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Quantum-Chemical Study of Gas-Phase 5/6/5 Tricyclic Tetrazine Derivatives

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The most important task for specialists in the field of energy-intensive compounds is the search for new high-energy density materials and the study of their properties. This paper continues the study of series of tetrazines condensed with different types of azoles and presents the results of study of molecule structure of high-energy 5/6/5 tricyclic 1,2,3,4- and 1,2,4,5-tetrazines annelated with nitro-substituted imidazoles. The enthalpies of formation of the given molecules in the gaseous phase have been determined by high-performance quantum-chemical calculations by various calculation methods within the Gaussian 09 program package: G4, G4MP2, ωB97XD/aug-cc-pVTZ, CBS-4M, B3LYP/6-311+G(2d,p), M062X/6-311+G(2d,p). Different calculation methods and approaches have been compared in terms of their accuracy and time consumption. In addition, vibrational IR spectra have been calculated for the given compounds, and the correspondence of characteristic absorption frequencies to key fragments and functional groups of the structures has been determined. Enthalpy of formation of one of the studied substances (4220 kJ/kg) is the highest one among entalpies of formation of energy-intensive bis(nitroazolo)tetrazines calculated up to date.

Keywords: high-performance computing, quantum-chemical calculations, enthalpy of formation, high-energy materials, tetrazines, nitroimidazoles, azides.

Introduction

The development of flat condensed polynitrogen polynuclear structures and their functionalization with explosophoric groups is one of the promising trends in the search for new high-energy density materials (HEDMs) [1–4]. Particularly, it is fused tricyclic tetrazines annelated with azoles that have a high energy potential [5, 6]. Since the energy properties of HEDMs largely depend on their enthalpy of formation ($\Delta H^\circ{}_f$), the accuracy of its determination is very important. Previously, we made a research of approaches to calculating $\Delta H^\circ{}_f$ for several series of tetrazines condensed with nitropyrroles and nitrotriazoles [7, 8]. It is obvious that derivatives of this class of tricyclic compounds containing nitroimidazole nuclei are also of interest, since the first synthesized representative of tricyclic imidazotetrazines, 3,8-diazido-2,9-dinitroimidazo[1,2-d:2',1'-f][1,2,3,4]tetrazine showed quite promising energy characteristics [9]. It is worth mentioning that in recent decades a significant progress has been made in the synthesis of energy-intensive nitroimidazoles [10, 11].

In the search for new high-energy materials, quantum chemical calculations are becoming increasingly important. In the largest computing centers, up to 40% of computing time is spent on quantum chemical calculations. Such calculations enable researchers to save time and material resources needed to produce the required quantities of the studied substances and to carry out labor-intensive thermochemical studies. They also help to design new molecules of promising compounds that have not yet been obtained in practice and to determine the physicochemical parameters of the mentioned substances with high accuracy. For example, the most accurate calculated values of the enthalpy of formation $\Delta H^\circ{}_f$ are obtained by quantum-chemical calcula-

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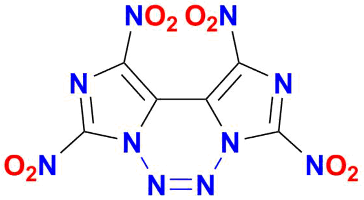
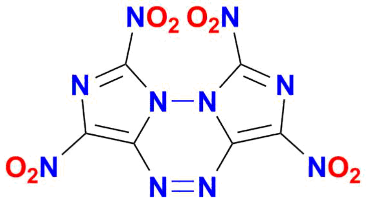
tions based on ab initio approaches. In the fundamental work of Curtiss [12], a thorough analysis of the accuracy of quantum-chemical calculations of thermochemical quantities on the example of 454 structures was performed using the G4 method within the Gaussian software, and it was shown that the average deviation of the calculation results from the experimental values in this case was only 0.8 kcal/mol, which for high-enthalpy substances was less than 1%. Over the past 15 years, many studies [13–15] of the approaches to calculate $\Delta H^\circ{}_f$ for a wide range of substances of various classes, using high-level calculations, have shown that methods of the Gaussian family, in particular G4, are effective to estimate $\Delta H^\circ{}_f$ of high-energy polynitrogen compounds.

