Quantum-Chemical Calculations of the Enthalpy of Formation of Some Tetrazine Derivatives

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Abstract. The paper addresses to the study of the physicochemical properties of new high-energy substances: nitro derivatives of various kinds of nitrogenous heterocyclic nuclei. The enthalpy of formation of the molecules in the gas phase is obtained using quantum-chemical calculations (Gaussian 09). Various methods for solving the stationary Schrödinger equation are used: G4MP2, G4, CBS-4M, CBS-QB3, ωB97XD/aug-cc-pVTZ, B3LYP/6-311+G(2d,p), M062X/6-311+G(2d,p). The results of calculations obtained by the atomization method and the method of isogyric reactions are comparatively assessed. Various calculation methods are compared in terms of accuracy and time costs.

Keywords: Enthalpy of formation · Quantum-chemical calculations · High-energy materials · Calculation efficiency

1 Introduction

One of the fundamental problems in the field of energy-intensive compounds is the search for new high-energy density materials (HEDMs) and the study of their properties. Most of the suggested new HEDMs are nitro derivatives of various nitrogenous heterocyclic nuclei. For example, several first representatives of a series of high-energy 5/6/5 tricyclic derivatives of 1,2,3,4-tetrazines have been recently proposed in [1–3] and reported to possess a number of attractive physicochemical and energetic properties. The high-energy potential of these compounds is determined by the fact that the presence of nitro groups in their structure provides an acceptable oxygen balance, and a large number of $C-N$, $N-N$ and N=N bonds of the heterocyclic system sets a high level of the enthalpy of formation. The first of these derivatives to be synthesized was 2,9-dinitrobis([1,2,4]triazolo)[1,5-d:5',1'-f][1,2,3,4]tetrazine (**1**) [1], the structure of which combines 1,2,3,4-tetrazine and two nitro-1,2,4-triazoles annelated with it. A preliminary assessment of the properties of this compound shows that it is not

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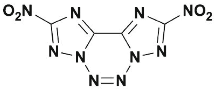
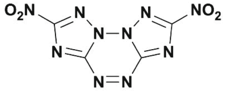
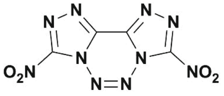
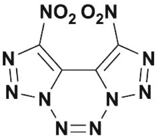
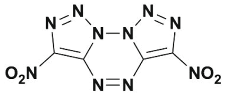
only characterized by a relatively high density, but is also comparable to HMX in terms of detonation characteristics; however, at the same time it has a noticeably lower sensitivity than both HMX and RDX. The above mentioned advantages of compound 1 make the entire range of energy-intensive 5/6/5 tricyclic derivatives of 1,2,3,4-tetrazines annelated with triazoles attractive for the search for new HEDMs. In addition, since the disadvantage of compound **1** is its relatively low thermal stability, it might be interesting to study the isomeric analogs of 5/6/5 tricyclic derivatives of unsymmetrical 1,2,3,4-tetrazine based on symmetric 1,2,4,5-tetrazine, as they can potentially provide greater thermal stability.

It should be noted that the key parameter that defines the energy capabilities of the HEDM is the enthalpy of formation, and the reliability of the results of calculating the energy characteristics of the compound depends on the accuracy of its value. Therefore, the purpose of this work was to determine the enthalpy of formation for 5/6/5 tricyclic derivatives of tetrazines annelated with nitrotriazoles (Table 1) $C_4N_{10}O_4$: 2,9-dinitrobis([1,2,4]triazolo)[1,5-d:5',1'-f][1,2,3,4]tetrazine (structure **1**), 2,7-dinitrobis([1,2,4]triazolo)[1,5-b:5',1'-f][1,2,4,5]tetrazine (structure **2**), 3,8-dinitrobis([1,2,4]triazolo)[4,3-d:3',4'-f][1,2,3,4]tetrazine (structure **3**), 1,8-dinitrobis([1,2,4]triazolo)[4,3-b:3',4'-f][1,2,4,5]tetrazine (structure **4**), 1,10-dinitrobis([1,2,3]triazolo)[1,5-d:5',1'-f][1,2,3,4]tetrazine (structure **5**) and 3,6-dinitrobis([1,2,3]triazolo)[1,5-b:5',1'-f][1,2,4,5]tetrazine (structure **6**) and in the gas phase at a temperature of 298 K and pressure p = 1 atm ($\Delta H^{298}_{f(g)}$) using various quantum-chemical methods and reveal regularities in the dependence of the value of ΔH_f on the structure of nitrotriazole isomers.

