Thermodynamics of Ethyl Decanoate

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The heat capacity of ethyl decanoate in the interval of (5 to 370) K was measured in an adiabatic calorimeter. The triple-point temperature $T_{\text{fus}} = (253.60 \pm 0.02)$ K and the enthalpy of fusion $\Delta_{\text{cr}}^{\text{liq}}H_{\text{m}}^{\circ} = (32.29 \pm 0.04)\ \text{kJ}\cdot\text{mol}^{-1}$ were determined. The vapor pressure over liquid ethyl decanoate in the interval of (294 to 323) K was measured by the Knudsen method. The calorimetric enthalpy of vaporization $\Delta_{\text{liq}}^{\text{g}}H_{\text{m}}^{\circ}(304.8\ \text{K}) = (69.9 \pm 0.7)\ \text{kJ}\cdot\text{mol}^{-1}$ was determined in an MID-200 Calvet-type microcalorimeter. The standard enthalpy of formation for liquid ethyl decanoate at 298.15 K $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq}) = (-682.7 \pm 2.4)\ \text{kJ}\cdot\text{mol}^{-1}$ was determined in a static bomb combustion calorimeter. From these data, the standard enthalpy of formation for gaseous ethyl decanoate was evaluated to be $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}) = (-612.2 \pm 2.4)\ \text{kJ}\cdot\text{mol}^{-1}$. The formation enthalpy was also calculated using quantum chemical methods via homodesmic reactions at different theory levels. The results are in excellent agreement with the experimental value.

Introduction

Ethyl decanoate ($C_{12}H_{24}O_2$, CASRN 110-38-3) is a widely used compound. It is contained in many fruits, such as banana, apple, cherry, and so on, and in some citrus, cacao, grape, watermelon, pear, pineapple, strawberry, plum, some nuts, and sea-buckthorn.[1] The light pleasant odor of the substance causes the odor of the majority of alcohol drinks (wine, brandy, whiskey).[2−6] Ethyl decanoate is a pheromone for the caddis fly (*Cheumatopsyche lepida*), some bugs (*Thamiaraea fuscicornis*, *Tramiathaea cornigera*, *Tramiathaea fuscicornis*), and bees and bumblebees (*Exoneura bicincta*, *Exoneura bicolor*, *Exoneura richardsoni*, *Bombus cyprarum*, *Bombus magnus*).[7] It is widely used in cosmetics as a fruit aromatizer and as part of perfume compositions.[8,9] In spite of such a wide use of this compound, its thermodynamic properties have not been sufficiently studied. The only paper has been devoted to the investigation of the thermodynamic properties of this compound.[10] In that paper, the liquid state formation enthalpy for ethyl decanoate was determined from the hydrolysis enthalpy, and its vapor pressure was measured in an ebulliometer. The analysis of the experimental results presented in the mentioned paper[10] is rather difficult due to incomplete description of the experimental procedures and unavailability of the primary experimental data. The investigation of the thermodynamic properties of this compound is necessary for justification of its synthesis and purification processes, as well as simulation of the process of ethyl decanoate dispersion in air when used as a pheromone. Moreover, this compound can be used as a reference substance in predicting schemes for thermodynamic properties of higher saturated fatty acid esters, which are the main components of liquid biodiesel fuels.

In the present work, the systematic study of the thermodynamic properties of ethyl decanoate in crystalline, liquid, and gaseous states including determination of heat capacity in the interval (5 to 370) K, enthalpies of phase transitions, enthalpies of formation in the liquid and gaseous states, vapor pressure, and vaporization enthalpy was carried out. The conformational contribution to the entropy of fusion was discussed.

Experimental Section

Sample. A commercial sample of ethyl decanoate (Fluka) with the stated mass fraction purity of 0.99 was dried over P_2O_5 for 2 months. The mass fraction purity of ethyl decanoate was found with a TSVET-800 chromatograph equipped with a flame ionization detector to be 0.995. A capillary column SUPELCOWAX-10, which is standard for the analysis of the esters of the higher fatty acids, of 60 m length and 0.53 mm diameter with 0.5 μm film thickness was used. The temperature of the column during the analysis was programmed to rise from (160 to 240) °C. The main impurities were the methyl and ethyl esters of other fatty acids. From the fractional melting experiments in an adiabatic calorimeter, the mole fraction purity of the sample was (0.984 ± 0.001).

Adiabatic Calorimetry. The heat capacity of ethyl decanoate under saturated vapor pressure (C_{s}) in the interval of (5 to 370) K and the fusion enthalpy were determined in a Termis TAU-10 adiabatic calorimeter. The apparatus and experimental procedures were described elsewhere.[11] The sample was loaded in the calorimetric container in a drybox. The uncertainty of the heat capacity measurements was ± 0.4 % in the main temperature interval of measurements.

Knudsen Method. The vapor pressure (p_{sat}) for ethyl decanoate in the interval of (294 to 323) K was measured by the integral Knudsen method. The apparatus and the experimental technique were described elsewhere.[12] The combined uncertainty of the measurements was established to be ± 5 %.

A nickel membrane with thickness $l = (50 \pm 1)\ \mu\text{m}$ and diameter $d = (0.1833 \pm 0.0004)$ mm was used in the effusion experiments.

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Table 1. Experimental Heat Capacities for Ethyl Decanoate ($M = 0.200318$ kg·mol^{-1})

