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Phase Equilibria and Thermodynamic Properties of Some Branched Alkyl Ethers[†]

Anastasia A. Efimova,[‡] Anna I. Druzhinina,[‡] Raisa M. Varushchenko,*[,‡] Olga V. Dorofeeva,[‡] and Eugenii L. Krasnyh[§]

Luginin's Laboratory of Thermochemistry, Department of Chemistry, Moscow State University, 119991, Moscow, Russia, and Samara State Technical University, 442010, Samara, Russia

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The low-temperature heat capacity and thermodynamic properties of the solid-to-solid transition and fusion of di-isobutyl ether (DIBE) were determined by adiabatic calorimetry in the temperature range from (8 to 373) K. The saturation vapor pressure of DIBE was determined by a comparative ebulliometry over the moderate pressure range from (10.8 to 99.6) kPa. A density of liquid DIBE was measured in the temperature interval from (298 to 313) K using a quartz pycnometer. The normal boiling temperature, $T_{\text{n.b.}}$, the enthalpy of vaporization at $T = 298.15$ K and $T_{\text{n.b.}}$, and the ideal gas thermodynamic functions (changes of the entropy, enthalpy, and Gibbs energy) at $T = 298.15$ K were derived. Appropriate thermodynamic functions over a wide temperature range from (150 to 1000) K and the standard enthalpy of formation at $T = 298.15$ K were computed by the methods of statistical thermodynamics (ST) and the density functional theory (DFT) on the level B3LYP/6-31G(d,p). The experimental data on the vapor pressure of DIBE were extended to the entire range of liquid phase from the triple to the critical temperatures by the corresponding states law and combined treatment of the *pT*-parameters and the low-temperature differences between the heat capacities of the ideal gas and liquid. The data on thermodynamic properties of some branched ethers, C_5 to C_9, studied earlier and in this work were critically analyzed for verification of their reliability and mutual consistency.

Introduction

An increased interest in thermodynamic study of the branched aliphatic ethers having a number of carbon atoms from 5 to 8 was recently due to their possible employment as environmentally friendly additives to the motor fuels.[1] The thermodynamic properties of the branched ethers were widely studied, especially for the tertiary species, like alkyl *tert*-butyl and alkyl *tert*-amyl ethers.[2−16] Data on the saturation vapor pressures and enthalpies of vaporization were published in refs 2 to 9. Our previous investigations of the low-temperature heat capacities, thermodynamic properties of the phase transitions, and the ideal gas thermodynamic functions, derived from the experimental data, were reported in refs 12 to 16. The standard enthalpies of formation and ideal gas thermodynamic functions were also obtained based on the B3LYP/6-31G(d,p) calculations and statistical thermodynamics.[14−16]

This paper deals with the thermodynamic study of the di-isobutyl ether by experimental and calculation methods. The experimental data on thermodynamic properties of di-isobutyl ether are scarce. There are some values of the normal boiling temperature, $T_{\text{n.b.}}$, 395.7 K,[17] 396.2 K,[8] and 395.2 K[18] of DIBE and the enthalpy of vaporization in ref 8: (40.85 and 33.95) $\text{kJ}\cdot\text{mol}^{-1}$ at 298.15 K and $T_{\text{n.b.}}$, respectively. In this paper, we report the low-temperature heat capacity, the saturation vapor pressure in the "atmospheric" pressure range, and the vapor pressure extended to the entire range of the liquid phase. These data, to the best of our knowledge, have not been reported before. A verification of the reliability and mutual consistency of the data on thermodynamic properties of the branched ethers in the section Discussion of Thermodynamic Properties of the Branched Ethers is of interest for both science and technology.

Experimental Section

Preparation of the Compound. Di-isobutyl ether (propane, 1,1′-oxybis[2-methyl]; CASRN 628-55-7) was synthesized by interacting an isobutyl sodium alcoholate with isobutyl bromine. The alcoholate was prepared beforehand by interaction of metallic sodium with isobutyl alcohol taken in 5-fold excess. A reaction mixture was boiled in a glass retort with a return condenser until completing the sodium bromine educing. The remaining alcohol was removed by repeated washing of the mixture with water and vacuum distillation. The yield of DIBE was 56 wt %. The ether was dried with calcium chloride and rectified in vacuum. The purity of the sample was analyzed by means of a Leco Pegasus IV D chromato-mass spectrometer (CMS) equipped with a gas chromatograph Agilen 6890 Series. A capillary column BPX5 has the column length of 30 m, an inside diameter of 250 μm, and a film thickness of 0.25 μm. CMS analysis showed the following mass fractions of ethers: 0.9898 (DIBE); 0.0025_6 (*n*-dibutyl ether, DBE); 0.0036_6 (isobutyl *tert*-butyl ether, IBTBE); 0.0039_9 (ethyl *tert*-amyl ether, ETAE). An obtained total mass of impurities fractions 0.0102_1 was supported within errors limits by the appropriate value 0.0096 ± 0.0012 determined by the calorimetric method of the fraction melting study (next section, Table 3). All attempts to purify the sample by rectifying were unsuccessful. An influence of impurities on experimental data was taken into consideration in determination of the heat capacity and the saturation vapor pressure of DIBE.

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* Corresponding author. E-mail: varusch@thermo.chem.msu.ru. Fax: +7 4959391240. Tel.: +7 4959395396.

[†] Part of the "William A. Wakeham Festschrift".

[‡] Moscow State University.

[§] Samara State Technical University.

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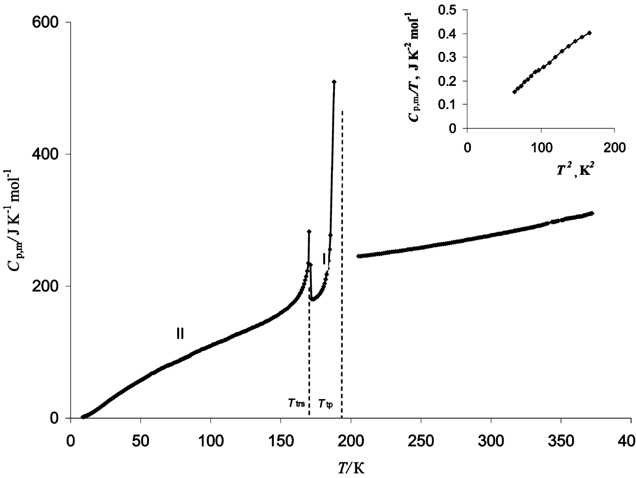


Figure 1. Molar heat capacity, $C_{p,\mathrm{m}}$, of di-isobutyl ether as a function of temperature, T, where T_{trs} and T_{tp} denote the temperatures of the λ-like transition and triple point. In the insert, a dependence of $C_{p,\mathrm{m}}/T$ on T^2 is given for the helium range of the temperatures.

Table 1. Equilibrium Melting Temperatures T_i, Reciprocal of the Sample Fraction Melted, $1/F_i$, and the $T_{i(\mathrm{calcd})}$ Values Calculated from the Linear Dependence of T_i on $1/F_i$ in One of Three Experiments for Di-isobutyl Ether

T_i/K	q_i^a/J	$(1/F_i)$	$T_{i(\mathrm{calcd})}$/K
188.013	4.406	13.00	
188.856^b	4.407	6.50^b	188.83
189.325^b	4.407	4.33^b	189.35
189.593^b	4.408	3.25^b	189.61
189.757^b	4.407	2.60^b	189.77
189.867^b	4.407	2.17^b	189.87
189.947^b	4.408	1.86^b	189.94
190.006^b	4.408	1.62^b	190.00
190.052^b	4.407	1.44^b	190.04
190.088^b	4.407	1.30^b	190.08
190.104	4.407	1.18	190.10
190.134	4.407	1.08	190.13
190.164	4.406	1.00	190.15
		0.00	190.39 ± 0.03

[a] The q_i denotes a quantity of energy used for melting the F_i substance fraction. [b] The T_i and $1/F_i$ values were used for calculation of N_2, T_{tp}, A_{cr}, and B_{cr} in the range of $1/F_i$ from 1.30 to ≤10 according to Aleksandrov.[22]

Measurement of the Low-Temperature Heat Capacity. The heat capacity of DIBE was measured in a fully automated set consisting of a vacuum adiabatic calorimeter and a data acquisition and control system, AK-6.25.[19] The sample was put in a titanium cylindrical container (volume ~1 cm^3) which was sealed by means of a brass lid and an indium gasket using a simple manifold. The temperature of the calorimeter was measured with the accuracy of $\pm 5 \cdot 10^{-3}$ K by a (rhodium + iron) resistance thermometer ($R_0 \sim 50\ \Omega$) calibrated on ITS-90. The temperature drop between the calorimeter and an adiabatic shield was measured by a four-junction (copper + 0.001 mass of iron)−Chromel thermocouple. A digital control of the adiabatic conditions by the AK-6.25 system allows keeping the temperature drop within $\pm$ (1 to 3)$\cdot 10^{-3}$ K in the whole temperature range studied. A small cryostat with the calorimeter was placed directly in the transport Dewar flasks with refrigerants (liquid helium or nitrogen). The vacuum seal of the cryostat was provided by cryosorption using an efficient charcoal getter.

The crystal phase of DIBE was obtained by cooling the liquid sample from room temperature to 77.4 K at a rate of (4 to 5)$\cdot 10^{-3}$ K$\cdot$s^{-1}. To obtain the stable phase, the solid specimen was annealed at the temperature by (15 to 20) K below the triple point for 24 h and then quenched at T = 77.4 K during the same period. In spite of this, the specimen continued to deliver heat in adiabatic conditions at a rate from ($3 \cdot 10^{-5}$ to $3 \cdot 10^{-6}$) K$\cdot$s^{-1} within 4 months that could be explained by a prolonged crystallization process. To accelerate this process, the specimen had being melted from (20 to 30) wt % for ~ 20 h which allowed completing the crystallization during ~ 24 h. The heat capacity of di-isobutyl ether was measured at the saturated vapor pressure over the temperature range from (8.8 to 351.5) K with uncertainties from (1.5 to 2) % between the temperatures (6 and 30) K; from (0.5 to 1) % in the temperature range (30 to 80) K; and from (0.2 to 0.3) % above 80 K. The difference $C_{\mathrm{sat,m}} - C_{\mathrm{p,m}} = T(\delta V/\delta T)_{\mathrm{p}}(\delta P/\delta T)_{\mathrm{sat}}$, estimated for the liquid phase at T = 298.15 K, was less than uncertainties of the $C_{\mathrm{sat,m}}$ values, and therefore it was not taken into account for the whole temperature interval studied. The heat capacity curve reveals a λ-like thermal anomaly and a fusion (Figure 1). Experimental values of the heat capacities are tabulated in the Supporting Information.