2 Calculation Method

At present, quantum-chemical calculations along with experimental measurement methods have become widespread as a means of determining the enthalpy of formation. The time-consuming synthetic production of the compounds under consideration is not required for such calculations, which advantages them greatly. Quantum-chemical calculations based on ab initio approaches (along with experimental data) enable the most accurate determination of the enthalpy of formation. The accuracy of such calculations by the G4 method of the Gaussian quantum-chemical package is assessed by Curtiss and his coauthors [4]. They use a test set of 454 substances to calculate thermochemical properties and compare the results with experimental data. A detailed analysis shows that the deviation of the calculation results from experimental data is less than 1 kcal/mol averagely (the deviation is less than 1% for high-enthalpy substances). Another noteworthy advantage of quantum-chemical methods is the possibility of designing molecules of new compounds that have not been yet synthesized, but look very promising. Their physicochemical characteristics (thermochemical properties, in particular) can be determined with high accuracy, and structural factors affecting such properties can be discovered.

Table 1. Molecules under consideration.

Formula	α^a	N%^{b}	№	Structural formula	№	Structural formula
$C_4N_{10}O_4$	0.500	55.56	**1**		**2**	
$C_4N_{10}O_4$	0.500	55.56	**3**		**4**	
$C_4N_{10}O_4$	0.500	55.56	**5**		**6**	

[a] - oxygen saturation coefficient of the $C_xH_yN_wO_z$ molecule, α = 2z/(4x + y);
[b] - mass content of nitrogen.

The enthalpy of formation can be calculated by examining reactions in which the test substance serves as a reagent or a product [5]. The standard enthalpy of formation of a substance can be determined by considering the energy balance equations of such reactions. This paper compares two approaches to evaluating the enthalpy of formation: 1) analysis of the atomization reaction of a substance (similar to our previous works [6–11]) and 2) analysis of the reaction of the substance formation from simple substances in standard states.

3 Results and Discussion

3.1 Enthalpy of Formation

The structures and the most significant geometric parameters of the molecules under consideration are calculated at the B3LYP/6-311+G(2d,p) level and shown in Fig. 1. The calculated values of the enthalpy of formation of the molecules in the gas phase, determined using various calculation methods (G4MP2, G4, ωB97XD/aug-cc-pVTZ, CBS-4M, CBS-QB3, B3LYP/6-311+G(2d,p), M062X/6-311+G(2d,p)), are presented in Table 2.

The enthalpy of formation of various isomers of the $C_4N_{10}O_4$ molecule are calculated by two approaches: ΔH_f(I) represents a calculation based on the change in the enthalpy for the reaction $4C(g) + 10N(g) + 4O(g) = C_4N_{10}O_4(g)$, and ΔH_f(II) represents a calculation based on the change in the enthalpy for the reaction $4C(g) + 5N_2(g) + 2O_2(g) = C_4N_{10}O_4(g)$. A comparison of the two calculation approaches shows that for all levels of calculation, the values of ΔH_f(I) are greater than the values of ΔH_f(II) by 7-101 kJ/mol, with the exception of the most accurate G4 method, for which the values of ΔH_f(II)

