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Thermodynamic properties Methyl- and Ethyladamantanes

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Abstract

The thermodynamic characteristics of the compounds and their total energy, transformation energies, entropies of transformations, and normal vibration frequencies have been calculated. It is shown that the calculated free Gibbs energies for the formation of isomerization products of per hydroaromatic hydrocarbons are in qualitative agreement with the experimental data of isomerate products.

Keywords: adamantane, methyladamantanes, ethyladamantanes, DFT calculation

Introduction

In the Gulf of Mexico found tiny black diamonds- according to scientists, they were formed from crude oil. These diamonds consist of a force of several dozen carbon atoms, which is less than one billionth of a carat. However, similar hydrocarbons of a diamond-like structure can also find practical application. Their artificial analogues are already used in medicines intended for the treatment of Parkinson's disease and viral infections [1, 2]. In addition, they can find application in the field of nanotechnology [3]. Diamond materials are derivatives of the saturated hydrocarbon adamantane, which was found in oil as far back as 1933. The spatial arrangement of carbon atoms in the adamantane molecule is the same as in the crystal lattice of diamond. Numerous adamantane molecules can join together, forming larger diamondoids.

When a large number of such molecules are combined, a diamond is formed-a characteristic regular lattice consisting of carbon atoms.

A group of scientists from ChevronTexaco's research division, led by Jeremy Dhala, discovered diamondoids consisting of several (up to 11) adamantane molecules in the oil deposits raised from the bottom of the Gulf of Mexico.

Before, under laboratory conditions, it was not possible to combine together more than four such molecules.

It is completely incomprehensible how diamondoids can be formed from hydrocarbon chains, of which oil consists. Perhaps, they are formed during reactions with methane, the catalyst in which the minerals that make up the clay are. If this is so, nothing prevents them from continuing their growth further, reaching quite sizeable dimensions. It was also found out that diamondoids can form black agglomerations with tiny crystals of diamonds called black technical diamonds. The latter, apparently, were formed not in the conditions of high temperatures and pressure, like ordinary diamonds. A number of scientists believe that they could form in space and get to Earth together with a meteorite substance.

The adamantane molecule has a high degree of symmetry. Some elements of symmetry of adamantane are preserved even when one or more substituents are introduced in the position of the nucleus.

Adamantane and its derivatives have been the object of many studies, both experimental and theoretical.

The molecular structure of adamantane was studied by gas-phase electron diffraction [4], ionization electron spectroscopy [5], photoelectronic spectroscopy [6], electron spin resonance [7], quantum calculations of ionization potentials (PI) and electron affinity (SE) [8].

The aim of this work is to conduct experimental studies and quantum chemical calculations by the method of functional of the energy from the electron density the DFT B3LYP/6-31G*, to study the structure and thermodynamic properties of alkyladamantanes composition C_{11} - C_{13} .

Experimental

Methyladamantanes are of great interest both for use as an artificial calculation field, and for determining the strain energy within this system. Schleiere and his colleagues calculated the strain energies for adamantane and 1,3,5,7-tetramethyladamantane (-6.9 kcal / mol and 5.0 kcal / mol, respectively) [9].

The data of the exact standard enthalpy of formation of these compounds plays a decisive role in the estimation of calculation methods.

The thermodynamic stability of some alkyladamantanes was determined by calculation and experimental methods, and then compared with each other [10].

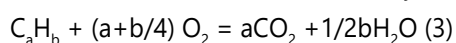
Alkyladamantanes of the composition $C_{12}H_{20}$ are obtained from perhydroacenaphthene upon passage of the latter over the alumina catalyst in a flow type plant with a metal reactor [11-14]. The products of this reaction include 1,3-dimethyladamantane, *trans*-1,4-dimethyladamantane, *cis*-1,4-dimethyladamantane,

The results of the calculations are presented in Table 1.

