






Quantum-Chemical Study of Some Trispyrazolobenzenes and Trispyrazolo-1,3,5-triazines

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Development of new high-energy density materials and study of their properties is an important task, since such materials are in high demand in various application areas. This paper continues the study of polynitrogen fused tetracyclic systems which include threeazole rings annelated with a benzene or azine ring. Such polycyclic structures attract special attention of scientists. This paper is dedicated to the study of properties of a number of promising high-energy tetracyclic compounds annelated with pyrazole nitro derivatives. For this study, we used quantum-chemical methods (the hybrid density functional B3LYP and the composite G4MP2 and G4 methods) within the Gaussian 09 and NWChem software packages at Lomonosov Moscow State University Supercomputer Complex. We used the atomization method and method of reactions to calculate the enthalpy of formation. We analyzed the dependence of the enthalpy of formation on the structural parameters of the compounds and calculated the optimized structures and IR absorption spectra. We also compare the Gaussian 09 and NWChem quantum chemical programs in terms of efficiency, parallelization and computational requirements. In the cases where the G4-level accuracy of the results is not required, the use of NWChem can significantly save computation time.

Keywords: quantum-chemical calculations, high-energy density materials, tris(azolo)benzenes, tris(azolo)azines, enthalpy of formation, high-performance computing.

Introduction

High-energy polynitrogen heterocyclic compounds have become a focus of study of scientists around the world over the last decades. The key characteristic of such compounds is the enthalpy of their formation, because it is on this value that the energetic possibilities of the compounds mainly depend. Research chemists, before synthesizing new compounds, need to preliminary assess their energetic possibilities, so as not to waste time and resources on objects that are not promising enough. In order to do so, it is necessary to know the enthalpy of formation, the best way to determine which is quantum-chemical calculations, the development of methods of which has been very rapidly progressing in recent decades. Even in the case of the already synthesized compounds, it is very important to estimate the enthalpy of formation by quantum-chemical calculations, since experimental measurements are not always reliable due to the insufficient purity of the experimental samples.

Our scientific group makes systematic studies of the energetic possibilities of polynitrogen structures consisting of three or four fused heterocycles [1–5]. In our previous works, we studied the properties of tris(pyrrolo)benzenes and -[1,3,5]triazines [4] and triimidazolobenzenes and -[1,3,5]triazines [5]. In this work, the objects of study are tris(pyrazolo)benzenes and [1,3,5]triazines, which consist of three pyrazole rings annelated with a central benzene or 1,3,5-triazine ring. We selected unsubstituted tetracycles **1a,b** and their hexanitro derivatives **2a,b,c** (Fig. 1) for quantum chemical calculations in order to assess the way the structural factors affect the

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of calculations of the composite G4MP2 method as given in [10, 12] and using the following formula to obtain the final energy of the molecule:

$$E_0[G4(MP2)] = CCSD(FC, T)/6 - 31G(d) + \Delta E_{MP2} + \Delta E_{HF} + \Delta E(SO) + E(HLC) + E(ZPE),$$

where $CCSD(FC, T)/6 - 31G(d)$ is the energy calculation is at the triples-augmented coupled cluster level of theory, CCSD(T), with the 6-31G(d) basis set, using frozen core; ΔE_{MP2} and ΔE_{HF} are the energy corrections calculated by the MP2 and HF methods accordingly, $\Delta E(SO)$ is the spin-orbit correction, $E(HLC)$ is the higher-level correction, and $E(ZPE)$ is the zero-point energy.

The IR absorption spectra were calculated using the hybrid density functional B3LYP with the 6-311+G(2d,p) basis and introducing a scaling factor of 0.967 [13].

To calculate the enthalpy of formation of the substances in the gas phase, we used two methods: 1) one based on the atomization reaction and 2) one based on reactions.

We used the method based on the atomization reaction in our previous works and for the $C_wH_xN_yO_z$ molecule it consists of the following steps:

1. The atomization energy is calculated

$$\sum D_0 = wE_0(C) + xE_0(H) + yE_0(N) + zE_0(O) - E_0(C_wH_xN_yO_z),$$

where $E_0(C), E_0(H), E_0(N), E_0(O), E_0(C_wH_xN_yO_z)$ are computed total energies of atoms and molecule.