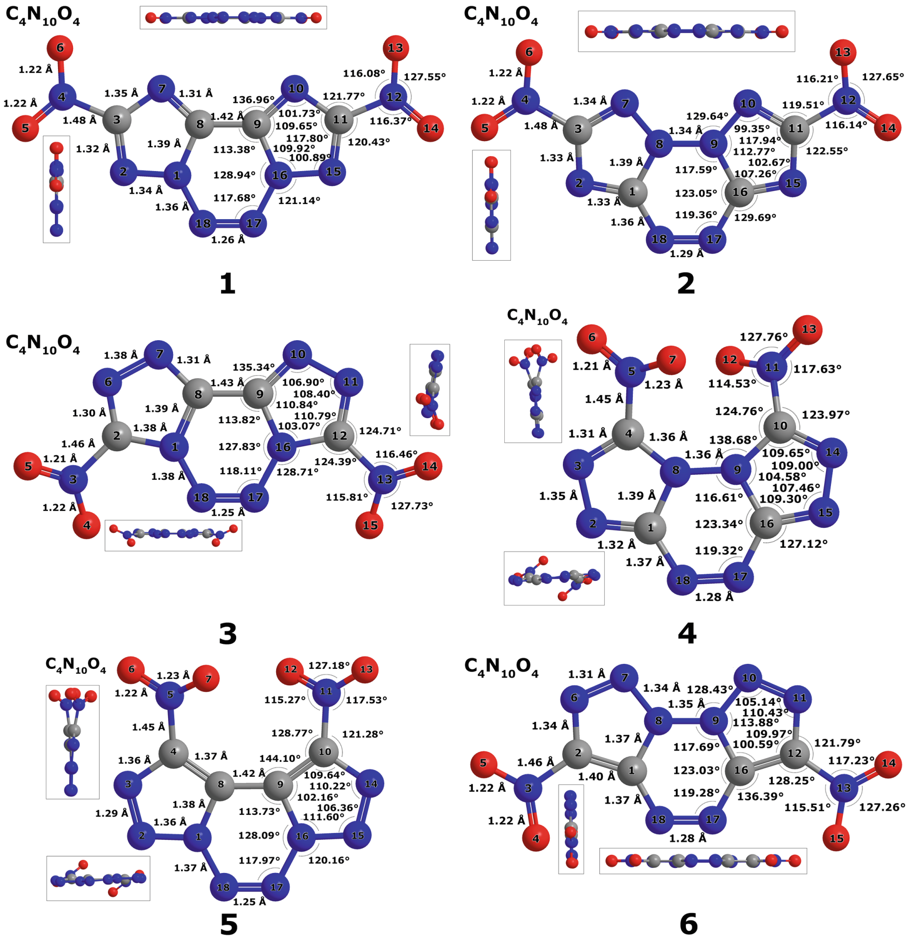


Fig. 1. Structures (in different angles) and most significant geometric parameters (in Å and °) of the calculated molecules (calculation level B3LYP/6-311+G(2d,p)).

are greater than the values of ΔH_f(I) by 3 kJ/mol. The more accurate the calculation is, the smaller is the difference between the ΔH_f(I) and ΔH_f(II) values, thus, for the CBS-4M method this difference is 101 kJ/mol, and for G4MP2 it is 7 kJ/mol.

All the considered $C_4N_{10}O_4(g)$ isomers (structures **1-6**) show similar tendencies of change in the values of the enthalpy of formation along the isomer series (Table 2). The enthalpy-of-formation values obtained at different levels of calculation increase in the following sequence CBS-4M < ωB97XD/aug-cc-pVTZ < CBS-QB3 < CBS-APNO < G4 < G4MP2 < M062X/6-311+G(2d,p) < B3LYP/6-311+G(2d,p), changing from structure **1** to structure **6** by approximately the same value 171-175 kJ/mol. Table 2 shows that the enthalpy of formation of various isomers increases from 867.5 kJ/mol to 1066.8 kJ/mol (G4).

