82	206.99	134.67
105.19	72.951	136.62	200.19	176.24	131.94	208.21	134.70
105.99	73.444	Liquid		177.05	132.02	209.44	134.91
106.80	73.907	148.50	132.34	177.87	132.00	211.89	135.23
107.61	74.351	149.32	132.30	178.69	131.84	213.12	135.31
108.42	74.808	150.13	132.22	179.50	132.01	214.35	135.57
109.23	75.273	150.95	132.24	180.31	132.07	215.58	135.80
110.04	75.732	151.76	132.17	181.13	132.11	216.81	135.97
110.85	76.229	152.58	132.02	181.94	132.15	218.03	136.10
111.66	76.689	153.40	131.98	182.76	132.22	219.26	136.32
112.47	77.249	154.21	131.92	183.57	132.23	220.49	136.50
113.28	77.735	155.03	131.82	184.39	132.28	221.72	136.73
114.09	78.265	155.85	131.80	185.20	132.31	222.95	137.00
114.90	78.764	156.66	131.65	186.02	132.40	224.18[c]	138.72[c]
115.71	79.268	157.48	131.58	186.83	132.43	225.41	137.41
116.52	79.825	158.30	131.66	187.64	132.44	226.64	137.68
117.32	80.300	159.11	131.65	188.46	132.57	227.87	137.96
118.13	80.878	159.93	131.66	189.27	132.67	229.10	138.17
118.94	81.391	160.74	131.66	190.08	132.73	230.33	138.37
119.75	81.873	161.56	131.59	190.90	132.86	231.56	138.98
120.56	82.423	162.38	131.65	191.71	132.86	232.79	138.82
121.37	82.910	163.19	131.54	192.52	132.90	234.03	139.04
122.18	83.450	164.01	131.61	193.34	133.04	235.26	139.38
122.99	83.950	164.82	131.62	194.15	133.11	236.49	139.60
123.80	84.422	165.64	131.58	194.97	133.17	237.73	139.86
124.61	84.867	166.46	131.64	195.78	133.28	238.96	140.10
125.42	85.176	167.27	131.67	196.59	133.39	240.20	140.31
126.23[c]	85.466[c]	168.09	131.61	197.41	133.43	241.43	140.55
127.04[c]	85.691[c]	168.90	131.72	198.22	133.49	242.67	140.84
127.85[c]	85.881[c]	169.72	131.64	199.03	133.58	243.90[c]	143.01[c]
130.26[c]	86.520[c]	170.53	131.66	199.84	133.72	245.13	141.34
131.07[c]	87.648[c]	171.35	131.73	200.86	133.85	246.37	141.62

Table S1 (continued)

T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ /(J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})
247.61	141.96	279.91	150.21	317.65	160.37
248.84	142.22	281.16	150.58	319.26	160.83
250.08	142.52	282.41	150.93	320.85	161.35
251.32	142.78	283.65	151.22	322.45	161.81
252.55	143.07	284.91	151.58	324.04	162.27
253.79	143.40	286.16	151.91	325.62	162.71
255.03	143.70	287.41	152.26	327.17	163.49
256.27	144.00	288.64	152.66	328.75	163.89
257.51	144.30	289.89	153.03	330.32	164.41
258.76	144.58	291.14 [c]	155.73 [c]	332.00	164.77
259.99[c]	147.09 [c]	292.39	153.77	333.41 [c]	164.12 [c]
261.23	145.32	293.65	154.19	334.95	165.41
262.48	145.52	294.90	154.51	336.41	166.01
263.72	145.82	296.15	154.89	337.93	166.65
264.96	146.12	297.41	155.34	339.45	167.08
266.20	146.45	298.66	155.67	340.96	167.29
267.44	146.81	299.92	156.00	342.46	168.70
268.69	147.12	301.40	155.73	343.95	168.46
269.93	147.44	303.04	156.09	345.45 [c]	165.98 [c]
271.18	147.73	304.68	156.57	346.86	169.12
272.42	148.06	306.32	157.94	348.32	170.04
273.67	148.41	307.95 [c]	157.56 [c]	349.78	170.39
274.91	148.70	309.58	158.00	351.12	170.98
276.1 [c]	151.44 [c]	311.20	159.24	352.57	171.44
277.40	149.54	312.82	159.00	354.02	171.96
278.66	149.85	314.44	159.50		

[a] The experimental points up to T = 79.25 K are measured in a helium bath, after this temperature in a nitrogen bath.
[b] The uncertainty in $C_{p,m}$ values at these temperatures is 0.5% due to the presence of argon in the calorimeter, not 0.2% as it was obtained for testing the calorimeter with reference samples of copper and n-heptane (see text for details).
[c] These points are defined as outliers and they are not shown in Fig. 2.

Table S2 Raw experimental molar heat capacity of 2-MTHF in the vitrified state (Molar mass = 86.1322 g·mol^{-1}, p^o = 101.3 kPa)

T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ /(J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})	T / K	$C_{p,m}$ / (J·K^{-1}·mol^{-1})
79.15	62.315	85.62	67.391	91.64	141.068	98.17	139.808
79.95	62.875	86.43	68.260	92.43	141.591	98.99	139.609
80.76	63.530	87.24	69.452	93.25	141.261	99.81	139.337
81.57	64.127	88.06	71.013	94.07	141.063	100.63	139.123
82.38	64.805	88.87	73.494	94.89	140.729	101.45	139.427
83.19	65.354	89.66	78.394	95.71	140.543		
84.00	65.975	90.38	94.906	96.53	140.306		
84.81	66.689	90.96	128.898	97.35	140.075		

