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Computer Design of Structure of Molecules of High-Energy Tetrazines. Calculation of Thermochemical Properties

Vadim M. Volokhov[1], ***Elena S. Amosova***[1], ***Alexander V. Volokhov***[1], ***Tatiana S. Zyubina***[1], ***David B. Lempert***[1], ***Leonid S. Yanovskiy***[1,2,3], ***Ilya D. Fateev***[4]

The article presents high-performance calculations, using quantum chemical ab initio methods, of thermochemical characteristics of high-energy compounds: $C_2N_6O_4$, $C_2N_6O_5$, $C_2N_6O_6$, $C_2H_2N_6O_4$, $C_3HN_7O_6$, $C_3HN_7O_4F_2$, $C_4N_{10}O_{12}$, $C_3HN_6O_4F$, $C_4N_{10}O_8F_4$, $C_4N_8O_8F_2$. The IR absorption spectra, structural parameters and atomic displacements for the most intense vibrations, as well as the enthalpies of formation are provided in the article. The calculations were performed at the B3LYP/6-311+G(2d,p) level and using the combined methods CBS-4M and G4 within the Gaussian 09 application package (Linda parallelization). It is shown that the enthalpy of formation depends on the molecule structure.

Keywords: high-performance computing, enthalpy of formation, quantum-chemical calculations, high-enthalpy compounds, IR spectra of gaseous molecules, combined CBS-4M method, combined G4 method.

Introduction

The rapidly developing new technologies, especially in the field of engines for advanced aircraft, stimulate great interest in the creation of high-energy materials for various purposes. In the recent time, modern computer technologies have played an increasingly important role in the creation of new materials with specific properties [1–3].

The value of the standard enthalpy of formation ΔH_f° of a chemical compound is one of the main criteria for its energy intensity, thus the determination of this value, both experimental and calculated, becomes a key task for assessing the efficiency of using a particular substance as a component of high-energy materials. In terms of thermochemistry, it is important to know how the enthalpy of formation of a substance changes with some structural changes. One of the most reliable methods for studying the dependences of the enthalpy of formation on various parameters characterizing molecules (along with the experiment) is quantum-chemical ab initio calculations using high-precision combined methods, such as CBS-4M and G4 within the Gaussian 09 package.

This work is dedicated to determination by quantum chemical methods of ΔH_f° of a number of high-enthalpy compounds with the common structure as shown in the Fig. 1. All these compounds were designed by the authors and are promising as components of fuel for various purposes. They have not been synthesized yet, and their thermochemical properties have been studied for the first time in this work. It should be noted that for molecules of such complexity, the spread of experimental data might be larger than that of calculated one, as it has been observed in one of our previous works [4].

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[1] Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia

[2] Central Institute of Aviation Motors, Moscow, Russia

[3] Moscow Aviation Institute (National Research University), Moscow, Russia

[4] Research Computing Center Lomonosov Moscow State University, Moscow, Russia

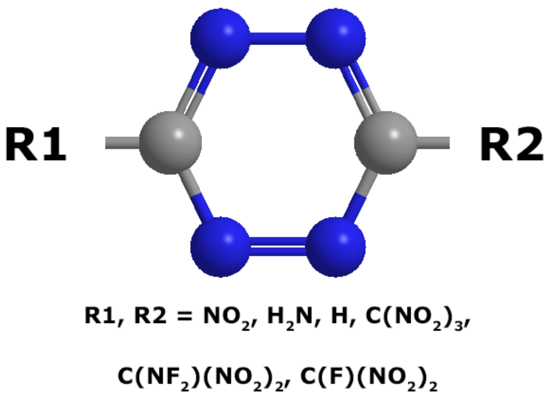


Figure 1. Structure of the studied molecules

The article is organized as follows. In Section 1 we describe the method we used to determine the enthalpy of formation of the given molecules. In Section 2 we discuss the results of our calculations: enthalpies of formation and IR spectra. Section 3 contains computational details of our calculations. Conclusion summarizes the study.

1. Calculation Method

The enthalpy of formation of the investigated gaseous molecules was calculated by the atomization method as was described in our previous works [4, 5]. The simulation was performed within the Gaussian 09 package [6] using the hybrid density functional B3LYP [7, 8] with the basis set 6-311+G(2d,p), which had already proven itself in molecular calculations, and the combined methods CBS-4M [9, 10] and G4 [11, 12].

