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# Thermodynamic properties of 1,1′-biadamantane

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## Abstract

A comprehensive study of thermodynamic properties of 1,1′-biadamantane in different phase states has been carried out. The heat capacity of the compound in the condensed state was measured in two adiabatic calorimeters in the temperature range from 5 to 370 K and in a single-cup scanning calorimeter from 315 to 610 K. Two solid-to-solid phase transitions at 336.3 ± 0.3 K with $\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\circ} = 1.154 \pm 0.019\,\mathrm{kJ\,mol^{-1}}$ and 509.6 ± 0.5 K with $\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\circ} = 1.30 \pm 0.03\,\mathrm{kJ\,mol^{-1}}$, and fusion at $T_{\mathrm{fus}} \sim 561$ K were revealed in this temperature interval. It was found that 1,1′-biadamantane did not form plastic crystals. The thermodynamic functions of the compound in the crystalline state were derived. The saturated vapour pressure of 1,1′-biadamantane from 393 to 443 K was determined by the Knudsen effusion method:

$$\ln\left(\frac{p}{\mathrm{Pa}}\right) = (32.82 \pm 0.37) - (13126 \pm 153)\left(\frac{K}{T}\right).$$

The sublimation enthalpy was obtained from the results of the effusion measurements: $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\circ}$ (417.8 K) = 109.1 ± 1.3 kJ mol$^{-1}$, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\circ}$ (298.15 K) = 113.8 ± 1.4 kJ mol$^{-1}$. The complete set of fundamentals was compiled from experimental spectral data and results of calculations in terms of the density functional theory (B3LYP/6-31G*). The combustion enthalpy of $C_{20}H_{30}$, $\Delta_{\mathrm{c}}H_{\mathrm{m}}^{\circ}$ (298.15 K, cr) = −(11801.3 ± 7.3) kJ mol$^{-1}$, was determined by the bomb-calorimetry method and the enthalpy of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ (298.15 K, cr) = −(356.4 ± 7.8) kJ mol$^{-1}$, was obtained. The thermodynamic properties of 1,1′-biadamantane in the ideal-gas state were calculated.

*Keywords:* 1,1′-Biadamantane; Heat capacity; Thermodynamics of sublimation; Formation enthalpy; Statistical thermodynamics; Thermodynamic properties

## 1. Introduction

Many adamantane derivatives are intermediates used in organic synthesis, in production of physiologically active substances, polymers, additives to lubricating oils and to special fuels [1]. Thermodynamic properties of adamantane [2], 1- and 2-adamantanols [3,4], 2-methyl-2-adamantanol [5], 2-adamantanone [6] and 1-bromoadamantane [7,8] have been studied in our laboratory recently. All the investigated compounds were found to form plastic crystals in various temperature ranges. Thermodynamic parameters of orientational disorder in plastic crystals of some adamantane derivatives have been determined [9].

Compounds containing several adamantane fragments are also synthesized. However, even the simplest of them, 1,1′-biadamantane ($C_{20}H_{30}$, 1,1′-bitricyclo[3.3.1.1$^{3,7}$]decane, Fig. 1), does not have thermodynamic properties studied in a wide temperature range. According to an X-ray diffraction analysis [10], the length of the central C–C bond in the molecule is 0.1578 nm, which exceeds the value typical for a C(sp$^3$)–C(sp$^3$) bond. Nevertheless, semi-empirical calculations (AM1 [11]) show that the barrier of rotation around this bond is rather high and amounts to 19.27 kJ mol$^{-1}$. It is also known [12] that condensation of adamantane molecules leads to the formation of stable polymeric compounds. That is why it would be worthwhile to obtain a thermodynamic description of the

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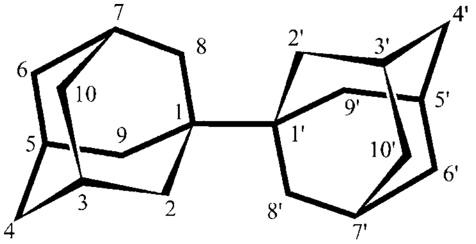

Fig. 1. The molecular structure of 1,1′-biadamantane.

condensation of adamantane into bi-, tri-, tetraadamantanes and its polymers that possess high thermostability and resistivity to various aggressive media. These polymeric materials can have other valuable properties and be used for the production of high-quality lubricating oils, additives to polymers, antirust protective covering for surfaces of machinary and its parts exploited under extreme conditions [13,14]. Thermodynamic investigation of 1,1′-biadamantane is of great interest for the development of the connection between the molecular structure and the ability to form plastic crystals.