Table S3 Fractional melting of 2-MTHF[a]
(Molar mass = 86.1322 g·mol^{-1}, m_{vacuum} = 0.74959$_3$ g, T_m = 137.20 K, p^o = 101.3 kPa)

I					II					III				
T_i/K	Q_{input}/J	Q_{fus}/J	F_i	$1/F_i$	T_i/K	Q_{input}/J	Q_{fus}/J	F_i	$1/F_i$	T_i/K	Q_{input}/J	Q_{fus}/J	F_i	$1/F_i$ [a]
122.55	3.075				127.761	3.075				127.623	4.820			
124.45	6.150				129.566	6.149				130.549	9.640			
126.326	9.225				131.346	9.224				133.628	14.459			
128.18	12.299				133.094	12.298				136.902	19.280	4.821	0.091	11.000[b]
130.008	15.373				134.784	15.372				137.019	24.101	9.642	0.182	5.500
131.803	18.447				136.383	18.447	3.075	0.056	18.000[b]	137.069	28.922	14.463	0.273	3.667
133.566	21.521				136.869	21.522	6.150	0.111	9.000	137.097	33.743	19.284	0.364	2.750
135.352	24.595				136.974	24.597	9.225	0.167	6.000	137.116	38.564	24.105	0.455	2.200
136.859	27.670	3.075	0.059	17.000[b]	137.027	27.673	12.300	0.222	4.500	137.131	43.385	28.926	0.545	1.833
136.98	30.744	6.149	0.118	8.500	137.061	30.748	15.376	0.278	3.600	137.146	48.206	33.747	0.636	1.571
137.033	33.819	9.224	0.176	5.667	137.084	33.823	18.451	0.333	3.000	137.16	53.027	38.568	0.727	1.375
137.064	36.893	12.298	0.235	4.250	137.102	36.898	21.526	0.389	2.571	137.174	57.848	43.389	0.818	1.222
137.086	39.968	15.373	0.294	3.400	137.115	39.973	24.601	0.444	2.250	137.186	62.668	48.210	0.909	1.100[b]
137.102	43.042	18.447	0.353	2.833	137.131	43.048	27.676	0.500	2.000	137.195	67.488	53.029	1.000	1.000[b]
137.115	46.117	21.522	0.412	2.429	137.139	46.123	30.751	0.556	1.800	138.802	72.307			
137.125	49.192	24.597	0.471	2.125	137.148	49.198	33.826	0.611	1.636	141.073	77.126			
137.137	52.266	27.671	0.529	1.889	137.157	52.273	36.901	0.667	1.500	143.332	81.943			
137.145	55.341	30.746	0.588	1.700	137.165	55.348	39.976	0.722	1.385	145.583	86.761			
137.152	58.416	33.821	0.647	1.545	137.174	58.423	43.051	0.778	1.286					
137.16	61.490	36.895	0.706	1.417	137.183	61.498	46.126	0.833	1.200					
137.168	64.565	39.970	0.765	1.308	137.192	64.573	49.201	0.889	1.125[b]					
137.175	67.640	43.045	0.824	1.214	137.201	67.648	52.276	0.944	1.059[b]					
137.183	70.714	46.119	0.882	1.133[b]	137.21	70.722	55.350	1.000	1.000[b]					
137.19	73.789	49.194	0.941	1.062[b]	137.768	73.796								
137.196	76.863	52.268	1.000	1.000[b]	139.217	76.870								
137.907	79.936				140.664	79.944								
139.356	83.009				142.107	83.017								
140.802	86.082													
142.244	89.155													

[a] Notation: T_i/K is the equilibrium temperature; Q_{input}/J is the heat introduced; Q_{fus}/J is the melted heat; F_i is the fraction of the melted sample; $1/F_i$ is the reciprocal fraction of the melted sample; this data were described by a linear dependence of the equilibrium temperature of fusion, T_i, on the reciprocal fraction of the sample melted: $T_i/\mathrm{K} = [(T_1/\mathrm{K}) - (T_m)/\mathrm{K}] \cdot (1/F_i) + (T_m/\mathrm{K})$, here, T_m = 137.20$_2$ K is the melting temperature of the pure sample, $[T_1 - T_m]$ = -0.034 K is a depression of the T_m value; T_1 denotes the melting temperature of the completely melted sample (F_i = 1). Linear regression coefficient equals r^2= 0.940.
[b] These points are not used in the construction of a linear relationship, $T_i = f(1/F_i)$ (Fig. 1S), in order to exclude experimental points with unstable equilibrium at the beginning and end of the melting process.

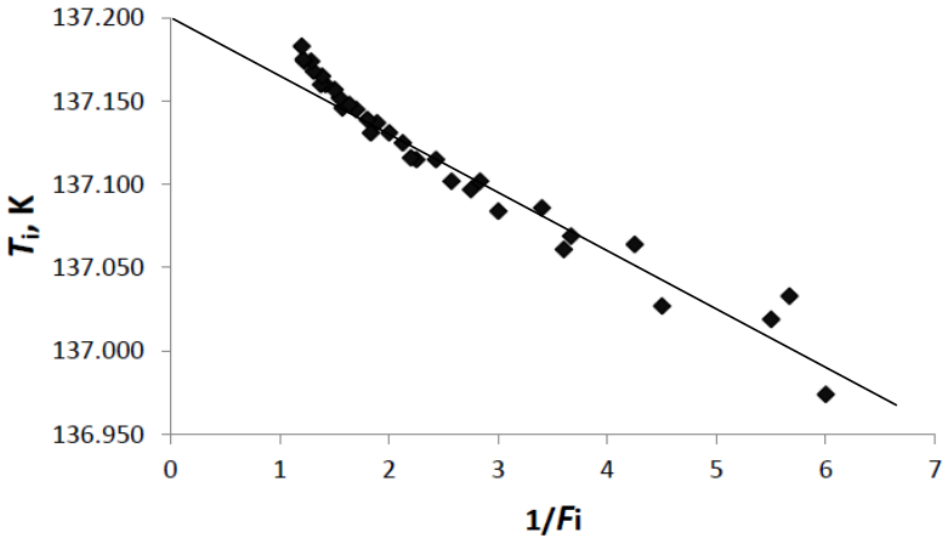

Fig. S1 The dependence of the equilibrium temperature of fusion, T_i, on the reciprocal fraction of the sample melted, $1/F_i$, for three experiments (Table S3)