The CBS series of methods was introduced by Petersson and colleagues [9, 10, 13–17] and includes three main methods listed in ascending order of accuracy and estimated time: CBS-4M, CBS-QB3, CBS-APNO. To obtain an accurate energy value, these methods use both additive and extrapolation schemes, and empirical corrections. We used the CBS-4M method in our work as the least demanding on computational resources. The CBS-4 [9] method which is a base for the CBS-4M one uses low level theory UHF/3-21G(*) for geometry optimization and zero-point energies and a series of further energy calculations for a given geometry using large basis sets for the SCF method, medium size ones for MP2 calculations, and small basis sets for the higher level method. The modifications introduced in the CBS-4M method are the use of the minimum population localization in the CBS extrapolation, the change in the two-electron empirical parameter and corrections for spin-orbit interactions in atomic energies [10].

The G4 method was introduced in 2007 by Curtiss and colleagues [11]. It uses calculations at the B3LYP/6-31G(2df,p) level for geometry optimization and zero-point energies. The Hartree-Fock energy limit is calculated using a linear two-point extrapolation scheme and Dunnings basis sets [18–22]. The G4 method for approximating the energies of more accurate calculations combines the CCSD (T) method with a sufficiently high level of electron correlation and a medium-sized basis set (6-31G (d)) with the energies from the calculations of a lower level of the theory (MP4 and MP2) with large basis sets. In addition, the remaining errors are taken into account by several empirical corrections that do not depend on the studied molecule.

The main steps of the calculation by the atomization method of the enthalpy of formation of compounds with the common formula $C_wH_xN_yO_zF_p$ are listed below:

1. Calculation of the atomization energy in the nonrelativistic approximation.

$$\sum D_0 = wE_0(C) + xE_0(H) + yE_0(N) + zE_0(O) + pE_0(F) - E_0(C_wH_xN_yO_zF_p), \qquad (1)$$

where $E_0(C), E_0(H), E_0(N), E_0(O), E_0(F)$ are calculated total energies of atoms. Total energy of the molecule $E_0(C_wH_xN_yO_zF_p)$ is calculated by the formula $E_0(C_wH_xN_yO_zF_p) = \varepsilon_0 + ZPE$, where ε_0 is a total energy of the molecule, and ZPE is a sum of zero-point energies of all vibrational modes of the molecule.

2. Calculation of the enthalpy of formation at $0K$

$$\begin{aligned}\Delta H_f^\circ(C_wH_xN_yO_zF_p, 0K) = {} & w\Delta H_f^\circ(C, 0K) + x\Delta H_f^\circ(H, 0K) + \\ & + y\Delta H_f^\circ(N, 0K) + z\Delta H_f^\circ(O, 0K) + p\Delta H_f^\circ(F, 0K) - \sum D_0,\end{aligned} \qquad (2)$$

where the first five summands are the enthalpies of formation of gaseous atomic components known from experiment.

3. Calculation of the enthalpy of formation at $298.15K$

$$\begin{aligned}\Delta H_f^\circ(C_wH_xN_yO_zF_p, 298K) = {} & \Delta H_f^\circ(C_wH_xN_yO_zF_p, 0K) + (H^0(C_wH_xN_yO_zF_p, 298K) - \\ & - H^0(C_wH_xN_yO_zF_p, 0K)) - w(H^0(C, 298K) - H^0(C, 0K)) - \\ & - x(H^0(H, 298K) - H^0(h, 0K)) - y(H^0(N, 298K) - H^0(N, 0K)) - \\ & - z(H^0(O, 298K) - H^0(O, 0K)) - p(H^0(F, 298K) - H^0(F, 0K)),\end{aligned} \qquad (3)$$

where the second summand is obtained from the calculation of the molecule, the third to seventh summands are known from experiment (or calculated from experimental molecular constants). The values of the enthalpy of formation of gaseous atoms and thermal corrections can be taken from various reference books or literature sources, for example [23–27].