A triple point temperature, T_{tp}, of the specimen and a mole fraction of impurities, N_2, were determined by the calorimetrical method of the fractional melting study.[19,20] An absence of some solution in the solid state of the ether was indicated by the Mastrangelo and Dornte method.[21] Three experiments were made for analyzing the linear dependence between the reciprocal fractions of the sample melted, $1/F_i$, and the equilibrium fusion temperatures, T_i. Table 1 lists an example of one experiment. According to Aleksandrov,[22] the data on T_i at the $1/F_i$ values from 1.3 to 6.5 were fitted in the linear equation

$$T_i = a + b \cdot (1/F_i), \quad R^2 = 0.9986 \tag{1}$$

Here $a = T_0(T_{\mathrm{tp}})$ is the triple point temperature of the pure compound; $b = (T_1 - T_0) \leq 0.26$ K is a depression of the T_{tp} value; and T_1 denotes the triple point temperature of the completely melted specimen under study ($F_i = 1$). Due to a short temperature interval between a λ-anomaly and a fusion, the number of the C_p values in the linear part of the heat capacity curve before melting was increased from 3 to 8 by supplying the calorimeter with the smaller energy increments. This allowed us to make the correct determination of the initial fusion temperature, T_i, and also the T_{tp} and N_2 values. A mean T_{tp} value equals to T_{tp} = (190.40 ± 0.06) K. The mole fraction of impurities, N_2, was calculated from the formula

$$N_2 = (\Delta_{\mathrm{fus}}H_{\mathrm{m}} \cdot \Delta T)/(R \cdot T_{\mathrm{tp}}^2) \tag{2}$$

where $R = 8.314472$ J$\cdot$K$^{-1}\cdot$mol^{-1}; $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ is the enthalpy of fusion; and ΔT denotes the depression of the triple point temperature of the substance.

The enthalpy of fusion was determined calorimetrically based on the total enthalpy adsorbed during transition of the substance from the crystal to liquid states with correction for the heating enthalpies of a hypothetic normal crystal and a liquid and adequate heating enthalpy of the empty container in the temperature interval of transition (Table 2). The mole fraction of impurities calculated from eq 2, $N_2 = 0.0096 \pm 0.0012$, agrees within error limit with that of CMS, N_2 (CMS) = 0.0102.

The λ-like anomaly occurs in the temperature interval from (160.2 to 173.5) K. The temperature of the solid-to-solid transition, T_{trs}, was attributed to the maximum C_p value in the

Table 2. Molar Enthalpy of Fusion, $\Delta_{fus}H_m$, of Di-isobutyl Ether[a] Calculated from the Equation $\Delta_{fus}H_m = \Delta_{tot}H - \Delta H_1 - \Delta H_2 - \Delta_{emp}H$ (3)

K		J·mol^{-1}				
T_{in}[b]	T_f[b]	$\Delta_{tot}H$[b]	ΔH_1[b]	ΔH_2[b]	$\Delta_{emp}H$[b]	$\Delta_{fus}H_m$
176.404	200.179	22224	2769	2432	5694	11330
176.372	200.391	22341	2775	2484	5753	11330

[a] M = 130.231 g·mol^{-1}, m = 0.60777 g is the mass of di-isobutyl ether. [b] T_{in} and T_f are the initial and final temperatures of calorimeter; $\Delta_{tot}H$ is the enthalpy increment in heating the calorimeter with the substances from T_{in} to T_f; $\Delta_{emp}H$ denotes the enthalpy increment needed for heating the empty calorimeter from T_{in} to T_f; ΔH_1 and ΔH_2 are the heating enthalpies calculated from the normal heat capacities of the crystal and liquid phases in the temperature intervals from T_{in} to T_{tp} and from T_{tp} to T_f, respectively.

Table 3. Thermodynamic Properties of the Phase Transitions of Di-isobutyl Ether, where T_{trs}, T_{tp}, $\Delta_{trs}H_m$, $\Delta_{fus}H_m$, $\Delta_{trs}S_m$, and $\Delta_{fus}S_m$ Denote the Temperatures, Enthalpies, and Entropies of the Solid-to-Solid Transition and the Fusion, N_2 Is Mole Fraction of Impurities, and A_{cr} and B_{cr} Are the Cryoscopic Constants

T_{tp}[a]/K	190.40 ± 0.06
$\Delta_{fus}H_m$/kJ·mol^{-1}	11.33 ± 0.11
$\Delta_{fus}S_m$/J·K^{-1}·mol^{-1}	59.51 ± 0.58
N_2[a]/mol fractions	0.0096 ± 0.0012
A_{cr}[a]/K^{-1}	0.03759 ± 0.00004
B_{cr}[a]/K^{-1}	0.00421 ± 0.00001
T_{trs}/K	170.71 ± 0.2
$\Delta_{trs}H_m$/kJ·mol^{-1}	1.80 ± 0.09
$\Delta_{trs}S_m$/J·K^{-1}·mol^{-1}	10.54 ± 0.53

[a] Average from three experiments.

heat capacity peak studied with a temperature step of 0.2 K. The changes of the enthalpy, $\Delta_{trs}H^0_m$, and the entropy, $\Delta_{trs}S^0_m$, were calculated by summing up these values in each experimental point of the heat capacity interval studied and followed by subtracting the appropriate heating functions for the normal (undisturbed) part of the C_p curve. The values of thermodynamic properties for the λ-transition and fusion are listed in Table 3. The λ-transition accompanied by small changes in the enthalpy and entropy could be attributed to a slight reorientation of the molecules in the crystal lattice.

The heat capacity of DIBE was extrapolated to $T \rightarrow 0$ with the equation

$$C_{p,m} = nD\left(\frac{\Theta_D}{T}\right) \qquad (4)$$

where D is the Debye function; $n = 7$ and $\Theta_D = 121.25$ K are the adjustable parameters calculated based on the heat capacities in the temperature interval from (8.82 to 12.88) K. The root-mean-square (rms) deviation of calculated $C_{p,m}$ values from experimental ones equals ± 2.1 % in this temperature interval.

Experimental values of the heat capacity (Supporting Information) were fitted by polynomials

$$C_{p,m} = \Sigma A_i\{(T - A_k)/B_k\}^i \qquad (5)$$

where $(T - A_k)/B_k$ is the normalizing term. The rms deviation between the experimental and calculated $C_{p,m}$ values equals 0.18 %. Smoothed values of $C_{p,m}$ and thermodynamic functions $S^0_m(T)$, $\{H^0_m(T) - H^0_m(0)\}$, and $\{G^0_m(T) - H^0_m(0)\}$ for the all temperature range studied are listed in Table 4. The thermodynamic functions of DIBE were calculated by numerical integrating of the $C_{p,m} = f(T)$ functions obtained by eqs 4 and 5 and adding the enthalpies and entropies of the λ-transition and fusion. The errors of thermodynamic functions were estimated by the law of the accumulation of random errors based upon the uncertainties of the heat capacity measurements.[23] The influence of the impurities content on thermodynamic functions of DIBE was evaluated using the mole fractions of impurities 0.0036_6 and 0.0039_9 for IBTBE and ETAE determined by CMS and the data on $C_{p,m}$, S^0_m, and $\Delta^0_T H^0_m$ values of these ethers,[14,13] respectively. The impurity of normal dibutyl (DBE) ether was excluded from evaluation due to lack of the data on the thermodynamic function of DBE. The correction values amounting to ≤ 0.07 % of the considered functions were not taken into account as they were in the error limits of the DIBE functions.

Table 4. Smoothed Molar Thermodynamic Properties of Di-isobutyl Ether

T	$C_{p,m}$	$\{H^0_m(T) - H^o_m(0)\}$	$S^0_m(T)$	$-[G^0_m - H$m0(0)]
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
		Crystal II		
10	2.519	0.00489	0.4387	0.00051
15	7.709	0.02946	2.360	0.00594
20	14.73	0.08497	5.506	0.0251
25	22.61	0.1782	9.633	0.0626
30	30.39	0.3109	14.45	0.1226
35	37.65	0.4812	19.69	0.2079
40	44.52	0.6867	25.17	0.3201
45	51.04	0.9258	30.79	0.4597
50	57.22	1.197	36.49	0.6275
55	63.54	1.498	42.24	0.8252
60	69.69	1.832	48.03	1.050
65	75.34	2.194	53.84	1.306
70	80.28	2.584	59.61	1.589
75	84.76	2.996	65.30	1.901
80	89.65	3.432	70.92	2.242
85	94.92	3.893	76.51	2.610
90	100.3	4.382	82.09	3.006
95	105.3	4.896	87.65	3.431
100	109.7	5.434	93.17	3.883
110	118.6	6.575	104.0	4.865
120	128.0	7.808	114.8	5.968
130	137.1	9.134	125.4	7.168
140	147.0	10.55	135.9	8.476
150	158.9	12.08	146.4	9.880
160	171.1	13.73	157.1	11.41
170.71	184.2	15.63	168.6	13.15
		Crystal I		
170.71	172.2	17.43	179.1	13.15
180	193.8	19.13	188.8	14.85
190.40	218.0	21.28	200.4	16.88
		Liquid		
190.40	241.1	32.61	259.9	16.88
200	243.7	34.99	272.1	19.43
210	246.3	37.43	284.0	22.21
220	248.9	39.89	295.5	25.12
230	251.9	42.38	306.6	28.14
240	255.0	44.91	317.3	31.24
250	258.3	47.47	327.8	34.48
260	261.8	50.07	338.0	37.81
270	265.3	52.70	348.0	41.26
280	269.0	55.37	357.7	44.79
290	272.8	58.08	367.2	48.41
298.15	276.08 ± 0.83	60.32 ± 0.15	374.8 ± 0.90	51.43 ± 0.28
300	276.8	60.83	376.5	52.12
310	280.8	63.62	385.6	55.92
320	285.0	66.45	394.6	59.82
330	289.5	69.32	403.5	63.84
340	294.7	72.24	412.1	67.87
350	300.0	75.21	420.8	72.07
360	304.4	78.24	429.3	76.31
370	308.9	81.30	437.7	80.65

Determination of the Saturated Vapor Pressure and the Density. Saturated vapor pressure in dependence on temperature was determined by comparative ebulliometry. The set consists of a differential ebulliometer that was used for measuring the boiling, T_b, and condensation, T_{cond}, temperatures and a mercury-contact manometer for automatic control and determination of the pressure inside the ebulliometer.[24] Argon is introduced into the system to keep up the constant pressure equal to that of the saturation vapor of the substance

Table 5. Saturated Vapor Pressures and Boiling Temperatures of Di-isobutyl Ether

$T_b{}^a$/K	$P_{exp}{}^b$/kPa	$P_{corr}{}^b$/kPa
330.897	10.801	10.750
336.085	13.429	13.367
341.657	16.831	16.757
347.208	20.877	20.788
352.090	25.072	24.972
357.887	30.910	30.787
363.268	37.264	37.121
(363.266)^c		
369.460	45.827	45.657
375.779	56.116	55.915
381.766	67.493	67.259
388.147	81.571	81.297
392.777	93.182	92.876
393.582	95.310	94.998
394.367	97.438	97.120
395.145	99.604	99.281

[a] Temperatures are expressed on the ITS-90. [b] P_{exp} and P_{corr} are the vapor pressures determined ebulliometrically and calculated from eq 6, respectively. [c] Boiling temperature measured repeatedly.

under study. The temperatures were automatically measured by platinum resistance thermometers ($R_0 \sim 100\ \Omega$). Glass protective tubes of the thermometers were soldered into the ebulliometer to increase the thermometric sensitivity. The measurement of the temperature was conducted by a computer-measuring system AK-6.25 with an accuracy of $S_T \leq 1 \cdot 10^{-2}$ K. The boiling temperatures of the liquid under study were measured at several fixed pressures, maintained automatically by the mercury-contact manometer. The pressure values appropriating to the manometer contacts were determined by calibration of the manometer with the standard substances: water (double distilled) and *n*-decane (99.9 % mol purity) for which the temperature dependences of the vapor pressure are well-known.[25,26] About 6.5 cm^3 and 9 cm^3 of liquid are required for measuring the boiling and condensation temperatures, respectively.