Therefore, in order to make a correct assessment of the energy potential of tricyclic tetrazine derivatives annelated with nitroimidazoles, the main purpose of this work was to establish the enthalpy of formation by various quantum chemical methods in the gas phase under normal conditions ($\Delta H^\circ{}_{f(g)}$) and to detect regularities in the dependence of this value on molecular structure of isomeric 5/6/5 tricyclic 1,2,3,4- and 1,2,4.5-tetrazines annelated with dinitroimidazole (the general formula $C_6N_{10}O_8$) as well as isomeric diazido derivatives (the general formula $C_6N_{14}O_4$) (Fig. 1).



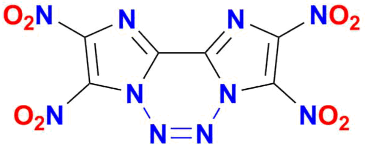
1a

1,3,8,10-tetranitroimidazo[1,5-d:5’,1’-f] [1,2,3,4]tetrazine



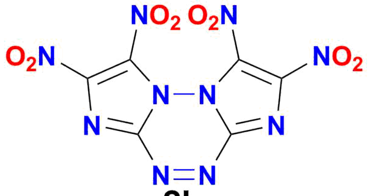
2a

1,3,6,8-tetranitroimidazo[1,5-b:5’,1’-f] [1,2,4,5]tetrazine



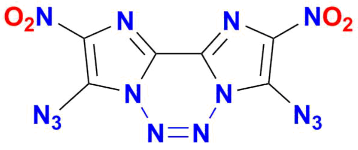
1b

2,3,8,9-tetranitroimidazo[1,2-d:2’,1’-f] [1,2,3,4]tetrazine



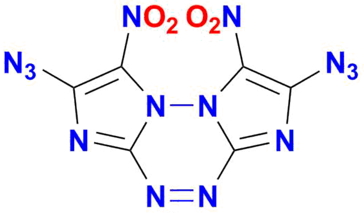
2b

1,2,7,8-tetranitroimidazo[1,2-b:2’,1’-f] [1,2,4,5]tetrazine



1c

3,8-diazido-2,9-dinitroimidazo[1,2-d:2’,1’-f] [1,2,3,4]tetrazine



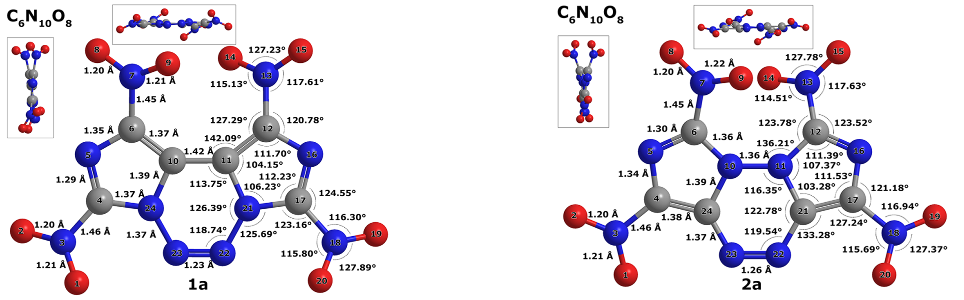
2c

2,7-diazido-1,8-dinitroimidazo[1,2-b:2’,1’-f] [1,2,4,5]tetrazine

Figure 1. Tricycle molecules under study

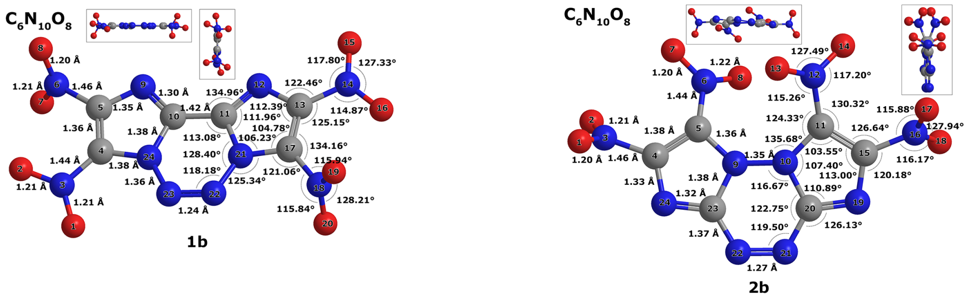
1. Calculation Method

To calculate physicochemical properties and thermochemical parameters of the compounds under study, we used the following quantum-chemical methods within the Gaussian 09 program package [16]: hybrid density functionals B3LYP [17, 18], M062X [19] and ωB97XD [20] that includes the empirical variance, with basis sets 6-311+G(2d,p) and aug-ccpVTZ correspondingly, and also the composite G4 and G4MP2 methods [12, 21, 22] and CBS-4M [23, 24] developed by Petersons group. The geometry of the studied molecules was obtained by fully optimizing all geometric parameters using the density functional theory by the ωB97XD/aug-cc-pVTZ method (Fig. 2). The subsequent calculation of vibrational frequencies using the analytical first and second derivatives