Table S4 Molar enthalpy, $\Delta_{cr}^{liq}H_m^\circ(T_m)$, and entropy, $\Delta_{cr}^{liq}S_m^\circ(T_m)$, of fusion of 2-MTHF [a]
(Molar mass = 86.132_2 g·mol^{-1}, m_{vac} = 0.74959_3 g, T_m = 137.20 K) [b]

T_{in} [c]	T_f [c]	ΔH_{tot} [d]	$\Delta_{T_{in}}^{T_m}H_m^\circ(cr)$ [e]	$\Delta_{T_m}^{T_f}H_m^\circ(liq)$ [e]	$\Delta_{T_{in}}^{T_f}H_{emp}$ [f]	$\Delta_{cr}^{liq}H_m^\circ(T_m)$	$\Delta_{cr}^{liq}S_m^\circ(T_m)$
K		J·mol^{-1}					J·K^{-1}·mol^{-1}
122.628	144.849	11079.0	1284.3	1014.9	2396.9	6383.0	46.523
125.372	147.446	11077.5	1052.3	1359.0	2409.8	6256.4	45.601
124.194	146.899	11158.2	1152.5	1286.5	2469.1	6250.2	45.555
119.911	144.81	11239.8	1509.4	1009.7	2667.8	6052.8	44.117
121.842	145.945	11238.6	1349.9	1160.1	2601.2	6127.4	44.660
					Mean	6203 [g]	45.21 [g]

[a] $\Delta_{cr}^{liq}H_m^\circ(T_m)$ value was calculated from the equation: $\Delta_{cr}^{liq}H_m^0(T_m)/(\mathrm{J\cdot mol^{-1}}) = \Delta_{tot}H - \Delta_{T_{in}}^{T_m}H_m(cr) - \Delta_{T_m}^{T_f}H_m(liq) - \Delta_{T_{in}}^{T_f}H_{emp}$

[b] The molar mass of the compound was calculated using relative atomic masses recommended by IUPAC (J. Meija, T. B. Coplen, M. Berglund, W. A. Brand, P. De Bièvre, M. Gröning, N. E. Holden, J. Irrgeher, R. D. Loss, T. Walczyk, T. Prohaska, *Pure Appl. Chem*., 2016, **88**, 265–291); standard uncertainties *u* are *u*(Molar mass) = 0.002 g·mol^{-1}; $u(m_{vac}) = 5\cdot10^{-5}$ g; the standard uncertainty of *u* is $u(T_m)$ = 0.02 K.

[c] T_{in} and T_f are the initial and final temperatures; the standard uncertainty of *u* is $u(T)$ = 0.02 K.

[d] ΔH_{tot} is the energy required to heat one mol of substance from T_{in} to T_f; the standard uncertainty of *u* is $u(\Delta H_{tot})$ = 22 J·mol^{-1}.

[e] $\Delta_{T_{in}}^{T_m}H_m(cr) = \int_{T_{in}}^{T_m} C_{p,m}(cr)dT$ and $\Delta_{T_m}^{T_f}H_m(liq) = \int_{T_m}^{T_f} C_{p,m}(liq)dT$ are the heating enthalpies calculated by the extrapolation to T_m based on the experimental values of the heat capacities of the crystal (120.56 -124.61 K) and liquid (142.31-149.65 K) obtained outside the pre-melting region.

[f] $\Delta_{T_{in}}^{T_f}H_{emp}$ is enthalpy of heating of an empty calorimeter from T_{in} to T_f.

[g] Combined expanded uncertainties U_c are $U_c(\Delta_{T_{in}}^{T_m}H_m^\circ(cr))$ = 2.5 J·mol^{-1}, $U_c(\Delta_{T_m}^{T_f}H_m^\circ(liq))$ = 2.3 J·mol^{-1}, $U_c(\Delta_{cr}^{liq}H_m^\circ(T_m))$ = 240 J·mol^{-1} and $U_c(\Delta_{cr}^{liq}S_m^\circ(T_m))$ = 1.7 J·K^{-1}·mol^{-1} (0.95 level of confidence).

