

# Syntheses, Geometrical and Electronic Structure of Alkyladamantanes and Their Thermodynamic Characteristic According to the Density Functional Theory

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**Abstract:** Propyladamantanes synthesized by of alkylation adamantane with isopropyl alcohol temperature range from 5 to 40°C in the presence of 96% sulfuric acid. Tetramethyl- and Dimethylethyladamantanes synthesized by of isomerization of Perhydroanthracene in the presence of aluminium oxide catalyst on the setting of the flow type. Isomers Butyladamantanes was obtained by the reaction of alkylation of the adamantane with n-butane and isobutane. Adamantane and its derivatives have been the subject of many experimental and theoretical studies. The molecular structure of adamantane was studied by gasphase electron diffraction, Penning ionization electron spectroscopy, photoelectron spectroscopy, electron spin resonance, and quantum calculations of ionization potentials (IP) and electron affinity (SE). The structure 1-n-propyladamantane (1), 1-isopropyladamantane (2), 2-n-propyladamantane (3), 1,2-di-n-propyladamantane (4), 1,3-dimethyl-5-ethyladamantane (5), 1,3,5,6-tetramethyladamantane (6), 1,3,5,7-tetramethyladamantane (7), perhydroanthracene (8), 1-n-butyladamantane (9), 1-isobutyladamantane (10), 1-sec-butyladamantane (11) has been studied using the Becke–Lee–Yang–Parr (B3LYP) hybrid energy functional of electron density with the 6-31G\* basis set. The geometric and electronic characteristics of the compounds and their total energy, normal vibration frequencies have been calculated. It has been shown that the calculated Gibb free energies of formation for the perhydroanthracene isomerization products are in qualitative agreement with the experimental product composition of the isomerate and alkylation of adamantane with isopropyl alcohol are in qualitative agreement with the experimental composition of the products. Obtained good agreement of calculated and experimental data on the composition of equilibrium mixtures.

**Keywords:** Propyladamantane, Dimethylethyladamantane, Tetramethyladamantane, Butyladamantane, DFT Calculations

## 1. Introduction

Alkyladamantanes and higher alkyladamantoids, are of interest not only as a component of energetic hydrocarbon fuels, e.g., RF-1, RF-2, etc. propellants, but also have great scientific importance. Because of the special thermodynamic properties of their isomers, they can be used for assessing the degree of catalytic transformation of oils and condensates by the action of natural clays and aluminosilicates and “fingerprinting” the fuels manufactured on their basis. In

addition, these hydrocarbons are useful as feedstock in fine organic and petrochemical syntheses [1]. The molecular structure of adamantane was studied by gasphase electron diffraction [2], Penning ionization electron spectroscopy [3], photoelectron spectroscopy [4], electron spin resonance [5], and quantum calculations of ionization potentials (IP) and electron affinity (SE) [6]. Since obtaining experimental data on the relative thermodynamic stability of isomers of polyalkyladamantanes and higher alkyladamantoids is fraught with certain difficulties, including those in the

identification of the isomers and determination of their spatial structure, computational methods are anticipated to play a very important role in solving these problems. In a previous papers [7, 8], we reported the results of studying the structure of perhydroacenaphthene, perhydrofluorene and its isomerization products C<sub>12</sub>H<sub>20</sub>-C<sub>13</sub>H<sub>22</sub> alkyladamantanes and presented calculated geometric and electronic characteristics, total energies, transformation energies, entropies of transformations, and normal vibration frequencies, as well as the equilibrium constant of isomerization of perhydroacenaphthene and perhydrofluorene into products.

In this paper we discuss the results of our quantum-chemical study of propyl-, tetramethyl-, dimethylethyl- and butyladamantanes, including comparison of the calculated and experimental compositions of equilibrium mixtures.