The most important issue for the development of new high-energy materials is to establish the relationship between the value of the enthalpy of formation and the molecule structure. Let us consider the sequence of isomers based on 1,2,3,4-tetrazine: structures **1**, **3**, **5**. The isomer with structure **5**, which contains a chain of eight nitrogen atoms, is characterized by the highest enthalpy of formation (1012.8 kJ/mol), The enthalpy of formation is 41 kJ/mol lower (867.5 kJ/mol) for structure **3** with a chain of four nitrogen atoms in the tetrazine ring and two chains of two nitrogen atoms in the triazole rings. The lowest enthalpy of formation (867.5 kJ/mol) is that of structure **1** with a chain of six nitrogen atoms and two separate nitrogen atoms in the triazole rings.

In the case of isomers based on 1,2,4,5-tetrazine with two oppositely located pairs of nitrogen atoms (structures **2**, **4**, **6**), the enthalpy of formation increases by 43 kJ/mol (structure **2** as compared to structure **1**), 37 kJ/mol (structures **3-4**), and 54 kJ/mol (structures **5-6**). However, as mentioned above, the structure with a chain of six nitrogen atoms (**6**) has the highest value of the enthalpy of formation (1066.8 kJ/mol)). The enthalpy of formation of structure **4** with two pairs of nitrogen atoms is 58 kJ/mol lower than that of structure **6**, and the lowest value is that of structure **2** with two isolated nitrogen atoms (910.8 kJ/mol).

Thus, it can be assumed that if all other structural parameters are equal:

1) the presence in the tetrazine ring of two oppositely located pairs of nitrogen atoms is preferable to their sequential arrangement in the form of a chain;
2) lengthening the chain of nitrogen atoms by triazole rings has a positive effect on the value of the enthalpy of formation;
3) the presence of pairs of nitrogen atoms in the triazole rings is preferable to single atoms.

3.2 IR Spectra and Frequency Analysis

Figures 2 and 3 show the IR absorption spectra and atom displacements for the most intense vibrations of the molecules under consideration, calculated at the B3LYP/6-311+G(2d,p) level.

Table 2. Enthalpies of formation of the molecules in the gas phase, calculated at different levels.