Table 1. Results of experiments on typical calorimetry at 298.15K

Property	1-methyl-adamantane	2-methyl-adamantane	1,3-dimethyl-adamantane	2,2-dimethyl-adamantane	1,3,5-trimethyl-adamantane	1,3,5,7-tetramethyl-adamantane
m(substance)/g	0.052167	0.054328	0.052458	0.050126	0.052339	0.053385
m(polyethylene)/g	0.016427	0.017204	0.017284	0.016824	0.016424	0.015484
m(cotton)/g	0.002794	0.002542	0.002248	0.002079	0.002061	0.002000
m(H ₂ O)/mole	0.05551	0.05551	0.05551	0.05551	0.05551	0.05551
$\Delta R/\Omega$	1.2996	1.3555	1.3202	1.2703	1.3001	1.3020
$-\Delta R_e$ (color)/kJ	-3.1010	-3.2342	-3.1500	-3.0309	-3.1020	-3.1066
$-\Delta R_e$ (cont)/kJ ⁶	-0.0156	-0.0163	-0.0157	-0.0153	-0.0160	-0.0170
$-\Delta E_w$ / kJ	0.0012	0.0012	0.0013	0.0010	0.0016	0.0018
$-\Delta E(ign)$ / kJ	0.0008	0.0016	0.0012	0.0012	0.0009	0.0012
$-e_e$ (substance)/kJ·g ⁻¹	44.2387	44.3424	44.3326	44.4975	44.3417	44.4024

The combustion reaction is described by the equation:



Derivatives from the standard molar combustion energy ΔE_b° , the standard molar enthalpy of combustion ΔH_b° and the molar standard enthalpy of formation of ΔH_f° compounds are presented in Table 2.

1,2-dimethyladamantane, 1-ethyladamantane and 2-ethyladamantane. As is known, alkyladamantanes $C_{13}H_{22}$ are usually obtained by isomerization of perhydrofluorene [11, 12, 15]. From isomerizate are allocated 1,3,5-trimethyladamantane, *cis*-1,3,6-trimethyladamantane, *trans*-1,3,6-trimethyladamantane, *cis*-1,3,4-trimethyladamantanes, *trans*-1,3,4-trimethyladamantane, 1,2,6-trimethyladamantane, 1,2,8-trimethyladamantan, 1-methyl-3-ethyladamantane, *cis*-1-methyl-4-ethyladamantanes, *trans*-1-methyl-4-ethyladamantanes.

Calculation results and Discussion

To minimize the errors in the calculations, 1- and 2-methyladamantanes, 2,2-dimethyladamantane, 1,3,5-trimethyladamantane were purified by standard methods (recrystallization, vacuum sublimation) before burning in the calorimeter, and 1,3-dimethyladamantane was purified by repeated fractional distillation under low pressure. Was used 1 cm³ of water was placed into the calorimetric bomb of internal volume 0.1 dm³ with calibration and additional equipment and then oxygen pressure up to 30 atmospheres at 298.15 K was established.

The vapor pressures of all the solid compounds were measured in a glass Bourdon gauge that was nulled against a mercury manometer. The vapor pressures of these compounds were fitted by least squares to the equation

$$\log_{10} (p/\text{Torr}) = A/T + B \quad (1)$$

and the enthalpy of sublimation was calculated assuming no vapour imperfection and negligible solid volume as [16]

$$\Delta H_{\text{sub}} = -R \ln 10 \quad (2)$$

The vapor pressure of 1,3-dimethyladamantane is determined by semi microebuliometric method [17].

Table 2. Oscillated molar condensation energy at 298.15 K

Compounds	$-\Delta E_b^\circ$, kJ/mole	$-\Delta H_b^\circ$, kJ/mole	$-\Delta H_f^\circ$, kJ/mole
1-Methyladamantane	6647,1±0,4	6658,4±0,4	242,7±0,4
2-Methyladamantane	6665,1±0,4	6676,4±0,4	224,7±0,4
2,2-Dimethyladamantane	7311,5±0,6	7324,1±0,6	256,5±0,6
1,3-Dimethyladamantane	7281,4±0,6	7293,9±0,6	286,6±0,6
1,3,5-Trimethyladamantane	7913,6±1,0	7927,4±1,0	332,6±1,0
1,3,5,7-Tetramethyladamantane	8545,4±0,9	8560,5±0,9	378,6±0,9

Derivatives from the sublimation enthalpies of methyladamantanes are presented in Table 3. The values of T_m are taken from the previously studied mean temperatures. The standard enthalpy of sublimation ΔH_s° (298.15 K) is determined by the equation:

$$\Delta H_s^\circ (298.15K) = \Delta H_s^\circ(T_m) + (298.15 K - T_m) (C_p^\circ(\text{gas}) - C_p^\circ(\text{solid})) \quad (4)$$

Table 3. The enthalpy of sublimation of methyladamantanes

Compounds	$\Delta H_s^\circ(T_m)/\text{kJ/mole}$	T/K	$\Delta H_s^\circ(298.15K)/\text{kJ/mole}$
1-Methyladamantane	16,0±0,2	300-340	16,2±0,3
2-Methyladamantane	16,1±0,2	300-340	16,3±0,3
2,2-Dimethyladamantane	17,2±0,2	300-360	17,6±0,3
1,3-Dimethyladamantane	16,2±0,2	-----	16,2±0,3
1,3,5-Trimethyladamantane	18,2±0,2	300-360	18,6±0,3
1,3,5,7-Tetramethyladamantane	19,5±0,2	310-350	20,0±0,3

Substitution of methyl groups on tertiary carbon atoms of adamantane nuclei increases thermochemical stability.