The boiling temperatures of the di-isobutyl ether were measured over the saturation vapor pressures from (10.8 to 99.6) kPa. The vapor pressure values were corrected for the impurities content using the Raoult law applied to the ideal solution of three components

$$P = P^0 \cdot (1 - \Sigma x_i) + \Sigma P_i x_i \tag{6}$$

where P, P^0, and P_i are the vapor pressures of the solution, the pure substance, and impurity, respectively, and Σx_i denotes a sum of the mole fractions of impurities. The values of x_i were given above. The data on the ln $p(T)$ equations of IBTBE, ETAE, and DBE impurities were taken from refs 14, 13, and 27. Table 5 lists the boiling temperatures, T_b, and the values of saturated vapor pressures determined experimentally, P_{exp}, and corrected for the impurities content, P_{corr}, respectively. A stability of the ether on prolonged boiling was demonstrated by an agreement within ± 2 mK between T_b values measured at the beginning and the end of the experiment at the same pressure 37.26 kPa. Depending on the temperature studied, an influence of the impurities amounts from (50 to 320) Pa in the pressure or from (0.10 to 0.12) K in the temperature. The *pT*-parameters of DIBE were fitted by a semiempirical equation derived from the Clausius−Clapeyron equation[24]

$$-RT \ln P = \Delta H_m(T_m) - \alpha_1 \cdot T + \alpha_2 \cdot \{T - T_m - T \ln(T/T_m)\} - \alpha_3 \cdot \{(1/2) \cdot (T^2 - T_m^2) - T \cdot T_m \ln(T/T_m)\} \tag{7}$$

where α_1, α_2, and α_3 are parameters, and T_m is the mean temperature of the experimental interval.

Table 6. Coefficients of Equations 8 to 9 and *F*-Criteria of Equation 11 for Di-isobutyl Ether

series	A	$-B$	$-C$	$10^3 \cdot D$	F^a	$F^a{}_{0.05}(1,f)$	$\sigma_p{}^b$/Pa
$T_b - P_{exp}$	160.7293	9759.57	23.65007	25.2571	59.24	4.84	9
$T_b - P_{calc}$	163.4804	9850.81	24.11185	25.8584	54.08	4.84	9

[a] $F_{0.05}(1,f)$ and F denote tabulated Fisher's criterion[23] and that estimated from eq 12, respectively. [b] σ_P is the root-mean-square difference between the experimental and calculated P values.

The treatment of the *pT*-parameters was conducted by the least-squares method (LSM) using orthogonal functions in turn with P_{exp} and P_{corr} values.[24] Final equations for the derived thermodynamic functions were transformed for compactness to the forms

$$\ln(P/\text{kPa}) = A + B \cdot (\text{K}/T) + C \cdot \ln(T/\text{K}) + D \cdot (T/\text{K}) \tag{8}$$

$$\Delta_{vap}H_m\ (\text{J} \cdot \text{mol}^{-1}) = R \cdot \{-B + C \cdot (T/\text{K}) + D \cdot (T/\text{K})^2\} \cdot \Delta Z \pm s\{\Delta H'_m(T) + s(\Delta Z) \cdot \Delta H'_m\} \tag{9}$$

$$\Delta C_{p,m}\ (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = C^0_{p,m}(\text{g}) - C^0_{p,m}(\text{liq}) = \text{R} \cdot \{C + 2D \cdot (T/\text{K})\} \pm s(\Delta C_{p,m}) \tag{10}$$

where the coefficients A, B, and C are linear combinations of the parameters in eq 7; the independent coefficient D equals to the minimum orthogonal parameter α_3 of eq 7; ΔZ is the difference between compression factors of the gas and liquid; $s\{\Delta H'_m(T)\}$ is the uncertainty of the value $\Delta_{vap}H_m$ resulting from errors of the *pT*-parameters; and $s(\Delta Z)$ is the error of the ΔZ value evaluated to be equal to about 1 %.[24]

The value of ΔZ that took into consideration the deviation of vapor from ideality and the volume changes of the gas and liquid was calculated from the formula

$$\Delta Z = \{P/(RT)\} \cdot \{V_m(\text{g}) - V_m(\text{liq})\} \tag{11}$$

where $V_m(\text{g})$ is the molar volume of the vapor evaluated based on Tsonopolous, Pitzer, and Cure's corresponding state equation[42] similarly to ref 7. The volume of the liquid, $V_m(\text{liq})$, was calculated from the density of DIBE.

An adequacy of the vapor pressure treatment with four-parametric eq 7 and, accordingly, eq 8 was verified[24] by statistical analysis of the coefficient D using Fisher's criterion F

$$F = D^2/\sigma^2(D) \geq F_{0.05}(1,f), \tag{12}$$

where $F_{0.05}(1, f)$ and F are tabulated[28] and estimated values of the *F*-criterion, and f is the number of degrees of freedom. Table 6 lists the parameters of eqs 8 to 10 and *F*-criterion values of eq 12. Comparing the F and $F_{0.05}(1,f)$ criteria shows that values of the D coefficient, having the largest uncertainties, are significant for both series of the *pT*-parameters which proves an adequate fit of the vapor pressures by eqs 7 and 8. The standard deviations of the fit ± 9 Pa in the pressure or ± 3 mK in temperature are within the experimental errors for both series of the *pT*-parameters.

Density, ρ, of DIBE was determined by means of a quartz pycnometer ($V \sim 1$ cm^3) that was placed in the air thermostat. The temperature of the thermostat was measured by platinum resistance thermometer and kept constant with accuracy ± (2 to 3)$\cdot 10^{-2}$ K. The density was determined in the temperature interval from (298 to 313) K with accuracy ≤ 0.1 %. The ρ values at different temperatures (Table 7) were treated by a linear equation using LSM

$$\rho\ (\text{g} \cdot \text{cm}^{-3}) = \alpha + \beta \cdot T\ (\text{K}) \tag{13}$$

where $\alpha = 1.0465$, $\beta = -0.0010$, and $R^2 = 0.9985$.

Table 7. Densities of Di-isobutyl Ether in Dependence on Temperature

T/K	ρ/g·cm^{-3}
293.15	0.7534[a]
298.22	0.74809
298.18	0.74869
298.14	0.74869
298.07	0.74849
298.09	0.74845
298.06	0.74862
298.15	0.7484[a]
302.68	0.74372
302.73	0.74419
302.79	0.74367
302.83	0.74350
302.81	0.74414
302.86	0.74347
303.15	0.7434[a]
308.15	0.7384[a]
312.99	0.73364
312.95	0.73353
312.72	0.73367
313.03	0.73400
313.02	0.73356
313.15	0.7334[a]

[a] Calculated from eq 13.

Table 8. Thermdynamic Functions of Vaporization of Di-isobutyl Ether for Two Series of the p,T-Parameters, where P_{sat}, $T_{\text{n.b.}}$, and $\Delta_{\text{vap}}H^0_{\text{m}}$ Denote the Saturation Vapor Pressure, Normal Boiling Temperature, and Enthalpy of Vaporization

properties	P_{exp}[a]	P_{corr}[a]	recommended values
P_{sat}(298.15 K)/kPa	2.176	2.161	2.169[b]
$T_{\text{n.b.}}$/K	395.76	395.88	395.82[b]
$\Delta_{\text{vap}}H^0_{\text{m}}$(298.15 K)/kJ·mol^{-1}	41.15 ± 0.66	41.20 ± 0.68	40.85 ± 0.20[8c]
$\Delta_{\text{vap}}H^0_{\text{m}}(T_{\text{n.b.}})$/kJ·mol^{-1}	34.51 ± 0.39	34.52 ± 0.40	

[a] P_{exp} and P_{corr} are the vapor pressure ebulliometrically determined and corrected by eq 6, respectively. [b] Mean values from two series of the pT-parameters. [c] Calorimetric value of the enthalpy of vaporization.[8]

The standard deviations of the eq 13 fit are $\pm 5 \cdot 10^{-4}$ g·cm^{-3}. The density of DIBE was used in calculation of the compressibility factor ΔZ by eq 11 and the critical parameters based on the corresponding states law.

Table 8 lists the vapor pressure at $T = 298.15$ K, the normal boiling temperature, $T_{\text{n.b.}}$, and enthalpies of vaporization of DIBE at $T = 298.15$ K and $T_{\text{n.b.}}$.

Calculations of Thermodynamic Functions of Di-isobutyl Ether

Ideal Gas Thermodynamic Functions. The absolute entropy, $S^0_{\text{m}}(T)$, the changes of the enthalpy, $\Delta^0_{\text{T}}H^0_{\text{m}}$, and the free Gibbs energy of DIBE in the ideal gas state at 298.15 K (Table 9) were calculated using the appropriate functions in the liquid state (Table 4) and the entropy of vaporization, $\Delta_{\text{vap}}S^0(T)$, estimated from the calorimetric $\Delta_{\text{vap}}H^0_{\text{m}}$ value and the entropy of compression, $\Delta S = R \cdot \ln\{P(T)/(101.325)\text{kPa}\}$, calculated from the vapor pressure data (Tables 8 and 9). Two series of the pT-parameters with experimental p values and those corrected by eq 6 were used for calculating the entropy and the free Gibbs energy. Differences between S^0_{m}(298 K)(g), $\{H^0_{\text{m}}(298\text{ K}) - H^0_{\text{m}}(0)\}$(g), and $\{G^0_{\text{m}}(298\text{ K}) - H^0_{\text{m}}(0)\}$(g) values calculated using two series of the pT-parameters are within the error limits: 1.1 J·K^{-1}·mol^{-1}, (0.51 and 1.1) kJ·mol^{-1}, respectively. The ideal gas standard entropy and Gibbs energy of formation (Table 9) were calculated based on the reaction

$$16\text{C(cr., graphite)} + 18\text{H}_2\text{(g)} + \text{O}_2\text{(g)} = 2\{(\text{CH}_3)_2\text{CHCH}_2\}_2\text{O(g)} \quad (14)$$

The absolute entropies of the reagents were taken from the handbook.[29]

Theoretical calculations of the thermodynamic functions were performed by the methods of statistical thermodynamics and the density functional theory (DFT) using the Gaussian 98 software package.[30] The structural parameters of di-isobutyl ether were fully optimized at the B3LYP/6-31G(d,p) level. Vibrational frequencies, zero-point energies, and thermal corrections were calculated at the same level. The scaling factors of 0.958 and 0.975 were applied to C−H stretchings and to all other frequencies, respectively. These values were obtained from fitting the experimental vibrational fundamentals of some related ethers.

