International Journal of Thermophysics, Vol. 25, No. 4, July 2004 (© 2004)

Ideal Gas Thermodynamic Properties of Propyl *tert*-Butyl Ethers from Density Functional Theory Results Combined with Experimental Data[1]

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Ideal gas thermodynamic properties, $S^\circ(T)$, $C_p^\circ(T)$, $H^\circ(T)-H^\circ(0)$, $\Delta_f H^\circ(T)$, and $\Delta_f G^\circ(T)$, are obtained on the basis of density functional B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculations for two propyl *tert*-butyl ethers. All torsional motions about C–C and C–O bonds were treated as hindered internal rotations using the independent-rotor model. An empirical approximation was assumed to account for the effect of the coupling of rotor potentials. The correction for rotor–rotor coupling was found by fitting to entropy values determined from calorimetric measurements. Enthalpies of formation were calculated using isodesmic reactions.

KEY WORDS: calorimetric measurements; DFT calculations; heat capacity; ideal gas; propyl *tert*-butyl ethers; thermodynamic properties.

1. INTRODUCTION

Ethers have been and are becoming more and more an interesting class of reactants and products in the science of combustion and its application. At the present time the chemical behavior of ethers as fuels and fuel additives is studied extensively. Detailed knowledge of their thermodynamics is important in modeling of complicated reaction systems, such as combustion and atmospheric oxidation processes.

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[1] Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

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In this work the ideal gas thermodynamic properties of *n*-propyl *tert*-butyl ether (NPTBE) and isopropyl *tert*-butyl ether (IPTBE) were obtained on the basis of density functional theory (DFT) calculations which have been successfully applied to a variety of organic compounds [1, 2]. Unfortunately, now it is not possible to obtain the accurate thermodynamic properties of NPTBE and IPTBE from theoretical calculations only. These molecules have seven internal rotations and the rigorous treatment requires a full analysis of rotor–rotor coupling, whereas a multi-dimensional model for calculating the energy levels of internal rotation has not yet been developed for such complicated cases. Hence, we used an independent-rotor approximation and an empirical correction was employed to account for the interaction between rotating groups. This correction was determined from comparison of calculated and experimental entropy values.

2. EXPERIMENTAL RESULTS

The heat capacities, $C_{\mathrm{p,m}}$, of two ethers were measured in the temperature range 10–353 K using an automated vacuum adiabatic calorimeter. The unit consists of a minicryostat with a calorimeter and an Aksamit system for controlling the heat capacity measurements and collecting and processing experimental data [3]. The temperature was measured with an iron–rhodium resistance thermometer ($R \sim 100\,\Omega$) accurate to $\leqslant 1 \times 10^{-2}$ K. The volume of the container for substances was $\sim 1\,\mathrm{cm}^3$. The instrumental errors of the heat capacity measurements are 0.5–1% at temperatures from 10 to 80 K and 0.1–0.3% above 80 K.

In the temperature range studied, NPTBE exists in metastable (I′) and stable (I) polymorphs and in vitreous and liquid states (Fig. 1a). The heat capacity curve of IPTBE reveals the metastable (II′) and stable (II) polymorphs and the liquid state (Fig. 1b). Since the stable crystalline phase II could not be obtained at temperatures below 85.7 K, the $C_{\mathrm{p,m}}$ values of IPTBE in the temperature range 10–86 K were calculated by a comparative method [5] based on the heat capacities of the metastable crystal (II′),

$$C_{\mathrm{p,m}}(\mathrm{II}) = (A + BT) \times C_{\mathrm{p,m}}(\mathrm{II}'). \tag{1}$$

The purity of the ethers determined by a calorimetric fractional melting study are 99.11 and 99.45 mol%, respectively. NPTBE and IPTBE were synthesized from 2-methylpropene and *n*-propanol and isopropanol, respectively, in the presence of KU-23 sulfocationite as a catalyst [4]. The major impurity in the samples was a dimer of 2-methylpropene. This was lately found in the studies of conditions of the pure ethers synthesis [6].

