

Liquid Organic Hydrogen Carriers: Thermophysical and Thermochemical Studies of Benzyl- and Dibenzyl-toluene Derivatives.

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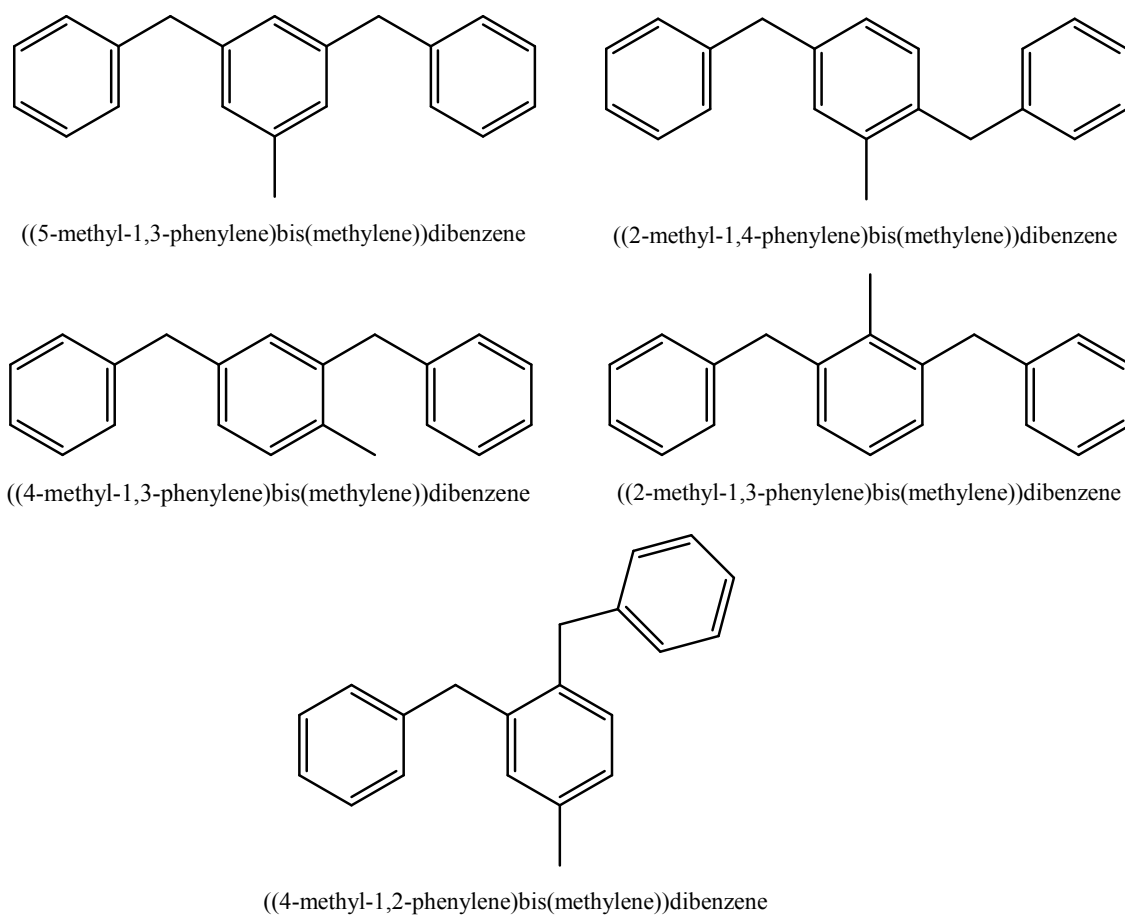


Figure S1. Possible structure isomers of dibenzyltoluene being present in Marlotherm SH[®].

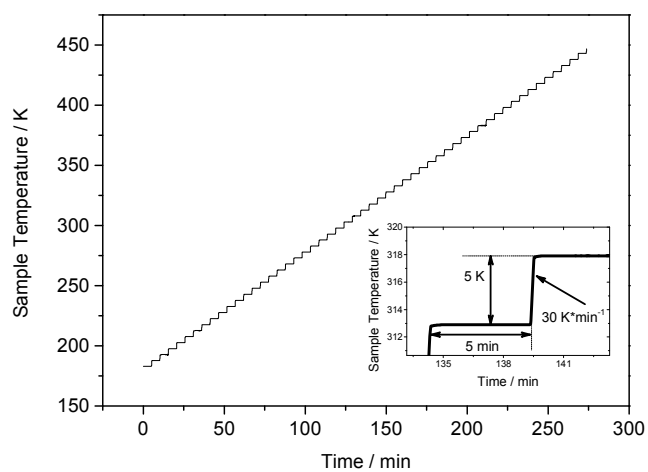


Figure S2. Temperature-time profile, consisting of a sequence of isotherm-heating segments. Inset shows closer view on one period.