Formula		$C_4N_{10}O_4$					
Structure		**1**	**2**	**3**	**4**	**5**	**6**
CBS-4M	kcal/mol	202.67^a	211.79^a	230.38^a	239.19^a	237.19^a	249.76^a
		178.45^b	187.57^b	206.16^b	214.98^b	212.98^b	225.55^b
	kJ/mol	*847.95*^{a}	*886.12*^{a}	*963.89*^{a}	*1000.78*^{a}	*992.41*^{a}	*1045.01*^{a}
		746.64^b	*784.81*^{b}	*862.58*^{b}	*899.47*^{b}	*891.09*^{b}	*943.70*^{b}
ωB97XD/ aug-cc-pVTZ	kcal/mol	208.26^a	218.05^a	234.31^a	244.39^a	244.69^a	256.53^a
		196.32^b	206.11^b	222.37^b	232.45^b	232.75^b	244.59^b
	kJ/mol	*871.37*^{a}	*912.32*^{a}	*980.36*^{a}	*1022.52*^{a}	*1023.79*^{a}	*1073.34*^{a}
		821.41^b	*862.36*^{b}	*930.38*^{b}	*972.55*^{b}	*973.83*^{b}	*1023.38*^{b}
CBS-QB3	kcal/mol	201.37^a	211.36^a	226.69^a	2336.02^a	235.66^a	248.11^a
		198.56^b	208.55^b	223.88^b	233.21^b	232.85^b	245.29^b
	kJ/mol	*842.53*^{a}	*884.35*^{a}	*948.48*^{a}	*987.52*^{a}	*986.02*^{a}	*1038.08*^{a}
		830.76^b	*872.58*^{b}	*936.71*^{b}	*975.75*^{b}	*974.25*^{b}	*1026.31*^{b}
CBS-APNO	kcal/mol	209.00^a	218.89^a	234.67^a	242.89^a	243.45^a	256.40^a
		203.51	213.40^b	229.18^b	237.40^b	237.96^b	250.91^b
	kJ/mol	*874.45*^{a}	*915.85*^{a}	*981.85*^{a}	*1016.27*^{a}	*1018.60*^{a}	*1072.77*^{a}
		851.47^b	*892.87*^{b}	*958.87*^{b}	*993.29*^{b}	*995.61*^{b}	*1049.79*^{b}
G4	kcal/mol	**206.64**^{a}	**216.99**^{a}	**231.58**^{a}	**240.39**^{a}	**241.37**^{a}	**254.28**^{a}
		207.34^b	**217.69**^{b}	**232.28**^{b}	**241.09**^{b}	**242.07**^{b}	**254.98**^{b}
	kJ/mol	***864.57***^{a}	***907.88***^{a}	***968.92***^{a}	***1005.80***^{a}	***1009.89***^{a}	***1063.89***^{a}
		867.50^b	***910.81***^{b}	***971.85***^{b}	***1008.73***^{b}	***1012.82***^{b}	***1066.82***^{b}
G4MP2	kcal/mol	211.34^a	222.02^a	236.37^a	245.90^a	245.94^a	258.84^a
		209.74^b	220.42^b	234.76^b	244.30^b	244.34^b	257.23^b
	kJ/mol	*884.27*^{a}	*928.94*^{a}	*988.96*^{a}	*1028.85*^{a}	*1029.01*^{a}	*1082.97*^{a}
		877.56^b	*922.24*^{b}	*982.26*^{b}	*1022.15*^{b}	*1022.31*^{b}	*1076.27*^{b}
M062X/ 6-311+ G(2d,p)	kcal/mol	231.79^a	241.11^a	258.09^a	266.42^a	270.16^a	281.44^a
		210.16^b	219.48^b	236.46^b	244.80^b	248.53^b	259.82^b
	kJ/mol	*969.81*^{a}	*1008.80*^{a}	*1079.84*^{a}	*1114.72*^{a}	*1130.34*^{a}	*1177.56*^{a}
		879.33^b	*918.32*^{b}	*989.36*^{b}	*1024.24*^{b}	*1039.85*^{b}	*1087.08*^{b}
B3LYP/ 6-311+ G(2d,p)	kcal/mol	224.04^a	232.87^a	249.20^a	259.62^a	260.33^a	270.28^a
		220.29^b	229.12^b	245.45^b	255.87^b	256.58^b	266.53^b
	kJ/mol	*937.37*^{a}	*974.32*^{a}	*1042.64*^{a}	*1086.24*^{a}	*1089.22*^{a}	*1130.85*^{a}
		921.69^b	*958.64*^{b}	*1026.97*^{b}	*1070.56*^{b}	*1073.54*^{b}	*1115.17*^{b}

$^a\Delta H_f$(I)
$^b\Delta H_f$(II)

According to Fig. 2 and 3, structure **1** is characterized by angular vibrations of the $N-O$ bonds of the nitro group NO_2 in the region of 841 cm^{-1}, vibrations of the $N-N$ bonds in the tetrazine ring in the region of 1220–1262 cm^{-1}, vibrations of the $N-N$ bonds in the triazole rings in the region 1317 cm^{-1}, vibrations of the $C-N$ bonds in the region of 1337–1377 cm^{-1}, and the vibrations of the $N-O$ bonds of the nitro group correspond to a peak in the region of 1620 cm^{-1}. Structure **2** is characterized by angular vibrations of the $N-O$ bonds of NO_2 fragments in the region of 845 cm^{-1}, vibrations of the $C-N$ bonds in the

