Theoretical estimation of energy parameters of nitro- and nitraza-substituted derivatives of stressless aliphatic caged structures

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Energy parameters of nitro- and nitraza-substituted derivatives of stressless and low-stress aliphatic caged structures were investigated. The effect of the degree of nitration on the density was studied.

Key words: caged structures, nitro compounds, nitraza compounds, high-energy compounds; density, enthalpy of formation; detonation velocity, blasting ability.

Computer search for new high-energy substances remains an urgent problem, despite numerous studies in this direction. One of the search methods is the selection of substances of a certain structural class and calculation of their goal parameters. The class for study is chosen, as a rule, starting from the already known compounds of this type with sufficiently high values of goal parameters.

The purpose of this work is to study energy possibilities of caged structures and their nitro- and nitraza-substituted derivatives and to find similar new high-energy substances. It had been supposed in the early sixties that potent energy-capacious substances can be obtained on the basis of caged structures. Several recent works on this topic should be mentioned: the quantum chemical study of several hypothetical caged compounds[1−2] and the synthesis and theoretical study of several nitro-substituted derivatives of cubane and cubane-like structures.[3]

However, quantum chemical calculations are limited by a few possible structures and cannot unveil their energy potentialities. Such limitation is explained by the absence of high-performance and sufficiently accurate methods for estimation of the goal physicochemical parameters and of a computer program that could provide automatic design of cage type structures (generator of structures). The latter directed the studies to existing hydrocarbon analogs and similar compounds.

The energy parameters of many nitro- and nitraza-substituted derivatives of caged structures were studied widely in this work. This has become possible due to the recently suggested methods of estimation of the density (ρ)[4] and enthalpy of formation ($\Delta_f H°$)[5] and to the GENESIS generator of structures developed by M. S. Molchanova. This generator allowed us to design all cageds studied. The density, enthalpy of formation, detonation velocity (D), and blasting ability (η)[6−8] have been studied. The structural dependences of these values and their relationship have been studied. D and η were chosen as the goal parameters for selection of the most promising compounds.

Calculation Procedure

We considered the structures $C_n H_{2n−k}$ without multiple bonds, where $n = 7 \div 12$ and $k = 2, 4, 6,$ and 8. The total number of isomers corresponding to these compositions, whith no multiple bonds and Me groups, was about 60000, but the further restrictions allowed us to reduce their number to the limits available for investigation: (1) the construction of hydrocarbon cageds only from the $-CH<$ and $-CH_2-$ fragments; (2) the size of the cycle was not less than four for $n = 7 \div 10$ and not less than five for $n = 11$ and 12; (3) the absence of insurmountable steric hindrances; and (4) the presence of any elements of symmetry. The latter requirement was not always fulfilled. There are data indicating that sometimes a decrease in symmetry results in an increase in the density of structural isomers.[3]

The hydrocarbon cageds designed are presented below. The values of ρ, $\Delta_f H°$, D, and η were calculated for these and various possible nitro- and nitraza-substituted derivatives. The accuracies of calculation of density ρ and the enthalpy of formation $\Delta_f H°$ were 0.05 g cm^{-3} and 25 kcal mol^{-1}, respectively.

The experimental and calculated values of ρ and $\Delta_f H°$ for several nitro- and nitraza-substituted derivatives of aliphatic hydrocarbons and several caged structures are presented in Tables 1 and 2. The detonation velocity and the blasting ability, which is related linearly to the detonation velocity, to a greater extent depend[6−8] on ρ than on $\Delta_f H°$. Therefore, a sufficiently low accuracy of calculation of the latter exerts no effect on the D and η parameters.

It is noteworthy that the mentioned accuracy of calculation of $\Delta_f H°$ is inappropriate in the case of high-stress structures such as cubane or spiropentane. The calculation procedure used gives decreased values, therefore, high-stress structures except cubane were not considered.