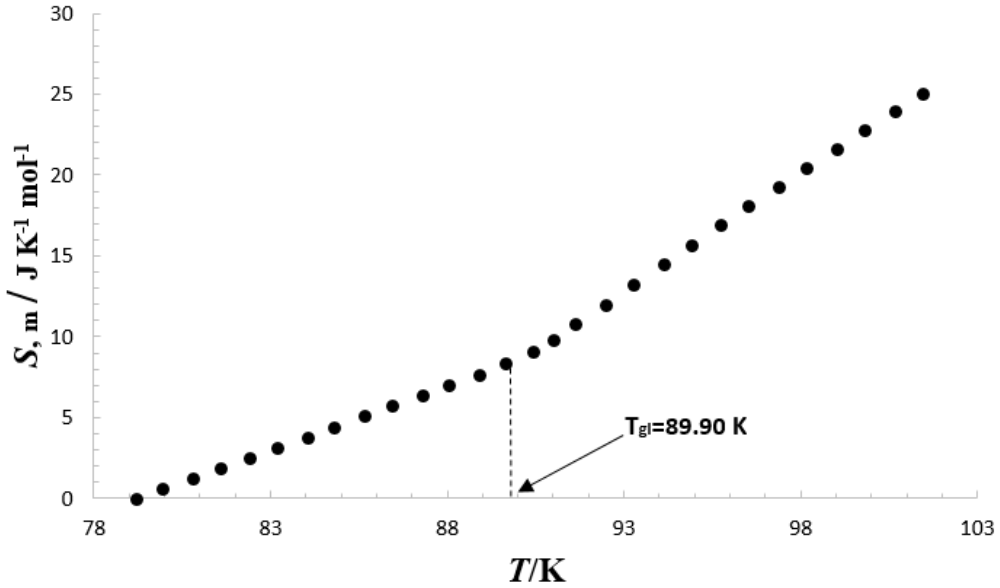

Fig. S2 Entropy of 2-MTHF in the G-transition region

Table S5 Coefficients of eqn (3) which approximate the experimental heat capacity of 2-MTHF

Temperature interval/ K[a]	*Crystal*			
	I	II	III	IV
	11.51-48.75	45.06-65.27	62.29-122.99	120.56-125.42
A0	3.89725333077217E+00	-1.62757605224256E+03	3.43724395363671E+02	1.2555542452758E+01
A1	-1.36588820011171E+00	1.64700592500753E+02	-1.78103645849477E+01	5.7995605854033E-01
A2	1.55386207614214E-01	-6.51942455403247E+00	4.03235628570565E-01	
A3	-4.40308474541435E-03	1.28236965673044E-01	-4.34226515175575E-03	
A4	5.76529958912840E-05	-1.24770662801790E-03	2.29021588730433E-05	
A5	-2.96566172813736E-07	4.80319036420137E-06	-4.72849263583557E-08	
RMSD[b]	0.030772029	0.071015286	0.042114827	0.077179892
RMSD,%	0.14	0.16	0.07	0.09

Table S5 (continued)

Temperature interval/ K[a]	*Liquid*		
	V	VI	VII
	148.5-159.11	150.13-232.79	222.95-354.02
A0	1.43652244180467E+02	-2.85856282119621E+02	-7.88414706460763E+02
A1	-7.60596543084794E-02	1.28628706218326E+01	1.84817447614847E+01
A2		-1.51395617217667E-01	-1.47157230843916E-01
A3		8.60734182800276E-04	5.76746974287415E-04
A4		-2.38691166056473E-06	-1.10516346087730E-06
A5		2.61256124085452E-09	8.32681566722261E-10
RMSD[b]	0.057037987	0.057778228	0.172360925
RMSD,%	0.04	0.04	0.11

[a] Adjacent temperature ranges overlap. The temperatures at which the difference between the heat capacity values calculated by the two neighboring polynomials is minimal in the entire overlap interval were chosen as the crosslinking temperatures of these ranges.
[b] RMSDs are the root-mean-square deviations between the calculated by eqn (3) and experimental $C_{p,m}$ values.

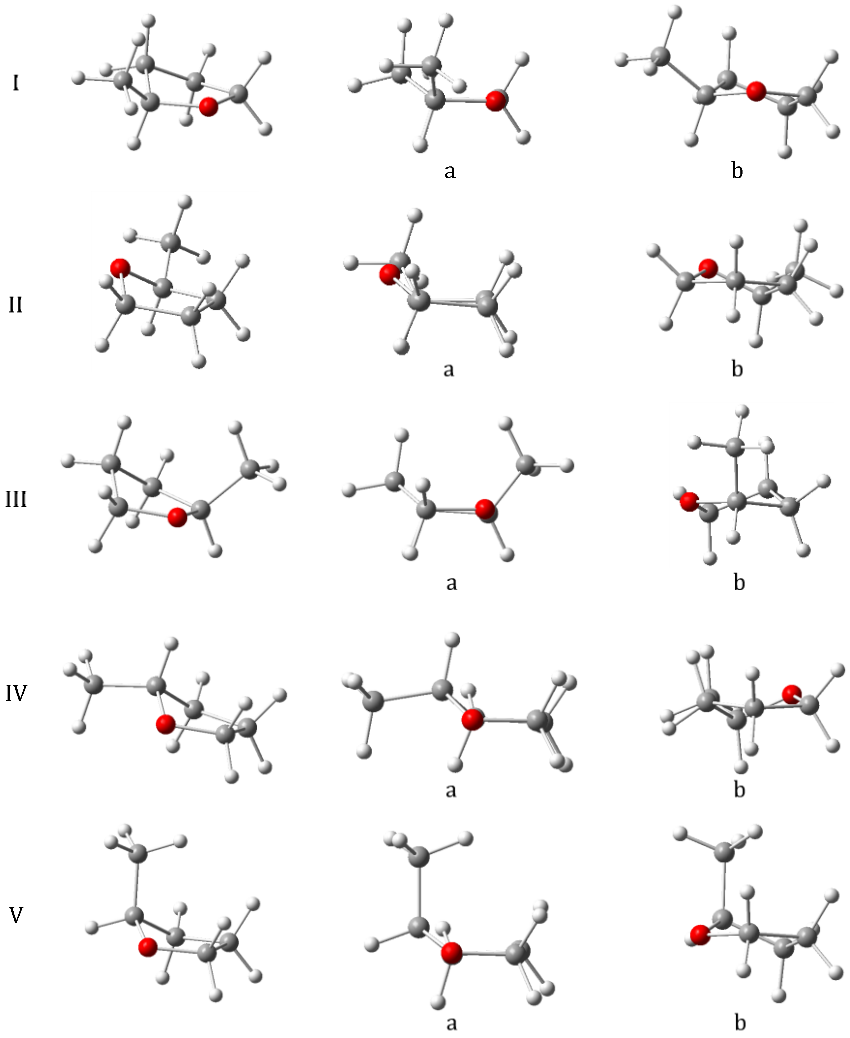

Fig. S3 Optimized structures of five stable conformers of 2-MTHF from different perspectives which are similar to a more or less distorted envelope (a) or twist (b) configuration