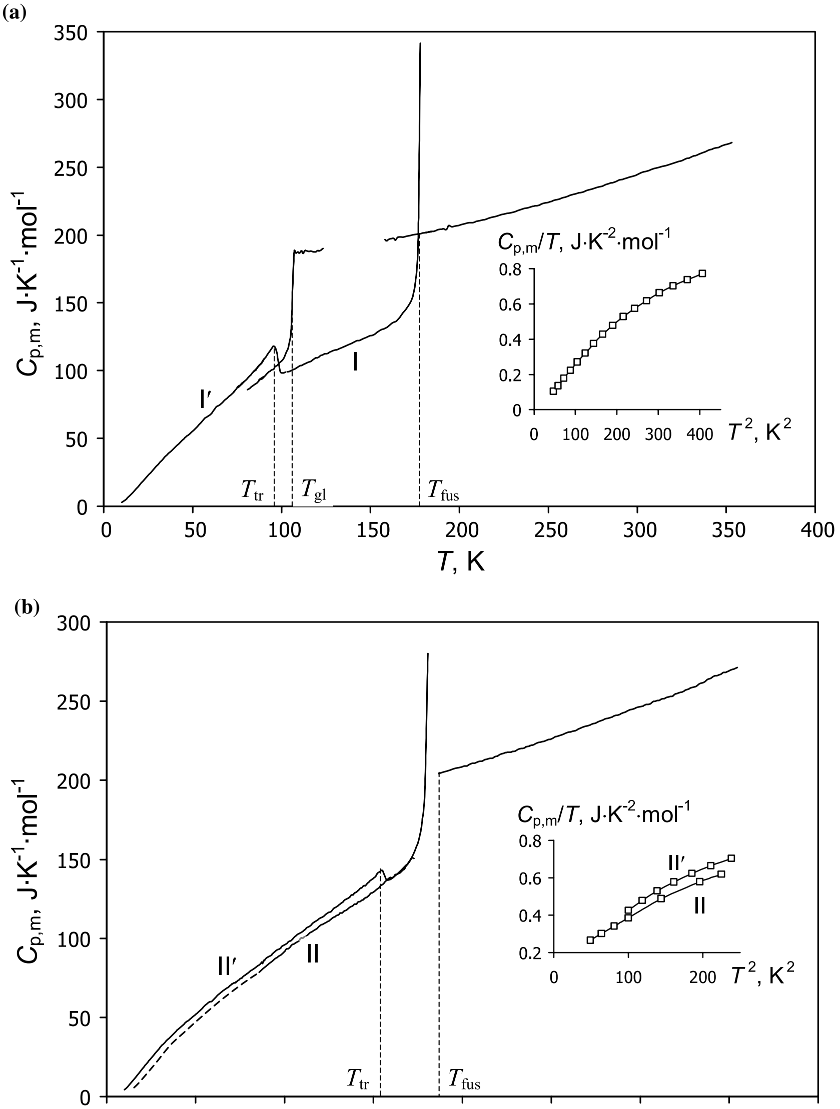


Fig. 1. Heat capacities of (a) NPTBE and (b) IPTBE as a function of temperature: stable (I, II) and metastable (I′, II′) polymorphs [4]. T_{tr}, T_{fus}, and T_{gl} are the temperatures of solid-to-solid transition, fusion, and vitrification, respectively. $C_{p,m}$ values calculated from Eq.(1) are shown by dash lines. Inserts: $C_{p,m}/T = f(T^2)$ dependences.

The errors in $C_{\mathrm{p,m}}$ values of NPTBE and IPTBE caused by impurities were estimated to be less than 0.1% at $T = 253\,\mathrm{K}$. Table I lists the temperatures of fusion, T_{fus}, transitions, T_{tr}, and vitrification, T_{gl}, and the enthalpies, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, and entropies, $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$, of fusion for two ethers. Taking into account the impurities, the repeatability errors were doubled.

The heat capacities of crystalline ethers were extrapolated from 10 K to $T \to 0$ with an uncertainty ~3% by the equation,

$$C_{\mathrm{p,m}} = \alpha T^3 + \gamma T. \tag{2}$$

The coefficient $\gamma = 0$ for the NPTBE and, as follows from the $C_{\mathrm{p,m}}T = f(T^2)$ dependence (Fig. 1a), polymorph I′ has $C_{\mathrm{p,m}} = 0$ at $T \to 0$. On the contrary, $\gamma \neq 0$ for the polymorphs II and II′ and IPTBE has nonzero $C_{\mathrm{p,m}}$ values when $T \to 0$ (Fig. 1b). This is likely to be explained by a substantial content of impurities in the IPTBE sample. Table II shows the smoothed heat capacities and entropy changes for ethers in crystalline and liquid states. The thermodynamic functions of the ethers in the liquid state were calculated by integrating the $C_{\mathrm{p,m}} = f(T)$ dependences for crystalline and liquid phases and adding the enthalpies and entropies of fusion, the changes of the corresponding functions in solid-to-solid transitions being computed by summing. The ideal-gas entropies were calculated from the entropies of the liquids using the entropy of vaporization, $\Delta_{\mathrm{v}}S^{\circ}_{\mathrm{m}}$, and the entropy of ideal-gas compression (Table I). The enthalpies of vaporization, $\Delta_{\mathrm{v}}H^{\circ}_{\mathrm{m}}$, were measured by a calorimetric method, and the entropies of compression were calculated using vapor pressure data for temperatures from 305 to 370 K [7]. The results of these two studies are thermodynamically consistent, which was verified by satisfactory agreement between

Table I. Thermodynamic Properties of NPTBE and IPTBE

	NPTBE	IPTBE
T_{fus} (K)	179.6 ± 0.2	184.78 ± 0.1
$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (kJ·mol^{-1})	9.87 ± 0.16	8.460 ± 0.01
$\Delta_{\mathrm{fus}}\ S_{\mathrm{m}}$ (J^{-1}·mol^{-1})	55.0 ± 0.8	45.78 ± 0.02
T_{tr} (K)	98.3	155.1
T_{gl} (K)	107.2	–
$\Delta_{\mathrm{v}}\ H^{\circ}_{\mathrm{m}}(298.15)$ (kJ·mol^{-1})	36.57 ± 0.20	34.48 ± 0.19
$\Delta_{\mathrm{v}}\ S^{\circ}_{\mathrm{m}}(298.15)$ (J·K^{-1}·mol^{-1})	122.66 ± 0.67	115.65 ± 0.67
R ln[p(298.15)/101325 Pa]^a	−23.28	−19.50
$\{S^{\circ}_{\mathrm{m}}(298.15\,\mathrm{K}) - S^{\circ}_{\mathrm{m}}(0)\}$ (g) (J·K^{-1}·mol^{-1})	429.6 ± 0.9	406.4 ± 0.9

[a] R ln[p(298.15)/101325 Pa] is the entropy of ideal gas compression.