The barriers for internal rotation of the CH_3 groups were determined from optimization of the corresponding transition states. The potential functions for internal rotation of i-C_3H_7 and i-C_4H_9 rotors were determined by scanning the torsion angles from (0 to 360)° at 15° increments and allowing all other structural parameters to be optimized at the B3LYP/6-31G(d,p) level. The calculated energy values were fitted to the Fourier function

$$V(\varphi) = V_0 + \frac{1}{2}\sum_n V_n(1 - \cos n\varphi) + \frac{1}{2}\sum_n V'_n(1 - \sin n\varphi) \quad (15)$$

where $V(\varphi)$ is potential energy function.

The entropies, $S°(T)$, heat capacities, $C^\circ_p(T)$, and enthalpies, $H°(T) - H°(0)$, for the temperatures $100\text{ K} \leq T \geq 1500\text{ K}$ were calculated by standard statistical thermodynamic formulas using the rigid-rotor harmonic-oscillator approximation with correction for the internal rotation. The torsion frequencies were omitted in the calculation of thermodynamic functions. Internal rotational contribution for each rotor was calculated by direct summation over the energy levels obtained by diagonalization of the one-dimensional Hamiltonian matrix associated with potential function from eq 15.

The enthalpy of formation, $\Delta_{\text{f}}H^\circ_{298}$, of DIBE (Table 9) was calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level using two isodesmic reactions and available experimental data on the enthalpies of formation for related ethers (Table 10).[31] As was shown in our previous studies,[14−16] such calculations led to reasonable accuracy. In spite of a poor group balance in the second reaction of Table 10, both of them give close $\Delta_{\text{f}}H^\circ_{298}$ values within error limits, and their average value is accepted for the enthalpy of formation of DIBE after correction for conformation mixture by Boltzman averaging

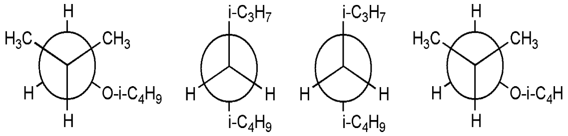
Table 9. Ideal Gas Thermodynamic Functions of Di-isobutyl Ether at $T = 298.15$ K Calculated from Calorimetric Data on the Heat Capacity and Enthalpy of Vaporization and the the Vapor Pressure Data

$\Delta_{\text{vap}}S_{\text{m}}(T)$/J·K^{-1}·mol^{-1}	137.01 ± 0.67
$R \cdot \ln\{P(T)/(101.325)\text{ kPa}\}$/J·K^{-1}·mol^{-1} [a]	−31.96
S^0_{m}(g)/J·K^{-1}·mol^{-1}	479.79 ± 1.1
$\Delta^0_{\text{T}}H^0_{\text{m}}$(g)/kJ·mol^{-1}	101.15 ± 0.51
$\{G^0_{\text{m}}(T) - H^0_{\text{m}}(0)\}$(g)/kJ·mol^{-1}	−41.90 ± 0.61
$\Delta_{\text{f}}S^0_{\text{m}}(T)$(g)/J·K^{-1}·mol^{-1}	−843.8 ± 3.2
$\Delta_{\text{f}}H^0_{\text{m}}(T)$(g)/kJ·mol^{-1} [b]	−345 ± 5
$\Delta_{\text{f}}G^0_{\text{m}}(T)$(g)/kJ·mol^{-1}	−93.62

[a] The compression entropy of the ideal gas from $P(298.15)$ to $P = 101.325$ kPa is the mean value calculated based on two series of the pT-parameters containing experimental p values and those corrected by eq 6. [b] See Table 10.

$$\Delta_f H^\circ_{298}(g) = (-345 \pm 5)\ \text{kJ·mol}^{-1}$$

It was found in calculation of the geometry, vibrational frequencies, and torsional potentials on the B3LYP/6-31G(d,p) level that the most stable conformer of DIBE is that of *gauche*$^+$−*trans*−*trans*−*gauche*$^+$ (G^+TTG^+) (C_2 symmetry). This conformer has *gauche* and *trans* locations of the bulky groups relative to two C−C bonds [$(CH_3)_2CH-CH_2OCH_2-CH(CH_3)_2$] and two C−O bonds [$(CH_3)_2CHCH_2-O-CH_2CH(CH_3)_2$], respectively.



The product of principal moments of inertia for optimized geometry and vibrational frequencies of the G^+TTG^+ conformer is given in Table 11. Next, low-energy stable conformers of DIBE are G^+TTG^- (C_s), $TTTG$ (C_1), and $TTTT$ (C_{2v}) with relative energies of (0.6, 1.5, and 3.0) kJ·mol^{-1} (46, 129, and 252) cm^{-1}, respectively. Potential energy curves obtained by scanning the torsion angles φ(C−O) and φ(C−C) of the G^+TTG^+ conformer are shown in Figure 2, and the V_n values in the expansion for the torsional potentials in eq 15 are given in Table 11. As seen from Figure 2 (the lower potential), two of three low energy conformers of DIBE, G^+TTG^- and $TTTG$, appear on the torsional potential, and therefore, these conformers will be taken into account in thermodynamic function calculation. To account for the $TTTT$ conformer, the geometry optimization and potential energy scan (Figure 3) were performed for this conformer; the corresponding molecular parameters are listed in Table 11. Thus, the thermodynamic functions of DIBE were calculated for an equilibrium mixture of G^+TTG^+, G^+TTG^-, $TTTG$, and $TTTT$ conformers. The vibrational−rotational contributions for G^+TTG^- and $TTTG$ conformers were accepted to be the same as for G^+TTG^+, whereas the difference in geometry and vibrational frequencies was taken into account for the $TTTT$ conformer. There are also higher-energy stable conformers of DIBE. One of them, $G^+G^+TG^+$ (Figure 3, the upper potential), was considered in this work; however, it had practically no effect on the calculated values of thermodynamic functions.

Table 10. Enthalpies of Reactions ($\Delta_r H^\circ_{298}$) and Enthalpies of Formation ($\Delta_f H^\circ_{298}$) of DIBE Calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) Level from Isodesmic Reactions

	kJ·mol^{-1}	
reaction	$\Delta_r H^\circ_{298}$	$\Delta_f H^\circ_{298}$
i-C_4H_9−O−i-C_4H_9 + CH_3−O−t-C_4H_9[a] = i-C_4H_9−O−t-C_4H_9[a] + CH_3−O−C_4H_9[a]	1.7	−345.1
i-C_4H_9−i-C_4H_9 + CH_3−O−CH_3[a] = i-C_3H_7−O−i-C_3H_7[a] + C_2H_5−O−C_2H_5[a]	−39.2	−348.0
average		−346.6
average value corrected for conformer mixture		−345.2

[a] The enthalpies of formation of ethers were taken from the handbook of Pedley.[31]

Table 11. Symmetry, Products of Moments of Inertia, Vibrational Frequencies, and Internal Rotational Molecular Constants of DIBE Calculated at the B3LYP/6-31G(d,p) Level

G^+TTG^+ conformer	
Point group: C_2	
Symmetry number: $\sigma = 2$	$I_AI_BI_C = 461825 \cdot 10^{-117}$ g^3·cm^6
Vibrational frequencies:[a] 3006, 3006, 2983, 2983, 2974, 2973, 2969, 2968, 2912, 2912, 2906, 2906, 2904, 2904, 2857, 2855, 2832, 2820, 1506, 1490, 1490, 1485, 1479, 1479, 1468, 1467, 1467, 1466, 1425, 1397, 1392, 1378, 1378, 1372, 1347, 1347, 1308, 1297, 1255, 1247, 1179, 1174, 1172, 1162, 1136, 1131, 1118, 1008, 959, 954, 943, 942, 915, 914, 910, 903, 825, 803, 526, 462, 415, 408, 361, 350, 260, 253, 245,[b] 225,[b] 215,[b] 211,[b] 155,[b] 129, 91,[b] 49,[b] 38[b]	
$TTTT$ conformer	
$\Delta E = 3.0$ kJ·mol^{-1}	Symmetry number: $\sigma = 2$
Point group: C_{2v}	$I_AI_BI_C = 401928 \cdot 10^{-117}$ g^{-3}·cm^6
Vibrational frequencies:[a] 3051, 3050, 3047, 3046, 3031, 3031, 3029, 3028, 2969, 2969, 2964, 2964, 2941, 2941, 2911, 2910, 2887, 2875, 1507, 1492, 1489, 1486, 1477, 1474, 1472, 1469, 1464, 1463, 1425, 1397, 1386, 1379, 1378, 1359, 1343, 1336, 1334, 1329, 1252, 1241, 1187, 1182, 1158, 1138, 1137, 1135, 1058, 979, 959, 951, 943, 941, 941, 937, 905, 901, 801, 775, 610, 538, 392, 378, 366, 366, 287, 268, 240,[c] 218,[c] 207,[c] 205,[c] 156,[c] 110, 97,[c] 53,[c] 26[c]	

[a] Scaling factor of 0.958 was used for C−H stretchings and 0.975 for other modes. [b] Instead of these torsional modes of the G^+TTG^+ conformer, the contributions due to the internal rotation were calculated using the following coefficients V_n in eq 15, reduced moment of inertia I_r, and symmetry number of rotor σ_m: CH_3 group (2): $I_r = 0.5147 \cdot 10^{-39}$ g·cm^2, $\sigma_m = 3$, $V_3 = 1496$ cm^{-1}; CH_3 group (2): $I_r = 0.5237 \cdot 10^{-39}$ g·cm^2, $\sigma_m = 3$, $V_3 = 1570$ cm^{-1}; i-C_4H_9 group (2): $I_r = 6.8418 \cdot 10^{-39}$ g·cm^2, $\sigma_m = 1$, $V_0 = -119.5$, $V_1 = 2247.2$, $V_2 = -631.0$, $V_3 = 782.8$, $V_4 = -68.5$, $V'_1 = 716.2$, $V'_2 = -556.4$, $V'_3 = 38.8$, $V'_4 = 83.8$ cm^{-1}; i-C_3H_7 group (2): $I_r = 7.2981 \cdot 10^{-39}$ g·cm^{-1}, $\sigma_m = 1$, $V_0 = -21.5$, $V_1 = -419.8$, $V_2 = 205.1$, $V_3 = 1593.5$, $V_4 = 74.6$, $V_5 = 17.1$, $V_6 = -61.5$, $V'_1 = 12.7$, $V'_2 = -11.2$, $V'_3 = 47.0$, $V'_4 = 12.8$, $V'_5 = -10.7$, $V'_6 = -8.4$ cm^{-1}. [c] Instead of these torsional modes of the $TTTT$ conformer, the contributions due to the internal rotation were calculated using the following coefficients V_n in eq 15, reduced moment of inertia I_r, and symmetry number of rotor σ_m: CH_3 group (4): $I_r = 0.5223 \cdot 10^{-39}$ g·cm^2, $\sigma_m = 3$, $V_3 = 1746$ cm^{-1}, i-C_4H_9 group (2): $I_r = 7.8900 \cdot 10^{-39}$ g·cm^2, $\sigma_m = 1$, $V_1 = 3011.6$, $V_2 = -864.3$, $V_3 = 731.4$, $V_4 = -44.0$, $V_5 = 51.2$, $V_6 = 12.1$ cm^{-1}, i-C_3H_7 group (2): $I_r = 8.3412 \cdot 10^{-39}$ g·cm^{-1}, $\sigma_m = 1$, $V_1 = -424.7$, $V_2 = 209.0$, $V_3 = 1589.5$, $V_4 = 70.2$, $V_5 = 13.2$, $V_6 = -61.8$ cm^{-1}.