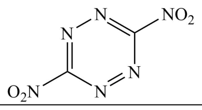
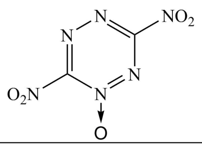
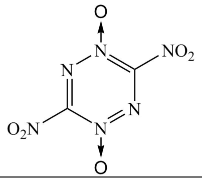
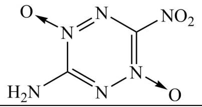
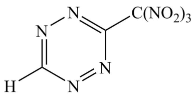
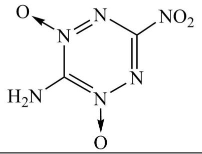
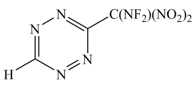
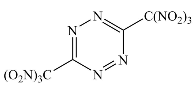
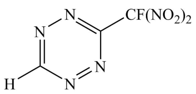
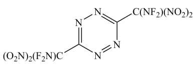
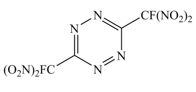
In this work, we used the experimental atomic enthalpies of formation from the NIST-JANAF thermochemical tables [24]. Since the theoretical calculation systematically overestimates the values of the zero-point frequencies, the frequencies are corrected using empirically selected coefficients. To obtain more accurate frequencies, it is necessary to correct the vibration frequencies when calculating the ZPE corrections and corrections $(H^0(C_wH_xN_yO_zF_p, 298K) - H^0(C_wH_xN_yO_zF_p, 0K))$. The values of the scaling factors are used for this, which are recommended in the literature for various calculation methods and various basis sets [6].

2. Results and Discussion

2.1. Enthalpy of Formation

Table 1 shows the structures of the calculated molecules, molecular weights, enthalpies of formation (in kcal/mol, kJ/mol, kJ/kg) obtained at different calculation levels: B3LYP/6-311+G(2d,p), CBS-4M and G4. Figure 2 and Fig. 3 show the structural parameters and the change in the enthalpies of formation of the calculated gaseous molecules.

Table 1. Chemical and structural formulae, molecular weights (Mw, in amu), enthalpies of formation ΔH_f° of calculated molecules (in kcal/mol – regular font, *kJ/mol – italic*, **kJ/kg – bold**), obtained at the B3LYP/6-311+G(2d,p), CBS-4M and G4 levels

N M_w	Structural formula	B3LYP/6-311+G(2d,p)	CBS-4M	G4
1 $C_2N_6O_4$ 172.06		139.88 *585.25* **3401.42**	130.04 *544.08* **3162.16**	128.76 *538.74* **3131.12**
2 $C_2N_6O_5$ 188.06		133.51 *558.59* **2970.28**	124.31 *520.10* **2765.61**	120.84 *505.59* **2688.49**
3 $C_2N_6O_6$ 204.06		136.4 *570.72* **2796.84**	128.14 *536.14* **2627.37**	122.72 *513.47* **2516.30**
4 $C_2H_2N_6O_4$ 174.07		105.24 *440.35* **2529.63**	104.93 *439.03* **2522.09**	97.67 *408.66* **2347.59**
5 $C_3HN_7O_6$ 231.08		152.63 *638.6* **2763.49**	125.99 *527.16* **2281.26**	124.95 *522.76* **2262.36**
6 $C_2H_2N_6O_4$ 174.07		99.38 *415.79* **2388.58**	94.61 *395.83* **2273.92**	91.53 *382.95* **2199.92**
7 $C_3HN_7O_4F_2$ 237.08		143.87 *601.96* **2539.06**	120.94 *506.00* **2134.29**	118.04 *493.86* **2083.10**
8 $C_4N_{10}O_{12}$ 380.1		192.74 *806.43* **2121.61**	142.90 *597.91* **1573.02**	138.54 *579.64* **1524.97**
9 $C_3HN_6O_4F$ 204.06		91.98 *384.86* **1885.86**	70.45 *294.84* **1444.75**	71.18 *297.81* **1459.29**
10 $C_4N_{10}O_8F_4$ 392.1		174.96 *732.02* **1866.94**	132.66 *555.05* **1415.58**	124.29 *520.05* **1326.33**
11 $C_4N_8O_8F_2$ 326.1		71.07 *297.35* **911.87**	31.74 *132.81* **407.28**	30.63 *128.14* **392.97**

