QUANTUM–CHEMICAL RESEARCH OF SOME IMIDAZOLE TETRAZINE DERIVATIVES

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Development of high-energy components of rocket fuels in IPCP RAS

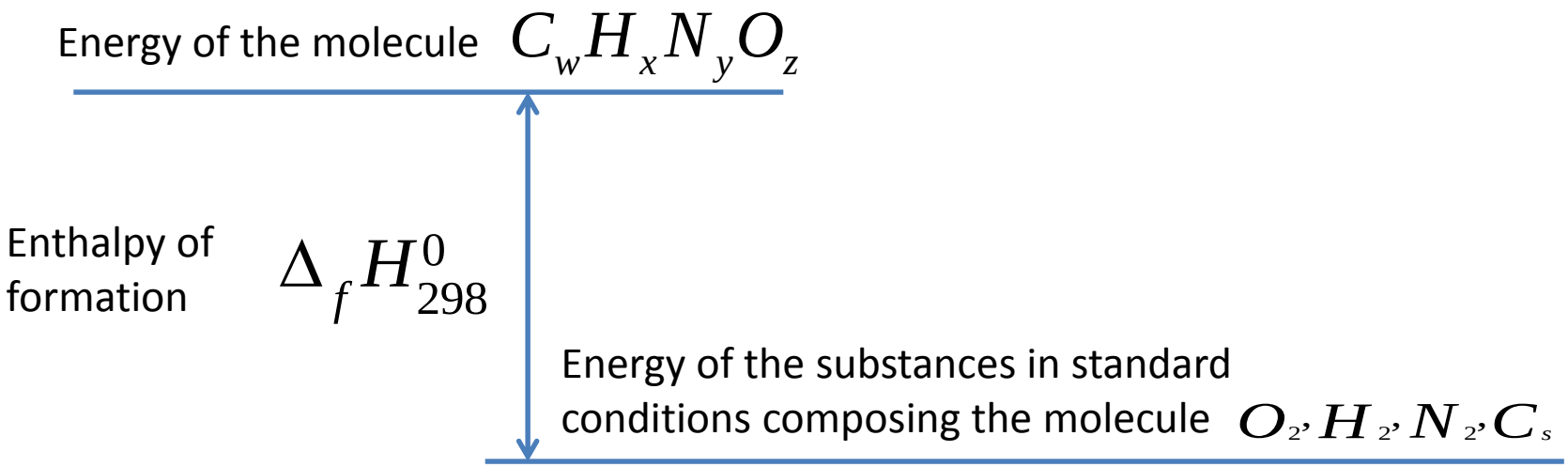
- IPCP RAS in collaboration with other RAS institutes (IOC) for more than 60 years has been developing high-energy substances.
- In recent years more attention is paid to quantum calculations of physical and chemical properties (Gaussian).
- Computer design of substances not yet synthesized.

FOCUS OF THE WORK – calculation of the enthalpy of formation, IR spectra and structure of new high-energy 5/6/5 tricyclic derivatives of 1,2,3,4- and 1,2,4,5-tetrazines by quantum-chemical ab initio methods (Gaussian 09).

Nowadays it is one of the most promising trends.

Enthalpy of formation

Compounds with a high enthalpy of formation are extremely demanded in rocket technology as fuel components, because when they burn, a lot of energy is released. The main characteristic of the released energy is the enthalpy of formation



Quantum-chemical ab initio calculations

Stationary Schrödinger Equation

$$H(\vec{r},\vec{R})\psi(\vec{r},\vec{R}) = E\psi(\vec{r},\vec{R})$$

Hamiltonian of a polyatomic molecule

$$H = \sum_i T_i + \sum_\alpha T_\alpha + \sum_{i>k} V_{ik} + \sum_{i,\alpha} V_{i\alpha} + \sum_{\alpha>\beta} V_{\alpha\beta} + V_{so}$$

Electronic and nuclear kinetic energies

Electronic and nuclear Coulomb interaction energies

Spin-orbital interaction

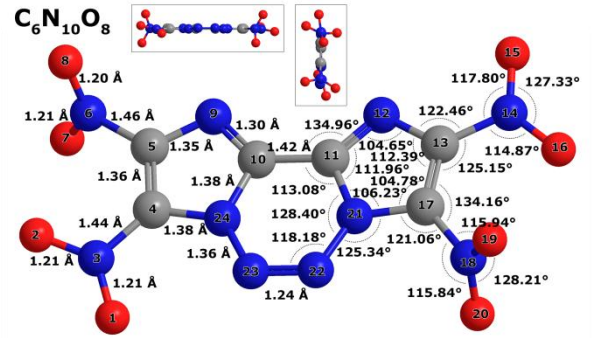
Approximations of ab initio calculations