## 2. Experimental

### 2.1. The Synthesis of Alkyladamantanes

Propyladamantanes were synthesized by alkylation of adamantane with isopropyl alcohol according [9] to figure 1. The reaction was carried out in the temperature range from 5 to 40 °C in the presence of 96% sulfuric acid.

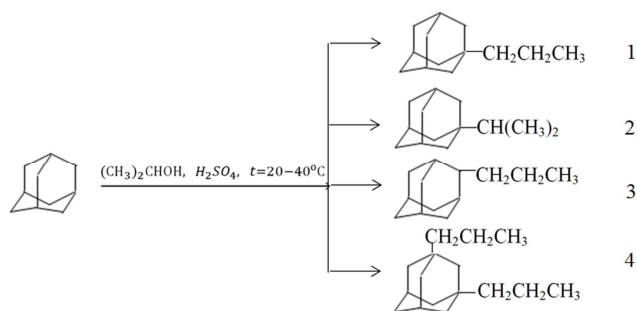
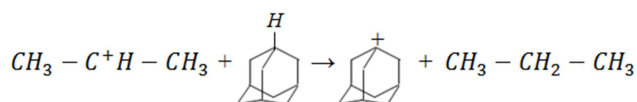
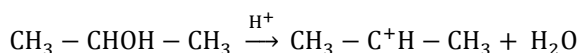


Figure 1. Synthesis of propyl- and dipropyladamantanes.

The main products of the alkylation of adamantane with isopropyl alcohol are 1-n-propyladamantane (yield 24%,  $n_D^{20} = 1.4902$ ) and 1,3-dipropyladamantane (yield 18%,  $n_D^{20} = 1.4882$ ), and in small amounts 1-isopropyl- and 2-n-propyladamantanes (yield 10% and 1%, respectively).

The structure of propyl radicals is clearly determined by IR spectra of hydrocarbons. The presence of the n-propyl group is indicated by the ordinary character of the 1380 cm<sup>-1</sup> band and the 740 cm<sup>-1</sup> band (Figure 2). The asymmetry of the 1380 and 1530 cm<sup>-1</sup> bands is associated with an impurity of 1-isopropyl adamantane.

Based on the composition of the alkylation products of adamantane with alcohols, the following reaction mechanism can be assumed. Alkylation proceeds along the tertiary carbon atom of the adamantane nucleus. The formation of a carbonium ion and the transfer of a positive charge to adamantane with the formation of an adamantyl-cation can be represented by the following scheme:



In addition, the alcohol is dehydrogenated to the corresponding olefin and attached along the nucleophilic mechanism to the adamantyl cation:

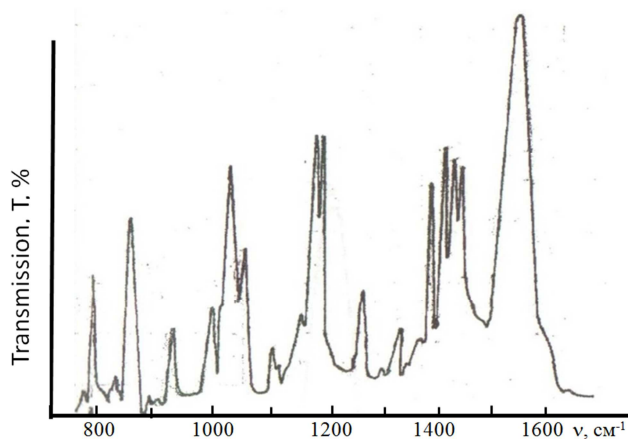
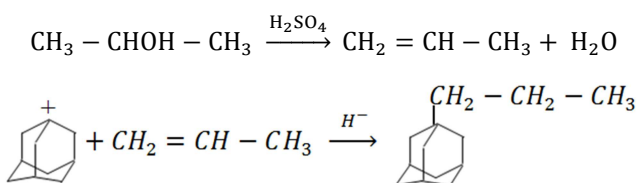


Figure 2. The experimental IR spectra of 1-n-propyladamantane.