without taking into account the correction for anharmonicity (absence of imaginary frequencies) confirmed the stability of the obtained configurations. The IR absorption spectra have been calculated at the ωB97XD/aug-cc-pVTZ level introducing a scaling factor of 0.956 to improve the agreement with experiment as recommended in [25].



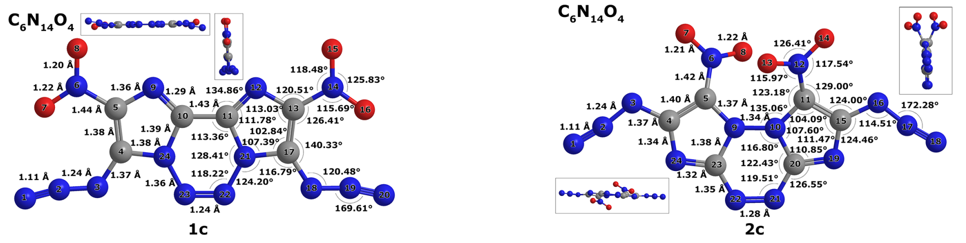
1,3,8,10-tetranitroimidazo[1,5-d:5’,1’-f][1,2,3,4]tetrazine

1,3,6,8-tetranitroimidazo[1,5-b:5’,1’-f][1,2,4,5]tetrazine



2,3,8,9-tetranitroimidazo[1,2-d:2’,1’-f][1,2,3,4]tetrazine

1,2,7,8-tetranitroimidazo[1,2-b:2’,1’-f][1,2,4,5]tetrazine



3,8-diazido-2,9-dinitroimidazo[1,2-d:2’,1’-f][1,2,3,4]tetrazine

2,7-diazido-1,8-dinitroimidazo[1,2-b:2’,1’-f][1,2,4,5]tetrazine

Figure 2. Structures (from different angles) and the most significant geometric parameters (in Å and °) of molecules **1a–c** and **2a–c**

In this work, we used two variants of calculating $\Delta H^\circ{}_{f(g)}$ of a substance of the general formula $C_xN_yO_z$, based on the energy balance of reactions involving the compound under study:

1) $\Delta H^\circ{}_{f(g)}(\mathrm{I})$ – using ΔH° of the reaction of atomization of the studied compound:

$$xC(g) + yN(g) + zO(g) = C_xN_yO_z(g);$$

2) $\Delta H^\circ{}_{f(g)}(\mathrm{II})$ – using ΔH° of the reaction of formation of the studied compound from simple substances:

$$xC(g) + (y/2)N_2(g) + (z/2)O_2(g) = C_xN_yO_z(g).$$

It should be noted that using two independent calculation schemes allows us to quantitatively compare the applied quantum-chemical calculation methods.

2. Results and Discussion

2.1. Enthalpy of Formation

For the structures under study, the oxygen saturation coefficient α ($\alpha = 2z/(4x + y)$ for $C_xH_yN_wO_z$) and the nitrogen mass fraction N% are 0.666 and 41.2%, respectively, in the case of isomers **1, 2a–b**, and 0.333 and 59.0% in the case of isomeric diazides **1, 2c**. Table 1 and Figure 3 present values of the enthalpy of formation of molecules **1a–c** and **2a–c** in the gas phase obtained by quantum-chemical calculations.