Table S6 Atomic coordinates of the stable conformers and transition states of 2-MTHF calculated at different levels of theory

Atom	x, Å	y, Å	z, Å	Atom	x, Å	y, Å	z, Å
B3LYP-D3(BJ)/def2-TZVPP							
	Conformer I				Conformer II		
C1	0.737821	0.056801	-0.397634	O1	0.010910	-1.110547	-0.180328
C2	-0.118967	1.196011	0.148501	C2	0.729242	-0.010380	0.378120
C3	-1.535211	0.665822	-0.080366	C3	-0.102890	1.220810	-0.007546
C4	-1.363288	-0.836560	0.171050	C4	-1.544593	0.675308	-0.112540
H5	0.790584	0.138641	-1.492444	C5	-1.365713	-0.847620	0.053279
H6	0.078063	1.324763	1.215496	C6	2.149320	-0.027648	-0.138810
H7	0.075150	2.143995	-0.351497	H7	0.732287	-0.115450	1.473628
H8	-2.278716	1.115551	0.575857	H8	-0.004430	2.023278	0.722281
H9	-1.843435	0.848800	-1.110888	H9	0.236980	1.602860	-0.970654
H10	-1.603964	-1.100787	1.204734	H10	-2.198714	1.082160	0.657363
H11	-1.983776	-1.445970	-0.489291	H11	-1.984461	0.917614	-1.078311
O12	0.016157	-1.137849	-0.064101	H12	-1.637655	-1.160524	1.069249
C13	2.139504	-0.038013	0.165165	H13	-1.943713	-1.438011	-0.655164
H14	2.651923	-0.916046	-0.227133	H14	2.714833	0.807390	0.276889
H15	2.719424	0.846183	-0.104902	H15	2.651177	-0.954191	0.138632
H16	2.106327	-0.116707	1.252575	H16	2.154216	0.056426	-1.226302
	TS1						
C1	0.793363	0.107389	-0.528206				
C2	-0.193161	1.262348	-0.273237				
C3	-1.435696	0.576902	0.342495				
C4	-1.089600	-0.921737	0.304952				
H5	1.292623	0.208399	-1.492291				
H6	0.234704	2.017677	0.384529				
H7	-0.451682	1.751375	-1.210831				
H8	-1.633364	0.914148	1.358859				
H9	-2.324346	0.786122	-0.250304				
H10	-0.774240	-1.276804	1.292533				
H11	-1.911263	-1.550206	-0.034122				
O12	-0.029699	-1.058485	-0.634623				
C13	1.839610	-0.046909	0.569312				
H14	2.432783	-0.945799	0.403305				
H15	2.510200	0.814013	0.579038				
H16	1.375078	-0.119002	1.554373				
B3LYP/cc-pVTZ							
	Conformer I				Conformer II		
C1	0.735546	0.051875	-0.390087	O1	0.015287	-1.110298	-0.176773
C2	-0.117334	1.198351	0.151049	C2	0.729368	-0.003707	0.376493
C3	-1.538611	0.671473	-0.071064	C3	-0.105884	1.221278	-0.024646
C4	-1.372166	-0.842964	0.137638	C4	-1.550262	0.674829	-0.094356
H5	0.769709	0.116317	-1.487725	C5	-1.366004	-0.853045	0.043909
H6	0.084755	1.334458	1.216195	C6	2.154793	-0.027310	-0.132157
H7	0.075086	2.143627	-0.355617	H7	0.728867	-0.097294	1.473492
H8	-2.270644	1.106308	0.608002	H8	0.003457	2.042374	0.683149
H9	-1.864915	0.884601	-1.090090	H9	0.219386	1.579215	-1.002340