2. The enthalpy of formation at 0K is calculated

$$\Delta H_f^\circ(C_wH_xN_yO_z, 0K) = w\Delta H_f^\circ(C, 0K) + x\Delta H_f^\circ(H, 0K) + y\Delta H_f^\circ(N, 0K) + z\Delta H_f^\circ(O, 0K) - \sum D_0,$$

where the first four summands are the enthalpies of formation of gaseous atomic components from the NIST-JANAF database of thermochemical parameters [14].

3. The enthalpy of formation at 298.15K is calculated

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

where the second summand is obtained from the molecule computation, the third to sixth summands are known from experiment (or calculated from experimental molecular constants).

According to Hess's law, the enthalpy of a reaction does not depend on the specific path of its occurrence, therefore any thermodynamic cycle that links the reactants with products in stable standard states can be used for calculations. In this case, to calculate the enthalpy of formation of the compound under study, it is necessary to obtain the values of the electron energy of all

members of the cycle, which are calculated using the lower level theory, as well as the values of the enthalpy of formation of the reactants, which can be calculated using the atomization method. Compared to direct calculation of the enthalpy of formation of the molecule under study by the atomization method, this approach allows for a significant reduction in the overall computational complexity. The reaction schemes used to calculate the enthalpy of formation are presented in Fig. 2.

2. Results and Discussion

2.1. Enthalpy of Formation

Geometric parameters of the optimized structure are pictured in Fig. 3. The results of calculation of the enthalpy of formation by various methods are gathered in Tab. 1.

Table 1. Results of the calculation of the enthalpy of formation of the studied tetracycles **C1–5**

№	Formula, {molecular mass [g/mol]}	$\Delta H_{f(g)}^{298}$ [kJ/mol (kJ/kg)]				
		B3LYP/6- 311+G(2d,p)	G4MP2	G4	NWChem G4MP2	Reactions G4MP2
1a	$C_9H_6N_6$ {198.065}	673.96	567.38	562.28	568.94	546.14
		(3402.70)	(2862.83)	(2837.08)	(2872.49)	(2757.37)
1b		775.00	664.44	658.30	665.47	642.16
		(3912.85)	(3352.59)	(3321.59)	(3359.83)	(3242.17)
2a	$C_9N_{12}O_{12}$ {467.976}	1138.19	936.50	–	941.90	935.38
		(2432.15)	(2000.33)		(2012.71)	(1998.77)
2b		1186.21	1002.27	–	1007.47	986.92
		(2534.76)	(2140.82)		(2152.81)	(2108.92)
2c		1087.87	894.87	–	898.81	886.84
		(2324.64)	(1911.42)		(1920.63)	(1895.06)

Values of $\Delta H_{f(g)}^{298}$ obtained using density functional theory proved to be overestimated (they exceed those obtained by G4MP2 method by 107–110 kJ/mol for compounds **1a,b** and by 183–202 kJ/mol for compounds **2a,b,c**). Still, they follow the general trend of the enthalpy of formation behavior and can be used for an initial comparison of the characteristics of compounds. Values of $\Delta H_{f(g)}^{298}$ obtained using the Gaussian G4MP2 and G4 methods (for compounds **1a,b**) and using NWChem are close (within 7 kJ/mol). The slight difference in the values obtained using the G4MP2 method in Gaussian and NWChem might be due to the fact that NWChem does not include the G4MP2 method and only follows the steps of the original G4MP2 method from Gaussian as it had been indicated in Introduction. Therefore, deviations may occur when calculating all the elements of the total energy. When using the G4MP2 method, the values of $\Delta H_{f(g)}^{298}$ obtained through the reactions are lower than those obtained through the atomization reaction by 1–15 kJ/mol for compounds **2a,b,c** and by 21–22 kJ/mol for compounds **1a,b**.