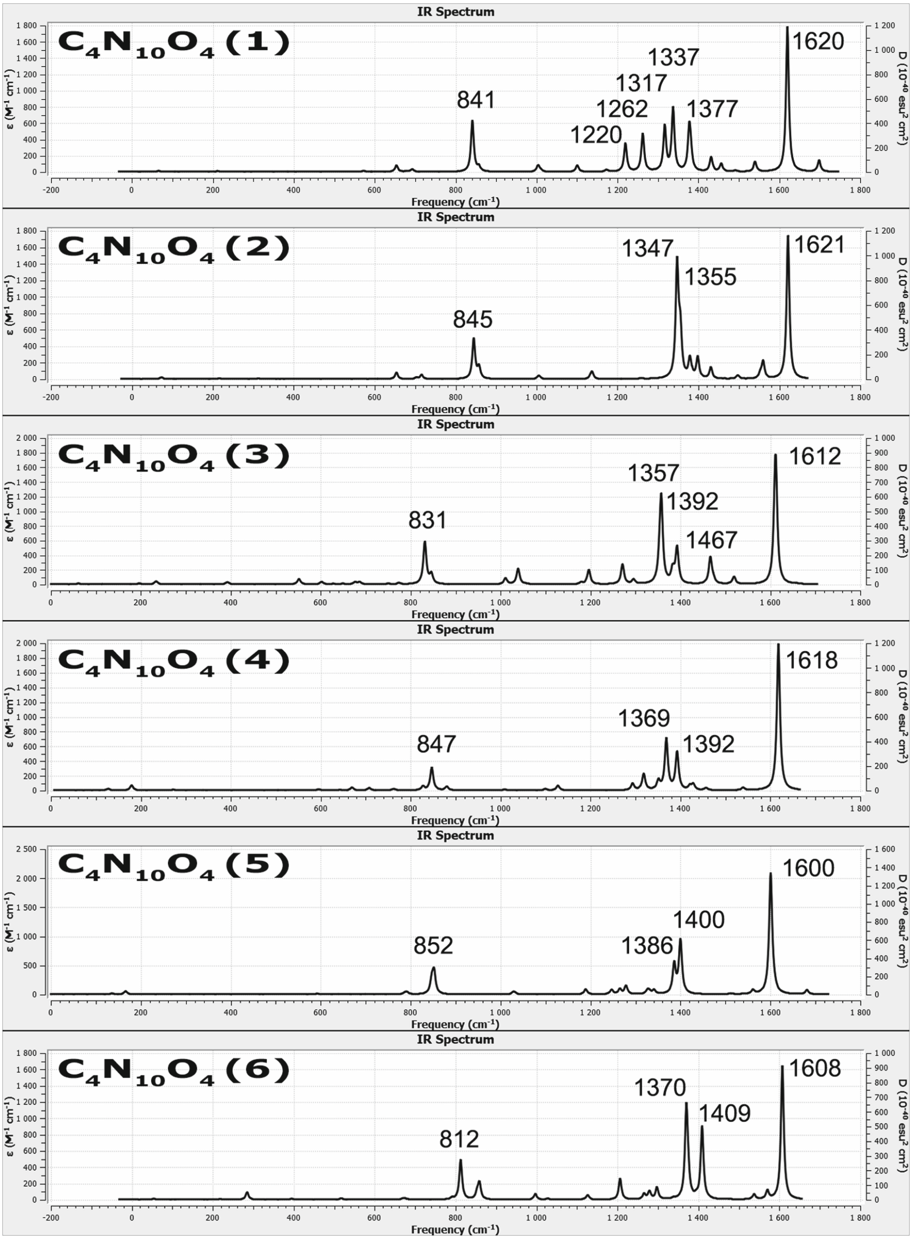


Fig. 2. IR absorption spectra.

region of 1347–1355 cm^{-1}, and vibrations of the $N-O$ bonds in the region of 1621 cm^{-1}. For structure **3**, the peak at 831 cm^{-1} corresponds to angular vibrations of the $N-O$ bonds of the nitro groups NO_2, the vibrations in the region