Tetramethyl- and dimethylethyladamantanes of the composition C<sub>14</sub>H<sub>24</sub> (5-7) were isomerized from perhydroanthracene [10], according to figure 3. The isomerization of perhydroanthracene was carried out at a temperature of 180-200°C in the presence of aluminum oxide.

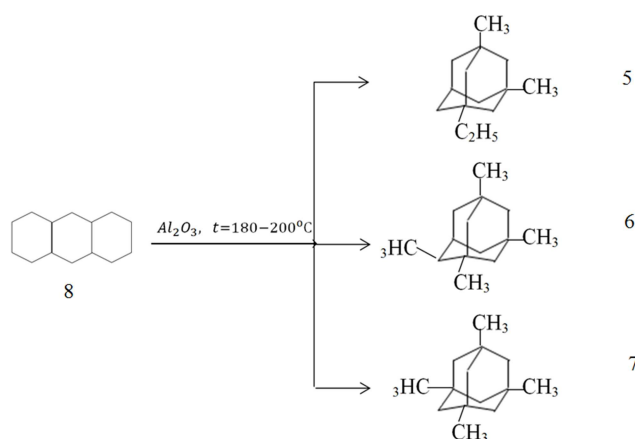


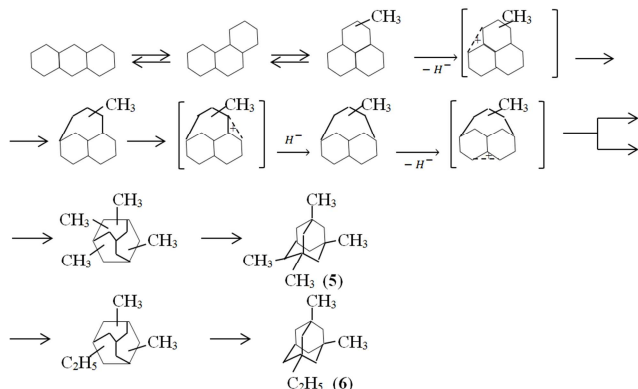
Figure 3. Synthesis of dimethylethyl- and tetramethyladamantanes by isomerization of perhydroanthracene.

The main reaction products are 1,3,5,6-tetramethyladamantane (yield 25%,  $n_D^{20} = 1.4800$ ) and 1,3-dimethyl-5-ethyladamantane (yield 35%,  $n_D^{20} = 1.4805$ ). The formation of the thermodynamically most stable isomer -

1,3,5,7-tetramethyladamantane kinetically is extremely difficult (yield 9%).

The structure of methyl and ethyl radicals is also clearly defined by IR spectroscopy [12, 13].

The mechanism of isomerization of perhydroanthracene can be schematically represented by the following scheme:



Alkylation of adamantane with isooctane was carried out in a swinging duck, thermostated at a given temperature. The adamantane was dissolved in isooctane and  $\text{AlCl}_3$  was added. The catalyst was activated with hydrochloric acid. The reaction was carried out for 2 hours. The main products are 1-n-butyladamantane (yield 66%,  $n_D^{20} = 1.4907$ ), 1-isobutyladamantane (yield 18%,  $n_D^{20} = 1.4890$ ), 1-sec-butyladamantane (yield 9%,  $n_D^{20} = 1.4870$ ). The reason for the lower thermodynamic stability of 1-isobutyl- and 1-sec-butyladamantane is probably the spatial 1.5-interaction of the protons of the methyl groups of the side chain and protons in the second carbon of the adamantane nucleus.

On the basis of the experimental data, the difference in the enthalpy of 1-n-butyl- and 1-isobutyl adamantanes is  $\approx 10.3$  kJ/mol.

Isomeric butyladamantanes (9-11) were obtained by the alkylation reaction of adamantane with isooctane [11]. The reaction equations are given in figure 4.