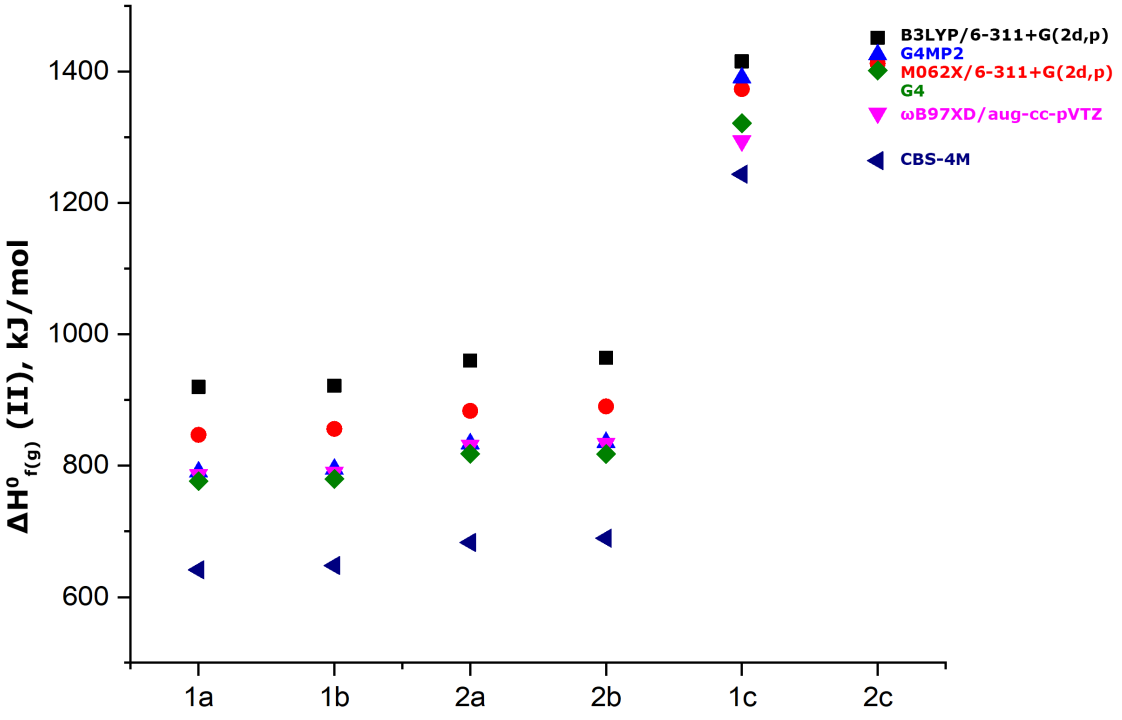


Figure 3. Values of the enthalpy of formation ($\Delta H^\circ{}_{f(g)}$) of molecules **1a–c** and **2a–c** in the gas phase calculated by different quantum-chemical methods

Table 1. Enthalpy of formation ($\Delta H^{\circ}{}_{f(g)}$) of molecules **1a–c** and **2a–c** in the gas phase calculated by different quantum-chemical methods

Calculation method	Enthalpy of formation, $\Delta H^{\circ}{}_{f(g)}$, kJ/mol					
	$C_6N_{10}O_8$				$C_6N_{14}O_4$	
	1a	**2a**	**1b**	**2b**	**1c**	**2c**
B3LYP/6-311+G(2d,p)	922.74^a	962.75^a	924.55^a	967.31^a	1442.41^a	1478.33^a
	919.84^b	959.85^b	921.65^b	964.41^b	1415.34^b	1451.27^b
M062X/6-311+G(2d,p)	942.98^a	979.59^a	952.30^a	986.38^a	1498.04^a	1537.07^a
	846.79^b	883.40^b	856.11^b	890.19^b	1373.30^b	1412.33^b
G4MP2	809.65^a	852.83^a	813.90^a	854.87^a	1394.94^a	1430.36^a
	790.48^b	833.66^b	794.73^b	835.70^b	1390.55^b	1425.96^b
ωB97XD/aug-cc-pVTZ	807.82^a	852.43^a	811.48^a	855.26^a	1375.62^a	1417.95^a
	786.39^b	830.99^b	790.04^b	833.82^b	1294.27^b	1336.59^b
G4	777.36^a	818.89^a	780.56^a	818.83^a	1315.56^a	1395.85^a
	776.40^b	817.92^b	779.89^b	817.86^b	1321.22^b	1401.51^b
CBS-4M	752.46^a	793.96^a	758.90^a	800.47^a	1381.72^a	1402.28^a
	641.60^b	683.09^b	648.03^b	689.60^b	1243.70^b	1264.26^b