Thermodynamic functions, $S^\circ(T)$, $C^\circ_p(T)$, and $H^\circ(T) - H^\circ(0)$, were calculated using the rigid-rotor harmonic-oscillator approximation for all rotation and vibration modes, except for internal rotation modes for which the independent-rotor model was employed. This model results in the overestimated values of thermodynamic functions as compared with $S^\circ(T)$ and $C^\circ_p(T)$ values determined from calorimetric measurements for alkyl ethers.[14−16] As in our previous works,[14−16] the correction for rotor−rotor coupling was introduced by multiplying the internal rotational contributions to the thermodynamic functions by the empirical factor K_{r-r}. The K_{r-r} value of 0.9875 was found by fitting to the experimental entropies of DIBE. The difference between experimental and thus calculated entropies is listed in Table 12. It should be noted that the K_{r-r} factor is the additive parameter, and it depends on the types and the number of atom groups in the ether. Since the calculated entropy values were fitted to the experimental ones, their uncertainty is close to that of the experimental values at temperatures from (298.15 to 350) K and should be ≤ 5 J·K^{-1}·mol^{-1} at higher temperatures. The uncertainty of calculated $C^\circ_p(T)$ values is estimated to be from (5 to 8) J·K^{-1}·mol^{-1}. The ideal gas thermodynamic functions including the enthalpy, $\Delta_f H^0$, and Gibbs energy, $\Delta_f G^0$, formation of DIBE in the wide temperature range from (0 to 1500) K are listed in Table 13.

Extrapolation of the Vapor Pressure to Entire Range of Liquid. The saturated vapor pressure of DIBE in the "atmospheric" pressure range was extended to the triple point temperature by simultaneous treatment of the pT-parameters and low-temperature differences between the heat capacities of the

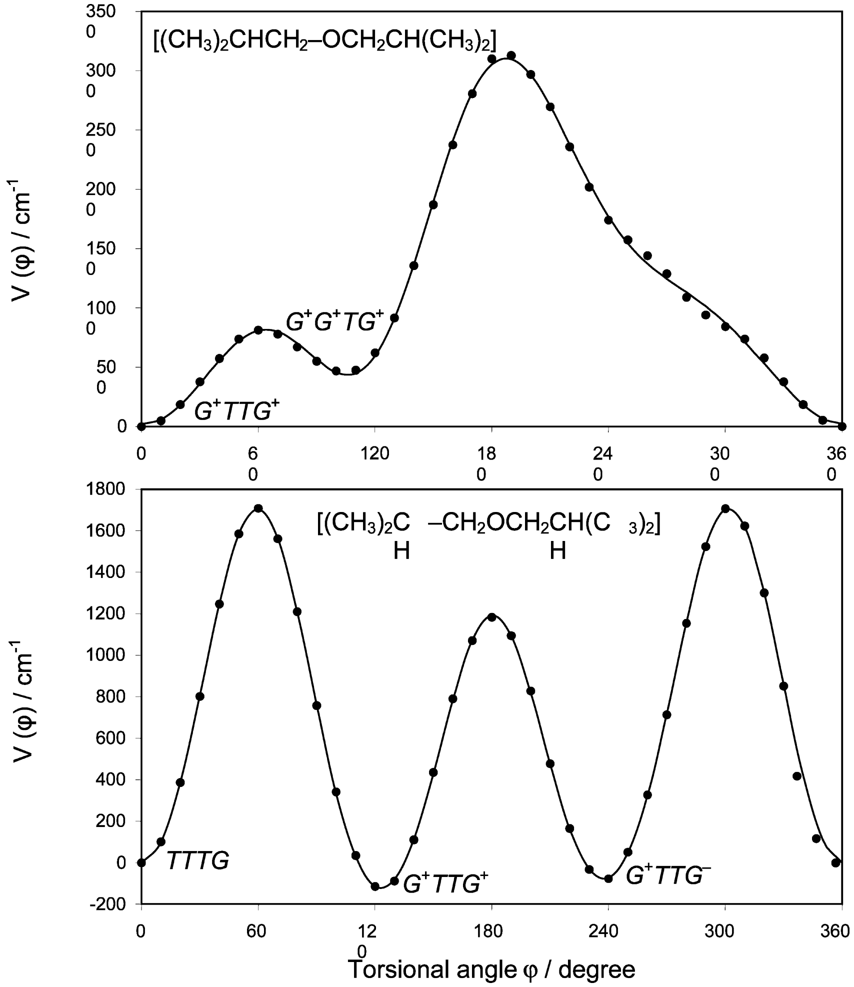


Figure 2. Torsional potential functions obtained by scanning the torsional angles φ(C−O) and φ(C−C) of the G^+TTG^+ conformer of DIBE. Points are the values calculated at the B3LYP/6-31G(d,p) level of theory. Line is the Fourier expansion with coefficients listed in Table 11.

ideal gas, $C^0_{p,\mathrm{m}}(\mathrm{g})$, and liquid, $C^0_{p,\mathrm{m}}(\mathrm{liq})$, using a system of two consistent equations

$$\ln(P/\langle P\rangle) = A' + B'/T + C'\cdot\ln T + D'\cdot T \qquad (16)$$

$$(\Delta C_{p,\mathrm{m}}/2)/R = (1/2)\cdot\{C^0_{p,\mathrm{m}}(\mathrm{g}) - C^0_{p,\mathrm{m}}(\mathrm{liq})\}\cdot R = C'/2 + D'\cdot T \qquad (17)$$

Here, the $\Delta C_{p,\mathrm{m}}$ value is the second derivative of the vapor pressure by the temperature; $\langle P\rangle$ is the vapor pressure at the mean temperature $\langle T\rangle$ of the experimental pT-interval; and A', B', C', and D' are the coefficients of the combined treatment of the vapor pressure and heat capacities. This method was shown[32] to give reliable results even when the vapor pressure of the narrow temperature interval ($\Delta T \le 50$ K) was extended to the wide temperature range ($\Delta T_{\mathrm{extr}} \ge 100$ K). Experimental data on the heat capacity of the liquid were taken for the temperature interval from (195 to 250) K (Table 4). The heat capacity of the ideal gas was computed by the above-mentioned statistical thermodynamic method

$$C^\circ_p(T) = a_1 + a_2T^{-2} + a_3T + a_4T^2 + a_5T^3 \qquad (18)$$

where $a_1 = 131.863$; $a_2 = -3.646\cdot10^5$, $a_3 = -0.1490$, $a_4 = 1.93\cdot10^{-3}$, and $a_5 = -1.803\cdot10^{-6}$.

The C°_p values used in calculation by eqs 16 and 17 are given in Table 14. The coefficients of these equations and their uncertainties calculated by LSM are listed in Table 15. For comparison, the corresponding values of eq 8 are also given in this table. As seen from Table 15, combined treatment of the pT-parameters and $\Delta C_{p,\mathrm{m}}$ values promotes the considerable decreasing of the uncertainties of approximated coefficients and therefore improves the extrapolation prediction of eqs 16 and 17. Nevertheless, eq 8 is more accurate when it is used as an interpolated one. The vapor pressure of diisobutyl ether evaluated at the triple point temperature $T_{\mathrm{tp}} = 190.40$ K equals $P_{\mathrm{tp}} = 0.06$ Pa. The error of extrapolation ≤ 10 % was evaluated by comparing the calculated and experimental P_{tp} values for some well-studied compounds.[32,43]

Extending the saturation vapor pressure of DIBE up to the critical region was carried out by a corresponding states law in Fillipov's version.[33] This method allowed us to compute the critical parameters T_{c}, V_{c}, and P_{c} and criterion of similarity A_{c} based on the saturated vapor pressures and the density of the liquid and to obtain an empirical equation of the binodal for extrapolation of the vapor pressure to the critical temperature.[33] The algorithm and the uncertainties of the critical parameters calculation were given in ref 34. The binodal equation[33] for calculating the saturation vapor pressure of DIBE between $T_{\mathrm{n.b.}}$ and T_{c} was determined

$$\lg(P^*/P) = a'\cdot\lg(T^*/T) + \{(T^*/T) - 1\}\cdot\{b' + c'\cdot(T^*/T)\} \qquad (19)$$

where P^* and T^* denote pseudocritical quantities and $a' = 3.9726$, $b' = 0.3252$, and $c' = 0.40529$ are the empirical coefficients. Table 16 reports the critical and pseudocritical parameters of DIBE. The uncertainties of the T_{c}, $V_{\mathrm{m,c}}$, and A_{c} values are from (1 to 2) %. The error of P_{c} estimation is within the limit from (3 to 4) %.