Analysis of the results of quantum chemical calculations of $\Delta H_{f(g)}^{298}$ of the structures under study shows that among unsubstituted tetracycles the $\Delta H_{f(g)}^{298}$ value of compound **1b** based on the 1,3,5-triazine ring is ~ 450 kJ/kg higher than that of its isomer **1a** with a benzene ring in the center of the molecule, which is quite natural, since **1b** contains a larger number of C–N bonds

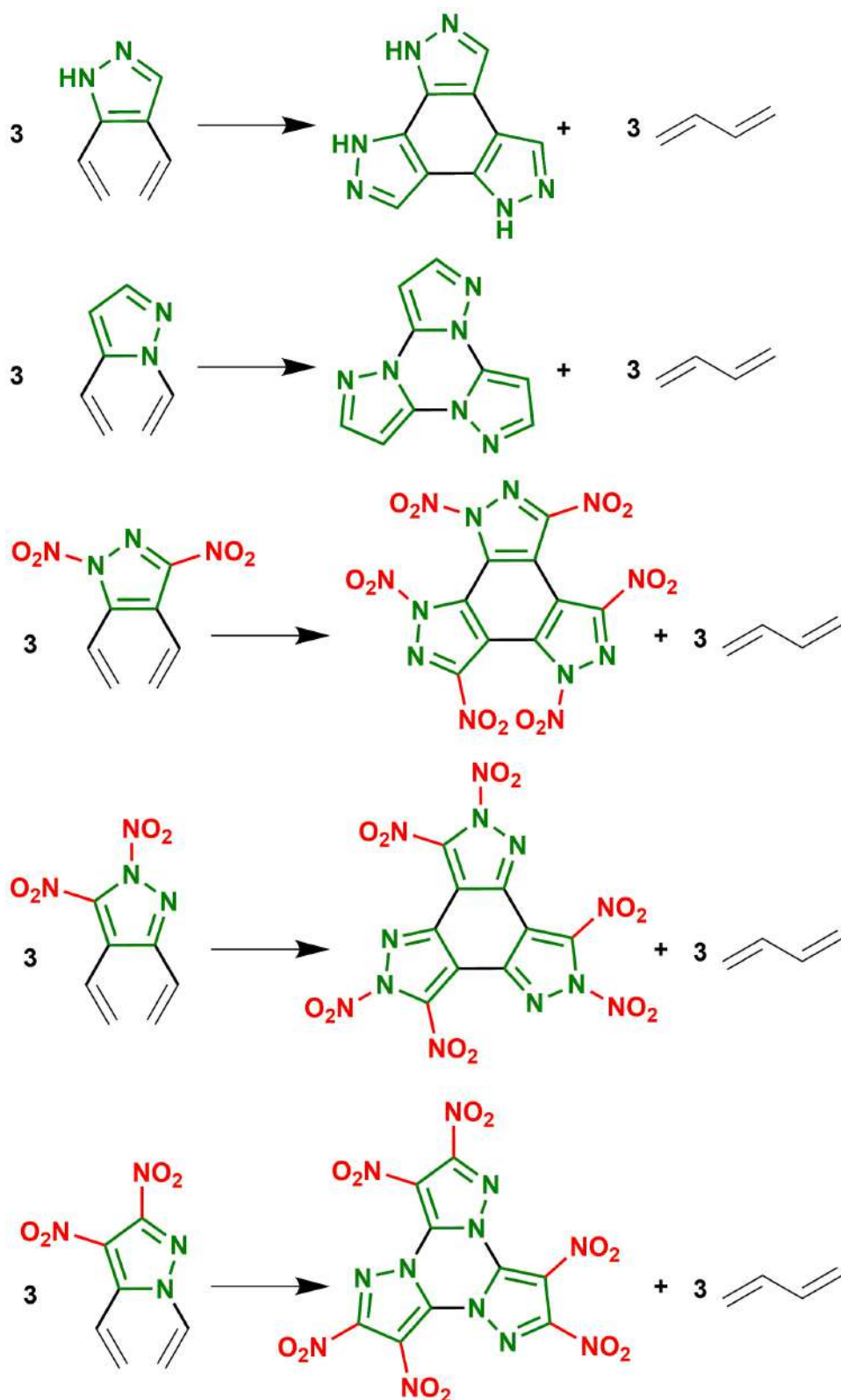


Figure 2. The reaction schemes used to calculate the enthalpy of formation

in its structure than its isomeric benzotriazole **1a**. At the same time, in the case of hexanitro derivatives of tetracycles **2a,b,c**, it is, on the contrary, isomer **2c** based on the 1,3,5-triazine ring that has the lowest $\Delta H_{f(g)}^{298}$ as compared to compounds **2a** and **2b** with a central benzene ring (the difference is ~ 40 – 110 kJ/mol or ~ 90 – 230 kJ/kg). This can be explained by the fact