**Table 1.** Experimental and calculated[5] values of $\Delta_f H^\circ$ for condensed substances

Substance	$\Delta_f H^\circ$/kcal g^{-1}	
	exp	calc
Cyclobutane	0.74[9]	−9.5
Spiropentane	37.7[9]	4.5
Norbornan-2-one	−53.8[9]	−58.0
Norbornane	−22.1[9]	−13.3
Cubane	140 (gas)	33.8
Adamantane	−46.3[9]	−24.4
Nitromethane	−27.0[9]	−21.8
Tetranitromethane	8.9[10]	13.1
Ethylenedinitramine	−25.7[11]	−15.7
2,4,6-Trinitro-1,3,5-triazine	14.7[20]	19.2
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane	18.0[20]	9.7
2,4,8,10-Tetranitroaza-spiroundecane[5,5]	5[12]	7.9

Results and Discussion

We designed 78 structures, some of which are known (for example, adamantane, cubane, and noradamantane), but they are mainly hypothetical caged structures. Their possible nitro- and nitraza-substituted derivatives were considered with the following structural restrictions: no nitro and nitraza groups linked with one carbon atom (NO_2—C—$N(NO_2)$); two nitro groups with one nitrogen

Table 2. Experimental and calculated values of density (ρ)

Substance	ρ/g cm^{-3}	
	exp	calc
Cubane	1.29[3]	1.14
Adamantane	1.07[18]	0.88
Congressane	1.2[18]	0.88
Tetranitromethane	1.64[13]	1.67
Trinitromethane	1.62[14]	1.70
Nitromethane	1.14[13]	1.12
Nitroethane	1.05[13]	1.10
1,1,1,2-Tetranitropropane	1.6[15]	1.80
Nitrocyclopropane	1.13[22]	1.23
Nitrocyclobutane	1.096[23]	1.16
1,3,5,7-Tetranitrocubane	1.81[3]	1.80
1,3,5-Trinitrocubane	1.74[3]	1.78
1,4-Dinitrocubane	1.66[3]	1.65
1,3-Dinitrocubane	1.65[3]	1.65
1-Nitro-1-(1-nitrocyclobutanyl)-cyclobutane	1.38[16]	1.42
5,5,10-Trinitropentacyclo-[4.2.2^{1,4}.0^{3,7}.0^{2,10}.0^{6,9}]decane	1.61[17]	1.69
1,3,5,7-Tetranitroadamantane	1.61[3]	1.68
Methylenedinitramine	1.74[19]	1.72
Ethylenedinitramine	1.75[19]	
2,4,6-Trinitro-1,3,5-triazine	1.82[20]	1.83
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane	1.87[20]	1.85
1-Nitro-10-hydroxyazotetra-cyclo[6.2.1^{1,4}.1^{6,9}.0^{11,12}]dodecane	1.46[23]	1.42
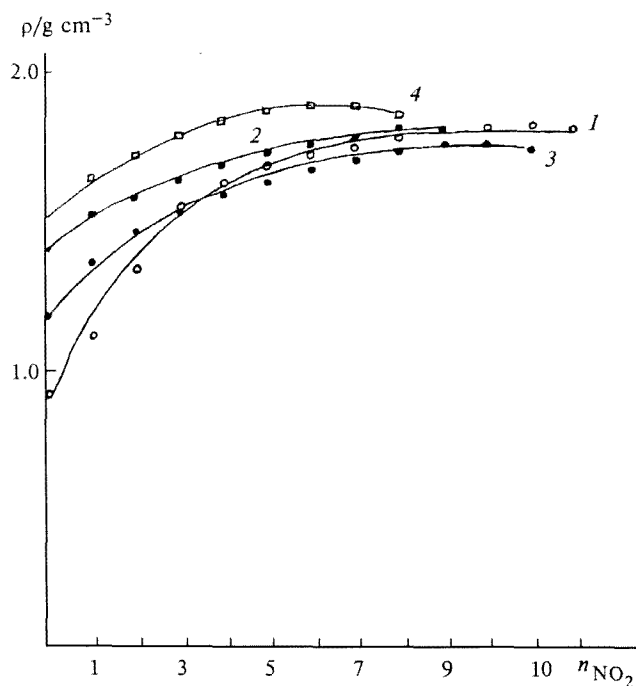
Fig. 1. Dependences of the density (ρ) of nitro-substituted derivatives of aliphatic hydrocarbons $C_{12}H_{12}$ (*1*) and their mononitraza- (*2*), dinitraza- (*3*), and trinitraza-substituted (*4*) derivatives on the number of nitro groups (n_{NO_2}).
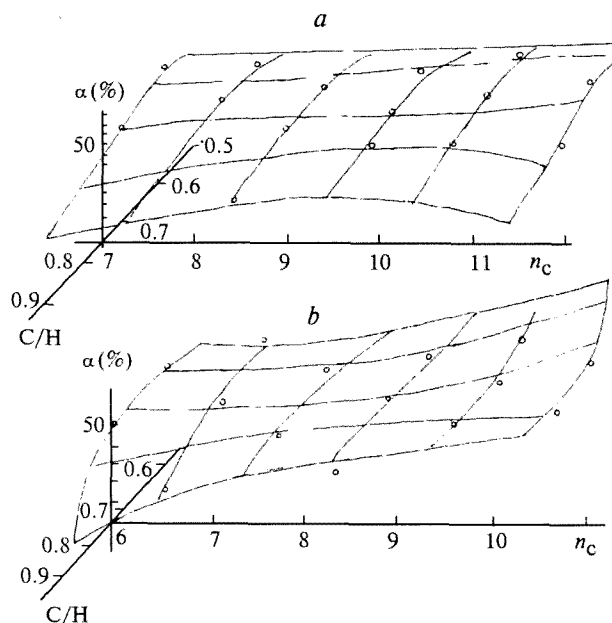