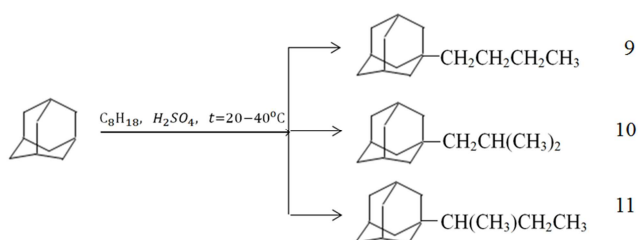
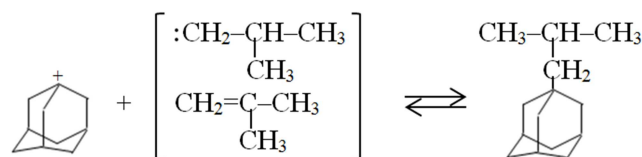


Figure 4. Synthesis of butyladamantanes.

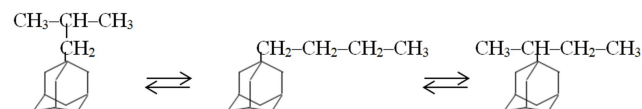
Identification of reaction products was carried out using mass-spectrometry, IR- and PMR-spectroscopy [12, 13].

Based on the studies carried out, it is possible to present the following mechanism for the formation of alkyladamantanes. The decomposition of paraffinic hydrocarbons in the presence of  $\text{AlCl}_3$  occurs along the heterolytic pathway. In this case, the  $\text{C}=\text{C}$  bonds, which are closer to the center of the molecule, are most easily exposed to the discontinuity.

Adamantane in the presence of  $\text{AlCl}_3$  readily forms adamantyl cation, which reacts with the products of the decomposition of paraffins (anion or olefin):



Alkyladamantanes under the reaction conditions are isomerized with a change in structure:



## 2.2. Quantum-chemical Calculations of the Synthesized Alkyladamantanes

Quantum-chemical calculations of compounds I-XI were performed using the density functional theory (DFT) using the B3LYP hybrid functional from the electron density with total energy optimization and calculation of the frequencies of normal vibrations and the 6-31G \* basis set. Calculations were performed using the program GAUSSIAN-98 [14]. For each molecule, geometric parameters of atoms were optimized using analytical methods of calculation. Calculating the frequencies of normal vibrations using the second derivatives, it was confirmed that the stationarity points, determined in optimization of geometry, corresponded to the minima of the potential energy surface.

The DFT B3LYP method is a combination of the Hartree-Fock method and the density functional theory using Becke's three-parameter (B3) gradient-corrected functional series [15] and the Lee-Yang exchange-correlation functional series (LYP) [16]. For each molecule, the geometric arrangement of atoms was optimized using analytical calculation methods. By calculating the normal vibration frequencies with the use of second derivatives, it was confirmed that the stationary points determined with geometry optimization are energy minima.

The DFT method using the B3LYP hybrid functional is widely used in the study of the kinetics and mechanism of reactions [17], the calculation and interpretation of vibrational spectra, the thermodynamics of compounds [18, 19], the molecular structure [20-22], the structural and electronic characteristics of compounds [23] and in other cases of research.

## 3. The Results of Calculations and Their Discussion

Table 1 shows the calculated electronic characteristics of the calculated molecules (1-11). Here are the energies of the boundary orbitals ( $E_{\text{homo}}$ ,  $E_{\text{lumo}}$ ), dipole moments ( $\mu$ ), zero-point energy (ZPC) and entropy values (S).

Table 2 shows the basic calculated energy characteristics of compounds 1-11. Here are values of complete energies ( $E_t$ ), complete energies with allowance for zero-point energy

( $E_{zpc}$ ), complete energies with allowance for enthalpy corrections ( $E_H$ ) and complete energies with allowance for Gibbs free energy corrections ( $E_G$ ) in atomic units.