T / K	C_s^a / J·K^{-1}·mol^{-1}	T / K	C_s^a / J·K^{-1}·mol^{-1}	T / K	C_s^a / J·K^{-1}·mol^{-1}	T / K	C_s^a / J·K^{-1}·mol^{-1}
Series 1							
Crystal							
130.37	189.7	159.59	214.4	187.04	236.4	214.52	261.2
132.31	191.5	161.55	215.9	189.00	238.0	216.49	263.3
134.25	193.3	163.50	217.4	190.96	239.7	218.46	265.4
136.19	195.0	165.46	218.9	192.93	241.4	220.42	267.6
138.13	196.6	167.42	220.4	194.89	243.1	222.39	270.0
140.08	198.3	169.38	222.0	196.85	244.7	224.36	272.5
142.02	200.0	171.34	223.6	198.81	246.5	226.33	275.1
143.97	201.6	173.30	225.1	200.77	248.3	228.29	277.8
145.92	203.3	175.26	226.6	202.74	249.9	230.26	280.8
147.87	205.0	177.23	228.3	204.70	251.8	232.23	284.0
149.82	206.5	179.19	229.8	206.66	253.6	234.19	287.3
151.77	208.2	181.15	231.3	208.63	255.4	236.16	291.1
153.72	209.7	183.11	233.1	210.59	257.3	238.11	296.8
155.68	211.2	185.07	234.7	212.56	259.1	240.07	303.0
157.63	212.8						
Series 2							
Crystal							
80.12	130.3	134.17	193.3	187.64	236.8	244.07	325.4
81.98	133.0	136.14	195.1	189.60	238.5	246.21	353.6
83.85	135.7	138.12	196.8	191.57	240.2	248.22	417.6
85.73	138.3	140.10	198.4	193.53	241.9	249.95	591.0
87.62	141.0	142.07	200.1	195.48	243.5	251.23	1085
89.51	143.6	144.06	201.8	197.44	245.2	252.01	2277
91.41	146.2	146.04	203.6	199.39	247.0	252.43	4498
93.31	148.8	148.02	205.3	201.35	248.7	252.66	7804
95.22	151.3	150.00	206.9	203.29	250.4	252.81	12043
97.14	153.8	151.98	208.5	205.24	252.1	252.91	16882
99.06	156.2	153.97	210.0	207.19	254.0	252.98	21501
100.98	158.7	155.95	211.5	209.14	255.7	253.04	24433
102.91	161.0	157.93	213.2	211.09	257.8	253.08	25205
104.84	163.3	159.92	214.8	213.04	259.7	253.12	29084
106.77	165.7	161.91	216.3	214.99	261.6	253.16	33371
108.71	167.9	163.89	217.8	216.93	263.7	253.19	38756
110.66	170.0	165.88	219.2	218.87	265.9	253.22	44814
112.60	172.2	167.86	220.8	220.81	268.3	253.24	51852
114.55	174.3	169.85	222.3	222.75	270.5	253.26	59055
116.50	176.4	171.83	223.9	224.69	272.9	253.28	67670
118.46	178.5	173.81	225.6	226.62	275.6	253.29	76555
120.41	180.4	175.79	227.1	228.54	278.3	253.31	88042
122.37	182.4	177.77	228.7	230.47	280.9	253.32	97883
124.33	184.3	179.74	230.3	232.58	284.3	253.33	116749
126.29	186.2	181.72	232.0	234.97	289.0	253.34	121233
128.26	188.0	183.69	233.6	237.29	294.1	253.35	127002
130.23	189.8	185.67	235.2	239.59	301.0	253.38	24262
132.19	191.6			241.85	310.4		
Liquid							
254.40	386.7	284.52	397.2	312.36	411.0	342.56	428.0
256.65	387.2	287.05	398.3	314.88	412.3	345.06	429.5
259.18	387.9	289.59	399.4	317.41	413.8	347.57	430.9
261.71	388.7	292.13	400.5	319.93	415.0	350.07	432.4
264.24	389.3	294.66	401.8	322.45	416.4	352.57	433.9
266.77	390.1	297.19	403.0	324.96	417.7	355.06	435.2
269.31	391.0	299.72	404.3	327.48	419.3	357.56	436.8
271.84	391.9	302.25	405.6	330.00	420.6	360.05	438.2
274.38	392.9	304.78	406.9	332.51	422.0	362.54	439.8
276.91	394.0	307.31	408.3	335.02	423.5	365.03	441.4
279.45	394.9	309.83	409.6	337.54	424.9	367.52	443.0
281.98	396.1			340.05	426.4		
Series 3							
Crystal							
180.73	230.9	194.53	242.6	206.25	253.2	219.87	267.5
182.71	232.5	196.49	244.4	208.20	255.2	221.82	269.7
184.69	234.2	198.44	246.2	210.15	257.0	223.76	272.3
186.66	235.8	200.40	247.8	212.10	259.0	225.69	274.9
188.63	237.5	202.35	249.5	214.05	261.0	227.62	277.6
190.60	239.3	204.30	251.3	215.99	263.2	229.55	280.1
192.56	240.9			217.93	265.3		
Liquid							
257.94	387.5	268.83	390.8	279.73	394.9	290.63	399.9
260.12	388.2	271.01	391.6	281.91	396.0	292.81	401.0
262.29	388.9	273.19	392.4	284.09	396.8	294.99	401.9
264.47	389.5	275.37	393.2	286.27	397.8	297.17	403.1
266.65	390.1	277.55	394.1	288.45	398.8		

Table 1.. Continued

T/K	C_s^a/J·K^{-1}·mol^{-1}	T/K	C_s^a/J·K^{-1}·mol^{-1}	T/K	C_s^a/J·K^{-1}·mol^{-1}	T/K	C_s^a/J·K^{-1}·mol^{-1}
Series 4							
Crystal							
181.61	231.8	195.42	243.3	207.14	254.0	220.75	268.4
183.59	233.4	197.38	245.0	209.09	255.7	222.68	270.8
185.57	235.1	199.33	246.7	211.04	257.6	224.61	273.3
187.54	236.7	201.28	248.3	212.98	259.7	226.54	276.1
189.52	238.4	203.24	250.1	214.93	261.7	228.46	278.4
191.49	240.0	205.19	252.0	216.87	263.9	242.20	1569
193.45	241.6			218.81	266.1		
Series 5							
Crystal							
191.61	240.1	201.46	248.6	211.71	258.4	221.86	269.6
193.58	241.8	203.52	250.4	213.75	260.3	223.88	272.1
195.54	243.5	205.57	252.3	215.78	262.5	225.89	274.9
197.50	245.2	207.62	254.3	217.81	264.8	227.90	277.8
199.46	246.8	209.67	256.4	219.84	267.1	229.89	280.6
Series 6							
Liquid							
255.37	387.0	282.36	396.2	308.07	408.7	335.78	424.0
257.10	387.4	284.34	397.1	310.05	409.6	337.76	425.1
258.76	387.7	286.32	397.8	312.02	410.7	339.74	426.2
260.59	388.3	288.30	398.7	314.00	411.8	341.72	427.3
262.56	388.9	290.28	399.7	315.98	412.8	343.70	428.7
264.54	389.4	292.26	400.7	317.96	414.0	345.68	429.8
266.52	390.0	294.23	401.6	319.94	415.0	347.66	431.0
268.50	390.8	296.21	402.5	321.92	416.3	349.64	432.2
270.48	391.6	298.19	403.4	323.90	417.2	351.62	433.3
272.46	392.3	300.16	404.4	325.88	418.2	353.61	434.3
274.44	393.0	302.14	405.5	327.86	419.2	355.59	435.6
276.42	393.8	304.12	406.5	329.84	420.3	357.57	436.8
278.40	394.5	306.09	407.7	331.82	421.5	359.55	438.0
280.38	395.3			333.80	422.7		
Series 7							
Crystal							
5.07	0.5226	10.32	4.888	22.70	26.32	51.09	82.94
5.31	0.6118	10.90	5.635	24.23	29.40	53.19	86.89
5.56	0.7121	11.48	6.424	25.75	32.51	55.30	90.74
5.81	0.8250	12.07	7.270	27.29	35.64	57.40	94.51
6.07	0.9558	12.66	8.157	28.39	37.87	59.52	98.20
6.36	1.118	13.26	9.088	29.64	40.42	61.64	101.8
6.69	1.318	13.87	10.03	31.35	43.96	63.76	105.3
7.02	1.545	14.47	11.01	33.22	47.77	65.89	108.8
7.35	1.796	15.09	12.05	35.10	51.55	68.01	112.1
7.70	2.073	15.81	13.35	36.98	55.32	70.14	115.4
8.04	2.376	16.64	14.88	38.87	59.03	72.38	118.9
8.40	2.709	17.48	16.38	40.75	62.74	74.72	122.4
8.76	3.071	18.32	17.92	42.73	66.71	77.07	125.9
9.12	3.453	19.16	19.47	44.82	70.83	79.44	129.4
9.48	3.859	20.01	21.05	46.90	74.94	81.80	132.9
9.85	4.299	21.18	23.32	49.00	78.99	84.15	136.2