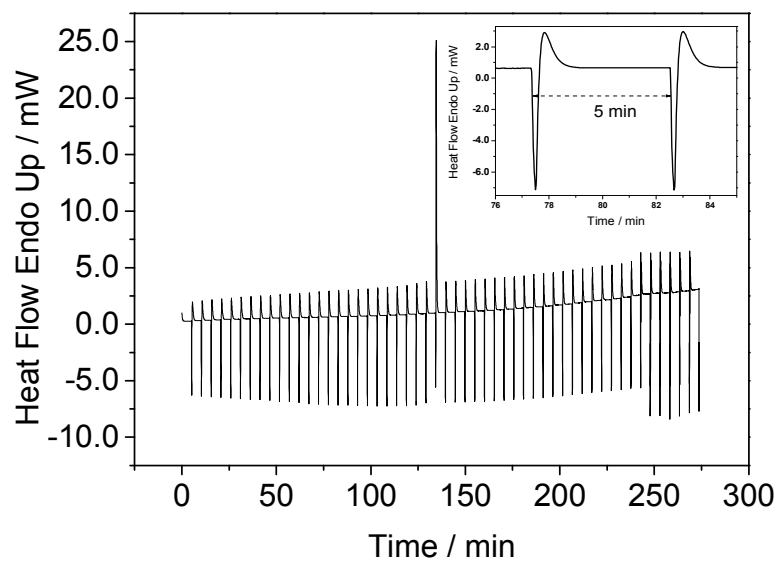


Figure S3. The resulting heat flow corresponding to the temperature time program from Figure 1. In the inset a zoomed step.

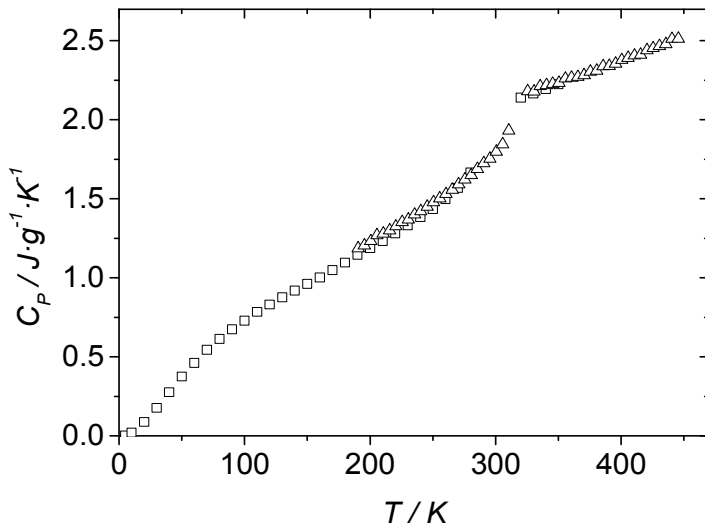


Figure S4. Test results for the heat capacity measurements for the methyl stearate:

□ - [1], Δ - this work.

**Table S1. Results of the Heat Capacity Measurements for the Marlotherm Fluids,
(in $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$)**