**Table 1.** Basic design the electronic characteristics of compounds 1-11.

Compound	$E_{\text{homo}}$ , ev	$E_{\text{LUMO}}$ , ev	$\mu$ , D	ZPC, ev	S, cal/mol-K
1	-0.24781	0.10188	0.1275	0.334733	108.667
2	-0.25001	0.08986	0.1236	0.331388	107.244
3	-0.24958	0.08836	0.1444	0.330616	107.239
4	-0.24906	0.06401	0.0772	0.306013	100.098
5	-0.25075	0.06379	0.1090	0.305508	100.056
6	-0.25047	0.06518	0.1450	0.306382	101.521
7	-0.24864	0.06577	0.0219	0.306100	99.872
8	-0.25324	0.08626	0.0098	0.330032	106.630
9	-0.25559	0.07514	0.0808	0.307316	103.962
10	-0.25327	0.06330	0.1036	0.304719	100.113
11	-0.25170	0.06446	0.0945	0.306018	100.965

These thermodynamic quantities are defined by the following formulas [24]:

$$E_{zpc} = E_t + ZPC \quad (1)$$

$$E_H = E_t + ZPC + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} \quad (2)$$

$$E_G = E_H - T S \quad (3)$$

where,  $E_{\text{vib}}$  – energy of oscillatory motion,

$E_{\text{rot}}$  – energy of rotational motion,

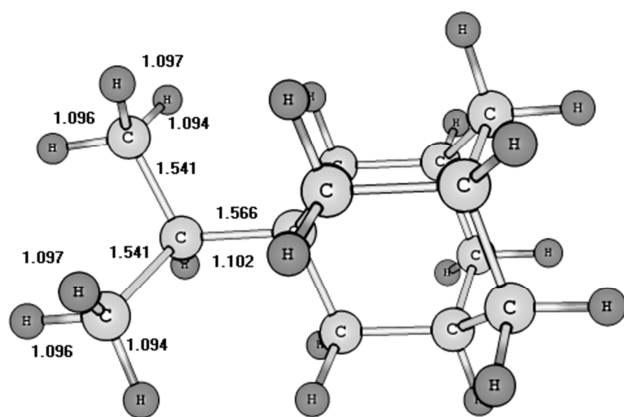
$E_{\text{trans}}$  – energy of translational motion,

S – entropy,

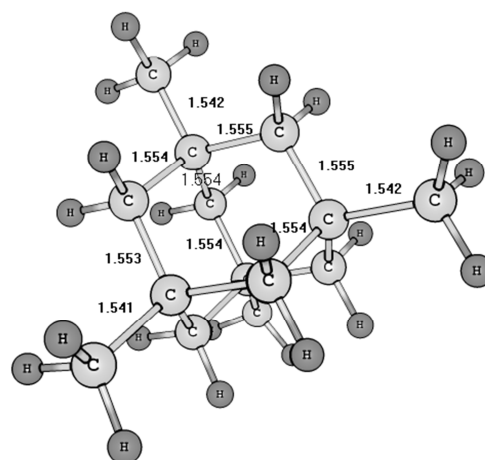
T – temperature on the Kelvin scale.

**Table 2.** Basic calculation of energy characteristics of compounds 1-11 in atomic units at the temperature of 298.15 °K.