The vapor pressures were calculated according to the equation[13]

$$p_{\text{sat}} = \left(\frac{1}{\alpha\gamma S_{\text{samp}}} + \frac{1}{k_{\text{W}} S_{\text{orif}}}\right)\frac{\Delta m}{\tau}\sqrt{\frac{2\pi RT}{M}} \qquad (1)$$

where p_{sat} is the vapor pressure for ethyl decanoate; Δm is the mass loss during the vacuum exposure time τ; S_{orif} is the cross sectional area of the orifice; T is the temperature of heat carrier in the thermostat where the copper block with effusion cell is placed; M is the vapor molar mass (M = 200.318 g·mol^{-1} according to IUPAC recommendations[14]); S_{samp} is the exposed sample surface; R = 8.31447 J·K^{-1}·mol^{-1}; and $\alpha\gamma$ is the product of the condensation coefficient (Langmuir) and the roughness coefficient for the sample surface. For liquid samples, the $\alpha\gamma$ is taken to be equal to unity. No correction for the discrepancy of wetting angle from 90° was introduced. So, the sample surface area was calculated as the cross-sectional area of the effusion cell.

The k_{W} transmission coefficient was determined according to Wahlbeck's theory of isotropy failure of a gas in the Knudsen cell.[15] The calculation technique was described earlier.[12] The effective diameter for the ethyl decanoate molecule (σ = 0.775 nm) was calculated from its excluded volume assuming the molecule to be spherical. The excluded volume was calculated in the Tinker 4.0 package[16] using the molecular geometry obtained in the quantum chemical calculations and the van der Vaals radii from ref 17.

Vaporization Calorimetry. For direct determination of vaporization enthalpy for ethyl decanoate, a differential Calvet type microcalorimeter MID-200 was used. The technique was established in our laboratory, and the special cell designed for these measurements was created.[18] In this study, the calorimeter was equipped with a more sensitive voltmeter having the measuring range between (1·10^{-9} and 2) V and relaxation time of (2 to 30) s. The sample of the compound of interest was placed into the hermetic cell made of stainless steel and covered

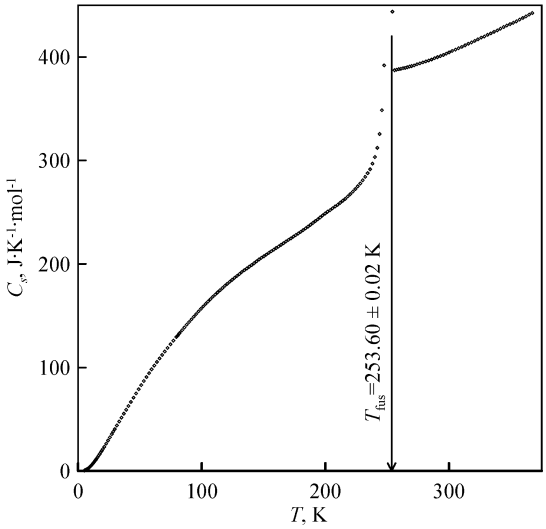


Figure 1. Temperature dependence of heat capacity of ethyl decanoate.

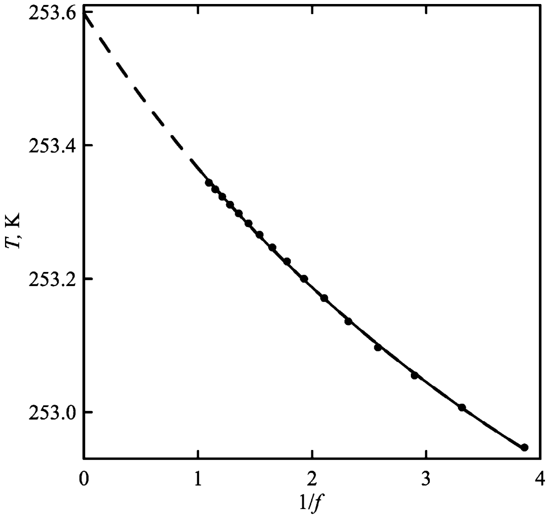


Figure 2. Results of the fractional-melting experiments for ethyl decanoate.

Table 2. Determination of the Molar Enthalpy of Fusion for Ethyl Decanoate

T_{start} / K	T_{end} / K	Q / $\text{J}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{liq}}H_{\text{m}}^{\circ}$ / $\text{J}\cdot\text{mol}^{-1}$
210.00	255.68	45281	32267[a]
210.00	256.90	45805	32318
210.00	254.89	44982	32273
210.00	254.62	44904	32300
Average			(32290 ± 38)

[a] From the fractional melting experiments.

with nickel foil. After preliminary thermostatting of the cell, the foil was punctured with a special rod, and the thermal flow caused by the evaporation of the sample was recorded. The calorimeter was calibrated in experiments with naphthalene and *n*-undecane recommended in ref 19. The uncertainty of measurements of the enthalpies of vaporization was estimated to be ± 1 %.