We have performed a comprehensive investigation of thermodynamic properties of 1,1′-biadamantane, which includes measurements of the heat capacity in the range from 5 to 580 K, of the saturated vapour pressure and the sublimation enthalpy, of the formation enthalpies of the compound in the crystalline and gaseous states. Quantum-chemical and statistical thermodynamics calculations have been carried out for obtaining the thermodynamic properties of 1,1′-biadamantane in the ideal gaseous state.

## 2. Experimental

### 2.1. Materials

1,1′-Biadamantane was synthesized by the Wurtz reaction [15] by boiling of 1-bromoadamantane in toluene over metallic sodium. Crystalline 1,1′-biadamantane obtained after removing the solvent by evaporation was purified by twice recrystallization from toluene and subsequent sublimation under vacuum conditions. The mass-fraction purity of the sample was >0.999 according to GLC (“Chrom-5” with a flame-ionization detector and a quartz capillary column (50 × 0.0002) m with a SE-30 stationary phase; helium as a carrier gas (0.15 MPa), temperatures of an evaporator and of a column are 543 and 493 K, respectively).

Benzoic acid (VNIIFTRI, Moscow, Russia; K-2 grade with mass-fraction purity >0.99993) and synthetic corundum (VNIIM, St. Petersburg, Russia; mass fraction purity >0.99995).

### 2.2. Apparatus and measurement procedures

### 2.2.1. Adiabatic calorimetry

The heat capacity of 1,1′-biadamantane between 5 and 105 K was measured in a TAU-1 vacuum adiabatic calorimeter made in VNIIFTRI (Moscow, Russia) and described in detail earlier [16–18]. The relative uncertainty of the heat-capacity measurements in the range from 40 to 105 K was ±0.4%, increased gradually with decreasing temperature from 40 K downwards but did not exceed ±2% from 5 to 10 K.

A low-temperature vacuum adiabatic calorimeter made by the Termis close corporation (Moscow, Russia) was used to obtain the heat of capacity, $C_\mathrm{s}$, of the compound in the temperature range 80–370 K [19]. It was found that the uncertainty of the $C_\mathrm{s}$ determination over this interval did not exceed 0.4% [19]. The temperature was measured with an iron-rhodium resistance thermometer ($R_0 = 50\,\Omega$) calibrated for the ITS-90 scale by VNIIFTRI. The corrections on reducing $C_\mathrm{s,m}$ to $C_{p,\mathrm{m}}$ and on sublimation of the substance were neglected because they are several orders of magnitude lower than the experimental error (the sum of the corrections is $<10^{-4}\ C_\mathrm{s,m}$ near 300 K).

### 2.2.2. Differential scanning calorimetry

The high-temperature heat capacity between 300 and 600 K of 1,1′-biadamantane was measured in an improved automatic one-cup scanning calorimeter [20]. The temperature scale of the device was tested by measuring the melting points of tin, lead, indium and benzoic acid. The heat-flow rate calibration [21] was carried out by the heat capacity of reference synthetic corundum (mass-fraction purity >0.99995).

In the measurements, a sample of 1,1′-biadamantane of 0.6897 g mass was placed in an aluminium ampoule. The average scanning rate was about 1 K $\mathrm{min}^{-1}$, the temperature step of the heat-capacity measurements did not exceed 0.3 K. The uncertainty of the heat-capacity determination in the scanning calorimeter was ±2%.

### 2.2.3. The Knudsen effusion method

The saturated vapour pressure of the compound was obtained by the integral effusion Knudsen method. The device description and the measurement procedure were presented earlier [22]. The uncertainty of the vapour-pressure determination was found to amount to ±5%. Three membranes were applied to the measurements ($l$ is a membrane thickness, $d$ is an orifice diameter):

- membrane 1: $l = 5.0 \times 10^{-5}$ m, $d = (1.833 \pm 0.004) \times 10^{-4}$ m;
- membrane 2: $l = 8.4 \times 10^{-5}$ m, $d = (4.467 \pm 0.005) \times 10^{-4}$ m;
- membrane 3: $l = 5.0 \times 10^{-5}$ m, $d = (8.370 \pm 0.004) \times 10^{-4}$ m.