[a] $\Delta H^{\circ}{}_{f(g)}$(I) calculated using the atomization reaction of the compound under study

[b] $\Delta H^{\circ}{}_{f(g)}$(II) calculated using the formation reaction of the compound under study from simple substances

Calculations of $\Delta H^{\circ}{}_{f(g)}$ by formulae I and II for each of the **1a–c** and **2a–c** compounds result in close values when the most high-level combined quantum-chemical G4 method is used (difference is no more than 1–6 kJ/mol). In the case when other methods are used to calculate the enthalpy of formation, difference between values of $\Delta H^{\circ}{}_{f(g)}$(I) and $\Delta H^{\circ}{}_{f(g)}$(II) slightly increases: 4–19 kJ/mol (0–2%) for G4MP2 method, 21–81 kJ/mol (3–6%) for ωB97XD/aug-cc-pVTZ, 3–27 kJ/mol (0–2%) for B3LYP/6-311+G(2d,p), 96–125 kJ/mol (9–11%) for M062X/6-311+G(2d,p) and 111–138 kJ/mol (11–16%) for CBS-4M. It should be noted that values of $\Delta H^{\circ}{}_{f(g)}$(I) are higher than those of $\Delta H^{\circ}{}_{f(g)}$(II) (see Tab. 1), with the only exception for corresponding values of the **1c** and **2c** structures calculated by the G4 method. It is known that the calculated values of the enthalpy of formation, as a rule, are higher than the experimental data, and therefore it can be assumed that quantum-chemical calculations using reaction II might be more accurate than calculations using reaction I. From the physical point of view, this seems quite logical, since the structure of the wave function in the case of the second reaction is divided into a smaller number of fragments.

In the case of calculations by the ωB97XD/aug-cc-pVTZ, G4MP2, M062X/6-311+G(2d,p), B3LYP/6-311+G(2d,p) and CBS-4M methods, the values of the enthalpy of formation $\Delta H^{\circ}{}_{f(g)}$(II) differ from the ones obtained using the referential G4 method by 1–2%, 2–5%, 1–10%, 4–18% and 6–17%, respectively. Thus, it can be preliminarily concluded that the methods that give the closest results to the ones obtained by the G4 methods for **1a–c** and **2a–c** compounds are ωB97XD/aug-cc-pVTZ and G4MP2. At the same time, the time required to complete G4 calculations is much longer than the calculation time using the ωB97XD/aug-cc-pVTZ and G4MP2 methods. Therefore, the latter two methods can be recommended for calculating $\Delta H^{\circ}{}_{f(g)}$ of structures of the type under study.

As it can be seen in Tab. 1 and Fig. 3, $\Delta H^{\circ}{}_{f(g)}$ values for the pairs of isomers **1a** and **1b**, **2a** and **2b**, with the same central cycle, are almost equal (the difference is within 1 kcal/mol), which is quite understandable, since the structures of the mentioned isomers contain an equal number of $C-NO_2$ groups, as well as $N-N$, $N=N$, $C-N$, $C=N$, $C-C$, and $C=C$ bonds. This is due to the fact that the structures of these isomeric pairs contain the same six-membered ring isomer (1,2,3,4-tetrazine for **1a** and **1b**, 1,2,4,5-tetrazine for **2a** and **2b**), and the imidazole rings annelated with them are not isomeristic.

At the same time, comparison of isomers pairs **1a** and **2a**, **1b** and **2b** shows that the values of $\Delta H^{\circ}{}_{f(g)}$ for them slightly differ, namely, by ~45 kJ/mol, and for a pair of **1c** and **2c**, by ~35 kJ/mol, and this difference is obviously caused by the type of the central cycle, on which the structure is based. Isomers **1a–1c** based on 1,2,3,4-tetrazine contain a $C-C$ bond, which greatly reduces the enthalpy of formation, while there is no such bond in similar isomers **2a–2c** based on symmetrical 1,2,4,5-tetrazine. Therefore, as can be seen from the results of calculations (see Tab. 1), $\Delta H^{\circ}{}_{f(g)}$ of isomer **2a** is greater than that of **1a**, respectively, $\Delta H^{\circ}{}_{f(g)}$ of structure **2b** is greater than that of **1b**, and $\Delta H^{\circ}{}_{f(g)}$ of **2c** is greater than that of **1c**.