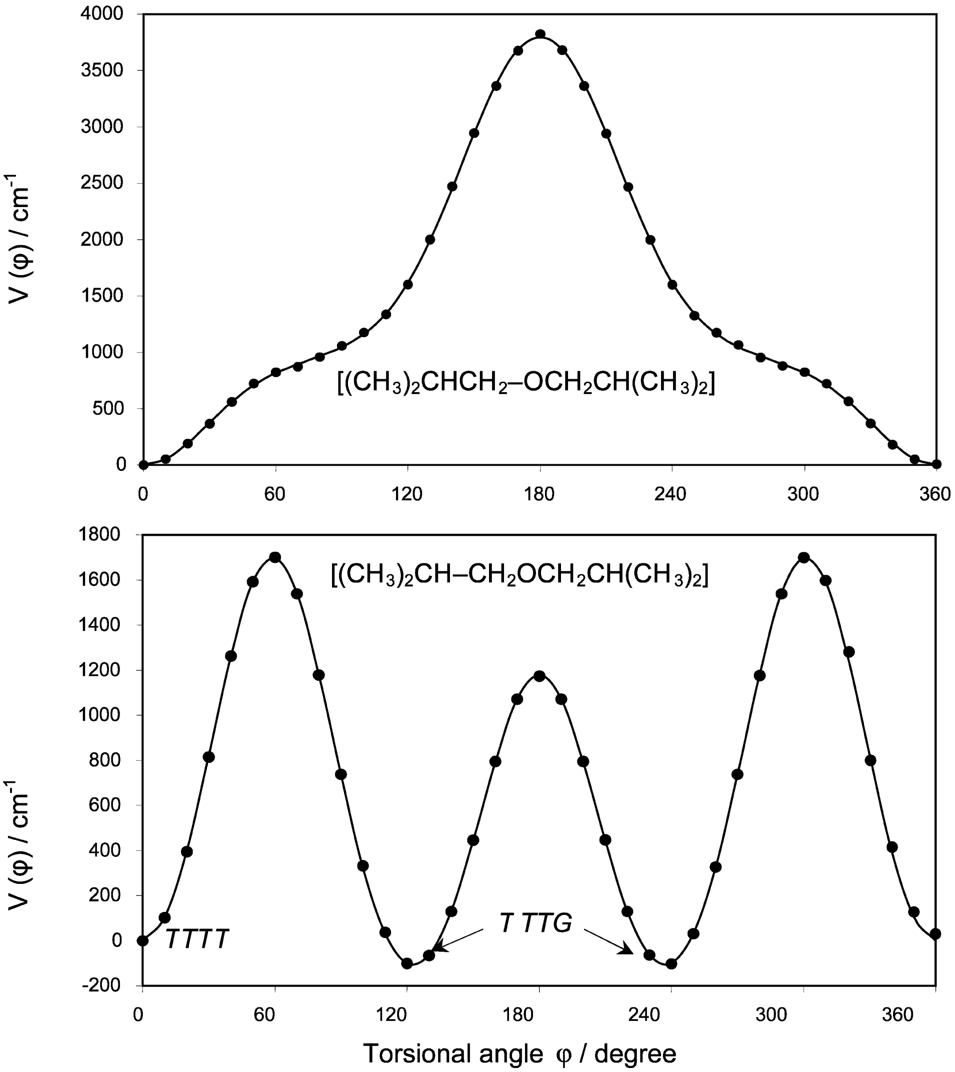


Figure 3. Torsional potential functions obtained by scanning the torsional angles φ(C−O) and φ(C−C) of the *TTTT* conformer of DIBE. Points are the values calculated at the B3LYP/6-31G(d,p) level of theory. Line is the Fourier expansion with coefficients listed in Table 11.

Table 12. Comparison between Experimental and Calculated Entropies of DIBE in the Ideal Gas State

T	J·K^{-1}·mol^{-1}		
K	S_{exp}	S_{calcd}	$S_{\text{exp}} - S_{\text{calcd}}$
298.15	479.79 ± 1.5[a]	480.49	−0.70
298.15	481.01 ± 2.5[b]	480.49	0.52
330	502.79 ± 1.6[b]	502.37	0.42
340	509.55 ± 1.5[b]	509.16	0.39

[a] Absolute entropies computed using the calorimetric $\Delta_{\text{vap}}S$ value. [b] Absolute entropies obtained using the $\Delta_{\text{vap}}S$ values derived from vapor pressure data (Table 5).

Discussion of Thermodynamic Properties of the Branched Ethers

This section deals with reviewing and summarizing the data on the vapor pressures, enthalpies of vaporization, heat capacities, and other thermodynamic functions of some branched ethers C_5 to C_9, which were studied recently in the series of papers (refs 2 to 16) as promising high octane enhancing additives to the motor fuels. The main attention is given to verification of the reliability and mutual consistency of the data on thermodynamic properties of the ethers.

Most of the ethers under review are tertiary ones. Table 17 lists the purity of the substances, the densities, ρ, and coefficients of molecular packing, K_{mp}, of the liquid ethers, the temperature interval of the experimental pT-parameters, the normal boiling temperatures, $T_{\text{n.b.}}$, the enthalpies of vaporization calculated from the vapor pressure, $\Delta_{\text{vap}}H^0_{\text{m}}(pT)$, and measured by calorimetric method, $\Delta_{\text{vap}}H^0_{\text{m}}(\text{calor})$, the temperature interval of the heat capacities, the triple point temperatures, T_{tp}, studied by adiabatic calorimetry, and the vapor pressures at T_{tp}, calculated by the system of eqs 16 and 17. The impurity contents in some ethers determined by the fractional melting technique are higher than those of the gas−liquid chromatography (GLC) that can be explained by less sensitivity of GLC. Considerable contents of impurities in three ethers, IPTBE, NPTBE, and DIBE, were taken into account by corrections estimated using eq 6 prior to approximation of the temperature dependence of the vapor pressure by eq 7. The coefficients K_{mp} were calculated similarly to Askadskii et al.[38] The saturation vapor pressures of the ethers were determined by comparative ebulliometry in narrow temperature intervals of $32 \leq (\Delta T/\text{K}) \leq 80$ of the "atmospheric" pressure range $6 \leq (\Delta P/\text{kPa}) \leq (101/202)$. The most accurate vapor pressure data of the organic compounds used to be measured in this pressure range that allows reliable extending of the pT-parameters to the entire range of the liquid phase from the triple to the critical temperatures. Due to less K_{mp} coefficients, the tertiary ethers

Table 13. Ideal Gas Thermodynamic Properties of Di-isobutyl Ether

T	C_p°	S°	$-[G^\circ - H^\circ(0)]/T$	$H^\circ - H^\circ(0)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
0	0.0	∞	0.0	0.0	−293.8	−293.8
100	101.9	321.0	250.9	7.0	−315.7	−247.7
150	130.5	367.9	282.3	12.8	−323.7	−212.0
200	155.7	409.0	308.9	20.0	−331.0	−173.6
250	181.0	446.4	332.7	28.4	−338.3	−133.4
298.15	207.0	480.5	353.9	37.8	−345.0	−93.3
300	208.0	481.8	354.6	38.1	−345.3	−91.8
350	235.8	515.9	375.3	49.2	−351.7	−49.0
400	263.0	549.2	394.9	61.7	−357.5	−5.4
450	288.8	581.7	413.9	75.5	−362.6	39.0
500	312.7	613.4	432.2	90.6	−367.1	83.8
600	354.4	674.2	467.5	124.0	−374.2	174.7
700	389.1	731.5	501.2	161.2	−379.3	266.6
800	418.3	785.4	533.4	201.6	−382.5	359.2
900	443.0	836.1	564.2	244.7	−384.1	452.0
1000	464.2	883.9	593.8	290.1	−384.5	544.9
1100	482.3	929.1	622.3	337.4	−383.8	637.8
1200	498.0	971.7	649.6	386.5	−382.3	730.6
1300	511.4	1012.1	676.0	437.0	−380.0	823.3
1400	523.1	1050.5	701.4	488.7	−377.3	915.8
1500	533.1	1086.9	725.9	541.5	−374.2	1008.0

Table 14. Ideal Gas Heat Capacities of Di-isobutyl Ether, Calculated from Equation 18

T/K	$C_p^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
195	153.22
200	155.69
205	158.17
210	160.65
215	163.15
220	165.66
225	168.18
230	170.71
235	173.27
240	175.84
245	178.43
250	181.04

Table 15. Coefficients of Equation 8 and the System of Equations 16 and 17 for Di-isobutyl Ether

	A'^a	$-B'^a$	$-C'^a$	$10^3\cdot D'^a$
eqs 16 and 17[b]	109.97555 ± 0.1	8497.71 ± 6	15.51471 ± 0.03	12.475 ± 0.06
eq 8	154.13637 ± 15	9681.53 ± 459	23.20218 ± 3	24.628 ± 3

[a] The A', B', and C' are the linear correlated coefficients; therefore, their uncertainties are inexact and can not be used for accurate calculations. [b] Equations were derived based on experimental T_b data and mean values of the vapor pressures calculated from the P_{exp} and P_{corr} data (Table 5).

Table 16. Critical T_c, P_c, and $V_{m,c}$ and Pseudocritical T*, P* Quantities, the Criterion of Thermodynamic Similarity A_c Triple Point Temperatures, T_{tp}, and Saturated Vapor Pressures, P_{tp} at T_{tp} for Di-isobutyl Ether

T_c	P_c	$V_{m,c}$	T^*	P^*		P_{tp}	T_{tp}
K	MPa	$\text{cm}^3\cdot\text{mol}^{-1}$	K	MPa	A_c	Pa	K
560	2.33	513	790	21.26	1.00	0.06	190.40

with an isomeric alkyl group have less $\Delta_{vap}H^0_m(298.15)$ values than those with a normal alkyl group.

Most of the data on heat capacity and the triple point temperatures were determined by R. V. Varushchenko, A. I. Druzhinina, and coauthors[12−16] in a fully automated adiabatic calorimeter described in this paper. The accuracy of the heat capacity data was on the average from (0.1 to 0.3) %. The triple points of the ethers are between the temperatures (157.7 and 190.4) K. The vapor pressures P_{tp} at T_{tp}, calculated by the above-mentioned method, vary in a wide pressure range from ($6\cdot 10^{-4}$ to 2.8) Pa (Table 17).

Testing the reliability and an internal consistency of thermodynamic functions in the series of ethers was carried out based on the methods of statistical thermodynamics and additivity principle. The compounds under study were divided into four families: *n*-alkyl-*tert*-amyl ethers, *n*-alkyl-*tert*-butyl ethers, *i*-alkyl-*tert*-butyl ethers, and di-iso-alkyl ethers (Table 17). A critical analysis of the data on the enthalpies of vaporization in the first family was carried out depending on the molar mass of the species. Figure 4 shows a distribution of the enthalpies of vaporization of *n*-alkyl-*tert*-amyl ethers relatively to a straight line obtained by the least-squares correlation of the calorimetric $\Delta_{vap}H^0_m(298.15)$ values of ETAE and *n*-BTAE and the $\Delta_{vap}H^0_m(298.15)$ value of MTAE calculated from the vapor pressure data of ref 3

$$\Delta_{vap}H^0_m(298.15)\ (\text{kJ}\cdot\text{mol}^{-1}) = 0.260\cdot M + 8.100, \qquad R^2 = 0.9996 \qquad (20)$$

where R^2 is a correlation coefficient.

Replacing the calculated $\Delta_{vap}H^0_m(298.15)$ value of MTAE by the appropriate calorimetric one[37] (Table 17) decreases the R^2 coefficient down to 0.9903 which proves a poor quality of the calorimetric data in ref 37.