The enthalpy of vaporization was obtained according to the equation

$$\Delta_{\text{liq}}^{\text{g}}H_{\text{m}}^{\circ} = K^{-1}\cdot M\cdot m^{-1}\cdot \int_{\tau=0}^{\tau} \Delta E\cdot \text{d}\tau \qquad (2)$$

where m is the vacuum mass of the sample; K is the calorimetric constant of the cell; ΔE is the difference of the potentials of thermocouples, which corresponds to the temperature imbalance between the cell and the thermostat of the calorimeter at the time τ; $\int_{\tau=0}^{\tau}\Delta E\cdot \text{d}\tau$ is the total signal value recorded during the experiment; and M is the molar mass of ethyl decanoate.

Table 3. Thermodynamic Properties of Ethyl Decanoate in the Condensed State

T / K	$C_{p,\text{m}}^{\circ}$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^{\text{T}}H_{\text{m}}^{\circ}/T$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^{\text{T}}S_{\text{m}}^{\circ}$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-\Delta_0^{\text{T}}G_{\text{m}}^{\circ}/T$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
		Crystal		
5	0.498	0.109	0.134	0.026
10	4.477	1.107	1.439	0.332
15	11.92	3.406	4.583	1.177
20	21.04	6.664	9.249	2.585
25	30.97	10.52	15.00	4.477
30	41.18	14.78	21.55	6.767
35	51.36	19.28	28.66	9.381
40	61.27	23.91	36.17	12.26
45	71.20	28.61	43.96	15.34
50	80.91	33.36	51.97	18.60
60	98.99	42.82	68.35	25.53
70	115.2	52.03	84.85	32.82
80	130.2	60.87	101.2	40.35
90	144.3	69.36	117.4	48.01
100	157.4	77.52	133.3	55.75
110	169.3	85.34	148.8	63.51
120	180.0	92.79	164.0	71.25
130	189.6	99.87	178.8	78.96
140	198.3	106.6	193.2	86.61
150	206.8	113.0	207.2	94.19
160	214.7	119.1	220.8	101.7
170	222.5	125.0	234.0	109.1
180	230.5	130.6	247.0	116.4
190	238.8	136.1	259.7	123.6
200	247.4	141.4	272.1	130.7
210	256.7	146.7	284.4	137.7
220	266.7	151.9	296.6	144.7
230	277.5	157.1	308.7	151.5
240	288.9	162.4	320.7	158.3
250	301.2	167.7	332.8	165.1
253.60	305.7	169.6	337.1	167.5
		Liquid		
253.60	386.5	296.9	464.4	167.5
260	388.1	299.2	474.1	174.9
270	391.3	302.5	488.8	186.3
280	395.2	305.8	503.1	197.3
290	399.6	308.9	517.0	208.1
298.15	403.5	311.4	528.2	216.7
300	404.4	312.0	530.7	218.7
310	409.6	315.1	544.0	228.9
320	415.0	318.1	557.1	239.0
330	420.6	321.1	569.9	248.8
340	426.4	324.1	582.6	258.4
350	432.3	327.2	595.0	267.9
360	438.3	330.2	607.3	277.1
370	444.5	333.2	619.4	286.2

Table 4. Vapor Pressures of Liquid Ethyl Decanoate by the Knudsen Method ($\lambda = 7.75\cdot 10^{-10}$ m, $S_{\text{sample}} = 7.85\cdot 10^{-5}$ m^2, $d_{\text{orifice}} =$ 0.183 mm)

T / K	τ / s	$10^6(\Delta m)$ / kg	k_{W}[a]	Kn[b]	p_{sat} / Pa
293.77	21600	2.88	0.826	4.9	1.69
298.67	7200	1.53	0.843	3.2	2.67
298.72	10800	2.30	0.843	3.2	2.67
303.68	14400	4.83	0.865	2.1	4.14
308.61	11700	6.29	0.893	1.3	6.48
313.57	7803	6.68	0.924	0.9	10.0
318.32	3600	4.80	0.957	0.6	15.2
323.24	3600	7.05	0.984	0.4	21.9

[a] Transmission probability factor was calculated according to Wahlbeck's theory.[15] [b] Kn is the Knudsen number, the ratio of the mean free path, and the orifice diameter.

Table 5. Results of Calorimetric Determination of the Vaporization Enthalpy of Ethyl Decanoate

	m	T	$\int_{\tau=0}^{\tau}\Delta E\cdot d\tau$		ΔH	$\Delta_l^g H_m^\circ$
no.	g	K	mV·s	cell	J	kJ·mol^{-1}
1	0.13787	304.80	8984	A	47.28	68.70
2	0.12199	304.85	8061	A	42.43	69.67
3	0.24501	304.80	16292	A	85.75	70.11
4	0.23235	304.95	15509	A	81.62	70.37
5	0.28036	304.65	18576	A	97.77	69.86
6	0.09726	304.70	6340	B	34.23	70.51

$$K_A = (190.0 \pm 1.1)\ \mathrm{mV{\cdot}s{\cdot}J^{-1}} \qquad K_B = (185.2 \pm 1.0)\ \mathrm{mV{\cdot}s{\cdot}J^{-1}}$$

$$\langle \Delta_l^g H_m^\circ(304.8\ \mathrm{K})\rangle = (69.9 \pm 0.7)\ \mathrm{kJ{\cdot}mol^{-1}}$$

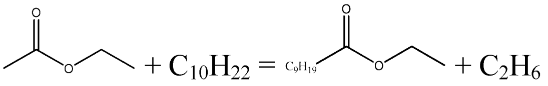
Combustion Calorimetry. The combustion enthalpy of liquid ethyl decanoate was measured in a modified commercial combustion calorimeter V-08 M with an isothermal water bath and a static bomb (of 326 cm^3 volume). Its design and the measurement procedure were described in detail earlier.[20] The calorimeter was calibrated with the use of reference benzoic acid (K-2 grade, mass-fraction purity of 0.99993). Gaseous oxygen of technical purity grade with ≥ 99.7 % of the main component was used. The main impurity was N_2. Water content in the gas was ≤ 0.007 %. The uncertainty of the combustion-enthalpy measurement was estimated to be ± 0.03 %. The uncertainty due to impurities in the sample was negligibly low because the major impurities were esters of higher fatty acids whose specific combustion energy was close to that for ethyl decanoate.