0H-MLH		12H-MLH		0H-MSH		18H-MSH	
T/K	$c_p/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	T/K	$c_p/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	T/K	$c_p/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	T/K	$c_p/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$
190.5	1.30112	190.53	1.38127	190.45	0.82118	190.45	0.89295
195.5	1.29401	195.53	1.41500	195.45	0.84856	195.45	0.91808
200.5	1.31422	200.53	1.41807	200.45	0.87985	200.45	0.93645
205.5	1.31322	205.53	1.45165	205.45	0.90253	205.45	0.94988
210.5	1.32374	210.53	1.46033	210.45	0.92588	210.45	0.97583
215.5	1.33767	215.53	1.46248	215.45	0.95540	215.45	0.99699
220.5	1.33766	220.53	1.49204	220.45	1.05049	220.45	1.01780
225.5	1.34632	225.53	1.51174	225.45	1.39662	225.45	1.06160
230.5	1.35643	230.53	1.51165	230.45	1.41940	230.45	1.25217
235.5	1.38086	235.53	1.53309	235.45	1.43175	235.45	1.37519
240.5	1.37799	240.53	1.56379	240.45	1.43005	240.45	1.37700
245.5	1.39085	245.53	1.56495	245.45	1.45088	245.45	1.40248
250.5	1.40772	250.53	1.58225	250.45	1.46278	250.45	1.40145
255.5	1.41100	255.53	1.60962	255.45	1.47042	255.45	1.41687
260.5	1.46963	260.53	1.62212	260.45	1.48080	260.45	1.44240
265.5	1.44711	265.53	1.62434	265.45	1.50133	265.45	1.44606
270.5	1.45709	270.53	1.64935	270.45	1.50843	270.45	1.45661
275.5	1.46194	275.53	1.66239	275.45	1.51358	275.45	1.48373
280.5	1.48603	280.53	1.66691	280.45	1.53239	280.45	1.49307
285.5	1.49655	285.53	1.69209	285.45	1.53284	285.45	1.50197
290.5	1.50015	290.53	1.71967	290.45	1.54871	290.45	1.53121
295.5	1.51894	295.53	1.72281	295.45	1.56128	295.45	1.53047
300.5	1.52412	300.53	1.74299	300.45	1.56821	300.45	1.54244
305.5	1.54119	305.53	1.77324	305.45	1.58292	305.45	1.56696
310.5	1.56774	310.53	1.76447	310.45	1.59733	310.45	1.58405
315.5	1.57924	315.53	1.79619	315.45	1.61064	315.45	1.59029
320.5	1.58787	320.53	1.82600	320.45	1.62146	320.45	1.60614
325.5	1.59962	325.53	1.82758	325.45	1.63909	325.45	1.63527
330.5	1.62684	330.53	1.85254	330.45	1.65432	330.45	1.63963
335.5	1.63799	335.53	1.88107	335.45	1.66412	335.45	1.66099
340.5	1.64985	340.53	1.89140	340.45	1.68564	340.45	1.69044
345.5	1.67933	345.53	1.89955	345.45	1.70181	345.45	1.68629
350.5	1.67865	350.53	1.93459	350.45	1.70408	350.45	1.71167
355.5	1.69044	355.53	1.95820	355.45	1.72439	355.45	1.74433
360.5	1.71524	360.53	1.95757	360.45	1.74353	360.45	1.74919
365.5	1.72636	365.53	1.97620	365.45	1.74901	365.45	1.76355
370.5	1.72358	370.53	2.00780	370.45	1.76237	370.45	1.79484
375.5	1.75424	375.53	2.00794	375.45	1.78669	375.45	1.80266
380.5	1.76208	380.53	2.03238	380.45	1.78876	380.45	1.81288
385.5	1.77949	385.53	2.06407	385.45	1.78950	385.45	1.85487
390.5	1.80027	390.53	2.05495	390.45	1.82821	390.45	1.85214
395.5	1.80892	395.53	2.10422	395.45	1.82035	395.45	1.86488
400.5	1.81441	400.53	2.08904	400.45	1.83398	400.45	1.89256

Table S2. Formula, Density ρ ($T = 293$ K), Specific Heat Capacity c_p ($T = 298.15$ K), and Expansion Coefficients $(\delta V/\delta T)_p$ of the Materials Used in the Present Study

Compound	Formula	ρ^a g·cm ⁻³	c_p^b J·K ⁻¹ ·g ⁻¹	$10^{-6} \cdot (\delta V/\delta T)_p$ dm ³ ·K ⁻¹
0H-MLH	C ₁₄ H ₁₄	0.996	1.54	1.0
12H-MLH	C ₁₄ H ₂₆	0.876	1.93	1.0
0H-MSH	C ₂₁ H ₂₀	1.044	1.56	1.0
18H-MSH	C ₂₁ H ₃₈	0.913	1.55	1.0
polyethylene ^c	CH _{1.93}	0.92	2.53	0.1
cotton ^d	CH _{1.774} O _{0.887}	1.50	1.67	0.1

^a From Table S3.

^b From Table S1.

^c Energy of combustion $\Delta_c u^\circ$ (polyethylene) = -46357.3 J·g⁻¹; $u(\Delta_c u^\circ) = 3.6$ J·g⁻¹.

^d Energy of combustion $\Delta_c u^\circ$ (cotton) = -16945.2 J·g⁻¹; $u(\Delta_c u^\circ) = 4.2$ J·g⁻¹.