Preliminary experiments revealed that the vapour pressure of 1,1′-biadamantane at $T = 300$ K was lower than $10^{-4}$ Pa. The main measurements were conducted with the use of a high-temperature massive thermostat that maintained a present temperature within ±0.02 K. The weighing of a container with the substance before and after an effusion experiment was performed with an accuracy of $\pm 2 \times 10^{-5}$ g. The thermostat temperature was measured with a platinum resistance thermometer ($R_0 = 10.0447\,\Omega$).

The saturated vapour pressure of the compound was calculated according to the following generalized equation that took into account vapour undersaturation in the Knudsen cell and failure of gas isotropy near the effusion orifice:

$$p_{\text{sat}} = \frac{\Delta m}{\tau}\left\{\frac{1}{kS_{\text{or}}} + \frac{1}{\alpha\gamma S_{\text{sub}}}\right\}\left(\frac{2\pi RT}{M}\right)^{1/2}, \qquad (1)$$

where $\Delta m$ is the mass loss of the sample during the effusion into vacuum; $\tau$ the duration of the effusion; $k$ the probability of the transmission of the molecules through the orifice (in terms of Wahlbeck's theory [23]); $S_{\text{or}}$ the cross-sectional area of the effusion orifice; $S_{\text{sub}}$ the geometrical surface from which the sublimation of the substance takes place; $\gamma$ the roughness coefficient; $\alpha$ the condensation coefficient; $T$ the temperature; $M$ is the molar mass of the effusing vapours (0.270452 kg mol$^{-1}$, calculated according to the molar masses of elements from [24]).

The calculation of $k$ coefficients was carried out according to the Wahlbeck theory on the failure of gas isotropy in an effusion cell [23] by the method of successive iterations [25]. The effective diameter of the molecule of 1,1′-biadamantane, $d_{\text{eff}} = 1.21$ nm, was estimated from the van der Waals volume obtained by the molecular mechanics using the MM3 force field [26] in the Tinker 4.0 package [27].

The experimental $p_{\text{sat}}$ values were approximated by the following equation:

$$\ln\left(\frac{p_{\text{sat}}}{\text{Pa}}\right) = A + B\left(\frac{T}{K}\right)^{-1}. \qquad (2)$$

The $A$ and $B$ coefficients in Eq. (2) and the product ($\alpha\gamma S_{\text{sub}}$) in Eq. (1) were determined by the least-squares method from the results of the effusion measurements conducted using the membranes with different parameters of the effusion orifices (see [6] for details).

### 2.2.4. *The bomb calorimetry*

The combustion enthalpy for 1,1′-biadamantane was determined by the bomb calorimetry in a semiautomatic isoperibol calorimeter with a static bomb and an air thermostat [28]. The bath temperature (300.65 K) was maintained during a whole experiment within ±0.02 K. The temperature of the calorimetric vessel used was measured with the use of a platinum resistance thermometer ($R = 500\ \Omega$). The energy equivalent of the calorimeter $\varepsilon$(calor) = 9834.6 ± 3.2 J K$^{-1}$, was obtained using reference benzoic acid (K-2 grade) with the standard combustion energy $\Delta_c U^\circ$(cr, 298.15 K) = −(26414 ± 5) J g$^{-1}$ (when a sample mass is adjusted to vacuum conditions), the specific density $\rho = 1320$ kg m$^{-3}$, the specific heat capacity $c_p$(cr, 298.15 K) = 1.21 J K$^{-1}$ g$^{-1}$ and $(\partial U/\partial p) = -0.116$ J MPa$^{-1}$ g$^{-1}$.