Weighing was carried out on a Mettler Toledo AG 245 electronic balance with an uncertainty of $\pm 2\cdot10^{-5}$ g. The liquid samples were burned in a platinum crucible in an oxygen atmosphere of 3.09 MPa pressure. Water of 1 cm^3 volume was initially added into the bomb. After the end of the experiment, all the water contained in the bomb was titrated using NaOH solution for taking into account the heat effect of nitric acid formation. The combustion products were controlled for soot traces. Its quantity did not exceed 0.07 mg and was determined from the mass of the dry crucible after an experiment.

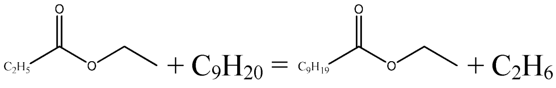
The calculations including the adjustment to the standard state and the correction due to the incomplete burning were performed by the method described in refs 21 and 22. The formation enthalpy of the compound was calculated using the standard formation enthalpies of gaseous carbon dioxide, $\Delta_f H^\circ(CO_2, g) = (-393.51 \pm 0.13)\ \mathrm{kJ\cdot mol^{-1}}$, and liquid water, $\Delta_f H^\circ(H_2O, liq) = (-285.83 \pm 0.04)\ \mathrm{kJ\cdot mol^{-1}}$.[23]

Quantum Chemical Calculations

The calculation of the formation enthalpy of ethyl decanoate in the ideal gas state was carried out by the homodesmic reaction method. Two reactions were used in calculations



(r1)



(r2)

The enthalpies of used reactions were calculated by the following equation

$$\Delta_r H_m^\circ(298.15\ \mathrm{K}) = \Big(\sum_{\text{products}} E_{\text{tot}} - \sum_{\text{reactants}} E_{\text{tot}}\Big) + \Big(\sum_{\text{products}} \mathrm{ZPVE} - \sum_{\text{reactants}} \mathrm{ZPVE}\Big) + \Big(\sum_{\text{products}} \Delta_0^{298.15} H_m^\circ - \sum_{\text{reactants}} \Delta_0^{298.15} H_m^\circ\Big) \quad (3)$$

where E_{tot} are the total energies of the used compounds at 0 K; ZPVE are the zero-point vibrational energies of intramolecular vibrations at 0 K; and $\Delta_0^{298.15} H_m^\circ$ are the enthalpy differences due to the heating of the compounds used in a homodesmic reaction from (0 to 298.15) K.

On the other hand, the enthalpy of the reaction can be calculated as the difference of the enthalpies of formation of the products and the reactants.

$$\Delta_r H_m^\circ = \Big(\sum_{\text{products}} \Delta_f H_m^\circ - \sum_{\text{reactants}} \Delta_f H_m^\circ\Big) \quad (4)$$

For enthalpy of formation of ethyl decanoate calculations, one needs to know the enthalpies of formation for the other substances in the homodesmic reaction.

The equilibrium geometries, the total energies, and the frequencies of normal vibrations for the most stable conformers of all participants of the homodesmic reactions were calculated at the B3LYP/6-31G(d,p)[24,25] and MP2/6-31G(d,p) theory levels in the PC GAMESS 7.0 program.[26] The most stable conformers of the molecules were found prior to these calculations using molecular mechanics force field MM2. The optimized molecular geometries are presented in the Supporting Information.

Normally, the calculated normal modes systematically differ from the experimental ones. To minimize these deviations, the calculated frequencies were scaled $\chi = \varpi_{\text{exptl}}/\varpi_{\text{calc}}$. For the B3LYP results, the scaling factors were calculated according to the equations

$$\chi = 1.011 \pm 0.006 \text{ below } 550\ \mathrm{cm^{-1}} \quad (5)$$

$$\chi = (1.084 \pm 0.008) - (3.43 \pm 0.64)\cdot10^{-5}(\varpi_{\text{calc}}/\mathrm{cm^{-1}}) \text{ from } (550 \text{ to } 2700)\ \mathrm{cm^{-1}} \quad (6)$$

$$\chi = 0.954 \pm 0.002 \text{ above } 2700\ \mathrm{cm^{-1}} \quad (7)$$

In the calculations based on the MP2 method, the scaling factors were calculated according to

$$\chi = 0.978 \pm 0.111 \text{ below } 550\ \mathrm{cm^{-1}} \quad (8)$$

$$\chi = (0.991 \pm 0.009) - (3.32 \pm 0.67)\cdot10^{-5}(\varpi_{\text{calc}}/\mathrm{cm^{-1}}) \text{ from } (550 \text{ to } 2700)\ \mathrm{cm^{-1}} \quad (9)$$

$$\chi = 0.924 \pm 0.010 \text{ above } 2700\ \mathrm{cm^{-1}} \quad (10)$$

The numerical values of the coefficients for eqs 5 to 10 were estimated by the authors from the experimental and calculated frequencies of normal modes for ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, iso-butane, 2,2-dimethyl propane, 2,2-dimethyl butane, and methyl acetate from an online database.[27]

The enthalpy of isobaric heating from (0 to 298.15) K was calculated by the statistical thermodynamic method. The contributions of internal rotation for tops were calculated in a harmonic approximation. No additional contribution for mixing of conformers was applied. It was assumed that the latter contribution can be neglected in calculation of the reaction enthalpies because the contributions on the left side and right side of the reactions will compensate each other.

Table 6. Results of Determination of the Standard Molar Combustion Energy for Ethyl Decanoate at $T = 298.15$ K[a]