Noticeable changes in the thermochemical characteristics occur when the nitro group in the imidazole rings is replaced by the azide group, i.e., in transition from structure **1b** to **1c** and from structure **2b** to **2c**, which leads to a significant increase in $\Delta H^{\circ}{}_{f(g)}$, by 541 and 584 kJ/mol, respectively. This increase in the enthalpy of formation is quite natural and is conditioned, firstly, by removal of the oxygen-containing $-NO_2$ group, which reduces $\Delta H^{\circ}{}_{f(g)}$, and, secondly, on the contrary, by introduction of the endothermic substituent $-N^{-}-N^{+}\equiv N$, which significantly enlarges $\Delta H^{\circ}{}_{f(g)}$ [26–28].

Earlier Shreeve and coauthors [9] described the synthesis of compound **1c**, and calculated $\Delta H^{\circ}{}_{f(g)}$ for this structure by the method of isodesmic reactions at the G2 level. The result of their calculation was 1390.8 kJ/mol, which is very close to our calculation results at the G4MP2 level (1390.5 kJ/mol), but in comparison with the value of $\Delta H^{\circ}{}_{f(g)}$ calculated by the high-level G4 method (1321.2 kJ/mol), it is obviously slightly overestimated (by 70 kJ/mol, i.e., by 5%).

2.2. IR Spectra and Frequency Analysis

Since most of the compounds under study have not yet been synthesized, providing IR spectra for them could be of great help for their future identification during synthesis. We also performed a quantum chemical analysis of vibrational spectroscopy in the gas phase for structures **1a–c** and **2a–c** (Fig. 4, Tab. 2). The intense absorption bands in the region of 1627–1581 cm^{-1} and 1392–1356 cm^{-1} can be attributed to asymmetric and symmetric stretching vibrations of the NO_2 nitro groups, respectively. The most intense peaks at ~2240 cm^{-1} in the spectra of structures **1c** and **2c** can be attributed to asymmetric stretching vibrations of N_3 azido groups, while the peaks at ~1230 cm^{-1} can be attributed to symmetric stretching vibrations of N_3 azido groups. The characteristic absorption frequencies of functional groups determined in our calculations correspond to the typical values given in the literature [29–32].

3. Computational Details

In this work, a number of computational sources have been used for the quantum-chemical calculations. The use of the Gaussian package led to some limitations in the calculations, since the parallelization within the program is implemented inefficiently. Test calculations (optimization