Table II. Smoothed Molar Thermodynamic Properties of NPTBE (I′, I) and IPTBE (II), $M = 116.204\,g \cdot \mathrm{mol}^{-1}$

T (K)	$C_{\mathrm{p,m}}$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$S^{\circ}_{\mathrm{m}}(T) - S^{\circ}_{\mathrm{m}}(0)$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	T (K)	$C_{\mathrm{p,m}}$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$S^{\circ}_{\mathrm{m}}(T) - S^{\circ}_{\mathrm{m}}(0)$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
	Crystal I′			Crystal II	
10	2.575	1.263	10	3.800	2.440
15	8.191	3.288	15	9.299	4.982
20	15.32	6.602	20	15.66	8.520
25	22.76	10.82	25	22.08	12.71
30	30.04	15.62	30	28.11	17.28
35	36.95	20.77	35	33.61	22.03
40	43.39	26.13	40	38.72	26.85
45	49.42	31.59	45	43.60	31.70
50	55.40	37.11	50	48.30	36.53
55	62.09	42.69	55	52.85	41.35
60	68.39	48.37	60	57.26	46.14
65	74.45	54.08	65	61.54	50.89
70	80.53	59.82	70	65.73	55.61
75	86.77	65.59	75	69.89	60.29
80	93.26	71.39	80	74.09	64.93
85	100.2	77.25	85	78.39	69.55
90	107.9	83.19	90	82.79	74.16
95	117.2	89.27	95	87.22	78.74
	Crystal I		100	91.68	83.33
100	98.51	95.67	110	100.0	92.47
110	102.9	104.5	120	107.6	101.5
120	109.4	113.7	130	114.7	110.4
130	115.0	122.7	140	121.8	119.2
140	120.2	131.4	150	129.4	127.8
150	125.8	139.9	160	138.0	136.4
160	133.0	148.2	170	148.0	145.1
170	139.7	156.5	180	159.8	153.9
179.6	142.7	164.0	184.78	166.0	158.1
	Liquid I			Liquid II	
179.6	201.3	219.0	184.78	203.7	203.9
180	201.5	219.5	190	205.5	209.6
190	204.4	230.4	200	208.7	220.2
200	207.4	241.0	210	212.0	230.5
210	210.2	251.2	220	215.4	240.4
220	213.6	261.0	230	219.0	250.1
230	217.2	270.6	240	222.6	259.5
240	220.7	279.9	250	226.3	268.7
250	224.4	289.0	260	230.3	277.6
260	228.3	297.9	270	234.3	286.4
270	232.2	306.6	280	238.5	295.0
280	236.2	315.1	290	242.5	303.4

Table II. (*Continued*)

T (K)	$C_{\mathrm{p,m}}$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$S^{\circ}_{\mathrm{m}}(T) - S^{\circ}_{\mathrm{m}}(0)$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	T (K)	$C_{\mathrm{p,m}}$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$S^{\circ}_{\mathrm{m}}(T) - S^{\circ}_{\mathrm{m}}(0)$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
290	240.4	323.5	298.15	245.7	310.3
298.15	244.0	330.2	300	246.4	311.8
300	244.8	331.8	310	250.3	320.0
310	249.1	339.9	320	254.4	328.0
320	253.0	347.8	330	259.0	335.9
330	257.4	355.7	340	264.3	343.7
340	262.4	363.4	350	269.4	351.4
350	266.8	371.1			

$\Delta_{\mathrm{v}} H^{\circ}_{\mathrm{m}}$ values measured calorimetrically and those calculated from the pT data [7].

3. THEORETICAL CALCULATIONS

3.1. Methods of Calculations

The DFT calculations were performed using the Gaussian 98 software package [8]. The structural parameters 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 ethers.

Potential functions for internal rotation about C–C and C–O bonds were determined by scanning the torsional 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 potential energy function thus obtained was then fitted to the Fourier series,

$$V(\varphi) = V_0 + \tfrac{1}{2}\sum_n V_n(1 - \cos n\varphi) + \tfrac{1}{2}\sum_n V'_n(1 - \sin n\varphi). \qquad (3)$$

The values of $S^{\circ}(T)$, $C^{\circ}_{\mathrm{p}}(T)$, and $H^{\circ}(T) - H^{\circ}(0)$ were calculated by standard statistical thermodynamic formulae using the rigid-rotor harmonic-oscillator approximation with correction for internal rotation. Internal rotational contributions for each rotor were calculated by direct summation over the energy levels, which were obtained by the diagonalization of the one-dimensional Hamiltonian with a fitted torsional potential (Eq. (3)).

Enthalpies of formation were calculated at the B3LYP/6-311+G(3df, 2p)// B3LYP/6-31G(d,p) level using isodesmic reactions. An isodesmic reaction is one in which the number of bonds of each type is conserved on the two sides of the reaction, and then one might expect the cancellation of errors arising from insufficient treatment of electron correlation and incompleteness of the basis sets [9].

3.2. Enthalpies of Formation

From analysis of available experimental data, rather different values were reported for the enthalpy of formation of IPTBE: $-358.1 \pm 3.0\,\mathrm{kJ\cdot mol^{-1}}$ [10] and $-342.3\,\mathrm{kJ\cdot mol^{-1}}$ [11]. Based on five isodesmic reactions given in Table III, the value of

$$\Delta_f H^\circ(\mathrm{IPTBE}, 298.15\,\mathrm{K},\ \mathrm{gas}) = -349 \pm 5\,\mathrm{kJ\cdot mol^{-1}},$$

was obtained in this work. Note, that in addition to being isodesmic, reactions 2 and 4 are homodesmotic reactions. Not only bond types are conserved in these reactions, but also the environment in which these bonds are located. Due to closer matching of bonding environments in reactants and products, as compared to the isodesmic reaction, the homodesmotic reaction gives more accurate estimates of the $\Delta_f H^\circ_{298}$ values.