We performed quantum-chemical calculations using the energy-functional method from the electron density of DFT B3LYP/6-31G* perhydroacenaphthene, perhydrofluorene and the products of their transformations [18, 19]. Optimization of the geometric structure of molecules and calculation of the frequencies of normal vibrations were carried out using atomic bases 6-31G*. Calculations were performed using the GAUSSIAN-98 program [20]. DFT B3LYP is a combination of the Charter-Fock method and the density functional theory using the gradient-corrected Beck function with three parameters (B3) [21] and the Li-Yang correlation functional series (LYP) [22]. For each molecule, the geometric arrangement of atoms was optimized using analytical calculation methods. By calculating the frequencies of normal vibrations using the second derivatives, it was confirmed that the stationarity points determined in the optimization of geometry are energy minima.

Table 4 shows the calculated electronic characteristics of the calculated molecules: the energy of the boundary orbitals (Ehomo, Elumo), dipole moments (μ), zero-point energy (ZPC) and entropy (S).

Table 4. Basic design electronic characteristics methyl and ethyl adamantanes of the composition $C_{12}H_{20}$ - $C_{13}H_{22}$

Compound	Ehomo, a.u.	Elumo, a.u.	μ , D	ZPC, a.u.	S, cal/(mol K)
1,3-Me ₂ Ad	0.27151	0.06866	0.1198	0.299901	93.688
trans-1,4-Me ₂ Ad	0.27015	0.06958	0.0985	0.300084	94.344
cis-1,4-Me ₂ Ad	0.26992	0.06852	0.1205	0.300210	94.114
1,2-Me ₂ Ad	0.26916	0.06955	0.0578	0.300276	93.831
1-EtAd	0.27072	0.06986	0.0457	0.300906	95.330
2-EtAd	0.26874	0.06956	0.0425	0.301490	95.188
1,3,5-Me ₃ Ad	0.27439	0.08067	0.0808	0.329916	103.962
cis-1,3,6-Me ₃ Ad	0.27189	0.06796	0.1036	0.327127	100.113
trans-1,3,6-Me ₃ Ad	0.26946	0.06860	0.1288	0.327594	100.532
cis-1,3,4-Me ₃ Ad	0.26919	0.06848	0.1090	0.327974	100.056
trans-1,3,4-Me ₃ Ad	0.27003	0.06968	0.1136	0.328036	99.937
1,2,6-Me ₃ Ad	0.27021	0.06928	0.0945	0.328522	100.965
1,2,8-Me ₃ Ad	0.26814	0.06888	0.0938	0.329022	101.298
1-Me-3-EtAd	0.26889	0.06997	0.1450	0.328912	101.521
cis-1-Me-4-EtAd	0.26737	0.06876	0.0772	0.328516	100.098
trans-1-Me-4-EtAd	0.26692	0.07061	0.0219	0.328610	99.872

Table 5 shows the calculated basic energy characteristics of compounds: the values for the total energy Et , the total energy with allowance for zero point energy $Ezpc$, the total energy with correction for enthalpy EH , and the total energy with correction for Gibbs free energy EG in atomic units of energy. Below are the formulas for determining these thermodynamic quantities [21]:

$$Ezpc = Et + ZPC, \quad (5)$$

$$EH = Et + ZPC + Evib + Erot + Etrans, \quad (6)$$

$$EG = EH - TS, \quad (7)$$

where, $Evib$ is the vibrational motion energy, $Erot$ is the energy of the rotational motion, $Etrans$ is the translational motion energy, S is the entropy and T is the Kelvin temperature.