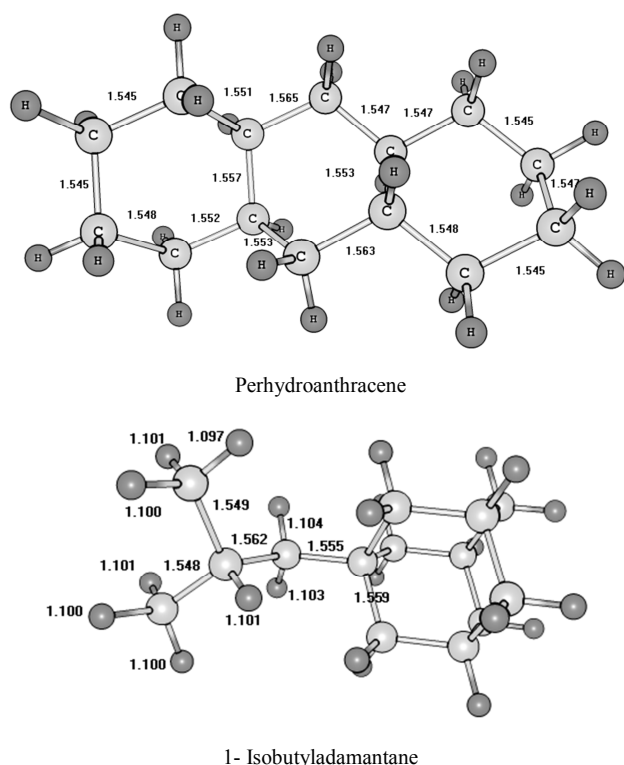
Compound	$E_t$ , a.u., ( $\Delta E_t$ )	$E_{zpc}$ , a.u., ( $\Delta E_{zpc}$ )	$E_H$ , a.u., ( $\Delta E_H$ )	$E_G$ , a.u., ( $\Delta E_G$ )
1	-547.8747539	-547.515212	547.501936	-547.553567
2	-547.8886614	-547.532903	-547.519003	-547.569958
3	-547.8883602	-547.533431	-547.519311	-547.570263
4	-547.8929792	-547.538677	-547.524623	-547.575287
5	-508.6655207	-508.336111	-508.323859	-508.372736
6	-508.6629781	-508.333033	-508.320840	-508.369816
7	-508.6612079	-508.331759	-508.319590	-508.367885
8	-508.6605242	-508.330749	-508.318633	-508.367042
9	-547.882752	-547.524897	-547.511158	-547.564131
10	-547.8794548	-547.521779	-547.508283	-547.559734
11	-547.8773523	-547.519630	-547.505964	-547.557543



Isopropyladamantane



1,3,5,7- Tetramethyladamantane



**Figure 5.** The geometric structure of 1-isopropyladamantane, perhydroanthracene, 1,3,5,7-tetramethyladamantane and 1-isobutyladamantane.

The thermodynamic characteristics obtained from our calculations are in qualitative agreement with the experimental data [25] of the isomerization of perhydroanthracene. Compound (7) as the product of isomerization has the greatest thermodynamic stability from all the others (5, 6), since it has the lowest values of  $E_t$ ,  $E_{zpc}$ ,  $E_H$ ,  $E_G$ , which also agrees with the experiment. The calculated data show that the yields of various alkyl adamantanes having the general formula  $C_{14}H_{24}$  in the isomerization reaction of perhydroanthracene are due to the difference in their thermodynamic stability. Proceeding from this, it can be concluded that this reaction is equilibrium. The experimental yields of these products are consistent with our calculations.

Figure 5 shows obtained from calculations the geometric structures of molecules 2, 7, 8 and 10. Here, for each structure, the nearest interatomic distances in angstroms are indicated.

## 4. Conclusions

The geometrical structure, electronic and energy characteristics (energy of boundary orbitals, dipole moments, zero-point energy, entropy values, values of total energies) of compounds (1-11) are calculated by the method of the density functional theory (DFT) using the B3LYP hybrid functional in 6-31G\* bases.

It was found that the calculated values of the Gibbs energies of the products of the isomerization of perhydroanthracene and the alkylation of adamantane with

alcohols are in qualitative agreement with the experimental composition of the products in isomerates.

The applicability of the calculation methods used for hydrocarbons of a diamond-like structure is shown and, consequently, these methods can later be used to determine the structure, thermodynamic stability, and compositions of equilibrium mixtures of isomers of higher alkyladamantoids, both contained in oils and gas condensates, and obtained synthetically.

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