H10	-1.674103	-1.151710	1.141767	H10	-2.178629	1.068865	0.703580
H11	-1.951733	-1.425290	-0.583287	H11	-2.023580	0.934261	-1.039909
O12	0.021427	-1.134655	-0.017941	H12	-1.653623	-1.188359	1.048437
C13	2.149506	-0.036937	0.147227	H13	-1.932692	-1.430549	-0.684555
H14	2.650380	-0.924349	-0.239382	H14	2.721489	0.808599	0.280572
H15	2.728348	0.838822	-0.151277	H15	2.651838	-0.953200	0.156715
H16	2.140050	-0.096338	1.236372	H16	2.169118	0.046199	-1.220415
		TS1					
C1	0.796085	0.099260	-0.525593				
C2	-0.190371	1.259618	-0.292393				
C3	-1.424795	0.589716	0.358103				
C4	-1.108282	-0.917673	0.295548				
H5	1.299324	0.188627	-1.489275				
H6	0.240279	2.040040	0.333969				
H7	-0.461710	1.715384	-1.243556				
H8	-1.579075	0.919320	1.384758				
H9	-2.330974	0.824894	-0.197604				
H10	-0.824962	-1.300889	1.282505				
H11	-1.937357	-1.520015	-0.073212				
O12	-0.031389	-1.064684	-0.625470				
C13	1.844836	-0.047532	0.573757				
H14	2.432883	-0.951488	0.415522				
H15	2.522037	0.808653	0.571690				
H16	1.385835	-0.107395	1.562436				
			MP2/6-311++G(d,p)				
		Conformer II				Conformer IV	
O1	-0.003504	-1.124612	-0.155861	O1	0.027108	-1.108270	-0.183581
C2	0.735567	-0.035988	0.402867	C2	0.714659	0.012678	0.369738
C3	-0.114209	1.227642	0.127245	C3	-0.104702	1.204854	-0.120850
C4	-1.500283	0.664857	-0.263139	C4	-1.548313	0.682890	0.000348
C5	-1.366709	-0.816826	0.101770	C5	-1.365945	-0.856905	0.009478
C6	2.119504	-0.021985	-0.211684	C6	2.157260	-0.026315	-0.086155
H7	0.807630	-0.193286	1.491437	H7	0.661630	-0.038792	1.471710
H8	-0.164143	1.863988	1.015135	H8	0.075426	2.114435	0.458816
H9	0.320321	1.816393	-0.685980	H9	0.154567	1.394665	-1.167685
H10	-2.326636	1.154219	0.258765	H10	-2.008158	1.021894	0.932716
H11	-1.663950	0.761488	-1.339359	H11	-2.176927	1.018420	-0.827607
H12	-1.594750	-0.978577	1.167337	H12	-1.687951	-1.282002	0.969742
H13	-1.982670	-1.485796	-0.501967	H13	-1.900974	-1.361852	-0.797408
H14	2.712352	0.794689	0.212080	H14	2.701039	0.838426	0.306563
H15	2.636085	-0.966095	-0.019885	H15	2.648299	-0.937281	0.265518
H16	2.040579	0.123671	-1.293032	H16	2.198427	-0.004959	-1.179067
		Conformer V				TS1	
C1	-1.760357	-0.053724	0.634865	C1	0.786761	0.117854	-0.534080
C2	-0.800284	0.022101	-0.547805	C2	-0.202241	1.267658	-0.252399
C3	0.158600	1.211340	-0.472620	C3	-1.451252	0.557324	0.325661
C4	1.244681	0.687458	0.482494	C4	-1.054461	-0.928716	0.325380
C5	1.185657	-0.843487	0.273926	H5	1.284494	0.234171	-1.501010
O6	0.071932	-1.110436	-0.589846	H6	0.225044	1.994640	0.443924
H7	-1.218682	-0.023612	1.585887	H7	-0.451171	1.792629	-1.177788

H8	-2.330204	-0.985731	0.594157	H8	-1.704690	0.907994	1.329378
H9	-2.460098	0.788416	0.611810	H9	-2.317454	0.720900	-0.319555
H10	-1.364226	0.002879	-1.485282	H10	-0.683990	-1.237777	1.312226
H11	-0.323007	2.126216	-0.116691	H11	-1.866197	-1.597476	0.032886
H12	0.578634	1.396123	-1.465578	O12	-0.028206	-1.052806	-0.654513
H13	1.009281	0.948846	1.517572	C13	1.830688	-0.041195	0.566927
H14	2.230571	1.096343	0.249858	H14	2.422610	-0.945078	0.399779
H15	1.055984	-1.372721	1.225545	H15	2.501649	0.824125	0.574983
H16	2.076514	-1.235403	-0.223661	H16	1.358381	-0.109227	1.552351
		TS2					
O1	0.085059	-1.149918	-0.487349				
C2	-1.797975	-0.051613	0.607597				
C3	1.269735	-0.788939	0.241081				
C4	1.204646	0.728455	0.494843				
C5	0.136303	1.187271	-0.506639				
C6	-0.797671	-0.023200	-0.542979				
H7	-1.288786	0.030184	1.573133				
H8	-2.353792	-0.992768	0.593481				
H9	-2.507797	0.777865	0.517732				
H10	1.314019	-1.360682	1.174442				
H11	2.131129	-1.062080	-0.377009				
H12	0.887223	0.940671	1.519370				
H13	2.170082	1.213962	0.333518				
H14	-0.372042	2.107744	-0.206942				
H15	0.579929	1.333926	-1.496420				
H16	-1.330667	-0.101319	-1.495930				
MP2(Full)/cc-pVTZ							
		Conformer I				Conformer III	
C1	0.729730	0.067500	-0.402703	C1	-1.948036	-0.034008	0.433996
C2	-0.124645	1.182741	0.164040	C2	-0.767751	-0.067342	-0.503900
C3	-1.522028	0.653020	-0.105234	C3	0.118510	1.176596	-0.408261
C4	-1.342378	-0.824453	0.201375	C4	1.253672	0.710521	0.491586
H5	0.786787	0.175101	-1.488181	C5	1.395158	-0.722438	0.030903
H6	0.052249	1.261557	1.234727	O6	0.062254	-1.178585	-0.137341
H7	0.076471	2.143532	-0.296190	H7	-1.613706	0.193907	1.441979
H8	-2.293085	1.115061	0.500014	H8	-2.441538	-0.999740	0.448293
H9	-1.774521	0.793612	-1.152219	H9	-2.664929	0.720664	0.123135
H10	-1.527339	-1.026622	1.255182	H10	-1.112505	-0.220367	-1.524588
H11	-1.991854	-1.462171	-0.390013	H11	-0.423297	2.030447	-0.017073
O12	0.018219	-1.134364	-0.096950	H12	0.512538	1.441166	-1.384901
C13	2.116356	-0.035236	0.170032	H13	0.951558	0.729701	1.534331
H14	2.633265	-0.897394	-0.237092	H14	2.160408	1.293525	0.378681
H15	2.691582	0.856063	-0.064058	H15	1.882642	-1.373395	0.746961
H16	2.058490	-0.145261	1.248373	H16	1.941485	-0.767207	-0.914033
		Conformer IV				TS1	
O1	0.024711	-1.099450	-0.198631	C1	0.783700	0.120070	-0.533409
C2	0.710634	0.006522	0.369360	C2	-0.200733	1.258687	-0.261515
C3	-0.101532	1.198614	-0.100319	C3	-1.430122	0.553271	0.335805
C4	-1.538314	0.677389	-0.021999	C4	-1.040797	-0.923550	0.321272
C5	-1.354045	-0.849604	0.027098	H5	1.292573	0.236886	-1.484352