Table 5. The main calculated electronic energy characteristics of methyl and ethyl adamantanes of the composition $C_{12}H_{20}$ - $C_{13}H_{22}$ at room temperature (298.15K) and relative isomerization energies (in kilocalories per mole)

Compound	Et , a.u. (ΔEt kcal/mol)	$Ezpc$, a.u. ($\Delta Ezpc$ kcal/mol)	EH , a.u. (ΔEH kcal/mol)	EG , a.u. (ΔEG kcal/mol)
1,3-Me ₂ Ad	-469.3577429 (-8.25)	-469.057841 (-8.92)	-469.046955 (-8.98)	-469.091469 (-8.23)
trans-1,4-Me ₂ Ad	-469.3533081 (-4.63)	-469.053224 (-6.03)	-469.042266 (-6.04)	-469.087092 (-5.48)
cis-1,4-Me ₂ Ad	-469.3534119 (-5.53)	-469.053202 (-6.01)	-469.042298 (-6.06)	-469.087014 (-5.43)
1,2-Me ₂ Ad	-469.3510802 (-4.07)	-469.050804 (-4.51)	-469.039936 (-4.58)	-469.084518 (-3.87)
1-EtAd	-469.3520422 (-4.67)	-469.051136 (-4.72)	-469.040277 (-4.79)	-469.085571 (-4.53)
2-EtAd	-469.3493798 (-3.00)	-469.047890 (-2.68)	-469.037126 (-2.81)	-469.082353 (-2.51)
1,3,5-Me ₃ Ad	-508.6738752 (-13.49)	-508.346748 (-13.39)	-508.334270 (-13.35)	-508.381836 (-12.20)
1,3,6-Me ₃ Ad	-508.6695449 (-8.98)	-508.341951 (-10.44)	-508.329471 (-10.34)	-508.377237 (-9.32)
cis-1,3,4-Me ₃ Ad	-508.667349 (-7.42)	-508.339375 (-8.80)	-508.326990 (-8.78)	-508.374530 (-7.62)
trans-1,3,4-Me ₃ Ad	-508.6675245 (-6.28)	-508.339489 (-8.89)	-508.327125 (-8.87)	-508.374608 (-8.59)
1-Me-3-EtAd	-508.6682485 (-8.16)	-508.339727 (-9.04)	-508.327415 (-9.05)	-508.375387 (-8.16)
cis-1-Me-4-EtAd	-508.6657517 (-6.42)	-508.336730 (-7.16)	-508.324460 (-7.19)	-508.372590 (-6.40)
trans-1-Me-4-EtAd	-508.665676 (-6.55)	-508.336764 (-7.18)	-508.324470 (-7.20)	-508.372706 (-6.47)
1,2,6-Me ₃ Ad	-508.6629347 (-4.83)	-508.334419 (-5.71)	-508.322091 (-5.71)	-508.369651 (-4.56)
1,2,8-Me ₃ Ad	-508.660226 (-3.13)	-508.331616 (-3.95)	-508.319308 (-3.96)	-508.366761 (-2.74)

The thermodynamic characteristics obtained in our calculations are in excellent qualitative agreement with experimental data on the isomerization of perhydroacenaphthene [1].

1,3-Dimethyladamantane as the product of isomerization has the greatest of all the other alkyladamantanes of the $C_{12}H_{20}$ composition with thermodynamic stability; it has the lowest values of Et , $Ezpc$, EH , EG . The yield of 1,3-dimethyladamantane is up to 80%. The cis and trans isomers of 1,4-dimethyladamantane have practically the same values of all the thermodynamic characteristics that we calculated. For these isomers, the isomerase composition is the same (about 4%). The stability of 1,2-dimethyladamantane

is lower than the stability of 1,3-adamantane and 1,4-adamantanes, which also agrees with the experiment. 1-ethyladamantane is more stable from calculations than 2-ethyladamantane. The experimental yields of these products are consistent with our calculations.

The thermodynamic characteristics obtained from our calculations are in excellent qualitative agreement with the experimental data on the isomerization of perhydrofluorene [1]. 1,3,5-Trimethyladamantane as the isomerization product has the greatest of all the other alkyladamantanes of the $C_{13}H_{22}$ composition with thermodynamic stability; it has the lowest values of Et, Ezpc, EH, EG. The yield of 1,3,5-trimethyladamantane is up to 50%. The cis and trans isomers of 1,3,6-trimethyladamantane and 1,3,4-trimethyladamantane have practically the same values of all the thermodynamic characteristics that we calculated. For these isomers, the isomerization composition is approximately the same (3 and 4%, respectively). The stability of 1-methyl-4-ethyladamantanes is lower than the stability of 1-methyl-3-ethyladamantane, which also agrees with the experiment. 1,2,6- and 1,2,8-trimethyladamantanes are not stable from the calculations. The experimental yields of these products are consistent with our calculations.

Thus, the results of the calculations presented above agree with the previously published experimental data that the number of different isomers of methyl- and ethyladamantane formed in the isomerization of perhydroaromatic hydrocarbons is due to the difference in their thermodynamic stability. It has been established experimentally that the reaction is an equilibrium process.

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