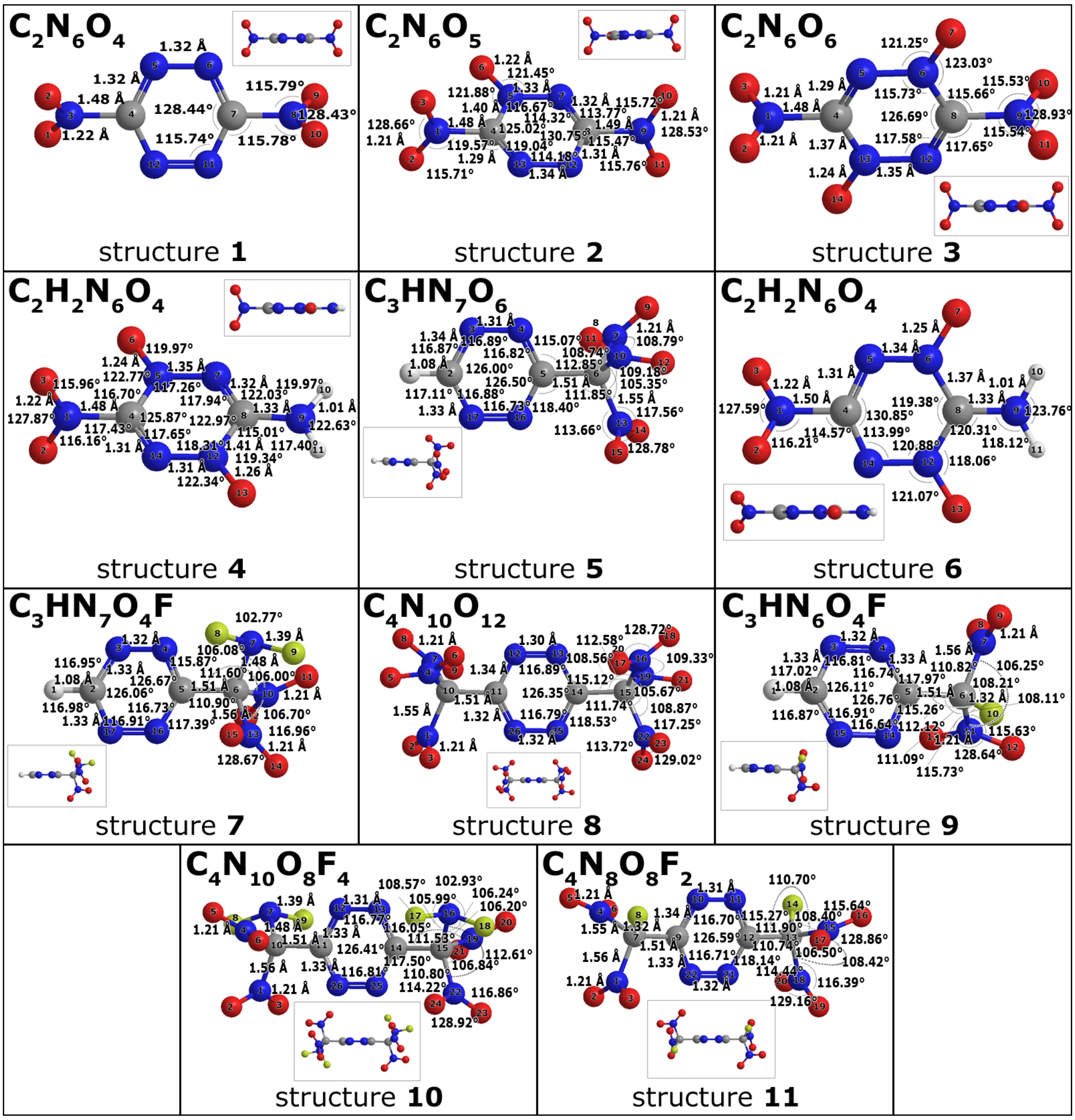


Figure 2. Structural parameters of the calculated molecules (in two angles)

Figure 3 and Tab. 1 show that the combined calculation methods (CBS-4M, G4) give similar results with difference being within 7% of the values obtained at the G4 level, while time spent on calculation by the CBS-4M method is up to 10 times less as compared to the G4 level. The values of enthalpy of formation obtained at the B3LYP/6-311+G(2d,p) level are higher than the ones of the CBS-4M method by 180-520 kJ/kg, which is from 8 to 57% as compared to the results at the G4 level, while time spent on calculations is more than that of the CBS-4M method, but less than that of the G4 method. The CBS-4M method uses the HF method with the basis set 3-21G* to calculate the frequencies, so we introduce the IR absorption spectra calculated at the B3LYP/6-311+G(2d,p) level.

Figure 3 and Tab. 1 show that the enthalpy of formation decreases with changes in structure **1** considered in the article. Let us discuss in more detail the trends observed in structures **1–11**.