A sample of 1,1′-biadamantane for the combustion was preliminary pressed into a pellet of about 0.10 g mass. The weighing was performed directly in a platinum crucible by means of a Mettler Toledo AG 245 balance with an accuracy of $2 \times 10^{-5}$ g. The correction from apparent mass to true mass (in vacuum) was applied using the value $\rho = 1140 \pm 30$ kg m$^{-3}$ measured in a pycnometer with the use of methanol at 293 K, which is in good agreement with the value 1190 kg m$^{-3}$ determined for 2,2′-biadamantane from crystallographic data at 243 K [29]. Since such a small sample of the compound gives an insufficient temperature rise during combustion experiments, 1,1′-biadamantane was burned together with an appropriate amount of benzoic acid (pellets of approximately 0.13 g). The calculations of the corrected temperature rise and of the Washborn corrections were conducted according to the standard techniques [30–32]. The molar masses of the substances were obtained from the molar masses of the elements recommended in [32]. The standard formation enthalpy of 1,1′-biadamantane was calculated with the use of the standard molar enthalpies of formation of $CO_2$ (g), −(393.51 ± 0.13) kJ mol$^{-1}$, and $H_2O$ (l), −(285.830 ± 0.042) kJ mol$^{-1}$, taken from [33].

## 3. Results

### 3.1. *The heat capacity and the parameters of the solid-to-solid transitions and fusion of 1,1′-biadamantane*

The temperature dependence of the molar heat capacity at saturated vapour pressure ($C_{\text{s,m}}$) for 1,1′-biadamantane in the temperature range from 5 to 600 K is presented in Fig. 2. The results of the $C_{\text{s,m}}$ measurements in the adiabatic calorimeters are summarized in Table S1 (in the Supporting Information).

Three phase anomalies connected with two solid-to-solid transitions and fusion were revealed in the $C_{\text{s,m}}$ *versus* $T$ curve (Fig. 2).

The calculation of the crIII–crII transition enthalpy was performed on the basis of the results of two series of the heat-capacity measurements (Table S1) and of two single experiments on continuous energy input (Table 1). The initial ($T_{\text{start}}$) and final ($T_{\text{end}}$) temperature of the latter experiments lay beyond the phase transition region; the temperature corresponding to the maximum value of the effective heat capacity in the phase transition was taken as the transition temperature (the average value of both series of the heat-capacity measurements):

$$T_{\text{trs}}(\text{crIII–crII}) = (336.3 \pm 0.3)\,\text{K}$$

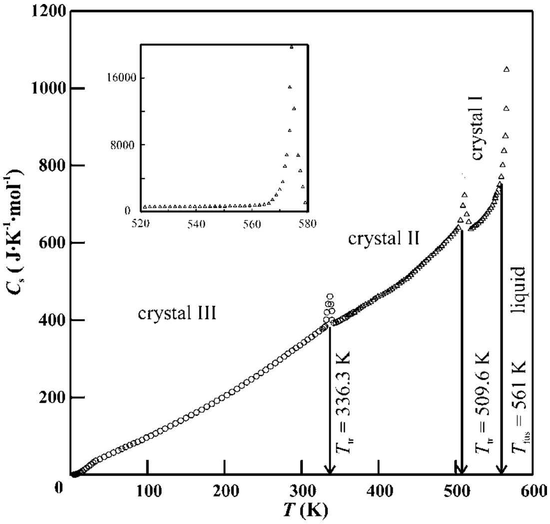

Fig. 2. The temperature dependence of the heat capacity for 1,1′-biadamantane. "○": adiabatic calorimetry; "△": DSC.

Table 1
Determination of the solid-to-solid (crIII → crII) phase transition enthalpy of 1,1′-biadamantane

| $T_{\mathrm{start}}$ (K) | $T_{\mathrm{end}}$ (K) | $Q$ (kJ mol$^{-1}$) | $\Delta_{\mathrm{trs}}H^\circ_{\mathrm{m}}$ (J mol$^{-1}$) |
|---|---|---|---|
| 319.74 | 349.96 | 12.73 | 1149 |
| 321.07 | 351.07 | 12.71 | 1171 |
| 320.14 | 351.67 | 13.27 | 1151 |
| 319.49 | 349.98 | 12.83 | 1145 |
| | | | $\langle\Delta_{\mathrm{trs}}H^\circ_{\mathrm{m}}\rangle = (1154 \pm 19)$[a] |

$M = 270.452$ g mol$^{-1}$, $Q$ is the quantity of heat supplied to the compound, $T_{\mathrm{start}}$ is the initial temperature of the experiment, $T_{\mathrm{end}}$ is the final temperature of the experiment.