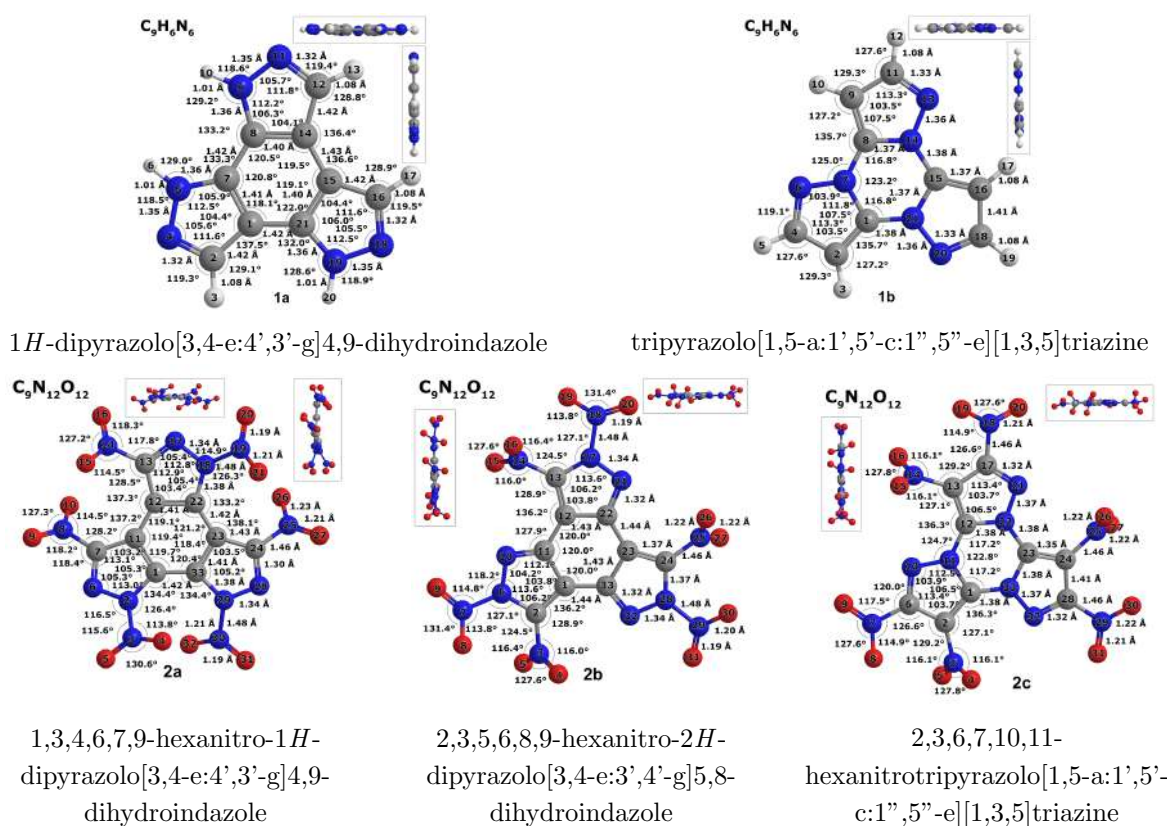


Figure 3. Structures and geometric parameters (in Å and °) of the studied tetracycles **1a,b** and **2a,b,c** (calculation level: B3LYP/6-311+G(2d,p))

that in addition to $C - NO_2$, there are also more endothermic $N - NO_2$ bonds in the structure of isomers **2a,b**, which are absent in **2c**. Meanwhile $\Delta H_{f(g)}^{298}$ of tetracycle **2a** is lower than that of **2b**, probably due to the position of nitro groups in each of the pyrazole rings. In the case of **2b**, the nitro groups are located in positions 1 and 2 in relation to each other, whereas in the case of isomer **2a** they are in position 1 and 3, while it is known that closer arrangement of nitro groups in isomers increases $\Delta H_{f(g)}^{298}$ [15].