Seven homodesmotic reactions were selected to determine the enthalpy of formation of NPTBE (Table III). The values in Table III are related to the most stable *TG* conformer. A correction for the mixture of *TG* and *TT* conformers ($0.2\,\mathrm{kJ\cdot mol^{-1}}$) was estimated from the conformational energy differences based on Boltzmann averaging. Thus, the value of

$$\Delta_f H^\circ(\mathrm{NPTBE}, 298.15\,\mathrm{K},\ \mathrm{gas}) = -339 \pm 5\,\mathrm{kJ\cdot mol^{-1}}.$$

was accepted in this work. This value is in close agreement with a value of $-339.3 \pm 2.1\,\mathrm{kJ\cdot mol^{-1}}$, calculated from the experimental enthalpy of reaction [11]. It should be noted that IPTBE with the value of $\Delta_f H^\circ_{298} = -349\,\mathrm{kJ\cdot mol^{-1}}$ calculated above is used as a reference molecule in reaction 12. Using the experimental $\Delta_f H^\circ_{298}$ values for IPTBE [10, 11] leads to a significant difference between enthalpies of formation of NPTBE calculated from reaction 12 ($-349.0\,\mathrm{kJ\cdot mol^{-1}}$ and $-333.2\,\mathrm{kJ\cdot mol^{-1}}$ for $\Delta_f H^\circ_{298}$ (IPTBE) from Refs. [10, 11] respectively) and reactions 6–11. This is additional evidence in support of the $\Delta_f H^\circ_{298}$ (IPTBE) value selected in this work.

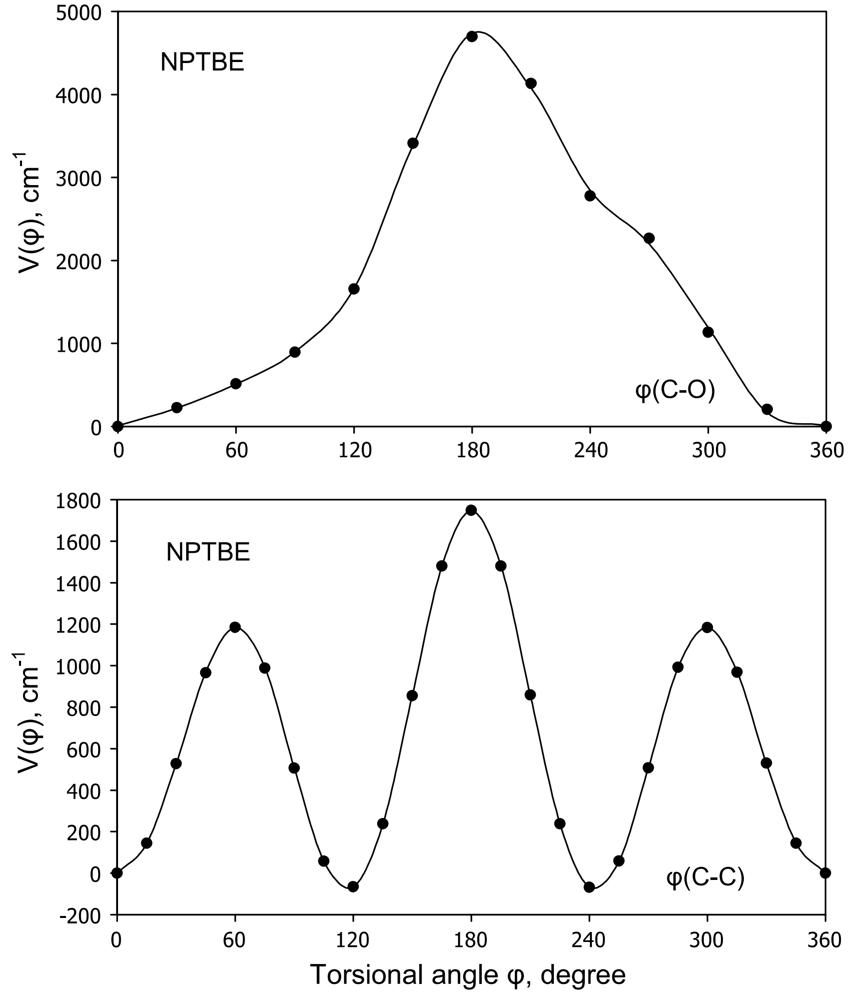


Fig. 2. Torsional potential functions of NPTBE. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansions with the coefficients listed in Table IV.