[a] The average value.

The transition enthalpy ($\Delta_{\mathrm{trs}}H^\circ_{\mathrm{m}}$) was calculated by

$$\Delta_{\mathrm{trs}}H^\circ_{\mathrm{m}} = Q - \int_{T_{\mathrm{start}}}^{T_{\mathrm{trs}}} C_{p,\mathrm{m}}(\mathrm{crIII})\ \mathrm{d}T - \int_{T_{\mathrm{trs}}}^{T_{\mathrm{end}}} C_{p,\mathrm{m}}(\mathrm{crII})\,\mathrm{d}T, \tag{3}$$

where $Q$ is the heat input for heating 1 mol of the compound from $T_{\mathrm{start}}$ to $T_{\mathrm{end}}$; $C_{p,\mathrm{m}}$(crIII) and $C_{p,\mathrm{m}}$(crII) are the heat-capacities baselines of the corresponding phases. The heat capacities of both phases were approximated by one common baseline,

$$C_{p,\mathrm{m}}(\mathrm{crIII,\ crII})/\mathrm{J\,K^{-1}\,mol^{-1}} = -6986.396 + 63.118\left(\frac{T}{K}\right) - 0.182998\left(\frac{T}{K}\right)^2 + 1.7877\times10^{-4}\left(\frac{T}{K}\right)^3, \tag{4}$$

obtained by the least-squares fitting from the experimental heat-capacity values from the ranges 309.1 to 319.3 K (crystal III) and from 346.3 to 361.3 K (crystal II). The enthalpy of the crIII–crII transition was thus derived to be

$$\Delta_{\mathrm{trs}}H^\circ_{\mathrm{m}}(\mathrm{crIII–crII}) = (1154 \pm 19)\,\mathrm{J\,mol^{-1}}.$$

The enthalpies of the high-temperature solid-phase transition crII–crI and of fusion were calculated from the heat-capacity measurements carried out in the scanning calorimeter (Table S2 in the Supporting Information).

The onset temperature was taken as the crII–crI transition temperature:

$$T_{\mathrm{trs}}(\mathrm{crII–crI}) = (509.6 \pm 0.5)\,\mathrm{K}.$$

The crII–crI transition enthalpy was obtained by the numerical integration of the excessive heat capacity in the phase-transition region. The heat capacities of the low- and high-temperature phases were fitted by the following linear polynomial:

$$C_{p,\mathrm{m}}(\mathrm{crII,\ crI})/\mathrm{J\,K^{-1}\,mol^{-1}} = -178.1907 + 1.58437\left(\frac{T}{K}\right), \tag{5}$$

from the experimental heat-capacity data from 435.4 to 465.0 K (crystal II) and 519.7 to 540.3 K (crystal I). Thus, the transition enthalpy is:

$$\Delta_{\mathrm{trs}}H^\circ_{\mathrm{m}}(\mathrm{crII–crI}) = (1.30 \pm 0.03)\,\mathrm{kJ\,mol^{-1}}.$$

The scanning-calorimetry measurements allowed us to estimate the melting point of the sample, $T_{\mathrm{fus}} \sim 561$ K (according to [15], the melting point of $C_{20}H_{30}$ lies in the range from 561 to 563 K). However, further heating led to seal failure of the calorimetric cell and to decomposition of the sample and, therefore, the fusion enthalpy was roughly estimated:

$$\Delta_{\mathrm{fus}}H^\circ_{\mathrm{m}}(561\,\mathrm{K},\ \mathrm{crI}) \sim (70 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

Thus, it was established that 1,1′-biadamantane did not form plastic crystals [8,9].