C6	2.140149	-0.025316	-0.088363	H6	0.223088	1.995872	0.411762
H7	0.659312	-0.059697	1.461416	H7	-0.463754	1.760974	-1.184777
H8	0.064751	2.088564	0.496271	H8	-1.663850	0.897548	1.336483
H9	0.174024	1.412715	-1.128691	H9	-2.300776	0.720736	-0.286292
H10	-2.037291	1.030637	0.873160	H10	-0.668746	-1.236901	1.297103
H11	-2.127184	0.988340	-0.875974	H11	-1.852202	-1.582712	0.039118
H12	-1.644909	-1.236039	1.004510	O12	-0.028217	-1.043509	-0.663207
H13	-1.913837	-1.377682	-0.734604	C13	1.802291	-0.042412	0.574181
H14	2.683595	0.827202	0.307302	H14	2.388598	-0.941542	0.417252
H15	2.629840	-0.934074	0.243813	H15	2.470939	0.813172	0.599426
H16	2.172658	0.010003	-1.172814	H16	1.313830	-0.112355	1.541930
		TS3					
O1	-0.005650	-1.153816	-0.085240				
C2	0.762871	-0.045955	0.383718				
C3	-0.133552	1.196543	0.224551				
C4	-1.433215	0.636575	-0.352535				
C5	-1.364092	-0.806070	0.101964				
C6	2.039457	0.004547	-0.410101				
H7	0.988289	-0.203147	1.439373				
H8	-0.311067	1.664437	1.186826				
H9	0.322340	1.933968	-0.426869				
H10	-2.317415	1.159505	-0.006446				
H11	-1.413110	0.664905	-1.436754				
H12	-1.643926	-0.891672	1.155751				
H13	-1.969455	-1.489736	-0.480375				
H14	2.683666	0.798608	-0.044532				
H15	2.571490	-0.937807	-0.335578				
H16	1.810670	0.191800	-1.454858				
CCSD(T)/def2-SVP							
		Conformer I				Conformer III	
O1	0.018324	-1.129035	0.184281	C1	-1.973739	0.087958	0.555421
C2	0.729191	0.080114	0.459201	C2	-0.790839	-0.061738	-0.391696
C3	-0.128161	1.184116	-0.164416	C3	0.187092	1.135773	-0.363044
C4	-1.539276	0.661487	0.116762	C4	1.312508	0.631807	0.548557
C5	-1.354314	-0.850445	-0.084243	C5	1.337537	-0.847212	0.168131
C6	2.142017	-0.047104	-0.081978	O6	-0.026786	-1.205763	0.015798
H7	0.771886	0.239707	1.560058	H7	-1.618841	0.331251	1.571344
H8	0.074709	2.179583	0.263741	H8	-2.538260	-0.856827	0.604721
H9	0.059901	1.226053	-1.253215	H9	-2.651480	0.889084	0.214328
H10	-1.818891	0.879966	1.162342	H10	-1.164788	-0.231416	-1.420982
H11	-2.314270	1.088316	-0.540324	H11	-0.293978	2.060753	-0.004771
H12	-1.997158	-1.449294	0.586294	H12	0.584610	1.330267	-1.374402
H13	-1.586427	-1.144562	-1.126528	H13	1.034368	0.740371	1.611338
H14	2.722395	0.866659	0.130904	H14	2.274689	1.144338	0.386181
H15	2.653941	-0.905330	0.381761	H15	1.785182	-1.501355	0.934369
H16	2.111578	-0.208345	-1.172364	H16	1.897721	-0.992684	-0.780662

Table S7 The relative energies of stable conformers and the barrier heights for transition states of 2-MTHF determined by different computational methods

Conformer	Lowest frequency cm^{-1}	E_e[a] Hartree	ΔE_e[b] $kJ{\cdot}mol^{-1}$	ZPE[c] Hartree	$H^\circ_{298} - H^\circ_0$[c] Hartree	ΔE_{tot}[d] $kJ{\cdot}mol^{-1}$
		B3LYP-D3(BJ)/def2-TZVPP				
I	46	-271.9019516	0.00	0.1415373	0.0073159	0.00[e]
II	41	-271.9019913	-0.10	0.1417221	0.0073110	0.37[e]
TS1 (I---II)	-73	-271.8998993	5.39	0.1418330	0.0064022	3.77[e]
TS (int rot CH_3, conf I)	-227	-271.8972401	12.37	0.1413563	0.0067395	10.38
		MP2(full)/cc-pVTZ				
I	49	-271.3024802	0.00	0.1411119	0.0072993	0.00[f]
IV	48	-271.3023861	0.25	0.1411623	0.0073505	0.51
III	54	-271.3022429	0.62	0.1412998	0.0071774	0.80[f]
TS1 (I---III)	-100	-271.3001363	6.15	0.1412605	0.0063864	4.15[f]
TS3 (I---IV)	-31	-271.3021142	0.96	0.1412447	0.0063419	-1.20
TS (int rot CH_3, conf I)	-241	-271.2971842	13.90	0.1408174	0.0067438	11.67
		MP2/6-311++G(d,p)				
IV	60	-271.0350446	0.00[g]	0.1410077	0.0073348	0.00
V	74	-271.0333831	4.36[g]	0.1411520	0.0072533	4.53
II	5	-271.0346869	0.94	0.1409436	0.0073345	0.77
TS1 (IV---II)	-96	-271.0324232	6.88[g]	0.1410926	0.0063833	4.61
TS2 (IV---V)	-63	-271.0333428	4.47	0.1409463	0.0064494	1.98
TS (int rot CH_3, conf IV)	-239	-271.0298407	13.66	0.1406448	0.0067266	11.11