3.3. Geometry, Vibrational Frequencies, and Torsional Potentials

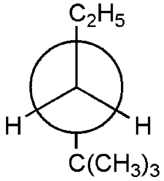
The DFT calculations predict the existence of two stable low energy conformers of NPTBE: the *trans-gauche* (*TG*) conformer of C_1 symmetry is 0.8 $\mathrm{kJ \cdot mol^{-1}}$ (67 $\mathrm{cm^{-1}}$) more stable than the *trans-trans* (*TT*) conformer

Table III. Enthalpies of Reaction and Enthalpies of Formation (in $kJ \cdot mol^{-1}$) for NPTBE and IPTBE calculated at B3LYP/6-311+G (3df,2p)//B3LYP/6-31G (d,p) Level from Isodesmic Reactions

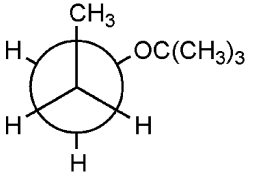
No.	Isodesmic reaction[a]	$\Delta_r H^\circ_{298}$	$\Delta_f H^\circ_{298}$
Isopropyl *tert*-butyl ether (IPTBE)			
1	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3 = (CH_3)_2CH\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$	−0.1	−349.0
2	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + (CH_3)_2CH\text{-}O\text{-}CH_3$	−2.4	−347.1
3	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 = (CH_3)_2CH\text{-}O\text{-}CH(CH_3)_2 + CH_3\text{-}O\text{-}C(CH_3)_3$	2.7	−353.5
4	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + (CH_3)_2CH\text{-}O\text{-}CH_3 = (CH_3)_2CH\text{-}O\text{-}CH(CH_3)_2 + CH_3\text{-}O\text{-}C(CH_3)_3$	−3.1	−347.8
5	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + (CH_3)_2CH\text{-}O\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}C(CH_3)_3$	3.5	−349.1
		Average	−349.3
n-Propyl *tert*-butyl ether (NPTBE)			
6	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_3 = CH_3\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	0.8	−338.5
7	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_3\text{-}CH_2\text{-}CH_3$	1.4	−340.7
8	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3 = CH_3\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	1.6	−340.2
9	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	2.4	−338.0
10	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	2.5	−336.3
11	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	2.6	−337.5
12	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH(CH_3)_2 = (CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_3$	4.8	−340.2
		Average	−338.8

[a] The experimental values of $\Delta_f H^\circ_{298}$ for species used in the isodesmic reactions were taken from Pedley [10], except for IPTBE, reaction 12 (see text).

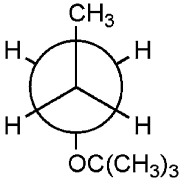
of C_s symmetry. Both conformers have *trans*-location of bulky groups relative to the C–O bond [$CH_3CH_2CH_2$–$OC(CH_3)_3$]:



and different relative positions of bulky groups around the C–C bond [CH_3CH_2–$CH_2OC(CH_3)_3$]:



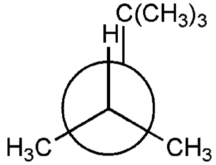
TG



TT

Calculated potential energy curves as a function of torsion angles φ(C–O) and φ(C–C) are shown in Fig. 2. For rotation about the C–C bond, the minima on the potential curve at 0° and 120° correspond to the *TT* and *TG* conformers, respectively. Moments of inertia for the optimized geometry, vibrational frequencies, and coefficients V_n in the expansion for the torsional potentials (Eq. (3)) are given in Table IV. The thermodynamic functions of NPTBE (Section 3.4) were calculated for an equilibrium mixture of *TG* and *TT* conformers. We did not take into account the difference between geometry and vibrational frequencies of *TG* and *TT* conformers of NPTBE because this results in insignificant changes of $S^\circ(T)$ and $C_p^\circ(T)$ values (0.2 and $0.5\,\mathrm{J}\cdot K^{-1}\cdot\mathrm{mol}^{-1}$, respectively, at 298.15 K). The energy of the next stable conformer of NPTBE, *gauche-trans* (*GT*), is $14\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ ($1150\,\mathrm{cm}^{-1}$) higher than that of the *TG* conformer. Since the *GT* conformer makes negligible contribution to the thermodynamic functions, we ignored it in thermodynamic function calculations.

For the IPTBE molecule, the branched groups lie on each side of the oxygen atom and nonbonded interactions result in a single stable low energy *eclipsed* conformer of C_s symmetry:



The potential energy curve as a function of the φ(C–O) torsional angle [$(CH_3)_2CH$–$OC(CH_3)_3$] is shown in Fig. 3. The minima on the potential curve at 0° and ~165° correspond to the *eclipsed* and near-*trans* conformers, respectively. The energy of the near-*trans* conformer is $25\,kJ{\cdot}mol^{-1}$ ($2090\,cm^{-1}$) higher than that of the *eclipsed* conformer. Calculated molecular parameters of IPTBE are given in Table IV.

3.4. Thermodynamic Functions

Thermodynamic functions, $S^\circ(T)$, $C^\circ_p(T)$, and $H^\circ(T) - H^\circ(0)$, were calculated within the framework of 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 overestimated values of thermodynamic functions as compared with $S^\circ(T)$ and $C^\circ_p(T)$ values determined from calorimetric measurements for alkyl ethers (Table V). The greater is the number of rotors, the greater are the discrepancies between calculated and experimental values. Especially large discrepancies are found for *tert*-alkyl ethers. It is most likely that the increased error is associated with the independent-rotor assumption.

To our knowledge, the theoretical models for computing the internal rotational contributions for species with three and more rotors have not been devised. Chen et al. [14] failed to reproduce the observed heat capacities and entropy of isobutane by assuming independent methyl rotation with any value of V_3. The authors [14] concluded that the interaction among methyl groups has a significant effect on thermodynamic functions. The rotor–rotor interactions in isobutane were approximated by the potential parameter V_6 which was determined empirically by comparison with experimental values of $S^\circ(T)$ and $C^\circ_p(T)$.