property	1	2	3	4	5	6
m_{comp}/g	0.47174	0.48532	0.31470	0.48336	0.47265	0.37280
m_{fuse}/g	0.00266	0.00332	0.00433	0.00273	0.00257	0.00300
m_{film}/g	0	0.03629	0.02214	0	0	0.04050
m_{soot}/mg	0	0	0	0.07	0	0
$p(\mathrm{O_2})$/MPa	3.09	3.10	3.09	3.09	3.10	3.05
T_{bath}/K	302.15	302.15	302.15	302.15	302.15	302.15
T_{i}/K	298.05354	298.06695	298.05308	298.05456	298.03614	298.04459
T_{f}/K	299.35753	299.52011	299.04046	299.38582	299.3365	299.22683
ΔT_{corr}/K	1.19572	1.34539	0.87011	1.22482	1.19791	1.07338
$10^5(K/\mathrm{s}^{-1})$	3.55	3.63	3.66	3.66	3.57	3.61
$\varepsilon_{\mathrm{i}}/\mathrm{J\cdot K^{-1}}$	14.89	15.01	14.62	14.91	14.92	14.65
$\varepsilon_{\mathrm{f}}/\mathrm{J\cdot K^{-1}}$	16.1	16.39	15.51	16.16	16.13	15.75
$\Delta_{\mathrm{ign}}U$/J	0.28	0.37	0.37	0.46	0.35	0.34
$[\varepsilon_{\mathrm{calor}}\cdot(-\Delta T_{\mathrm{corr}})]$/J	−17593.70	−19795.93	−12802.71	−18021.88	−17625.93	−15793.61
$[\varepsilon_{\mathrm{cont}}\cdot(-\Delta T_{\mathrm{corr}})]$/J	−19.13	−21.94	−13.41	−19.67	−19.18	−16.79
$\Delta_{\mathrm{IBP}}U$/J	−17612.55	−19817.5	−12815.75	−18041.09	−17644.76	−15810.06
$(m_{\mathrm{soot}}\cdot\Delta_{\mathrm{c}}U_{\mathrm{soot}})$/J	0	0	0	−2.3	0	0
$[\Delta U(\mathrm{HNO_3})]$/J	1.49	1.02	0.836	0.956	1.02	0.896
$(\Delta_{\mathrm{st.state}}U)$/J	5.65	6.4	4.2	5.81	5.67	4.83
$\Delta_{\mathrm{c}}U^\circ/\mathrm{J\cdot g^{-1}}$	−37224.6	−37240.6	−37217.2	−37219.4	−37225.3	−37227.3
$\Delta_{\mathrm{c}}U^\circ_{\mathrm{m}}/\mathrm{J\cdot mol^{-1}}$	−7456.75	−7459.95	−7455.27	−7455.71	−7456.89	−7457.29

[a] m_{comp}, m_{fuse}, and m_{film} are the masses of the sample of the investigated compound, cotton fuse, and polyethylene bag adjusted to vacuum conditions (estimated density of the compound is $\rho = 0.864\ \mathrm{g\cdot cm^{-3}}$, cotton fuse $\rho = 1.52\ \mathrm{g\cdot cm^{-3}}$, polyethylene $\rho = 0.90\ \mathrm{g\cdot cm^{-3}}$); m_{soot} is the mass of the soot formed in the experiment; $p(\mathrm{O_2})$ is the pressure of oxygen in the bomb; T_{bath} is the temperature of the calorimeter; T_{i} and T_{f} are the initial and final temperature in the reaction period; ΔT_{corr} is the corrected temperature rise; K is the cooling constant of the calorimeter; ε_{i} and ε_{f} are the energy equivalent of the contents of the bomb in the initial and final states, respectively; $\Delta_{\mathrm{ign}}U$ is the electrical energy for igniting the sample; $\varepsilon_{\mathrm{calor}}$ is the energy equivalent of the calorimeter ($\varepsilon_{\mathrm{calor}} = (14713.9 \pm 3.2)\ \mathrm{J\cdot K^{-1}}$); $\varepsilon_{\mathrm{cont}}\cdot(-\Delta T_{\mathrm{corr}}) = \varepsilon_{\mathrm{i}}\cdot(T_{\mathrm{i}} - 298.15) + \varepsilon_{\mathrm{f}}\cdot(298.15 - T_{\mathrm{i}} - \Delta T_{\mathrm{corr}})$; $\Delta_{\mathrm{c}}U_{\mathrm{soot}}$ is the average combustion energy of the soot ($-33\ \mathrm{kJ\cdot g^{-1}}$ [ref 30]); $\Delta_{\mathrm{IBP}}U$ is the change of internal energy for the isothermal bomb process; $\Delta U(\mathrm{HNO_3})$ is the energy required for decomposition of the $\mathrm{HNO_3}$ solution formed; $\Delta_{\mathrm{st.state}}U$ is the energy correction to the standard state (the sum of Washburn's corrections, $c_{\mathrm{p}} = 2.01\ \mathrm{J\cdot K^{-1}\cdot g^{-1}}$; $(\partial U/\partial p)_T = -0.35\ \mathrm{J\cdot MPa^{-1}\cdot g^{-1}}$); $\Delta_{\mathrm{c}}U^\circ$ and $\Delta_{\mathrm{c}}U^\circ_{\mathrm{m}}$ is the standard massic and molar combustion energies of ethyl decanoate, respectively.

Table 7. Results of Quantum Chemical Calculation of Formation Enthalpies in the Gaseous State for Ethyl Decanoate

property	ethane	nonane	decane	ethyl acetate	ethyl propanoate	ethyl decanoate
B3LYP/6-31G(d,p)						
$-E_{\mathrm{tot}}$/Hartree [a]	79.838736	355.054582	394.371062	307.718563	347.036051	622.251612
ZPVE/$\mathrm{kJ\cdot mol^{-1}}$	189.4	697.6	769.7	300.0	372.8	879.1
$\Delta_0^{298.15}H^\circ_{\mathrm{m}}/\mathrm{kJ\cdot mol^{-1}}$	11.64	35.01	38.67	21.66	25.31	50.18
$\Delta_{\mathrm{f}}H^\circ_{\mathrm{m}}(\mathrm{g})/\mathrm{kJ\cdot mol^{-1}}$	−83.82 [b]	−228.86 [b]	−249.53 [b]	−444.7 [c]	−466.5 [c]	−612.1[d] −611.2[e]
MP2/6-31G(d,p)						
$-E_{\mathrm{tot}}$/Hartree[a]	79.543401	353.817818	392.999892	306.807608	345.990535	620.264844
ZPVE/$\mathrm{kJ\cdot mol^{-1}}$	190.0	696.4	768.5	299.0	372.3	877.1
$\Delta_0^{298.15}H^\circ_{\mathrm{m}}/\mathrm{kJ\cdot mol^{-1}}$	11.60	35.48	39.11	21.96	25.33	50.60
$\Delta_{\mathrm{f}}H^\circ_{\mathrm{m}}(\mathrm{g})/\mathrm{kJ\cdot mol^{-1}}$	−83.82[b]	−228.86[b]	−249.53[b]	−444.7[c]	−466.5[c]	−611.7[d] −611.4[e]

[a] 1 Hartree = 2625.5 kJ·mol⁻¹. [b] Recommended value from ref 30. [c] Experimental value from ref 10. [d] Calculated from reaction r1. [e] Calculated from reaction r2.

Results and Discussion

Heat Capacity and Parameters of Fusion. The experimental heat capacities for ethyl decanoate in the interval of (5 to 370) K are listed in Table 1 and shown in Figure 1.