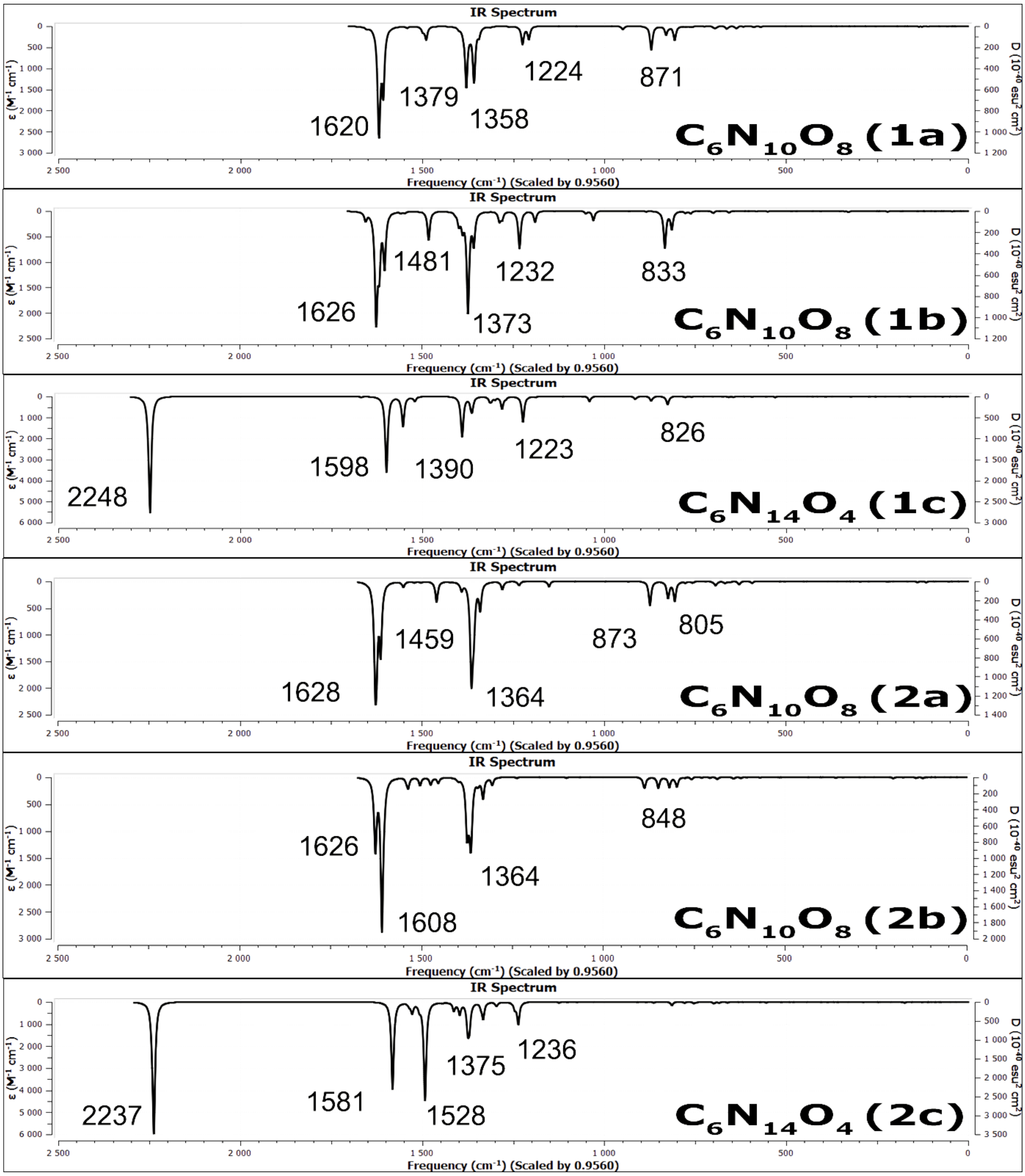


Figure 4. IR absorption spectra for structures **1a–c** and **2a–c**, calculated by the ωB97XD/aug-cc-pVTZ method

of a 28-atom molecule by the B3LYP method) on various resources carried out in the course of our previous work showed that a significant change in performance occurs only when increasing the number of computational cores from 1 to 8. A further increase in the number of cores does not lead to the expected rise of performance. Additional comparison of calculation by the G4MP2 method on 8 and 32 cores confirmed the previous observations and conclusions, and in this work we used 8 cores per task for each calculation method. Calculations by the B3LYP/6-311+G(2d,p) and CBS-4M methods were performed on the local computational resourses of FRC PCP MC RAS. For other calculations, we used high-performance computing resourses