In this work the contribution to the thermodynamic functions due to coupling of rotor potentials was taken into account by multiplying the partition function for uncoupling internal rotations by the empirical factor $K_{r\text{–}r}$. The $K_{r\text{–}r}$ values of 0.867 and 0.774 were found by fitting to the experimental entropies of NPTBE and IPTBE, respectively. The difference

Table IV. Moments of Inertia, Vibrational Frequencies and Internal Rotational Molecular Constants of NPTBE and IPTBE Calculated at B3LYP/6-31G(d,p) Level

NPTBE: *TG* conformer

Point group: C_1	$I_\mathrm{A} = 25.1031 \times 10^{-39}\,\mathrm{g \cdot cm^2}$
Symmetry number: $\sigma = 1$	$I_\mathrm{B} = 77.2003 \times 10^{-39}\,\mathrm{g \cdot cm^2}$
Ground electronic state: $\tilde{X}^1A$	$I_C = 81.1320 \times 10^{-39}\,\mathrm{g \cdot cm^2}$
Molecular weight: 116.2028	$I_\mathrm{A} I_\mathrm{B} I_C = 157231 \times 10^{-117}\,\mathrm{g^3 \cdot cm^6}$

Vibrational frequencies:[a] 3004, 3000, 3000, 2994, 2992, 2989, 2985, 2978, 2948, 2926, 2919, 2918, 2915, 2912, 2890, 2859, 1502, 1492, 1487, 1477, 1476, 1471, 1464, 1461, 1456, 1450, 1401, 1396, 1384, 1373, 1370, 1351, 1285, 1249, 1245, 1228, 1203, 1150, 1117, 1078, 1025, 1017, 1003, 937, 913, 901, 890, 870, 868, 766, 716, 506, 458, 445, 385, 337, 331, 290, 264,[b] 254,[b] 232,[b] 207,[b] 166,[b] 144, 80,[b] 21 [b]

CH_3 group: $I_\mathrm{r} = 0.5200 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3 = 1127\,\mathrm{cm^{-1}}$
CH_3 group: $I_\mathrm{r} = 0.5212 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3=1107\,\mathrm{cm^{-1}}$
CH_3 group: $I_\mathrm{r} = 0.5203 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3=1002\,\mathrm{cm^{-1}}$,
CH_3 group: $I_\mathrm{r} = 0.5229 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3=1163\,\mathrm{cm^{-1}}$,
C_2H_5 group: $I_\mathrm{r} = 3.6882 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=1$, $V_1 = 355.5$, $V_2 = -333.0$, $V_3 = 1414.7$, $V_4 = -86.6$, $V_5 = -24.7$, $V_6 = -32.5$ (in $\mathrm{cm^{-1}}$),
t-C_4H_9 group: $I_\mathrm{r} = 5.2310 \times 10^{-39}\,\mathrm{g \cdot cm^{-1}}$, $\sigma_\mathrm{m}=3$, $V_3=973\,\mathrm{cm^{-1}}$,
C_3H_7 group: $I_\mathrm{r} = 7.0462 \times 10^{-39}\,\mathrm{g \cdot cm^{-1}}$, $\sigma_\mathrm{m}=1$, $V_0 = -201.2$, $V_1 = 4085.7$, $V_2 = -824.6$, $V_3 = 640.3$, $V_4 = -272.6$, $V_1' = 1075.6$, $V_2' = -357.9$, $V_3' = -224.0$, $V_4' = -69.2$ (in $\mathrm{cm^{-1}}$).

IPTBE: *eclipsed* conformer

Point group: C_s	$I_A = 28.8592 \times 10^{-39}\,\mathrm{g \cdot cm^2}$
Symmetry number: $\sigma=1$	$I_B = 62.3435 \times 10^{-39}\,\mathrm{g \cdot cm^2}$
Ground electronic state: $\tilde{X}^1A'$	$I_C = 70.4758 \times 10^{-39}\,\mathrm{g \cdot cm^2}$
Molecular weight: 116.2028	$I_A\ I_B I_C = 126799 \times 10^{-117}\,\mathrm{g^3 \cdot cm^6}$

Vibrational frequencies: [a]A' 3000, 2999, 2994, 2990, 2987, 2926, 2920, 2919, 2906, 1494, 1484, 1478, 1472, 1463, 1401, 1393, 1378, 1356, 1251, 1204, 1175, 1119, 1028, 1012, 902, 871, 809, 720, 508, 461, 404, 346, 291, 266,[b] 250,[b] 185, A'' 3001, 2996, 2993, 2982, 2982, 2916, 2914, 1476, 1464, 1460, 1456, 1449, 1378, 1373, 1330, 1226, 1127, 1021, 939, 919, 906, 887, 467, 388, 311, 259,[b] 216,[b] 199,[b] 84,[b] 37[b]

CH_3 groups (2): $I_\mathrm{r} = 0.5209 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3=1109\,\mathrm{cm^{-1}}$
CH_3 groups (2): $I_\mathrm{r} = 0.5204 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3=1217\,\mathrm{cm^{-1}}$,
CH_3 group: $I_\mathrm{r} = 0.5214 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3=1166\,\mathrm{cm^{-1}}$,
t-C_4H_9 group: $I_\mathrm{r} = 7.6445 \times 10^{-39}\,\mathrm{g \cdot cm^2}$, $\sigma_\mathrm{m}=3$, $V_3=985\,\mathrm{cm^{-1}}$,

Table IV. (*Continued*)

i-C_3H_7 group: $I_r = 6.8367 \times 10^{-39}\,g \cdot cm^2$, $\sigma_m = 1$, $V_1 = 2557.0$, $V_2 = 908.1$,
$V_3 = -695.8$, $V_4 = 141.6$, $V_5 = 264.4$, $V_6 = -59.4$ (in cm^{-1}).