While cooling the sample from 370 K, the spontaneous crystallization of the supercooled liquid began at $T = (240$ to $243)$ K. The sample was kept at $T = 253$ K until the heat evolution had stopped, which took (4 to 6) h.

The triple-point temperature for ethyl decanoate $T_{\mathrm{fus}} = (253.60 \pm 0.02)$ K was determined by the fractional melting method (Figure 2). The results could not be satisfactorily described by the van't Hoff equation taking into account solid-insoluble impurities. So, the fractional melting data for ethyl decanoate were fitted according to the Mastrangelo equation.[28]

$$T_{\mathrm{fus}} - T_{\mathrm{i}} = \frac{x_2 R {T_{\mathrm{fus}}}^2}{\Delta_{\mathrm{cr}}^{\mathrm{liq}}H^\circ_{\mathrm{m}}\left(f_{\mathrm{i}} + \dfrac{k}{1-k}\right)} \tag{11}$$

where f_{i} is a fraction melted; k is a distribution coefficient; and x_2 is a molar fraction of impurity in the sample. The use of the Mastrangelo equation demonstrates that the main impurities in ethyl decanoate are soluble in the liquid and crystalline ethyl decanoate. The physical properties of the impurities are expected to be very close to the properties of the main compound due to similar structure. So, the error in the thermodynamic properties caused by the impurities will be rather low.

The fusion enthalpy $\Delta_{\mathrm{cr}}^{\mathrm{liq}}H^\circ_{\mathrm{m}}(253.60\ \mathrm{K}) = (32.29 \pm 0.04)\ \mathrm{kJ\cdot mol^{-1}}$ was determined from several experiments (Table 2). The following equation was used to calculate $\Delta_{\mathrm{cr}}^{\mathrm{liq}}H^\circ_{\mathrm{m}}$

$$\Delta_{\mathrm{cr}}^{\mathrm{liq}}H^\circ_{\mathrm{m}} = Q - \int_{T_{\mathrm{start}}}^{T_{\mathrm{fus}}} C_{p,\mathrm{m}}(\mathrm{cr})\mathrm{d}T - \int_{T_{\mathrm{fus}}}^{T_{\mathrm{end}}} C_{p,\mathrm{m}}(\mathrm{liq})\mathrm{d}T \tag{12}$$

where Q is the energy needed to heat 1 mol of ethyl decanoate from T_{start} to T_{end}. The initial T_{start} and final T_{end} temperatures lay in the temperature intervals with "normal" heat capacity (without fusion enthalpy contribution). The following equations were applied to describe the heat capacity for crystalline and liquid ethyl decanoate

$$C_{p,\mathrm{m}}(\mathrm{cr})/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 215.71 - 0.57497(T/\mathrm{K}) + 3.6671{\cdot}10^{-3}(T/\mathrm{K})^2 \quad (13)$$

$$C_{p,\mathrm{m}}(\mathrm{liq})/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 511.4 - 1.240(T/\mathrm{K}) + 2.945{\cdot}10^{-3}(T/\mathrm{K})^2 \quad (14)$$

The numerical coefficients were obtained from the experimental data in the interval of (189 to 212) K and (255 to 300) K, respectively.

Thermodynamic Functions of the Condensed State. For calculation of the entropy and the enthalpy for the phases, one has to extrapolate the experimental heat capacities below $T = 5$ K. For extrapolation purposes, the experimental heat capacity values in the region (5.1 to 5.9) K were fitted by the equation

$$C_p{\cdot}T^{-2}/\mathrm{J{\cdot}K^{-3}{\cdot}mol^{-1}} = -(7.61 \pm 0.07){\cdot}10^{-3} + (5.51 \pm 0.01){\cdot}10^{-3}(T/\mathrm{K}) \quad (15)$$

The experimental heat capacities in the interval (5 to 370) K were fitted by polynomials. The smoothed values of the thermodynamic functions for ethyl decanoate in the crystalline and liquid states are listed in Table 3.

Vapor Pressure and Enthalpy of Vaporization. The results of vapor pressure determination by the integral Knudsen method are presented in Table 4. The results of calorimetric determination of vaporization enthalpy are shown in Table 5.

To evaluate the temperature dependence of vapor pressure, the Clarke and Glew[29] equation was used

$$-RT\ln\left(\frac{p_{\mathrm{sat}}}{p^\circ}\right) = AT/\theta - B[(T/\theta) - 1] - C[\theta - T + T\ln(T/\theta)] \quad (16)$$

where θ is the reference temperature and p° is a standard pressure, 1 bar. For vapor pressure < 100 Pa, coefficients A, B, and C are equal to the changes in Gibbs energy $\Delta_{\mathrm{liq}}^{\mathrm{g}}G_{\mathrm{m}}^{\circ}(\theta)$, enthalpy $\Delta_{\mathrm{liq}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\theta)$, and heat capacity $\Delta_{\mathrm{liq}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\circ}(\theta)$ when going from liquid to gas at a standard pressure and temperature θ, respectively.

The joint treatment of the vapor pressure and calorimetric enthalpy of vaporization was carried out. The A and B parameters in eq 16 for liquid ethyl decanoate were calculated by minimizing the function $\sum_i(\Delta_{\mathrm{liq}}^{\mathrm{g}}G_{\mathrm{m}}^{\circ}(\mathrm{exptl}) - \Delta_{\mathrm{liq}}^{\mathrm{g}}G_{\mathrm{m}}^{\circ}(\mathrm{calcd}))^2 w_i^2 + \sum_i(\Delta_{\mathrm{liq}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\mathrm{exptl}) - \Delta_{\mathrm{liq}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\mathrm{calcd}))^2 \upsilon_j^2$, where w_i and υ_i are the statistical weights for the used data ($w_i^{-1} = (0.05RT_i/\mathrm{J{\cdot}mol^{-1}})$ and $\upsilon_j^{-1} = 700/6$). $\Delta_{\mathrm{liq}}^{\mathrm{g}}G_{\mathrm{m}}^{\circ}(\mathrm{exptl})$ were calculated as $\Delta_{\mathrm{liq}}^{\mathrm{g}}G_{\mathrm{m}}^{\circ}(\mathrm{exptl}) = -RT\ln(p_{\mathrm{sat}}/p^\circ)$. The θ temperature was assumed to be 298.15 K. The heat capacity change was estimated to be $\Delta_{\mathrm{liq}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\circ}(\theta) = -100\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The literature data on vapor pressure of ethyl decanoate obtained with an ebulliometer[10] were not used in joint treatment because they lay much higher in temperature than the results of the effusion method. The obtained parameters of eq 16 are

$$\Delta_{\mathrm{liq}}^{\mathrm{g}}G_{\mathrm{m}}^{\circ}(\theta) = (26.24 \pm 0.03)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_{\mathrm{liq}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\theta) = (70.52 \pm 0.09)\ \mathrm{kJ{\cdot}mol^{-1}}$$