Table S3. Densities of the (Di)Benzyltoluene Derivatives at Different Temperatures

T/K	$\rho_{0HMSH}^a / \text{g} \cdot \text{cm}^{-3}$	$\rho_{18\text{-MSH}} / \text{g} \cdot \text{cm}^{-3}$	$\rho_{0H\text{-MLH}}^a / \text{g} \cdot \text{cm}^{-3}$	$\rho_{12H\text{-MLH}} / \text{g} \cdot \text{cm}^{-3}$
273.15	1.058		1.01	
293.15	1.044	0.91342	0.996	0.87620
298.15		0.91014		
303.15		0.90694		0.86921
313.15	1.03	0.90061	0.98	0.86224
323.15		0.89422		0.85531
333.15	1.016	0.88783	0.966	0.84837
343.15		0.88145		0.84138
353.15	1.001		0.95	0.83446
373.15	0.987		0.936	
393.15	0.973		0.92	
413.15	0.958		0.906	
433.15	0.944		0.89	
453.15	0.93		0.873	
473.15	0.915		0.856	

^a From Sasol^{26, 27}

Table S4. Dynamic Viscosities of the (Di)benzyltoluene Derivatives

T	η_{0H-MSH}^a	η_{0H-MLH}^a	T	$\eta_{18H-MSH}$	T	$\eta_{12H-MLH}$
K	mPa·s		K	mPa·s	K	mPa·s
273.15	340	8.38	282.91	1520	284.99	9.12
			287.74	790	287.60	8.18
293.15	49	3.98	293.15	425	292.76	6.75
			298.39	242	297.89	5.62
			303.22	155	303.00	4.80
313.15	17	2.55	313.55	72.1	313.22	3.63
			323.69	38.2	323.42	2.86
333.15	8.2	1.84	334.03	22.4	333.63	2.33
			344.56	14.4	343.83	1.96
353.15	4.7	1.43	354.89	9.99	354.04	1.67
			365.24	7.31	364.24	1.45
373.15	3.1	1.03	373.25	6.03	373.92	1.28
			385.38	4.43	384.35	1.15
393.15	2.2	0.79	393.18	3.89	394.45	1.04
			403.52	3.17	404.65	0.94
413.15	1.7	0.64	413.85	2.65	414.85	0.85
			423.38	2.36	423.35	0.78
433.15	1.3	0.54	433.98	2.07		
			444.35	1.80		
453.15	1.1	0.47				

^aFrom Sasol^{27,28}**Table S5. Surface Tension of the (Di)benzyltoluene Derivatives at Different Temperatures**

T	σ_{0H-MSH}	T	σ_{0H-MLH}	T	$\sigma_{18H-MSH}$	T	$\sigma_{12H-MSH}$
K	mN·m ⁻¹	K	mN·m ⁻¹	K	mN·m ⁻¹	K	mN·m ⁻¹
297.35	41.6	298.35	37.2	298.63	35.1	296.24	31.8
308.08	40.5	308.22	36.3	308.16	33.7	307.68	30.6
318.14	39.3	318.12	35.4	318.17	32.7	317.99	29.8
328.32	37.9	327.89	34.5	328.24	31.8	327.84	28.9

Table S6. Results for Combustion Experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for 0H-MLH^a

m (substance) /g	0.31126	0.262765	0.368431	0.273448	0.425874	0.258725
m^i (cotton) /g	0.001106	0.00096	0.001082	0.000914	0.001098	0.001029
m'' (polyethylene) /g	0.363193	0.389782	0.348547	0.385405	0.306709	0.401358
ΔT_c /K	2.00047	1.94826	2.11303	1.96335	2.1439	1.9727
$(\epsilon_{\text{calor}}) \cdot (-\Delta T_c)$ /J	-29790.2	-29012.6	-31466.2	-29237.4	-31926	-29376.6
$(\epsilon_{\text{cont}}) \cdot (-\Delta T_c)$ /J	-32.55	-31.89	-34.87	-32.3	-35.13	-32.37
$\Delta U_{\text{decomp HNO}_3}$ /J	47.18	47.18	53.75	47.78	52.56	48.38
ΔU_{corr} /J	11.11	10.53	12.13	10.73	12.65	10.65
$-m^i \cdot \Delta_c u^i$ /J	18.74	16.27	18.33	15.49	18.61	17.44
$-m'' \cdot \Delta_c u''$ /J	16836.65	18069.24	16157.7	17866.34	14218.2	18605.87
$\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	-41473.4	-41486.7	-41416.7	-41431.5	-41465.5	-41459.6
$-\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	41455.6 \pm 10.8					