The smoothed values of the heat capacity of 1,1′-biadamantane are listed in Table S3 (in the Supporting Information). The Debye function with three degrees of freedom, $C_{\mathrm{v,m}} = 3RD(\langle\Theta_{\mathrm{D}}\rangle/T)$, was used for extrapolation of the heat capacity at $T < 5$ K, The average characteristic Debye temperature, $\langle\Theta_{\mathrm{D}}\rangle = 86.6 \pm 0.2$ K, was determined from the experimental values of the heat capacity in the range from 5.12 to 7.26 K (the maximum deviation is $|C_{p,\mathrm{exp.}} - C_{p,\mathrm{calc.}}| < 0.01C_{p,\mathrm{exp.}}$). The standard molar thermodynamic functions of crystalline 1,1′-biadamantane at $T = 298.15$ K are:

- $C_{p,\mathrm{m}} = (335.3 \pm 1.3)\,\mathrm{J\,K^{-1}\,mol^{-1}}$,
- $\Delta_0^{298.15}S^\circ_{\mathrm{m}} = (289.9 \pm 1.3)\,\mathrm{J\,K^{-1}\,mol^{-1}}$,
- $\Delta_0^{298.15}H^\circ_{\mathrm{m}} = (45.88 \pm 0.20)\,\mathrm{kJ\,mol^{-1}}$.

### *3.2. The thermodynamics of sublimation for 1,1′-biadamantane*

The saturated vapour pressure of 1,1′-biadamantane was measured by the effusion Knudsen method between $T = 392.8$ and 442.7 K (Table S4 in the Supporting Information).

The temperature dependence of the saturated vapour pressure can be described by the following equation:

$$\ln\left(\frac{p}{\mathrm{Pa}}\right) = (32.82 \pm 0.37) - (13126 \pm 153)\left(\frac{T}{K}\right)^{-1}. \tag{6}$$

From Eq. (6) the vapour pressure at the average temperature $\langle T\rangle = 417.8$ K is

$$p_{\mathrm{sat}}(417.8\,\mathrm{K}) = (4.068 \pm 0.057)\,\mathrm{Pa},$$

and the molar standard ($p^\circ = 10^5$ Pa) sublimation enthalpy and entropy amount to

$$\Delta_{\mathrm{sub}}H^\circ_{\mathrm{m}}(417.8,\ \mathrm{crII}) = (109.1 \pm 1.3)\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_{\mathrm{sub}}S^\circ_{\mathrm{m}}(417.8\,\mathrm{K},\ \mathrm{crII}) = (176.9 \pm 3.1)\,\mathrm{kJ\,mol^{-1}}.$$

The sublimation enthalpy of 1,1′-biadamantane was adjusted from $\langle T\rangle = 417.8$ K to $T = 298.15$ K using the heat-capacity difference $\Delta_{\mathrm{gas}}^{\mathrm{crII}}C_p$ from 417.8 to 336.3 K, the solid-phase transition enthalpy at 336.3 K and the difference $\Delta_{\mathrm{gas}}^{\mathrm{crIII}}C_p$ in the range 336.3–298.15 K. In these calculations, the heat capacity of the crystalline compound was obtained experimentally and that of the gas by the statistical thermodynamics. The value to be found was:

$$\Delta_{\text{sub}}H^{\circ}_{\text{m}}(298.15\,\text{K},\ \text{crIII}) = (113.8 \pm 1.4)\,\text{kJ}\,\text{mol}^{-1}.$$

The standard entropy of 1,1′-biadamantane in the gaseous state,

$$\Delta_0^{417.8}S^{\circ}_{\text{m}}(\text{gas}) = 606.7 \pm 3.6\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1},$$

was calculated on the basis of the heat-capacity and vapour-pressure data.

### 3.3. Experimental determination of the enthalpy of formation of 1,1′-biadamantane

The results of the combustion experiments are summarized in Table S5 (in the Supporting Information), according to which the combustion energy and the standard molar combustion enthalpy were derived with regard to the corresponding combustion reaction

$$C_{20}H_{30}(\text{cr}) + 27.5O_2(\text{g}) = 20CO_2(\text{g}) + 15H_2O(\text{l}). \qquad (7)$$

$$\Delta_{\text{c}}U^{\circ}_{\text{m}}(298.15\,\text{K},\ \text{crIII}) = -(11782.7 \pm 7.3)\,\text{kJ}\,\text{mol}^{-1},$$

$$\Delta_{\text{c}}H^{\circ}_{\text{m}}(298.15\,\text{K},\ \text{crIII}) = -(11801.3 \pm 7.3)\,\text{kJ}\,\text{mol}^{-1}.$$