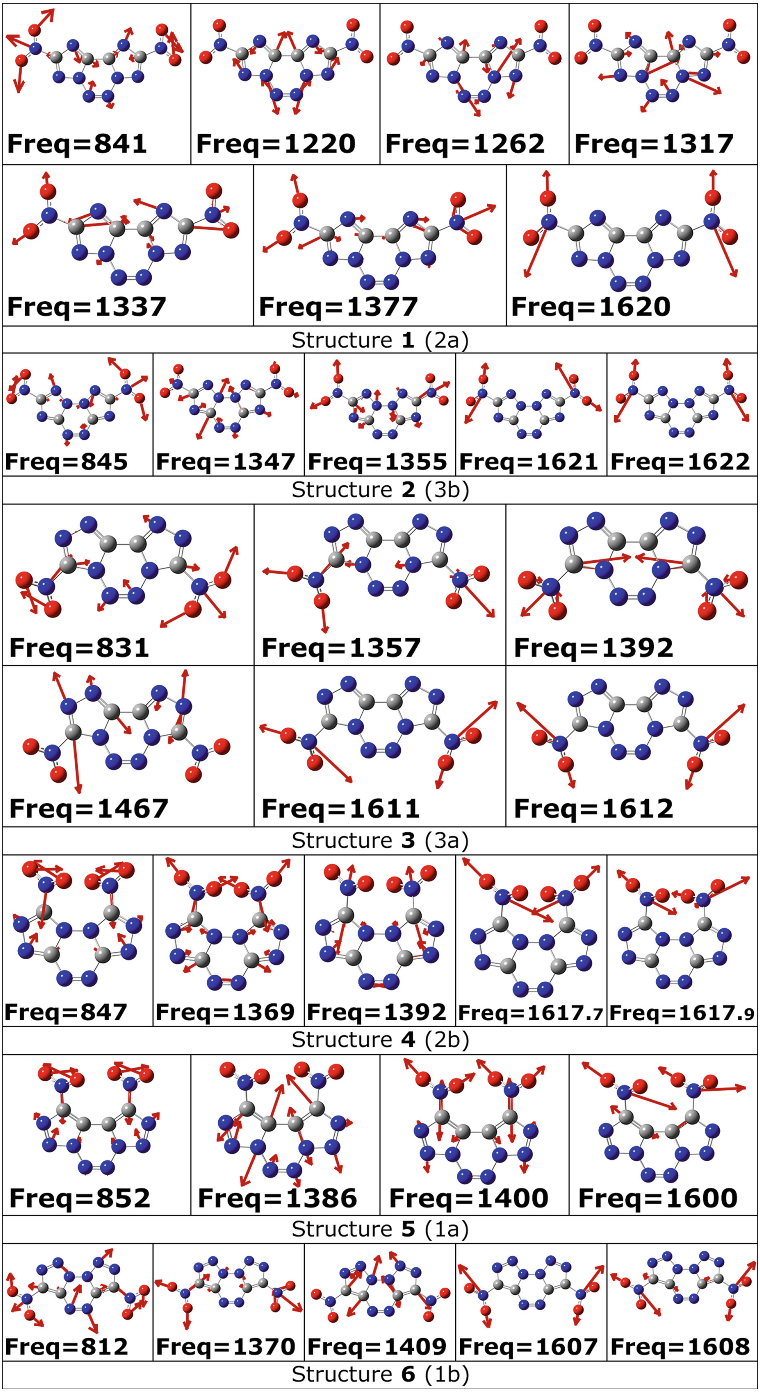


Fig. 3. Atom displacements for the most intense vibrations.

of 1357–1467 cm^{-1} correspond to vibrations of the $C - N$ bonds, and the peak at 1612 cm^{-1} corresponds to vibrations of the $N - O$ bonds in the nitro groups. Structure **4** is characterized by angular vibrations of the $N - O$ bonds in the region of 847 cm^{-1}, vibrations of the $C - N$ bonds in the region of 1369–1392 cm^{-1}, and vibrations of the $N - O$ bonds in the region of 1618 cm^{-1}. For structures **5** and **6**, the peaks at 852 cm^{-1} and 812 cm^{-1}, respectively, correspond to angular vibrations in the nitro groups, and the peaks at 1600 cm^{-1} and 1608 cm^{-1} for vibrations of the $N - O$ bonds. The vibrations of the $C - N$ bonds on the crosslinking of the tetrazine and triazole rings correspond to peaks at 1386 cm^{-1} (for structure **5**) and 1409 cm^{-1} (for structure **6**), and the vibrations of the $C - N$ bonds of the nitro groups correspond to 1400 cm^{-1} (structure **5**) and 1370 cm^{-1} (structure **6**).