[a] Scaling factor of 0.958 was used for C–H stretchings and 0.975 for other modes.

[b] Instead of these torsional modes, the contributions due to the internal rotation were calculated from the potential (Eq. (3)) and parameters for rotors given in this Table.

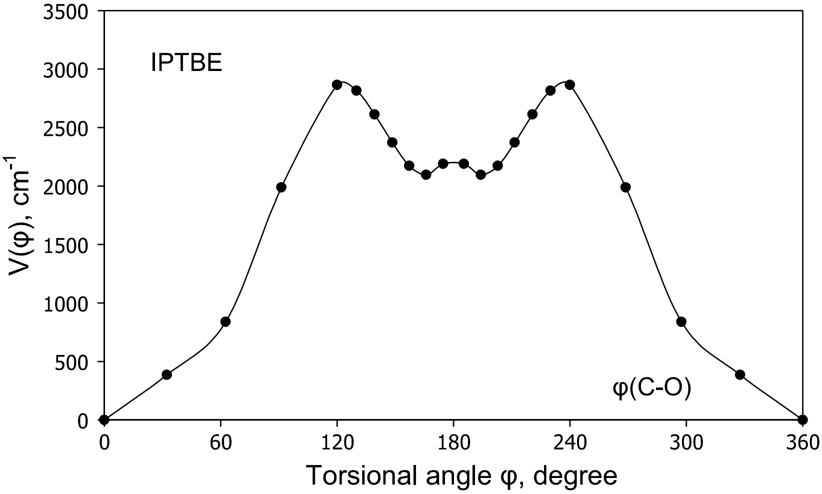


Fig. 3. Torsional potential function of IPTBE. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion with the coefficients listed in Table IV.

between experimental and thus calculated entropies is shown in Table V. It should be noted that the employed procedure for correction of the thermodynamic functions does not violate well-known thermodynamic relations between calculated values of $S^\circ(T)$, $C_p^\circ(T)$, and $H^\circ(T) - H^\circ(0)$.

Table VI lists the thermodynamic properties of NPTBE and IPTBE calculated using molecular constants (Table IV) and enthalpies of formation (see Section 3.2) estimated in this work. Since the calculated entropy

Table V. Deviation of Entropies and Heat Capacities of Ethers Calculated by B3LYP/6-31G(d,p) Method from Experiment (in $J \cdot K^{-1} \cdot mol^{-1}$)

	CH_3-CH_2-O-CH_2-CH_3				$(CH_3)_2CH$-O-$CH(CH_3)_2$		
	Exp	Exp − calc			Exp	Exp − calc	
	Ref. [12]	No correction	Corrected ($K_{r-r}=0.964$)		Ref. [13]	No correction	Corrected ($K_{r-r}=0.892$)
$S^\circ(342.31)$	342.3	−1.7	0.4	$S^\circ(298.15)$	399.3	−7.0	−0.2
$C^\circ_p(309.98)$	121.9	−2.1	−0.4	$S^\circ(340.00)$	420.8	−7.7	−0.4
$C^\circ_p(350.00)$	131.3	−1.9	−0.3	$C^\circ_p(360.04)$	182.5	−4.6	−0.4
$C^\circ_p(400.04)$	143.3	−1.5	0.1	$C^\circ_p(380.01)$	191.0	−4.3	−0.1
$C^\circ_p(450.04)$	155.1	−1.0	0.5	$C^\circ_p(399.98)$	199.3	−4.1	0.2
				$C^\circ_p(449.98)$	219.1	−3.6	0.7
	CH_3-CH_2-CH_2-O-$C(CH_3)_3$				$(CH_3)_2CH$-O-$C(CH_3)_3$		
	This work[a]	No correction	Corrected ($K_{r-r}=0.867$)		This work[a]	No correction	Corrected ($K_{r-r}=0.774$)
$S^\circ(298.15)$	429.6	−14.3	−0.4	$S^\circ(298.15)$	406.4	−20.4	−0.8
$S^\circ(313.15)$	439.5	−13.6	0.6	$S^\circ(313.15)$	415.6	−20.7	−0.4
$S^\circ(323.15)$	444.9	−14.4	0.1	$S^\circ(323.15)$	421.9	−20.7	0.1
$S^\circ(333.15)$	450.6	−14.8	0.0	$S^\circ(333.15)$	428.1	−20.7	0.5
$S^\circ(343.15)$	456.6	−14.9	0.2	$S^\circ(343.15)$	434.3	−20.7	0.9
$S^\circ(353.15)$	462.7	−14.8	0.5	$S^\circ(353.15)$	440.4	−20.7	1.3

[a] For 298.15 K the entropies of vaporization were calculated using enthalpies of vaporization measured by calorimetric method at 298.15 K [7]; for other temperatures the entropies of vaporization were calculated from vapor pressure data [7].