**Fig. 2.** Dependences of the degrees of nitration (α) at which the maximum density of nitro-substituted derivatives of aliphatic hydrocarbons (*a*) and their mononitraza-substituted derivatives (*b*) are achieved on the number of carbon atoms (n_C) in a molecule and the ratio of the number of carbon and hydrogen atoms in the initial structures (C/H).
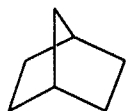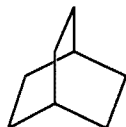
C_7H_{17} C_7H_{10} C_8H_{14} C_8H_{10} C_8H_8
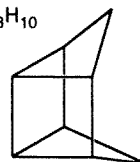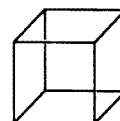
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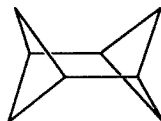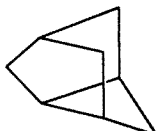
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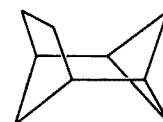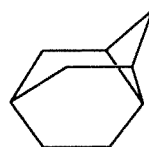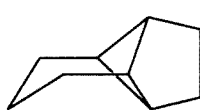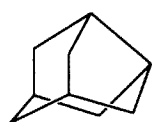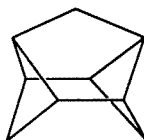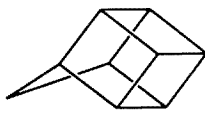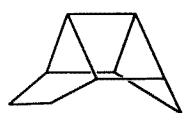
C_9H_{12} C_9H_{10}
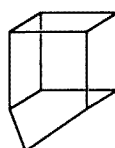
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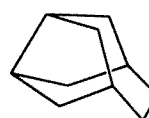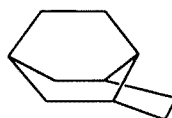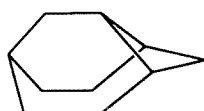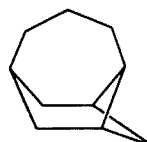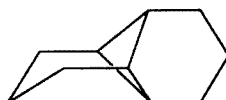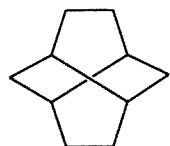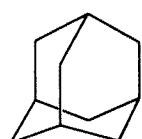
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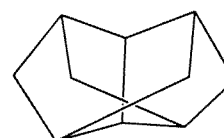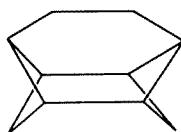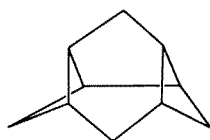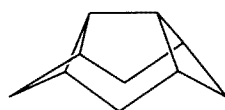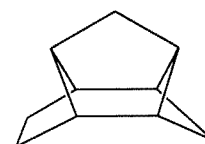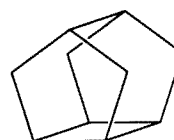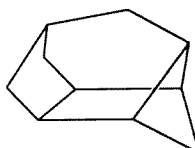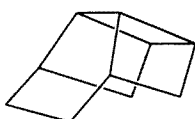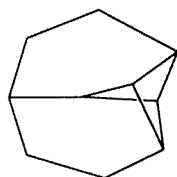
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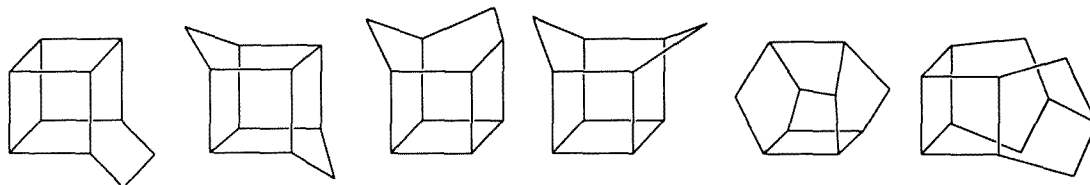
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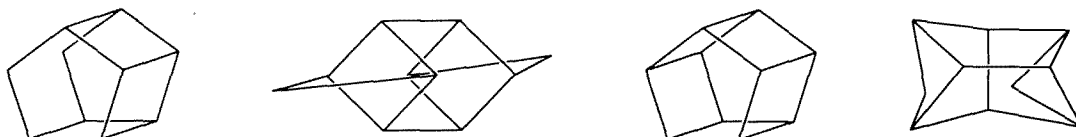
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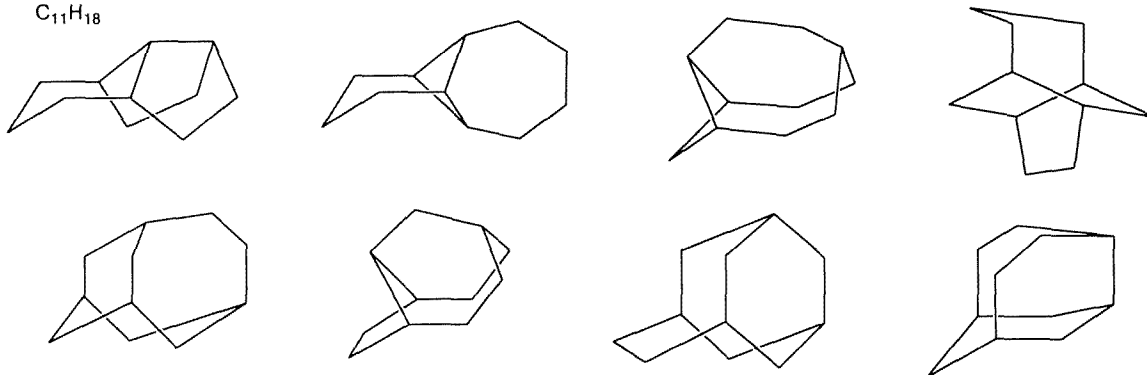
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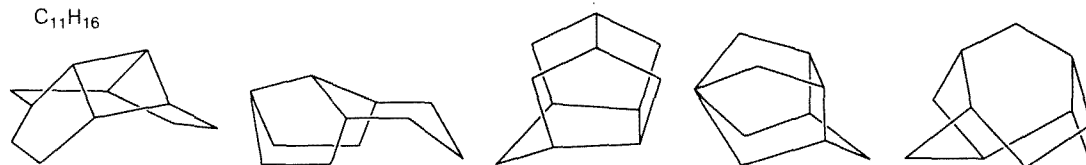
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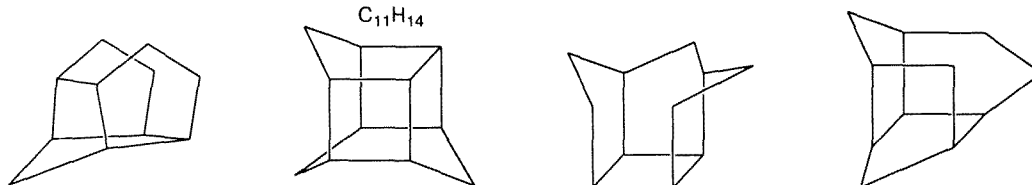
C$_{12}$H$_{18}$