^a The definition of symbols assigned according to ref.¹⁴ is as follows: m (substance), m^i (cotton) and m'' (polyethylene) are, respectively, the mass of compound burnt, the mass of fuse (cotton), and the mass of the polyethylene bag used in each experiment; masses were corrected for buoyancy; V (bomb) = 0.32 dm³ is the internal volume of the calorimetric bomb; p^i (gas) = 3.00 MPa is the initial oxygen pressure in the bomb; m^i (H₂O) = 1.00 g is the mass of water added to the bomb for dissolution of combustion gases; $\epsilon_{\text{calor}} = (14891.55 \pm 0.95) \text{ J} \cdot \text{K}^{-1}$ is the energy equivalent of the calorimeter; $\Delta T_c = T^f - T^i + \Delta T_{\text{corr}}$ is the corrected temperature rise from initial temperature T^i to final temperature T^f , with the correction ΔT_{corr} for heat exchange during the experiment; ϵ_{cont} is the energy equivalents of the bomb contents in their initial ϵ_{cont}^i and final states ϵ_{cont}^f ; the contribution for the bomb content is calculated with $(\epsilon_{\text{cont}}) \cdot (-\Delta T_c) = (\epsilon_{\text{cont}}^i) \cdot (T^i - 298.15) + (\epsilon_{\text{cont}}^f) \cdot (298.15 - T^f + \Delta T_{\text{corr}})$. $\Delta U_{\text{decomp HNO}_3}$ is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states.

Table S7. Results for Combustion Experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for 12H-MLH^a

m (substance) /g	0.269927	0.339253	0.256365	0.291792	0.289056	0.253473
m^i (cotton) /g	0.001054	0.001	0.000814	0.00112	0.001101	0.001232
m'' (polyethylene) /g	0.300483	0.297831	0.329959	0.304501	0.303549	0.308743
ΔT_c /K	1.76626	1.97147	1.81701	1.84614	1.83442	1.74185
$(\epsilon_{\text{calor}}) \cdot (-\Delta T_c)$ /J	-26302.4	-29358.2	-27058.1	-27491.9	-27317.4	-25938.8
$(\epsilon_{\text{cont}}) \cdot (-\Delta T_c)$ /J	-28.77	-32.86	-30.04	-30.61	-30.31	-28.58
$\Delta U_{\text{decomp HNO}_3}$ /J	44.79	47.18	47.78	48.38	44.79	44.79
ΔU_{corr} /J	7.36	8.38	7.68	7.77	7.73	7.29
$-m^i \cdot \Delta_c u^i$ /J	17.86	16.95	13.79	18.98	18.66	20.88
$-m'' \cdot \Delta_c u''$ /J	13929.58	13806.64	15296.01	14115.84	14071.71	14312.49
$\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	-45684.9	-45723.7	-45727.2	-45688.4	-45682.6	-45693
$-\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	45700.0 \pm 8.2					

^a For the definition of symbols see Table S6; $\epsilon_{\text{calor}} = 14891.55 \pm 0.95 \text{ J} \cdot \text{K}^{-1}$.

Table S8. Results for Combustion Experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for 0H-MSH^a

m (substance) /g	0.242118	0.278037	0.278037	0.367052	0.265265	0.201418	0.275426
m' (cotton) /g	0.001028	0.001281	0.001281	0.001231	0.000996	0.001131	0.001139
m'' (polyethylene) /g	0.396955	0.418865	0.418865	0.333016	0.394507	0.420208	0.342922
ΔT_c /K	1.90848	2.07636	2.07636	2.05471	1.96569	1.86841	1.83229
$(\epsilon_{\text{calor}}) \cdot (-\Delta T_c)$ /J	-28420.3	-30920.2	-30920.2	-30597.8	-29272.1	-27823.6	-27285.7
$(\epsilon_{\text{cont}}) \cdot (-\Delta T_c)$ /J	-31.33	-34.61	-34.61	-33.75	-32.3	-30.29	-29.53
$\Delta U_{\text{decomp HNO}_3}$ /J	44.2	47.78	47.78	47.78	50.17	48.98	45.39
ΔU_{corr} /J	10.36	11.55	10.44	12.03	10.8	9.76	10.1
$-m' \cdot \Delta_c u'$ /J	17.42	21.71	21.71	20.86	16.88	19.16	19.3
$-m'' \cdot \Delta_c u''$ /J	18401.76	19417.45	19417.45	15437.72	18288.28	19479.71	15896.94
$\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	-41210.7	-41204.5	-41208.5	-41174.3	-41235.4	-41189.1	-41185.1
$-\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	41201.1 \pm 7.6						

^a For the definition of symbols see Table S6; $\epsilon_{\text{calor}} = 14891.55 \pm 0.95 \text{ J} \cdot \text{K}^{-1}$.