Table VI. Ideal Gas Thermodynamic Properties of NPTBE and IPTBE ($p^\circ = 101.325\,\text{kPa}$)

T (K)	$C_p^{\circ *}$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	S° ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$-[G^\circ - H^\circ(0)]/T$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$H^\circ - H^\circ(0)$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta_f H^\circ$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta_f G^\circ$ ($\text{kJ}\cdot\text{mol}^{-1}$)
NPTBE						
0	0.0	0.0	∞	0.0	−291.0	−291.0
150	108.1	335.1	265.5	10.4	−318.8	−219.2
200	130.7	369.3	287.2	16.4	−325.8	−184.9
250	154.0	400.9	306.8	23.5	−332.6	−148.9
298.15	177.2	430.0	324.4	31.5	−339.0	−113.0
300	178.1	431.1	325.0	31.8	−339.2	−111.6
350	202.1	460.4	342.3	41.3	−345.4	−73.1
400	225.3	488.9	358.8	52.0	−350.9	−33.8
500	267.0	543.8	390.4	76.7	−360.5	46.6
600	302.4	595.7	420.3	105.2	−368.0	128.7
700	332.3	644.6	448.9	137.0	−373.8	212.0
800	358.1	690.7	476.3	171.5	−377.9	295.9
900	380.3	734.2	502.6	208.5	−380.7	380.4
1000	399.6	775.3	527.8	247.5	−382.4	465.0
1100	416.3	814.2	552.1	288.3	−383.0	549.8
1200	430.8	851.0	575.5	330.7	−382.8	634.6
1300	443.4	886.0	598.0	374.4	−381.9	719.4
1400	454.3	919.3	619.8	419.3	−380.5	804.0
1500	463.8	951.0	640.8	465.2	−378.7	888.6
IPTBE						
0	0.0	0.0	∞	0.0	−299.6	−299.6
150	102.6	314.5	251.5	9.4	−328.4	−225.7
200	127.4	347.4	271.4	15.2	−335.6	−190.3
250	151.8	378.5	289.7	22.2	−342.6	−153.2
298.15	175.4	407.2	306.4	30.1	−349.0	−116.2
300	176.3	408.3	307.0	30.4	−349.2	−114.7
350	200.6	437.3	323.6	39.8	−355.4	−75.1
400	223.8	465.6	339.6	50.4	−361.1	−34.7
450	245.5	493.3	355.1	62.2	−366.2	6.4
500	265.5	520.2	370.3	74.9	−370.8	48.1
600	300.8	571.8	399.6	103.3	−378.5	132.6
700	330.7	620.5	427.7	134.9	−384.4	218.2
800	356.4	666.4	454.7	169.3	−388.7	304.6
900	378.5	709.6	480.7	206.1	−391.7	391.5
1000	397.6	750.5	505.6	244.9	−393.5	478.6
1100	414.1	789.2	529.7	285.5	−394.3	565.9
1200	428.4	825.9	552.8	327.7	−394.3	653.2
1300	440.8	860.7	575.2	371.1	−393.7	740.5

Table VI. (*Continued*)

T (K)	$C_p^{\circ *}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	S° ($J \cdot K^{-1} \cdot mol^{-1}$)	$-[G^\circ - H^\circ(0)]/T$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$H^\circ - H^\circ(0)$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ$ ($kJ \cdot mol^{-1}$)	$\Delta_f G^\circ$ ($kJ \cdot mol^{-1}$)
1400	451.5	893.7	596.8	415.6	−392.6	827.7
1500	460.9	925.2	617.6	461.4	−391.1	914.8

*At temperatures from 150 to 500 K thermodynamic functions can be calculated using equation $C_p^\circ(T) = a_1 + a_2T^{-2} + a_3T + a_4T^2 + a_5T^3$ with $a_1 = 70.900$, $a_2 = -1.042 \times 10^5$, $a_3 = 0.1482$, $a_4 = 1.04 \times 10^{-3}$, $a_5 = -1.099 \times 10^{-6}$ for NPTBE and $a_1 = 61.507$, $a_2 = -1.660 \times 10^5$, $a_3 = 0.2148$, $a_4 = 8.67 \times 10^{-4}$, $a_5 = -9.571 \times 10^{-7}$ for IPTBE.

values were fitted to the experimental ones, their uncertainty is close to the uncertainty of the experimental values at temperatures 298.15–350 K and should not exceed 3–5 $J \cdot K^1 \cdot mol^1$ at higher temperatures. A comparison of trends in heat capacity values for alkanes and ethers shows that calculated $C_p^\circ(T)$ values for NPTBE and IPTBE agree with correlations utilizing empirical group additivity contributions. The uncertainty of calculated $C_p^\circ(T)$ values is estimated to be 5–8 $J \cdot K^1 \cdot mol^1$.

4. CONCLUSION

The enthalpies of formation for two $C_7H_{16}O$ ethers were obtained from B3LYP calculations with isodesmic reactions. The method is satisfactory, and the results compare well with those available from experiment [10, 11] and estimated by group additivity methods [11, 15]. The group additivity methods are valuable and are inexpensive techniques for estimation of thermodynamic properties. Unfortunately, even for hydrocarbons and ethers, many group values remain unknown. In the past 20 years the experimental thermochemical database has not grown much and so it has become important to devise alternative methods to estimate group values. It seems likely that the missing group contributions can be derived from theoretical calculations similar to those performed in this work.

Thermodynamic functions of NPTBE and IPTBE were obtained by combining the DFT results with experimental $S^\circ(T)$ values determined from calorimetric investigations. Since a multi-dimensional model for the energy levels of internal rotation has not yet solved, an empirical correction for rotor–rotor coupling was used. The preliminary calculations for other alkyl ethers suggest that there is a trend in empirical corrections for the rotor–rotor coupling. We believe that further calculations for ethers would allow us to estimate the missing groups and to develop a group additivity scheme for accurate estimation of thermodynamic properties of alkyl ethers.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research under Grants No. 02-02-17009 and 02-03-32227.

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