$C_{12}H_{16}$
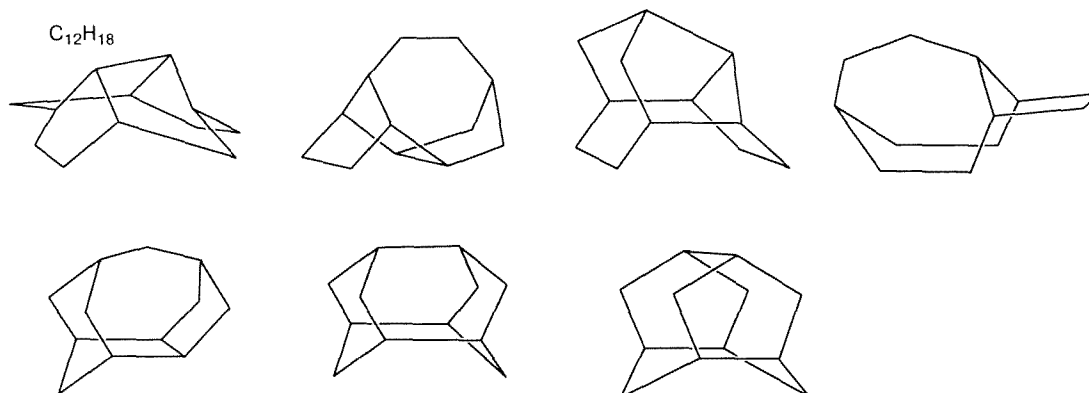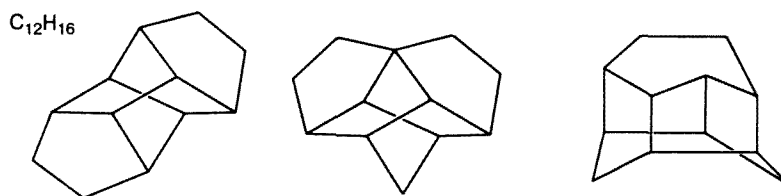
atom ($N(NO_2)_2$) and two adjacent nitraza groups (($NO_2)N—N(NO_2)$) were allowed. An unexpected result of the calculation of ρ, $\Delta_f H^\circ$, D, and η of the initial structures and their nitro and nitraza-substituted derivatives is the fact that the maximum density is reached not at a 100% degree of nitration, but at ~50—60 %, and then it decreases. Typical curves showing the dependence of the density on the degree of nitration are presented in Fig. 1.