Table S9. Results for Combustion Experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for the 18H-MSH^a

m (substance) /g	0.27784	0.260305	0.230754	0.29964	0.172472	0.165202	0.154428
m' (cotton) /g	0.000856	0.000994	0.00092	0.001121	0.001174	0.001188	0.000979
m'' (polyethylene) /g	0.311356	0.359349	0.30179	0.316087	0.342155	0.361092	0.360739
ΔT_c /K	1.82015	1.91549	1.64578	1.90178	1.59445	1.63064	1.59725
$(\epsilon_{\text{calor}}) \cdot (-\Delta T_c)$ /J	-27100.5	-28519.9	-24504.2	-28315.8	-23739.9	-24278.7	-23781.6
$(\epsilon_{\text{cont}}) \cdot (-\Delta T_c)$ /J	-30.15	-31.43	-26.73	-31.55	-25.75	-26.49	-25.85
$\Delta U_{\text{decomp HNO}_3}$ /J	49.57	50.77	43.6	48.98	43	42.41	42.7
ΔU_{corr} /J	7.78	8.35	6.92	8.19	6.72	6.95	6.77
$-m' \cdot \Delta_c u'$ /J	14.5	16.84	15.59	19	19.89	20.13	16.59
$-m'' \cdot \Delta_c u''$ /J	14433.62	16658.45	13990.17	14652.95	15861.38	16739.25	16722.89
$\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	-45440.3	-45396.4	-45393.3	-45448.7	-45425.6	-45377.7	-45448.6
$-\Delta_c u^\circ$ (liq) /($\text{J} \cdot \text{g}^{-1}$)	45418.7 \pm 11.1						

^a For the definition of symbols see Table S6; $\epsilon_{\text{calor}} = 14889.1 \pm 1.0 \text{ J} \cdot \text{K}^{-1}$.

Table S10. Experimental Vapor Pressures of 18H-MSH Measured by the Static Method

T	p	$u(p)$ ^a	$\Delta_1^g H_m^\circ(T)$ ^b
K	Pa	Pa	$\text{kJ}\cdot\text{mol}^{-1}$
343.50	0.426	0.016	82.37
346.01	0.515	0.018	82.05
346.01	0.485	0.017	82.05
348.50	0.619	0.020	81.73
351.00	0.762	0.024	81.41
351.00	0.720	0.023	81.41
353.49	0.910	0.028	81.10
355.99	1.115	0.033	80.78
355.99	1.069	0.032	80.78
358.49	1.323	0.038	80.46
360.99	1.622	0.046	80.14
360.99	1.565	0.044	80.14
363.48	1.993	0.055	79.82
363.48	1.914	0.053	79.82
365.98	2.339	0.063	79.50
365.98	2.269	0.062	79.50
368.47	2.831	0.076	79.18
368.48	2.745	0.074	79.18
370.97	3.346	0.089	78.86
370.98	3.259	0.086	78.86
373.47	3.996	0.105	78.54
373.47	3.902	0.103	78.54

^a Uncertainties of vapor pressures were calculated according to the following equation:
 $u(p/\text{Pa}) = 0.0005 + 0.005(p/\text{Pa})$

^b The vaporization enthalpy $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (88.2 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}$ was calculated using eqs 8 and 10

Table S11. Vapor pressures of Marlotherm Fluids from Sasol

$$\begin{aligned} & \text{0H-MLH} \\ & \Delta_1^g H_m^\circ(298.15 \text{ K}) = (73.3 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1} \\ \ln(p/\text{Pa}) = & \frac{325.81}{R} - \frac{98264.58}{R \cdot (T/\text{K})} - \frac{83.6}{R} \ln\left(\frac{T/\text{K}}{298.15}\right) \end{aligned}$$

T/K	p/Pa
373.2	220
393.2	600
413.2	1500
433.2	3300

453.2	6800
473.2	13100
493.2	23700
513.2	40800
533.2	67200
553.2	106100
573.2	161900
593.2	239400
613.2	344200
633.2	482600

0H-MSH

$$\Delta_1^g H_m^\circ (298.15 \text{ K}) = (112.8 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{421.13}{R} - \frac{148901.18}{R \cdot (T/\text{K})} - \frac{121.1}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$$

T/K	p/Pa
413.2	10
433.2	50
453.2	170
473.2	500
493.2	1200
513.2	2700
533.2	5400
553.2	9800
573.2	20000
593.2	31500
613.2	56000
633.2	86000