$C_2N_6O_4$. The successive addition of one or two oxygen atoms to the ring part of structure **1** is modeled in a series of structures **1–3**. In this case, the enthalpy of formation decreases sequentially by 429 and 594 kJ/kg, respectively (we compare here the values obtained by the G4

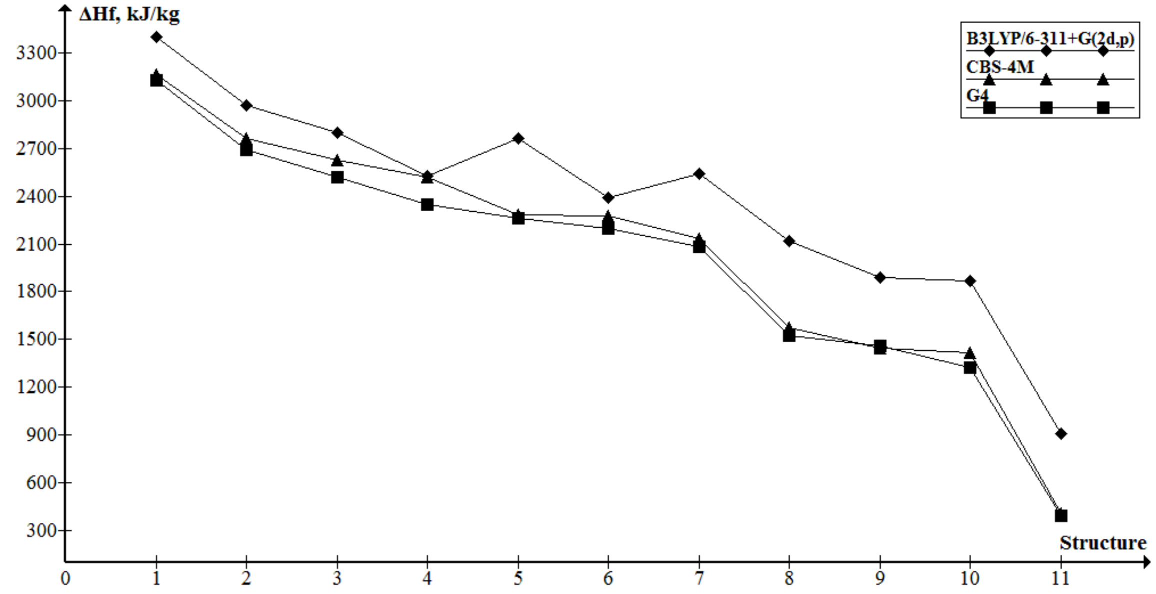


Figure 3. Enthalpies of formation of structures **1–11**

method). The addition of the first oxygen atom lowers the enthalpy of formation by 429 kJ/kg, and the effect of the addition of the second one is significantly lower (166 kJ/kg).

The transition from structure **3** to **4** by replacing one of the NO_2 fragments with NH_2 leads to a decrease in the enthalpy of formation by 172 kJ/kg.

In the case when oxygen atoms are located opposite each other (structure **4**), the enthalpy of formation is higher (by 153 kJ/kg) than the one for the isomer with structure **6**, where both oxygen atoms are located near the NH_2 fragment.

$C_3HN_7O_6$. The molecules in the series from structure **1** to structure **5** are rearranged by replacing one NO_2 fragment with H and the other with $C(NO_2)_3$. This rearrangement is accompanied by a decrease in the enthalpy of formation by 854 kJ/kg. Replacement in structure **5** of one of the NO_2 fragments by NF_2 (structure **7**) or F (structure **9**) leads to a decrease in the enthalpy of formation by 193 kJ/kg and 825 kJ/kg, respectively. The presence of two oppositely located $C(NO_2)_3$ groups in structure **8** leads to a decrease in the enthalpy of formation in comparison with structure **5** by 718 kJ/kg.

2.2. IR Absorption Spectra

The IR absorption spectra and displacements of atoms for the most intense vibrations are shown in Fig. 4, Fig. 5, Fig. 6 and Fig. 7 correspondingly.

The highest frequencies (from 1628 cm^{-1} to 1670 cm^{-1}) with noticeable intensities are observed in the NO_2 groups, which are part of the $R1$ and $R2$ fragments in almost all the structures under consideration. The exceptions are structures **4** and **6**, in which the most intense vibrations are with frequency of 1457 cm^{-1} for structure **4** and 1398 cm^{-1} for structure **6**, corresponding to the vibrations of the NO bond of nitrogen atoms in the ring. Vibrations along the $C-N$ bond of the nitrogen atom belonging to the NO_2 group are characterized by frequencies with lower intensity: 1333 cm^{-1} for structure **5**, 1330 cm^{-1} for structure **8**, 1350 cm^{-1} for structure **9**, 1335 cm^{-1} for structure **10**, and 1348 cm^{-1} for structure **11**. Asynchronous vibrations of carbon and nitrogen atoms included in the ring are also characterized by frequencies with noticeable intensity: 1355 cm^{-1} for structure **2** and 1455 cm^{-1} for structure **3**.