The results obtained can be explained by steric hindrances appeared due to the interaction of nitro groups in highly nitrated compounds. All calculations were performed only up to the degree of nitration that provides the maximum density in the given series of nitro-substituted derivatives. The studies of more completely nitrated compounds are hardly worthwhile due to the extremely low stability of such compounds rather than worsening of energy parameters.

Only two completely nitrated saturated hydrocarbons are known: tetranitromethane and hexanitroethane, and the latter is distinguished by the extremely low stability.
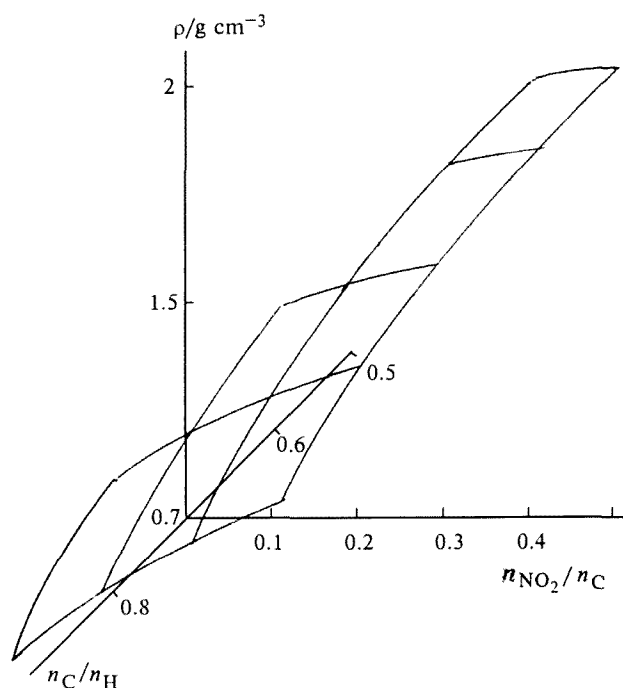
All attempts to obtaine completely nitrated derivatives for more complicated saturated hydrocarbons were unsuccessful. As a rule, the maximum degree of nitration was 50—60 %.

The dependences of the degree of nitration, at which the maximum density is achieved, on the number of carbon atoms and the ratio of carbon and hydrogen atoms (C/H) for the initial structures (a) and their mononitraza-substituted derivatives (b) are shown in Fig. 2. The results obtained make it possible to draw the conclusion that it makes no sense to achieve a degree of nitration higher than 50—60 % upon synthesis of powerful energy-capacious substances based on nitro-substituted derivatives.

The dependences of ρ on the relative content of nitraza groups and the ratio of carbon and hydrogen atoms in the initial cageds are presented in Fig. 3. It can be seen from the plot that the highest values of the density and, hence, the D and η values are achieved when the maximum possible number of nitraza groups is introduced.

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ρ/g cm^{-3}

Fig. 3. Dependences of the density (ρ/g cm^{-3}) on the ratio of the number of nitraza groups and carbon atoms (n_{NO_2}/n_C) in the structures studied and of carbon and hydrogen atoms (n_C/n_H) in the initial hydrocarbon frameworks.

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