Table S12. Vapor Pressures of (4-Methylphenyl)-Phenylmethane (as one of the Main Components of the 0H-MLH). Data Measured by the Transpiration Method [2]

$$\Delta_1^g H_m^\circ (298.15 \text{ K}) = (69.9 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{315.51}{R} - \frac{94788.79}{R \cdot (T/\text{K})} - \frac{83.6}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$$

T/K	p/Pa
293.2	0.484
298.2	0.733
303.2	1.183
308.2	1.833
313.2	2.854
318.2	4.307
323.2	6.456
328.2	9.445
333.2	13.88

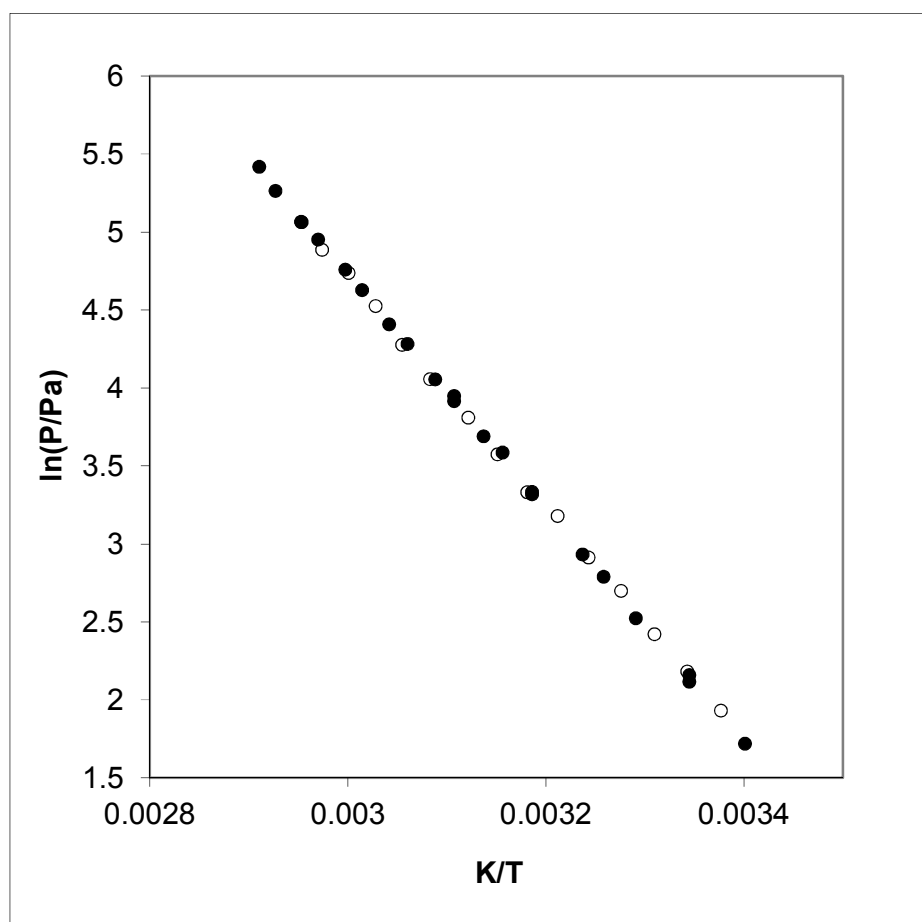


Figure S5. Comparison of vapor pressures of (4-Methylphenyl)-Phenylmethane (as one of the Main Components of the 0H-MLH and those for 0H-MLH from Sasol: ● - data from Sasol; ○ - data from the transpiration method [2].

Table S13. Group Additivity Values for the Calculation of Enthalpies of Vaporization and Enthalpies of Formation of Marlotherm Fluids at 298.15 K (in kJ·mol⁻¹)

GAV	$\Delta_f^g H_m^\circ$ [3]	$\Delta_f H_m^\circ$ (g) [4]
CH ₃ [C]	6.33	-42.05
CH ₂ [2C]	4.52 ^a	-21.46
CH[3C]	1.24 ^b	-9.04
C[4C]	-2.69	-1.26
CH ₂ [2C _B]	4.52 ^c	-19.42 ^d
C _B H[2C _B]	5.65	13.72
C _B [C, 2C _B]	3.44	23.51

^a For cyclic increment the value CH₂[2C] = 5.52 kJ·mol⁻¹ was evaluated from the vaporization enthalpy of cyclohexane [5]

^b For cyclic increment the value CH[3C] = 1.51 kJ·mol⁻¹ was evaluated from the vaporization enthalpy of methylcyclohexane [5]