2.2. IR Spectra and Frequency Analysis

The IR absorption spectra are shown in Fig. 4. Compounds **1a,b** containing hydrogen are characterized by the intense absorption bands associated with vibrations of hydrogen bonds. Thus the most intense peak in the region of $\sim 3553 \text{ cm}^{-1}$ of the spectrum of compound **1a** corresponds to stretching vibrations of $N - H$ bonds, and the peak in the region of $\sim 398\text{--}358 \text{ cm}^{-1}$ corresponds to out-of-plane bending vibrations of the same bonds. The intense absorption bands in the region of $\sim 911 \text{ cm}^{-1}$ are associated with bending vibrations in the pyrazole rings, and in region of $\sim 1604 \text{ cm}^{-1}$ – with stretching vibrations of $C = C$ bonds in the benzene ring. The intense peak in the region of $\sim 1591 \text{ cm}^{-1}$ of the **1b** spectrum can be attributed to the stretching vibrations of the $C = C$ bonds in the pyrazole rings, and the peaks in the region of $\sim 1444\text{--}1297 \text{ cm}^{-1}$ to the bending vibrations of $C - H$ bonds. Compounds **2a,b,c** are characterized by intense absorption bands associated with vibrations in nitro groups. The intense absorption bands in the region of $\sim 1667\text{--}1555 \text{ cm}^{-1}$ and $\sim 1263\text{--}1255 \text{ cm}^{-1}$ of the **2a** and **2b**

spectra can be attributed, respectively, to asymmetric and symmetric stretching vibrations of $N - O$ bonds of nitro groups, and peaks in the region of $\sim 827 - 776 \text{ cm}^{-1}$ to bending vibrations of the same bonds. Peaks in the region of $\sim 1340 - 1328 \text{ cm}^{-1}$ of the **2a,b,c** spectra are associated with the stretching vibrations of $C - N$ bonds between the pyrazole rings and nitro groups. Peaks in the region of $\sim 1568 - 1550 \text{ cm}^{-1}$ of the **2c** spectrum can be attributed to the stretching vibrations of $N - O$ bonds of nitro groups, and peaks in the region of $\sim 840 - 797 \text{ cm}^{-1}$ with the bending vibrations in nitro groups. Peak in the region of $\sim 1605 \text{ cm}^{-1}$ corresponds to stretching vibrations of $C = C$ bonds in the pyrazole rings.