Using the recommended values of the standard enthalpies of formation for $CO_2$(g) and $H_2O$(l) [33] and the sublimation enthalpy for 1,1′-biadamantane obtained above, the formation enthalpies for the compound in the crystalline and gaseous states were calculated

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(298.15\,\text{K},\ \text{crIII}) = -(356.4 \pm 7.8)\,\text{kJ}\,\text{mol}^{-1},$$

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(298.15\,\text{K},\ \text{g}) = -(242.6 \pm 7.9)\,\text{kJ}\,\text{mol}^{-1}.$$

Rather a great uncertainty of the formation-enthalpy value obtained could be connected with the small amount of the sample used in the calorimetric measurements and with the small number of the combustion experiments.

### 3.4. The thermodynamic properties in the ideal gaseous state

The calculations of the thermodynamic properties of 1,1′-biadamantane in the ideal gaseous state by the statistical thermodynamics were performed in the ‘rigid rotator–harmonic oscillator’ approximation [34]. A molecule of 1,1′-biadamantane belongs to the $D_{3d}$ point group with the symmetry number $\sigma = 6$. The calculations of the equilibrium geometries and the fundamentals for $C_{20}H_{30}$ were performed in terms of the density functional theory (DFT) using the B3LYP functional [35] in the 6-31G* basis set. Among a number of possible potentials for DFT [36], B3LYP was chosen because it is used the most frequently for calculations of spectral and thermodynamic properties of hydrocarbons and allows obtaining reliable data on them. All the calculations were done using the PC GAMESS package (version 6.4) [37]. The product of the principal inertia moments of the molecule, $I_AI_BI_C = 1.24 \times 10^{-131}\,\text{kg}^3\,\text{m}^6$, and the reduced inertia moment of the adamantyl top, $I_r = 246 \times 10^{-45}\,\text{kg}\,\text{m}^2$ (the symmetry number of the internal rotation is 3), were obtained from the geometry optimized by the B3LYP/6-31G* method. The same method was applied to compute the fundamentals and the corresponding IR intensities. Ref. [11] comprises results of the experimental IR and Raman of 1,1′-biadamantane. In the present work, a comparison of the calculated wave numbers (B3LYP/6-31G*) with the experimental ones [11] was carried out taking into account the symmetry of each vibration, their degeneracy and their intensity (Table S6 in the Supporting Information). There was some ambiguity in attributing some calculated wave numbers to the experimental bands from [11]. This can be related either to calculation limitations or to the experimental error.

After establishing the correspondence between the experimental and calculated fundamentals, the scaling factor was found to be 0.978. For the calculations by statistical thermodynamics, the experimental spectrum supplemented with the scaled calculated wave numbers (Table S6) was used.

The internal rotation in 1,1′-biadamantane around the central C–C bond has not been investigated yet. Bistričić et al. [11] gave only a value of the potential barrier height for the rotation ($V_0 = 19.3\,\text{kJ}\,\text{mol}^{-1}$) found by the semi-empirical AM1 method. In the present work, the AM1 method was also applied, resulting in $V_0 = 23.2\,\text{kJ}\,\text{mol}^{-1}$ and a luck of reproduction of the calculated vibrational spectrum presented in [11]. That is why the fundamentals were computed in terms of DFT at the B3LYP/6-31G* level (Table S6).

In this work, the potential barrier, $V_0 = 22.4\,\text{kJ}\,\text{mol}^{-1}$, was obtained by the molecular mechanics method using MM3 force field [26] in the Tinker 4.0 package [27]. This value is close to that from [11]. Based upon the wave number for the torsion vibration $\nu_0 = 32\,\text{cm}^{-1}$ (B3LYP/6-31G*, scaled with the factor 0.978), an estimation of the potential barrier of the top rotation was also made according to [34]

$$\nu_0 = \frac{n_r}{2\pi}\sqrt{\frac{V_0}{2I_r}}, \qquad (8)$$

where $I_r$ is the reduced inertia moment; $n_r$ is the number of maxima in the potential energy curve for the internal rotation.