[a] Electronic energy determined from quantum chemical calculation.
[b] Relative energies calculated without any corrections.
[c] ZPE and ($H^\circ_{298} - H^\circ_0$) corrections scaled by the factors of 0.981, 0.961, and 0.962 for B3LYP-D3(BJ)/def2-TZVPP, MP2(Full)/cc-pVTZ, and MP2/6-311++G(d,p) methods, respectively.
[d] Relative energies calculated including ZPE and thermal corrections.
[e] These values of conformer energies and barrier height give the coefficients V_1 = 0.37 $kJ{\cdot}mol^{-1}$ and V_2 = 3.58 $kJ{\cdot}mol^{-1}$ for pseudorotational potential.
[f] These values of conformer energies and barrier height give the coefficients V_1 = 0.80 $kJ{\cdot}mol^{-1}$ and V_2 = 3.75 $kJ{\cdot}mol^{-1}$ for pseudorotational potential.
[g] These values of conformer energies and barrier height give the coefficients V_1 = 4.36 $kJ{\cdot}mol^{-1}$ and V_2 = 4.46 $kJ{\cdot}mol^{-1}$ for pseudorotational potential.

Table S8 Ideal gas thermodynamic properties of 2-MTHF[a]

T K	$C^{\circ}_{p,m}(T)$ J·K^{-1}·mol^{-1}	$S^{\circ}_{m}(T)$ J·K^{-1}·mol^{-1}	$-[G^{\circ}_{m}(T) - H^{\circ}_{m}(0)]/T$ J·K^{-1}·mol^{-1}	$H^{\circ}_{m}(T) - H^{\circ}_{m}(0)$ kJ·mol^{-1}	$\Delta_f H^{\circ}_{m}$ kJ·mol^{-1}	$\Delta_f S^{\circ}_{m}$ J·K^{-1}·mol^{-1}	$\Delta_f G^{\circ}_{m}$ kJ·mol^{-1}
0	0	0	∞	0	-189.88	0.00	-189.88
100	54.79	260.29	215.71	4.46	-202.18	-334.70	-168.71
150	63.71	284.19	234.72	7.42	-207.28	-376.22	-150.85
200	74.34	303.90	249.61	10.86	-212.34	-405.28	-131.28
250	88.18	321.92	262.28	14.91	-217.47	-428.21	-110.42
298.15[b]	**103.88**	**338.77**	**273.28**	**19.53**	**-222.30**	**-445.88**	**-89.36**
300	104.51	339.41	273.68	19.72	-222.48	-446.48	-88.54
350	121.94	356.83	284.32	25.38	-227.16	-460.92	-65.84
400	139.24	374.25	294.47	31.91	-231.42	-472.32	-42.50
450	155.70	391.61	304.30	39.29	-235.25	-481.34	-18.64
500	170.99	408.81	313.89	47.46	-238.65	-488.52	5.61
600	197.89	442.44	332.53	65.94	-244.28	-498.80	55.01
700	220.44	474.69	350.55	86.89	-248.51	-505.35	105.24
800	239.49	505.40	368.01	109.92	-251.52	-509.40	155.99
900	255.69	534.57	384.91	134.70	-253.49	-511.72	207.06
1000	269.53	562.24	401.27	160.97	-254.58	-512.88	258.30
1100	281.40	588.50	417.11	188.54	-254.94	-513.23	309.61
1200	291.61	613.44	432.44	217.20	-254.70	-513.02	360.93
1300	300.40	637.13	447.28	246.81	-253.97	-512.45	412.21
1400	307.99	659.68	461.65	277.24	-252.87	-511.63	463.41
1500	314.57	681.16	475.58	308.37	-251.46	-510.66	514.53

[a] These thermodynamic properties were calculated using molecular parameters from Table 6 and experimental value of $\Delta_f H^{\circ}_{m}$(2-MTHF, g, 298.15 K) = 222.3 ± 2.0 kJ·mol^{-1} from ref. 16.

[b] The contributions to the thermodynamic functions of the different motions at 298.15 K are summarized in Table S9.

Table S9 Contributions to the thermodynamic functions of the different types of motion at 298.15 K for 2-MTHF

Motion	$C^{\circ}_{\mathrm{p},m}(T)$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$S^{\circ}_{m}(T)$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$-[G^{\circ}_{m}(T) - H^{\circ}_{m}(0)]/T$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$H^{\circ}_{m}(T) - H^{\circ}_{m}(0)$ $\mathrm{kJ\cdot mol^{-1}}$
Translational	20.786	164.427	143.641	6.197
Rotational	12.472	109.943	97.471	3.718
Vibrational	55.682	28.095	9.192	5.636
CH_3 internal rotational	8.990	10.174	4.470	1.701
Psedorotational	5.952	26.130	18.504	2.274
Total	103.882	338.769	273.278	19.526