Table 2. Allocation of the IR spectra of structures **1a–c** and **2a–c**

Compound	Frequency, cm^{-1}	Allocation of absorption frequencies in the IR spectrum
1a	1620–1607	asymm. stretch. vibrations NO_2
	1489	stretch. vibrations $C-N$ in imidazole rings
	1378–1356	symm. stretch. vibrations NO_2
	1224	asymm. stretch. vibrations $N-N$ in tetrazine ring
	1207	symm. stretch. vibrations $N-N$ in tetrazine ring
1b	1654	stretch. vibrations $C-C$ in tetrazine ring
	1625–1602	asymm. stretch. vibrations NO_2
	1481	stretch. vibrations $C-N$ and $C-C$ in imidazole rings
	1388–1357	symm. stretch. vibrations NO_2
	1231	stretch. vibrations $C-N$ and $N-N$ in tetrazine ring
	1189	asymm. stretch. vibrations $N-N$ in tetrazine ring
	1028	asymm. stretch. vibr. $N-N$ in tetrazine ring, deform. vibr. in imidazole rings
1c	2248	asymm. stretch. vibrations N_3
	1598	asymm. stretch. vibrations NO_2
	1552	asymm. stretch. vibrations $C-C$ and $C-N$
	1392	symm. stretch. vibrations NO_2
	1362	symm. stretch. vibrations $C-N$ and NO_2
	1280	symm. stretch. vibrations N_3 and deform. vibrations of imidazole rings
	1223	symm. stretch. vibrations N_3 and deform. vibrations of triazole rings
	1040	asymm. stretch. vibrations $N-N$ in tetrazine ring
	914	deform. vibrations in tetrazine ring
2a	1627–1624	asymm. stretch. vibrations NO_2
	1550	stretch. vibrations $C-C$ in imidazole rings
	1459	stretch. vibrations $C-N$ and $N-N$ in imidazole rings
	1390	stretch. vibrations $C-N$ in imidazole rings
	1364–1357	symm. vibrations NO_2
	1339	stretch. vibrations $C-N$ and $N-N$ in imidazole rings
2b	1626–1608	asymm. stretch. vibrations NO_2
	1503–1473	stretch. vibrations $C-C$ and $C-N$ in imidazole rings
	1453	stretch. vibrations $N-N$ in tetrazine ring
	1364	symm. stretch. vibrations $NO_2$and $C-C$ in imidazole rings
	1362–1304	stretch. vibrations $C-N$ in tetrazine and imidazole rings
	847–796	angular vibrations NO_2, stretch. vibrations $C-N_{NO_2}$
2c	2237	asymm. stretch. vibrations N_3
	1581	asymm. stretch. vibrations NO_2
	1527	asymm. deform. vibrations in tetrazine and imidazole rings
	1492	asymm. stretch. vibrations $N_{N_3}-C$
	1413	symm. stretch. vibrations $C-N$ and $N-N$
	1397	asymm. stretch. vibrations $C-N$ and $N_{NO_2}-C$
	1374	symm. stretch. vibrations NO_2
	1370	asymm. vibrations $C-N$
	1332	symm. stretch. vibr. NO_2 and asynch. deform. vibr. in imidazole rings
	1245	deform. vibrations of imidazole rings
	1236	symm. stretch. vibrations N_3

of the Lomonosov Moscow State University. Computation time varied from several hours for M062X/6-311+G(2d,p) method to several months by G4 method.

Conclusions

Quantum-chemical methods for calculating the enthalpy of formation of tricyclic bis(imidazo)tetrazines **1a–c** and **2a–c** in the gas phase at different calculation levels have been systematically studied, which made it possible to determine $\Delta H^{\circ}{}_{f(g)}$ for the given substances and discover its dependence on the structure of the compounds. The performed studies have shown that $\Delta H^{\circ}{}_{f(g)}$ of isomers with identical substituents and a central tetrazine ring (pairs **1a, b** and **2a, b**) are almost equal. At the same time, replacement of 1,2,3,4-tetrazine in the structure with 1,2,4,5-tetrazine, i.e., in transition from **1a, b** to **2a, b** (as well as from **1c** to **2c**) leads to increase in the calculated $\Delta H^{\circ}{}_{f(g)}$ by 8 (13) kcal/mol. Moreover, the replacement of one nitro group in each imidazole ring of the tricycle structure by an azide substituent, i.e., in transition from **1a, b** to **1c** and from **2a, b** to **2c** leads to a significant increase in $\Delta H^{\circ}{}_{f(g)}$ by 129–140 kJ/mol, as a result of which it is possible to achieve values of the enthalpy of formation up to 1400 kJ/mol (4220 kJ/kg), which is the largest value of $\Delta H^{\circ}{}_{f(g)}$ among energy-intensive bis(nitroazolo)tetrazines calculated up to date.

IR spectra have been calculated for the tricycles under study **1a–1c** and **2a–2c**, and the frequencies of the characteristic vibrations bands have been allocated to the corresponding structural fragments of the compounds under study, primarily to nitro groups (asymm. 1625-1580 cm^{-1} and symm. 1390–1350 cm^{-1}) and to azido groups (asym. 2250–2240 cm^{-1} and sym. 1225–1235 cm^{-1}).

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