4 Computational Details

The Lomonosov-2 compute node with the following configuration: Intel(R) Xeon(R) Gold 6140 CPU @ 2.30 GHz, RAM 259 GB, 20 Tb disk space, was used for calculations.

In regard to the parallelization degree of the executed calculations, it should be noted that the Gaussian package uses its own Linda software for parallelization. Some observations concerning the efficiency of calculations were made. While running a number of test tasks, a stable acceleration on pools up to 8 cores was noted, but further the acceleration effect decreased (Fig. 4). Thus, we used 8 cores per task in our calculations. The calculation speed also depends

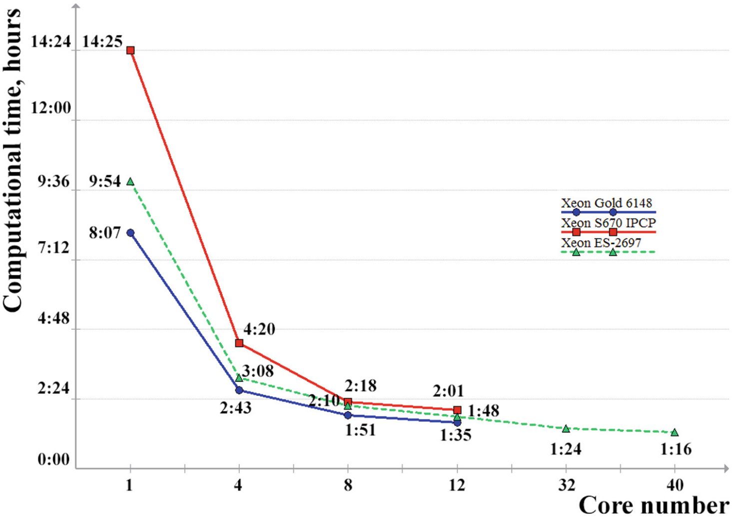


Fig. 4. Comparison of the computational time for the standard task in the Gaussian package on various computational configurations.

on processors' support of the avx2 and sse42 instructions, the former one, in particular, can profit by 8–10 times on some tasks using processors with a close clock rate [12]. In the calculation process, the Gaussian package creates enormous intermediate files, which size up to 2TB. It can take up to 35–50 min to write them to an SSD disk and noticeably longer to SATA arrays. Thereby, SSD disks or high-speed SAS disks with a large amount of allocated disk memory are very advisable for calculations.

The calculation time by the given conditions for the structures under consideration varied from 300–600 core-hours (1–3 days) for the CBS-4M and M062X/6-311+G(2d,p) methods to 3000–6000 core-hours (17–33 days) for the most time-consuming G4 and CBS-APNO methods.

5 Conclusions

The study of quantum-chemical methods for calculating the enthalpy of formation of dinitrobistriazoletetrazines made it possible for this group of compounds to determine the isomeric series of the increasing enthalpy of formation and reveal structural factors affecting the value of their ΔH_f, such as the structure of the nitrotriazole fragment (1,2,4-triazoles or 1,2,3-triazole) and the type of tetrazine nucleus (1,2,3,4- or 1,2,4,5-tetrazine). The highest value in the series of considered isomers differs from the lowest one by 199 kJ/mol (calculation by the G4 method). Calculations were carried out by methods of varying complexity and by two different approaches for establishing the enthalpy of formation. The results of calculation by two approaches differ by 3–101 kJ/mol, and the observation has been made that the more accurate the calculation is, the smaller is this difference. Analysis of IR absorption spectra and atom displacements for the most intense vibration has been made.

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