The standard entropy of vaporization was calculated from the obtained parameters to be $\Delta_{\mathrm{liq}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ} = (148.5 \pm 0.3)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The corresponding standard entropy of gaseous ethyl decanoate is $S_{\mathrm{m}}^{\circ}(\mathrm{g{,}298.15\ K}) = (676.7 \pm 2.1)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

The vaporization enthalpy obtained from the results by Wiberg and coauthors[10] is $\Delta_{\mathrm{liq}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(422\ \mathrm{K}) = (58.4 \pm 0.1)\ \mathrm{kJ{\cdot}mol^{-1}}$. If one uses $\Delta_{\mathrm{liq}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\circ} = -100\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, that enthalpy value is adjusted to $T = 298.15$ K to be 70.8 kJ·mol^{-1}, which is in excellent agreement with the value (70.5 ± 0.5) kJ·mol^{-1} obtained in this paper.

Enthalpies of Combustion and Formation. The results of the determination of the combustion energy for liquid ethyl decanoate are presented in Table 6. The average molar energy and enthalpy of combustion at $T = 298.15$ K are

$$\Delta_{\mathrm{c}}U_{\mathrm{m}}^{\circ}(\mathrm{liq,\ 298.15\ K}) = (-7457.0 \pm 1.7)\ \mathrm{kJ{\cdot}mol^{-1}},\ \Delta_{\mathrm{c}}H_{\mathrm{m}}^{\circ}(\mathrm{liq,\ 298.15\ K}) = (-7469.4 \pm 1.7)\ \mathrm{kJ{\cdot}mol^{-1}}$$

The formation enthalpy of the compound in the liquid state, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{liq,\ 298.15\ K}) = (-682.7 \pm 2.4)\ \mathrm{kJ{\cdot}mol^{-1}}$, was calculated from its combustion reaction.

$$\mathrm{C_{12}H_{24}O_2(liq) + 17O_2(gas) = 12CO_2(gas) + 12H_2O(liq)}$$

The standard enthalpy of formation of ethyl decanoate in the gaseous state was evaluated using the experimental enthalpy of vaporization $\Delta_{\mathrm{liq}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\ 298.15\ \mathrm{K}) = (70.52 \pm 0.09)\ \mathrm{kJ{\cdot}mol^{-1}}$ (Table 5). The adjusted formation enthalpy was found to be $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{g,\ 298.15\ K}) = (-612.2 \pm 2.4)\ \mathrm{kJ{\cdot}mol^{-1}}$.

The total energies, ZPVEs, and $\Delta_0^{298.15}H_{\mathrm{m}}^{\circ}$ values for all participants of the reaction and the formation enthalpy value for ethyl decanoate are shown in Table 7. The resulting formation enthalpy of ethyl decanoate [the mean value $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{g,\ 298.15\ K}) = -611.6\ \mathrm{kJ{\cdot}mol^{-1}}$] agrees perfectly with the experimental value.

Using the data reported in this paper, we can calculate the entropy and the Gibbs energy of formation for ethyl decanoate

$$\Delta_{\mathrm{f}}S_{\mathrm{m}}^{\circ}(\mathrm{liq,\ 298.15\ K}) = -(1314 \pm 3)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{liq,\ 298.15\ K}) = -(290.9 \pm 2.5)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_{\mathrm{f}}S_{\mathrm{m}}^{\circ}(\mathrm{g,\ 298.15\ K}) = -(1166 \pm 3)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{g,\ 298.15\ K}) = -(264.7 \pm 2.5)\ \mathrm{kJ{\cdot}mol^{-1}}$$

Conformational Contribution to the Entropy of Ethyl Decanoate. Ethyl decanoate is known to form many conformers. It is rather difficult to calculate a conformational contribution to thermodynamic properties for such long-chain molecules. However, in the case of ethyl decanoate, one may evaluate this contribution by combining experimental and theoretical results obtained in this work. It is also possible to find out how important this contribution to the fusion entropy is.

The conformational contribution to the entropy is defined in this paper as the entropy of mixing of conformers. It can be calculated assuming the conformational compositions of liquid and gas are equal. The standard entropy of liquid ethyl decanoate at the fusion temperature is $S_{\mathrm{m}}^{\circ}(\mathrm{liq}) = (464.4 \pm 2.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. According to the temperature dependence of vapor pressure for ethyl decanoate (eq 16, Table 5), the standard entropy of vaporization is $\Delta_{\mathrm{liq}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ} = (164.7 \pm 0.5)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The corresponding entropy of ethyl decanoate in the gaseous state at T_{fus} is $S_{\mathrm{m,exp}}^{\circ}(\mathrm{g}) = (629.1 \pm 2.1)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

The standard entropy of the main conformer of ethyl decanoate in the ideal gas state $S_{\mathrm{m}}^{\circ}(\mathrm{g}) = (568.4 \pm 5.7)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ was calculated from the results of the quantum-chemical calculations using the method of statistical thermodynamics. The uncertainty of the value was estimated to be 1 %. The conformational contribution is the difference between the latter two values and is equal to $S_{\mathrm{m}}^{\circ}(\mathrm{conf}) = S_{\mathrm{m,exp}}^{\circ}(\mathrm{g}) - S_{\mathrm{m}}^{\circ}(\mathrm{g}) = (60.7 \pm 6.1)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

The difference between $\Delta_{\mathrm{cr}}^{\mathrm{liq}}S_{\mathrm{m}}^{\circ} = (127.3 \pm 0.2)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and $S_{\mathrm{m}}^{\circ}(\mathrm{conf})$ is a contribution of the other types of disorder except conformational disorder. This value equal to (66.6 ± 6.1) $J \cdot K^{-1} \cdot mol^{-1}$ is close to the entropy of fusion (50 to 60) $J \cdot K^{-1} \cdot mol^{-1}$ typical for molecular compounds without internal rotation.

Supporting Information Available:

The figures of the main conformers used in the estimation of the enthalpy of formation of ethyl decanoate molecules and the tables of atom coordinates for used compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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