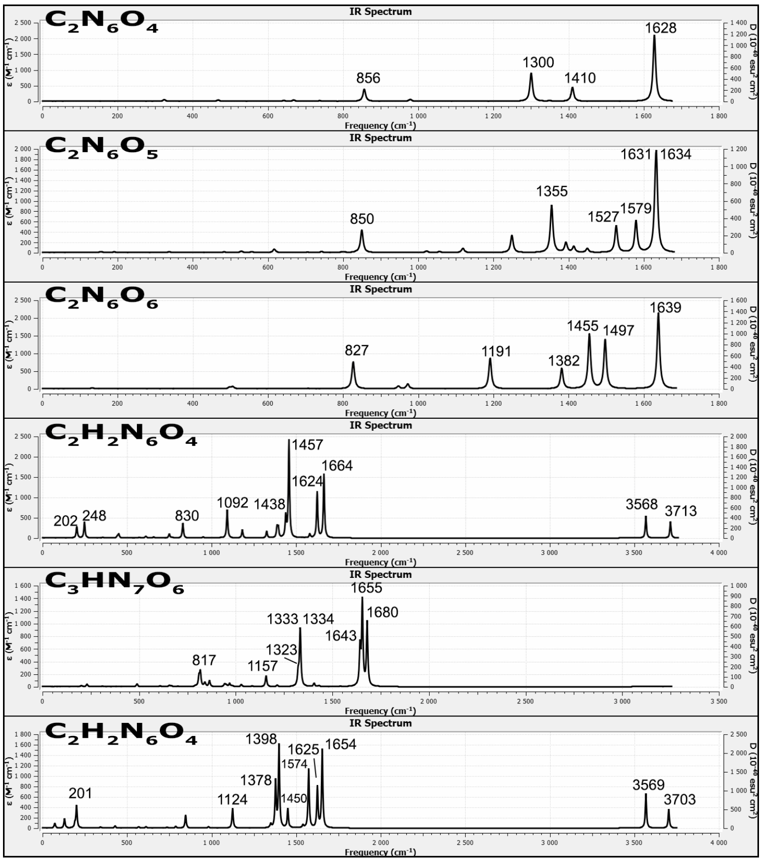


Figure 4. IR absorption spectra for the calculated compounds (structures **1–6**)

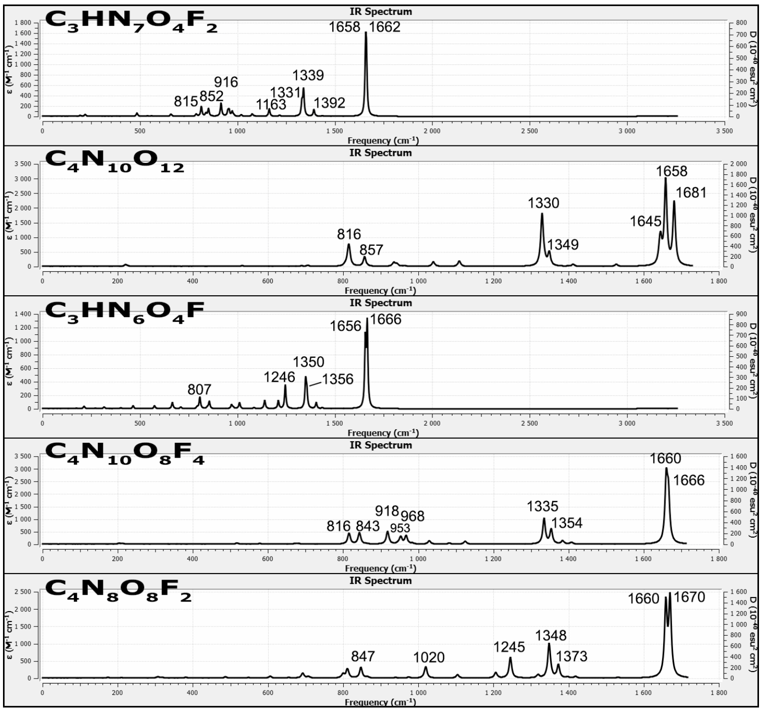


Figure 5. IR absorption spectra for the calculated compounds (structures **7–11**)