The reliability and internal consistency of the $\Delta_{vap}H^0_m(298.15)$ values in all four series of ethers were verified using a second-order group-additivity method, originally introduced by S. W. Benson.[39] Table 18 lists the recommended experimental and calculated enthalpies of vaporization and the values of group increments $\Delta(\Delta_{vap}H^0_m)$ evaluated based on the group increments for enthalpies of formation in the liquid and ideal gas states by Domalski and Hearing.[40] Two $\Delta(\Delta_{vap}H^0_m)$ increments for $C-(O)(C)_3$ and $C-(O)(C)_2(H)$ groups (Table 18) were defined more accurately in this work using the enthalpies of vaporization of *i*-BTBE, DIBE, and DIPE. The mean deviation of the calculated $\Delta_{vap}H^0_m(298.15)$ values from the recommended ones equals 3.3 %. When using the increment of 8.71 kJ·mol^{-1} for the $C-(O)(C)_3$ group from ref 40, the appropriate mean deviation increased to 25 %. This can be explained by the erroneous value of this increment since there was a small number of the experimental $\Delta_{vap}H^0_m(298.15)$ values of the branched ethers at the time, when monograph 40 was written. A mean deviation, 3.9 %, similar to that in our work, was obtained when using appropriate group increments by Cohen.[41]

Table 17. Thermodynamic Properties[a] of Some Branched Ethers

		$\rho(T)$(298.15)		$\Delta T(p\text{-}T)$	$T_{\text{n.b.}}$	$\Delta_{\text{vap}}H^\circ_{\text{m}}$(298.15) $(p\text{-}T)$[e]	$\Delta_{\text{vap}}H^\circ_{\text{m}}$(298.15) (calor)	$\Delta T\ (C_{p,\text{m}} - T)$	T_{tp}	P_{tp}
compounds[b]	purity[c,d]	$\text{g}\cdot\text{cm}^{-3}$	K_{mp}[g](298.15)	K	K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	K	K	Pa
$CH_3OC(CH_3)_3$ MTBE	99.95[c]	0.7352[35]	0.5420	287 − 351[2]	328.30[2] 328.32[3] 328.2[36]	29.96 ± 0.39 30.24 ± 0.35 30.23[11]	30.04 ± 0.2[8]	11 − 308[11]	164.56 ± 0.01	–
$CH_3OC(CH_3)_2CH_2CH_3$ MTAE		0.77074[9] (at 293.15 K)	–	294 − 359[9] 306 − 359[3]	359.58[9] 359.39[3]	34.75 ± 0.38 35.05 ± 0.70	35.8[37,f]	–	–	–
$(i\text{-}C_3H_7)_2O$ DIPE	99.91[c] 99.86[d]	0.7256[27] (at 293.15 K)	0.5329	308 − 340[7]	341.63[7] 341.64[2]	32.73 ± 0.50	32.26 ± 0.2[8]	14 − 450[10]	187.77 ± 0.01	2.8[7]
$C_2H_5OC(CH_3)_3$ ETBE	99.9[c] 99.91[d]	0.7351[7] 0.7353[35]	0.5416	343 − 398[7]	345.85[7] 345.86[3]	33.10 ± 0.36 32.98 ± 0.58	32.97 ± 0.2[8]	8 − 344[13]	179.33 ± 0.01	0.65[7]
$i\text{-}C_3H_7OC(CH_3)_3$ *i*-PTBE	99.97[c] 99.11[d]	0.7354[4]	0.5420	305 − 360[4]	360.67[4] 360.43[3] 360.7[8]	34.47 ± 0.55 35.06 ± 0.67	34.48 ± 0.20[4] 34.67 ± 0.18[8]	10 − 353[12]	184.78 ± 0.5	0.10[g]
$n\text{-}C_3H_7OC(CH_3)_3$ *n*-PTBE	99.97[c] 99.45[d]	0.7455[4]	0.5490	315 − 370[4]	370.89[4]	37.13 ± 1.05	36.57 ± 0.20[4] 36.76 ± 0.18[8]	10 − 353[12]	179.6 ± 0.1	0.64[g]
$C_2H_5OC(CH_3)_2CH_2CH_3$ ETAE	99.9[c] 99.87[d]	0.7614[5] 0.7609[35]	0.5607	318 − 374[5]	374.82[5] 374.70[3]	38.03 ± 0.57 38.07 ± 1.02	38.19 ± 0.16[5]	8 − 344[13]	157.7 ± 0.1	$1\cdot10^{-3}$[g]
$i\text{-}C_4H_9OC(CH_3)_3$ *i*-BTBE	99.92[c] 99.92[d]	0.7486[7]	0.5505	311 − 385[7]	386.06[7] 386.12[6]	39.13 ± 0.51	39.12 ± 0.2[8] 39.17 ± 0.27[6]	8 − 353[14]	162.33 ± 0.01	$6\cdot10^{-4}$[7]
$(i\text{-}C_4H_9)_2O$[g] DIBE	99.56[c] 99.04[d]	0.7484	0.5489	331 − 395	395.82	41.18 ± 0.67	40.85 ± 0.2[8]	8 − 373	190.40 ± 0.04	0.06
$n\text{-}C_4H_9OC(CH_3)_3$ *n*-BTBE	99.9[c]	0.7582[6]	0.5582	359 − 395[6]	396.58[6]	41.82 ± 1.7	41.58 ± 0.15[6]	–	–	–
$n\text{-}C_4H_9OC(CH_3)_2CH_2CH_3$ *n*-BTAE	99.9[c]	0.7748[6]	0.5703	331 − 419[6]	422.21[6]	45.96 ± 1.5	45.65 ± 0.47[6]	–	–	–

[a] Thermodynamic properties: density of liquid, $\rho(T)$; coefficient of molecular packing, K_{mp}; temperature interval of pT-parameters, $\Delta T(p\text{-}T)$; normal boiling temperature, $T_{\text{n.b.}}$; enthalpy of vaporization calculated from pT-parameters, $\Delta_{\text{vap}}H^\circ_{\text{m}}(p\text{-}T)$; calorimetric value, $\Delta_{\text{vap}}H^\circ_{\text{m}}$(calor); temperature interval of the heat capacity, $\Delta T(C_{p,\text{m}} - T)$; triple point temperature,T_{tp}; vapor pressure at T_{tp}, P_{tp}. [b] The ethers under study: methyl-*tert*-butyl, MTBE; methyl-*tert*-amyl, MTAE; di-*iso*-propyl, DIPE; ethyl-*tert*-butyl, ETBE; *iso*-propyl-*tert*-butyl, *i*-PTBE; *n*- propyl-*tert*-butyl, *n*-PTBE; ethyl-*tert*-amyl, ETAE; *iso*-butyl-*tert*-butyl, *i*-BTBE; di-*iso*-butyl, DIBE; *n*-butyl-*tert*-butyl, *n*-BTBE; *n*-butyl-*tert*-amyl, *n*-BTAE. [c] GLC, mass %. [d] Calorimetry, mol %. [e] The $\Delta_{\text{vap}}H^\circ_{\text{m}}(298.15)(p\text{-}T)$ values were calculated in this work by eq 9 using pT-data of references cited in column with $T_{\text{n.b.}}$ values. [f] An uncertainty of the value was not ascertained. [g] Values obtained in this work.

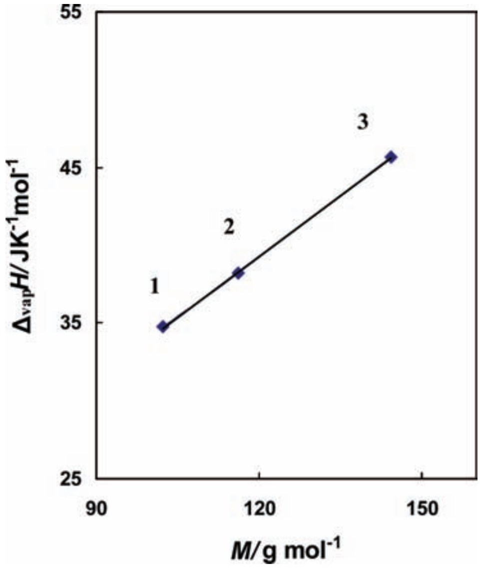


Figure 4. Change of the enthalpies of vaporization in the series of alkyl-*tert*-amyl ethers: methyl-*tert*-amyl ether[9] (1), ethyl-*tert*-amyl ether[5] (2), and *n*-butyl-*tert*-amyl ether[6] (3). The straight line was computed from eq 20. M is a molar mass of the compound.

The result of this analysis proves a mutual consistency of the enthalpies of vaporization within ≤ 4 % for the series of branched ethers studied.

The critical analysis of the data on the absolute entropies of the ethers was carried out for the liquid and ideal gas states (Table 19). The entropies in the liquid state determined from the heat capacity data, S^0_{m}(liq)(calor), were compared with those calculated by Benson's group-additivity method, S^0_{m}(liq)(calcd), and obtained by statistical thermodynamics based on B3LYP/6-31G(d,p) calculations, S^0_{m}(g)(stat. therm.). Calorimetric values of S^0_{m}(liq)(298.15) agree within errors limits with those calculated by the group-additivity method for all compounds excepting *i*-propyl-*tert*-butyl ether. There are two values of absolute entropy for this ether caused by the existing two polymorphs revealed on the heat capacity curve of this compound (Figure 5).[12] Due to uninterrupted change of the heat capacity curve of the polymorph II before the fusion, this polymorph was interpreted by mistake as a stable one. The S^0_{m}(liq)(298.15) values of polymorphs II and II′ deviate from appropriate absolute entropy, calculated by the group-additivity method, by 4 % and 1.5 %, respectively (Table 19). Taking into account a far larger deviation for polymorph II and experimental fact that it could be obtained only once,[12] this polymorph should be considered as a metastable one. The heat capacities of the stable polymorph II′[12] were fitted by polynomials (5). The rms deviation between the experimental and calculated $C_{p,\text{m}}$ values equals 0.18 %. Smoothed values of $C_{p,\text{m}}$ and thermodynamic functions $S^0_{\text{m}}(T)$, $\{H^0_{\text{m}}(T) - H^0_{\text{m}}(0)\}$, and $\{G^0_{\text{m}}(T) - H^0_{\text{m}}(0)\}$ for the whole temperature range studied are listed in Table 20.

The ideal gas entropies determined based on S^0_{m}(liq)(calor) values, entropies of vaporization, and the entropies of the ideal gas compression, S^0_{m}(g)(calor), are conformed within error limits to those obtained by statistical thermodynamics and B3LYP/6-31G(d,p) calculations (Table 19). An agreement between absolute entropies obtained by different methods for the liquid and ideal gas states proves the reliability of these data and the all values used for calculation of the S^0_{m}(g)(calor) values, namely, the heat capacities, enthalpies of vaporization, and vapor pressures for all ethers considered in Table 19.