^c Evaluated from the vaporization enthalpy of the diphenylmethane from ref. [6]

^d Evaluated from the enthalpy of formation of the diphenylmethane from ref. [7]

Table S14. Data used for Correction of the Enthalpies of Formation Calculated with the G3MP2 (Using the Atomization Procedure), kJ·mol⁻¹

Compounds	$\Delta_f H_m^\circ$ (g) AT	$\Delta_f H_m^\circ$ (g) exp
biphenyl [6]	165.3	180.3±3.3
di-phenyl-methane [2,7]	150.2	165.0±1.5
1,2-diphenylbenzene [8]	253.5	279.5±1.3
1,4-diphenylbenzene [8]	252.5	272.9±2.6
1,3-diphenylbenzene [8]	252.0	279.9±2.0

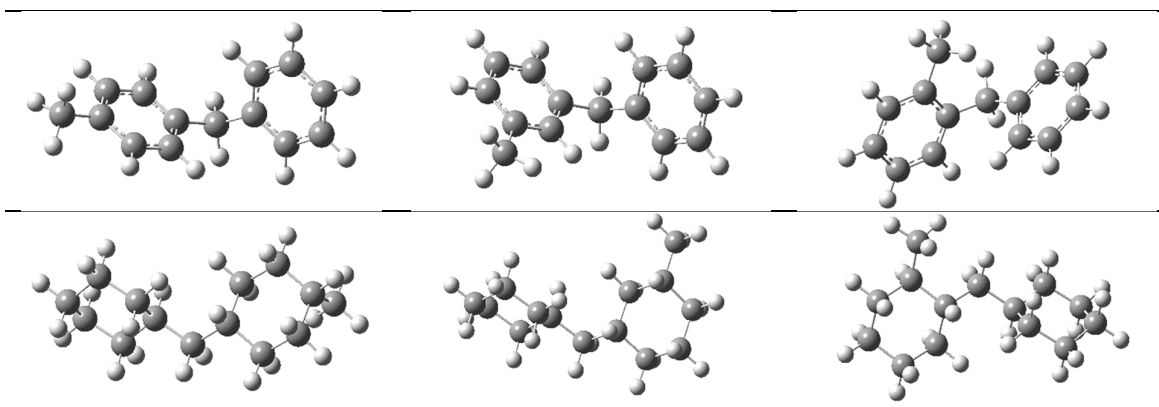


Figure S6. Optimized structure of isomers constituted 0H-MLH and 12H-MLH

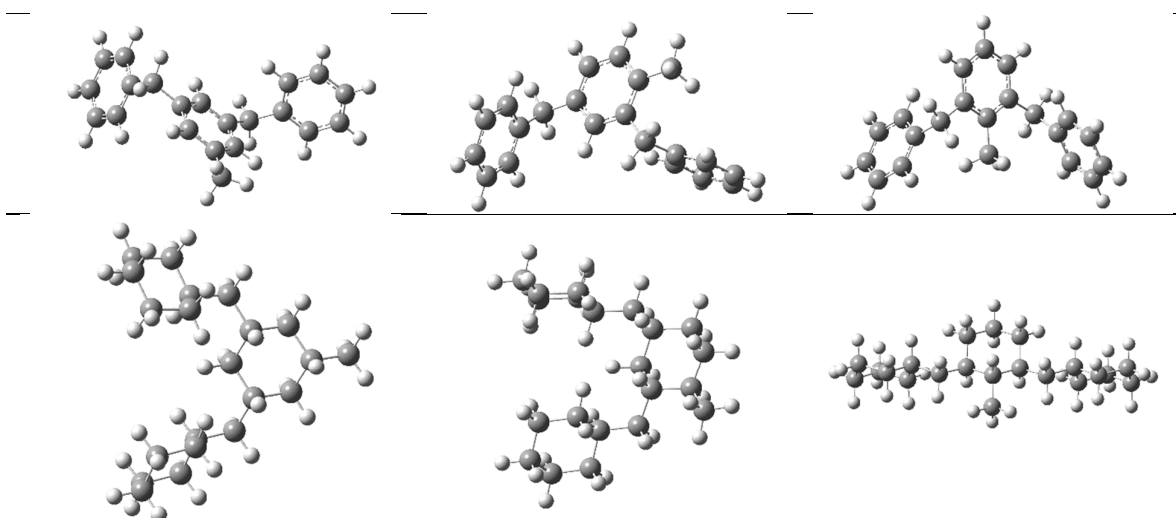


Figure S7. Optimized structure of isomers constituted 0H-MSH and 18H-MSH

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