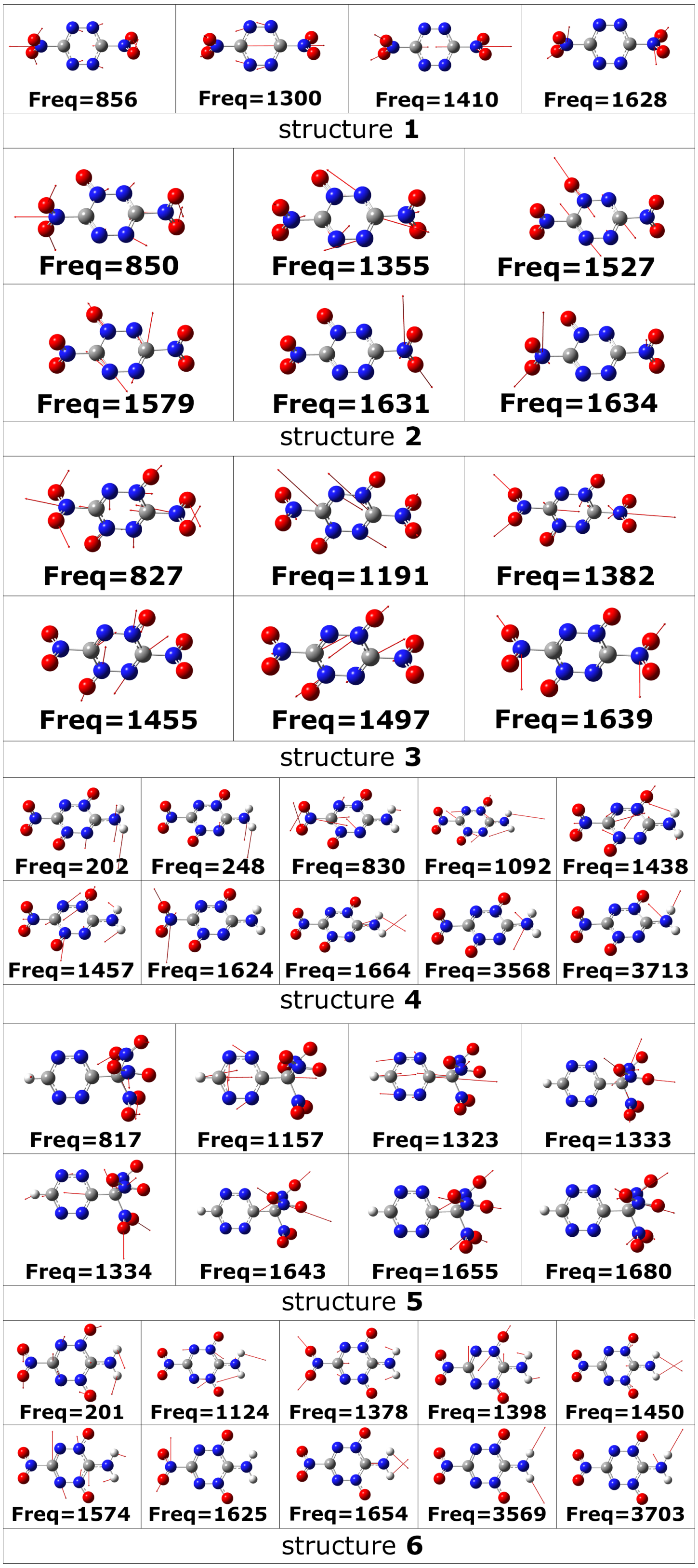


Figure 6. Displacement vectors for the indicated frequencies (structures **1**–**6**)

3. Computational Details

Various computational sources have been used for the quantum chemical simulation depending on the complexity of the task. Simulations of the simpler molecules have been performed on