Table 18. Recommended Experimental $\Delta_{\mathrm{vap}}H^0_{\mathrm{m}}$(298.15) Values of Some Branched Ethers and Those Calculated Based on Benson's Group Additive Values $\Delta(\Delta_{\mathrm{vap}}H^0_{\mathrm{m}})$[40]

compounds[a]	$\Delta_{\mathrm{vap}}H^0_{\mathrm{m}}$(298.15)/kJ·mol^{-1} (recommended)[b]	$\Delta_{\mathrm{vap}}H^0_{\mathrm{m}}$(298.15)/kJ·mol^{-1} (calculated)	$\Delta(\Delta_{\mathrm{vap}}H^0_{\mathrm{m}})$/kJ·mol^{-1} group molecules	$\Delta(\Delta_{\mathrm{vap}}H^0_{\mathrm{m}})$/kJ·mol^{-1} group values
$CH_3OC(CH_3)_3$ MTBE	30.08 ± 0.31	30.17	C−(C)(H)$_3$	5.35
$CH_3OC(CH_3)_2CH_2CH_3$ MTAE	34.86 ± 0.51	35.27	C−(C)$_2$(H)$_2$	5.10
(*i*-$C_3H_7)_2O$ DIPE	32.39 ± 0.32	32.39	C−(C)$_3$(H)	3.60
$C_2H_5OC(CH_3)_3$ ETBE	33.02 ± 0.38	33.07	C−(O)(H)$_3$	5.35
i-$C_3H_7OC(CH_3)_3$ *i*-PTBE	34.65 ± 0.42	36.31	C−(O)(C)$_3$	−0.64[c]
n-$C_3H_7OC(CH_3)_3$ *n*-PTBE	36.73 ± 0.42	38.17	C−(O)(C)(H)$_2$	2.90
$C_2H_5OC(CH_3)_2CH_2CH_3$ ETAE	38.15 ± 0.30	38.17	C−(O)(C)$_2$(H)	0.79[c]
i-$C_4H_9OC(CH_3)_3$ *i*-BTBE	39.14 ± 0.32	42.02	O−(C)$_2$	9.41
(*i*-$C_4H_9)_2O$ DIBE	40.93 ± 0.37	43.81		
n-$C_4H_9OC(CH_3)_3$ *n*-BTBE	41.60 ± 0.50	43.91		
n-$C_4H_9OC(CH_3)_2CH_2CH_3$ *n*-BTAE	45.72 ± 0.84	48.37		

[a] Symbols of compounds are analogous to those in Table 17. [b] Recommended $\Delta_{\mathrm{vap}}H^0_{\mathrm{m}}$(298.15) values were evaluated as average weighed experimental values excepting that of MTAE from ref 37. [c] The increments of (−0.64 and 0.79) kJ·mol^{-1} for C−(O)(C)$_3$ and C−(O)(C)$_2$(H) groups were evaluated on the basis of the enthalpies of vaporization of *i*-BTBE, DIBE, and DIPE.

Table 19. Entropies of Some Branched Ethers in Liquid and Ideal Gas States at T = 298.15 K

compounds	J·K^{-1}·mol^{-1} S^0_{m}(liq) (calor)[a]	S^0_{m}(liq) (calcd)[a]	S^0_{m}(g) (calor)[b]	S^0_{m}(g) (stat. therm.)[b]
$CH_3OC(CH_3)_3$ MTBE	265.30 ± 1.6	266.3	357.8 ± 2.2[2]	357.8[f]
$CH_3OC(CH_3)_2CH_2CH_3$ MTAE	–	–	–	–
$C_2H_5OC(CH_3)_3$ ETBE	295.8 ± 1.8	297.9	391.5 ± 2.8	391.4[16]
(*i*-$C_3H_7)_2O$ DIPE	304.6 ± 1.8	309.4	399.3 ± 2.8	399.1[f]
i-$C_3H_7OC(CH_3)_3$ *i*-PTBE	318.6 ± 1.9[c,f] 310.3 ± 2.1[d]	323.3	414.8 ± 2.4 406.4 ± 2.4	415.6[e,f] 407.2[15]
n-$C_3H_7OC(CH_3)_3$ *n*-PTBE	330.3 ± 2.0	330.3	431.1 ± 2.9	430.0[15]
$C_2H_5OC(CH_3)_2CH_2CH_3$ ETAE	332.7 ± 2.0	330.3	435.8 ± 2.6	433.4[16]
i-$C_4H_9OC(CH_3)_3$ *i*-BTBE	354.1 ± 2.1	357.3	457.0 ± 2.8	456.9[14]
(*i*-$C_4H_9)_2O$ DIBE	374.8 ± 2.2	377.4	479.8 ± 2.7	480.5[f]
n-$C_4H_9OC(CH_3)_3$ *n*-BTBE	–	–	–	–
n-$C_4H_9OC(CH_3)_2CH_2CH_3$ *n*-BTAE	–	–	–	–

[a] S^0_{m}(liq)(calor) and S^0_{m}(liq)(calcd) values were determined using calorimetric data on the heat capacities and Benson's group additivity method,[40] respectively. [b] S^0_{m}(g)(calor) and S^0_{m}(g)(stat. therm.) values were obtained using the heat capacities, vapor pressure, and enthalpies of vaporization and statistical thermodynamics based on B3LYP/6-31G(d,p) calculations, respectively. [c] S^0_{m}(liq)(calor) value for the stable polymorph II′. [d] S^0_{m}(liq)(calor) values for the metastable polymorph II. [e] The S^0_{m}(g)(stat. therm.) entropy was evaluated using that value for polymorph II, 406.4, and difference between S^0_{m}(g)(calor) values of polymorph II′ and II. [f] Values obtained in this work.

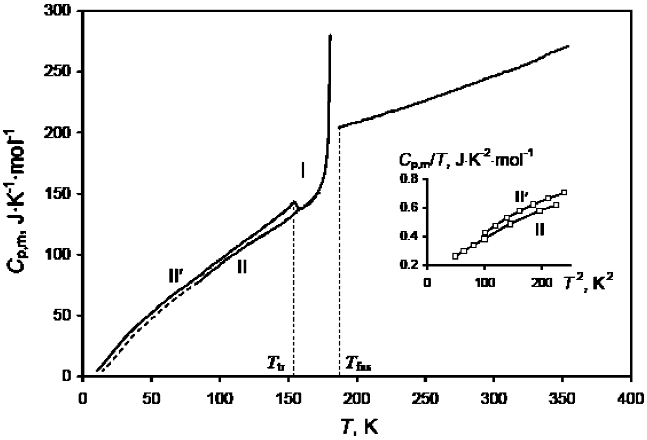


Figure 5. Heat capacity of *i*-propyl-*tert*-butyl ether as a function of temperature, where T_{tr} is the phase transition temperature and T_{fus} is the temperature of fusion. The inset contains the $C_{p,\mathrm{m}}/T = f(T^2)$ dependence in the region of helium temperatures.

Conclusion

A set of the thermodynamic properties of di-isobutyl ether (DIBE) have been defined for the first time by experimental and calculation methods. The low-temperature heat capacity and thermodynamic properties of the phase transitions of DIBE have been measured by adiabatic calorimetry. The temperature dependence of the saturation vapor pressure has been determined by comparative ebulliometry over the moderate temperature and pressure ranges. The pT-parameters of the ether were corrected for the impurities content of related ethers (~1 mol %). The density of liquid DIBE was measured at the ambient temperatures using a quartz pycnometer. The normal boiling temperature, the temperature dependence of the enthalpy of vaporization, the critical parameters, and the ideal gas thermodynamic functions S^0_{m}(g), $\{H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(0)\}$(g), and $\{G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(0)\}$(g) at T = 298.15 K have been derived from experimental data. The calculated $\Delta_{\mathrm{vap}}H^0_{\mathrm{m}}$ value of DIBE agrees with the calorimetric literature value within the error limits that proves the reliability of the data of both methods. The ideal gas thermodynamic functions $C^0_{\mathrm{p}}(T)$, S^0_{m}(g), and $\{H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(0)\}$(g) over the wide temperature range have been computed by statistical thermodynamics and DFT on the level B3LYP/6-31G(d,p). The vapor pressure of DIBE in the "atmospheric" pressure range was extended to the whole range of the liquid phase from the

Table 20. Smoothed Molar Thermodynamic Properties of *i*-Propyl-*tert*-butyl Ether

T	$C_{p,\mathrm{m}}$	$\{H^0_\mathrm{m}(T) - H^0_\mathrm{m}(0)\}$	$S^0_\mathrm{m}(T)$	$-[G^0_\mathrm{m} - H^0_\mathrm{m}(0)]$
K	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
		Crystal II′		
10	4.183	0.01399	2.336	0.00937
15	11.00	0.05162	5.290	0.02773
20	17.52	0.1230	9.350	0.06400
25	24.28	0.2273	13.98	0.1222
30	31.14	0.3660	19.02	0.2045
35	37.72	0.5385	24.32	0.3128
40	42.02	0.7399	29.69	0.4478
45	47.14	0.9628	34.94	0.6094
50	52.17	1.211	40.17	0.7972
55	57.04	1.484	45.37	1.011
60	61.69	1.781	50.53	1.251
65	66.11	2.101	55.65	1.516
70	70.33	2.442	60.70	1.807
75	74.41	2.804	65.69	2.123
80	78.47	3.186	70.62	2.464
85	82.63	3.589	75.51	2.829
90	87.10	4.013	80.35	3.219
95	91.60	4.460	85.19	3.633
100	95.84	4.929	90.00	4.071
110	104.3	5.930	99.53	5.019
120	112.5	7.015	109.0	6.061
130	120.6	8.180	118.3	7.197
140	129.0	9.427	127.5	8.427
150	138.3	10.76	136.7	9.748
155.1	142.9	11.48	141.4	10.46
		Crystal I		
160.3	137.3	12.07	145.1	11.20
170	148.1	13.45	153.5	12.70
180	159.0	14.99	162.3	14.28
184.78	164.2	15.76	166.5	15.01
		Liquid		
184.78	203.7	24.22	212.3	15.01
190	205.4	25.29	218.0	16.20
200	208.7	27.36	228.6	18.44
210	212.0	29.46	238.9	20.78
220	215.4	31.60	248.9	23.22
230	219.0	33.77	258.5	25.76
240	222.6	35.98	267.9	28.40
250	226.3	38.22	277.1	31.13
260	230.3	40.51	286.0	33.94
270	234.3	42.83	294.8	36.85
280	238.5	45.19	303.4	39.84
290	242.5	47.60	311.8	42.92
298.15	245.7 ± 0.8	49.59 ± 0.30	318.6 ± 0.9	45.40 ± 0.30
300	246.5	50.04	320.1	46.09
310	250.3	52.53	328.3	49.23
320	254.4	55.05	336.3	52.55
330	259.0	57.62	344.2	55.96
340	264.3	60.23	352.0	59.44
350	269.4	62.90	359.7	63.00

triple to the critical points using the corresponding states low in L. Filippov's version and the method of simultaneous treatment of the pT-parameters and low-temperature differences between heat capacities of the ideal gas and liquid.

A review and summarization of some thermodynamic properties of the branched ethers, enhancing the octane number of the fuel, have been carried out. Critical analysis of the data realized by group-additivity and statistical thermodynamic methods confirmed the reliability and mutual consistency of the majority of the data on the enthalpies of vaporization and absolute entropies of the ethers studied.

Supporting Information Available:

Table for experimental molar heat capacities of di-isobutyl ether. This material is available free of charge via the Internet at http://pubs.acs.org.

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