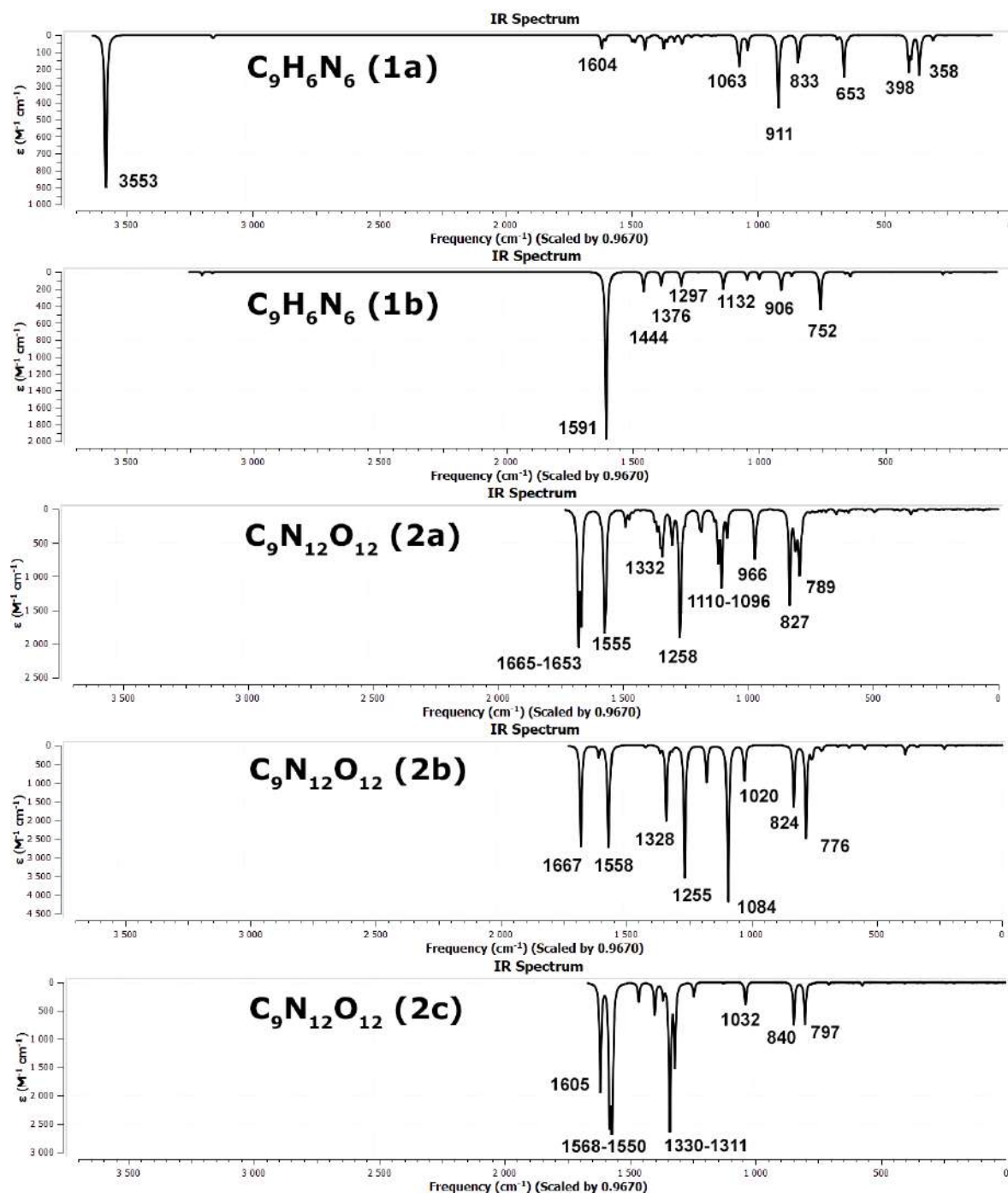


Figure 4. IR absorption spectra of the studied tetracycles **1a,b** and **2a,b,c** (calculation level: B3LYP/6-311+G(2d,p))

3. Computational Details

Quantum-chemical computations were carried out at Lomonosov Moscow State University Supercomputer Complex [16–18] (project 2312) and at the Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry of the Russian Academy of Sciences. Computations by the G4 and G4MP2 method using the Gaussian software package and by the G4MP2 method using the NWChem software package were carried out on the *volta2* section of the Lomonosov-2 supercomputer, equipped with Intel Xeon Gold 6240 processors (18 cores, 2.60 GHz, 1497.6 GFlop/s) and Nvidia Tesla V100 graphics accelerators (900-2G500-0010-000, 1246 MHz, 7 TFlop/s).

Gaussian uses its own Linda software for parallelization, but the distribution of tasks between processors of one node is not very efficient. G4MP2 calculations for compounds **1a,b** took about 7 hours, and G4 calculations took about 17 hours.

NWChem allows tasks to be distributed between several nodes using MPI, leading to a significant reduction in the time required to complete calculations. NWChem computations for compounds **1a,b** used two nodes and took about an hour, which is significantly faster than in the case of Gaussian. NWChem computations for molecules **2a,b,c** with large number of heavy atoms required four nodes for each task and took about 30–35 hours depending on the molecule.

Due to time limitations in the *volta2* section and particular qualities of the G4MP2 method within Gaussian program package computations using this method for compounds **2a,b,c** were carried out on a separate computing resource equipped with an Intel(R) Xeon(R) Gold 6140 CPU (2.30 GHz), 259 Gb RAM, and 20 TB of disk space, and took about 40 days. In such circumstances, it was impossible to perform the computation for **2a,b,c** substances using the most accurate G4 method (the computation time was estimated at several months approximately).

Conclusions

We computed the optimized geometry, IR absorption spectra, and enthalpy of formation in the gaseous phase of a series of tetracycles with a central benzene or [1,3,5]triazine ring annelated with three pyrazole rings. We analyzed the dependence between the enthalpy of formation and the structural parameters of the molecule (number and types of bonds, presence of functional groups). Gaussian and NWChem program packages were compared in terms of accuracy and time costs. In the cases, where the G4-level accuracy of the results is not required (the deviation from experimental data reaches 4 kJ/mol), the use of NWChem can significantly save computation time owing to the efficient distribution of tasks between nodes while maintaining an acceptable accuracy of the results. Within the Gaussian software package, time savings can be achieved using reactions in calculations, but the accuracy of the results, in this case, is reduced compared to NWChem. The obtained data on the enthalpy of formation becomes the basis for predicting the energetic possibilities of the considered compounds in high-energy compositions.

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