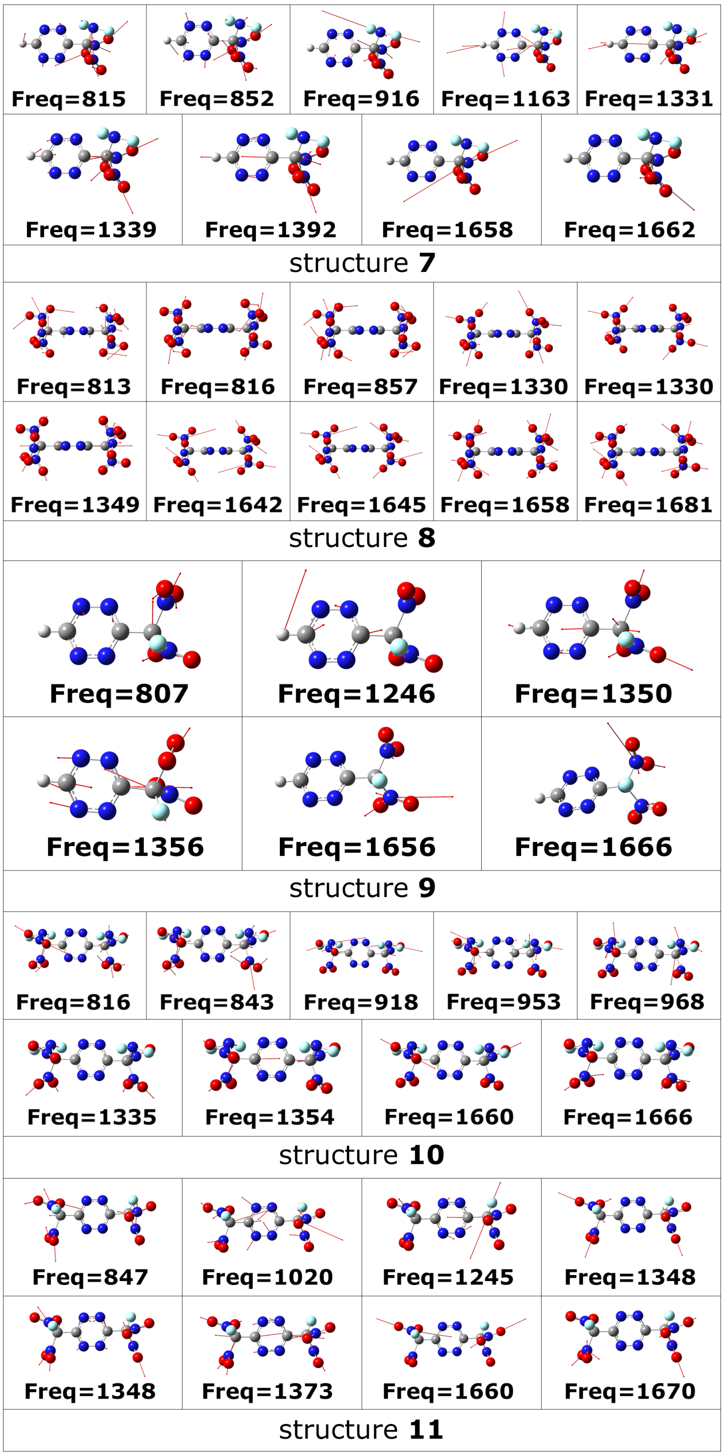


Figure 7. Displacement vectors for the indicated frequencies (structures **7–11**)

the local computational resources of the Institute of Problems of Chemical Physics of the Russian Academy of Sciences using the minicluster with computational nodes consisting of two Intel Xeon®X5675@3.46GHz processors, 48 Gb RAM and two GPU Nvidia Tesla C2075 per node, and computational cluser with nodes consisting of Intel Xeon®5450-5670@3GHz processors and 8 and 12 Gb RAM. The computation time for the given tasks have amounted to several hours approximately. For the computationally intensive tasks, we have used the high-performance computing resourses of the Lomonosov Moscow State University with computational nodes consisting of Intel Xeon®Gold 6140 CPU @2.30GHz processors and 256 Gb per node. The computation time on the heaviest structures by the most expensive G4 method amounted to two months.

Conclusion

Thermochemical data of high-energy compounds: $C_2N_6O_4$, $C_2N_6O_5$, $C_2N_6O_6$, $C_2H_2N_6O_4$, $C_3HN_7O_6$, $C_3HN_7O_4F_2$, $C_4N_{10}O_{12}$, $C_3HN_6O_4F$, $C_4N_{10}O_8F_4$, $C_4N_8O_8F_2$ has been obtained as a result of high-precision quantum-chemical calculations. It is shown that the enthalpy of formation decreases with increasing complexity of the structure of the molecules of the studied series. The IR absorption spectra, structural parameters, and atomic displacements for the most intense vibrations are also calculated. The calculations have been performed at the B3LYP/6-311+G(2d,p) level and using the combined CBS-4M and G4 methods. It has been demonstrated that the use of the CBS-4M calculation level for the selected class of molecules gives results that are close (within 7%) to those obtained at the G4 level and leads to a significant (up to 10 times) savings in the calculation time, although the values of the enthalpy of formation obtained by this method are either overstated or understated in comparison to the results of the G4 calculation. All molecules have been designed in the work for the first time and their physicochemical properties have been calculated and described for the first time.

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