The value $V_0 \cong 12\,\text{kJ}\,\text{mol}^{-1}$ was thus obtained. The lower potential barrier for 1,1′-biadamantane correlates well with the established fact that the C(4)–C(4) bond length in this molecule, $R_{\text{C–C}} = 1.578\,\text{Å}$, is much greater than the average value 1.5(3) Å for a single C–C bond. This enabled us to achieve good agreement between the calculated value of the ideal-gas entropy, $\Delta_0^{417.8}S^{\circ}_{\text{m}}(\text{g, calc.}) = 604.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ (Table 2, the internal rotation contribution was calculated by the energy levels of the top [34]), and the experimental one, $\Delta_0^{417.8}S^{\circ}_{\text{m}}$ (g, exp.) $= 606.7 \pm 3.6\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$.

The results of the calculations by the statistical thermodynamics are listed in Table S7 (in the Supporting Information).

Table 2
The potential barrier of internal rotation ($V_0$) in the molecule of 1,1′-biadamantane, the ideal-gas entropy, calculated by the statistical thermodynamics using this barrier, and the internal rotation contribution to the entropy ($\Delta_{\mathrm{int.rot.}}S$)

| $V_0$ (kJ mol$^{-1}$) | Method for $V_0$ calculations | $\Delta_0^{417.8} S_m^\circ(g)$ (J K$^{-1}$ mol$^{-1}$) | $\Delta_{\mathrm{int.rot.}}S$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| 19.3 | AM1 [11] | 601.5 | 25.8 |
| 22.42 | MM3 [26], this work | 600.7 | 24.9 |
| 11.98 | By Eq. (8), $\nu_0 = 32$ cm$^{-1}$ | 604.2 | 28.5 |
| – | Experiment | 606.7 ± 3.6 | – |

Table 3
The thermodynamic parameters of different reactions of 1,1′-biadamantane synthesis ($p^\circ = 10^5$ Pa)

| Reaction[a] | $T$ (K) | $\Delta_r H_m^\circ$ (kJ mol$^{-1}$) | $\Delta_r S_m^\circ$ (J mol$^{-1}$ K$^{-1}$) | $K^\circ$ |
|---|---|---|---|---|
| (9) | 298.15 | 26.60 | −39.95 | $1.8 \times 10^{-7}$ |
| | 400 | 29.22 | −32.17 | $3.2 \times 10^{-6}$ |
| (10) | 298.15 | 54.30 | −28.22 | $1.0 \times 10^{-11}$ |
| | 400 | 53.61 | −30.06 | $2.7 \times 10^{-9}$ |
| (11) | 298.15 | −38.94 | −28.36 | $2.2 \times 10^{5}$ |
| | 400 | −38.61 | −27.34 | 4109 |
| (12a) | 298.15 | −699.4 | −202.4 | $10^{111}$ |
| (12b) | 400 | −674.4 | −219.4 | $10^{76}$ |

[a] The thermodynamic properties of the participants of the reactions were taken from [2,38] for $C_{10}H_{16}$, [38,39] for $Br_2$ and NaBr, [7] for 1-$C_{10}H_{15}Br$, [4] for 1-$C_{10}H_{15}OH$.

The data from Table S7 were used for obtaining the equilibrium constants of four reactions of 1,1′-biadamantane synthesis (Table 3).

$$2C_{10}H_{16}(g) = C_{20}H_{30}(g) + H_2(g) \tag{9}$$

$$2\ 1\text{-}C_{10}H_{15}Br = C_{20}H_{30} + Br_2 \tag{10}$$

$$C_{10}H_{16}(g) + 1\text{-}C_{10}H_{15}OH(g) = C_{20}H_{30}(g) + H_2O(g) \tag{11}$$

$$2\ 1\text{-}C_{10}H_{15}Br(g) + 2Na(cr) = C_{20}H_{30}(g) + 2NaBr(cr) \tag{12a}$$

$$2\ 1\text{-}C_{10}H_{15}Br(g) + 2Na(liq) = C_{20}H_{30}(g) + 2NaBr(cr) \tag{12b}$$

It is evident from the data presented in Table 3 that the formation of 1,1′-biadamantane is thermodynamically favorable in the case of the reaction of intermolecular dehydration of 1-adamantanol (11) and of the Wurtz reaction (12a) and (12b). At the same time, the direct dimerization of adamantane (9) and the debromination reaction (10) are thermodynamically forbidden at $T < 400$ K.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.03.018.

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