- Adiabatic approximation - the kinetic energy of nuclei is neglected
- Self-consistent field - the electron moves in the effective field of the remaining electrons
- Rectification of the electron correlation

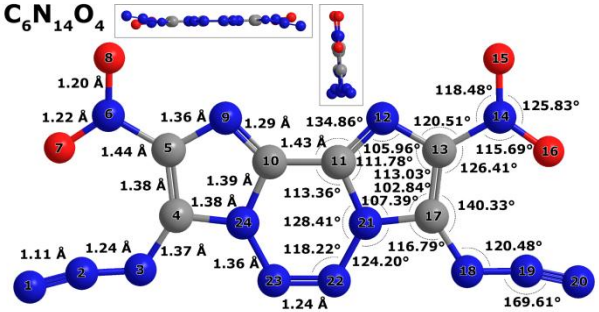
Molecules under consideration $C_6N_{10}O_8$ and $C_6N_{14}O_4$

Calculation level: **ωB97XD/aug-cc-pVTZ**

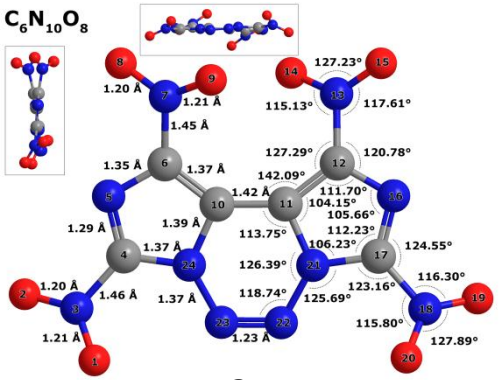
1,2,3,4-tetrazines



1a

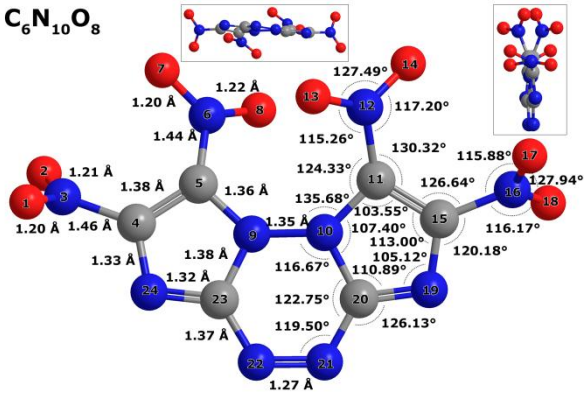


2a

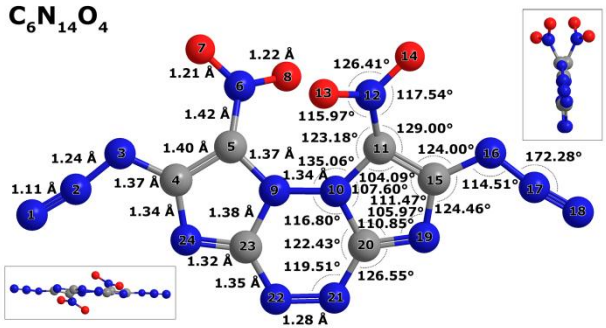


3a

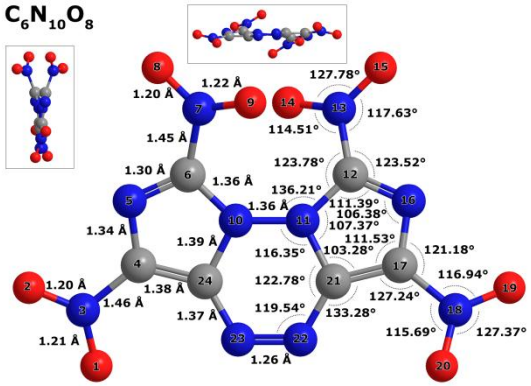
1,2,4,5-tetrazines



1b



2b



3b

Two approaches to calculating the enthalpy of formation

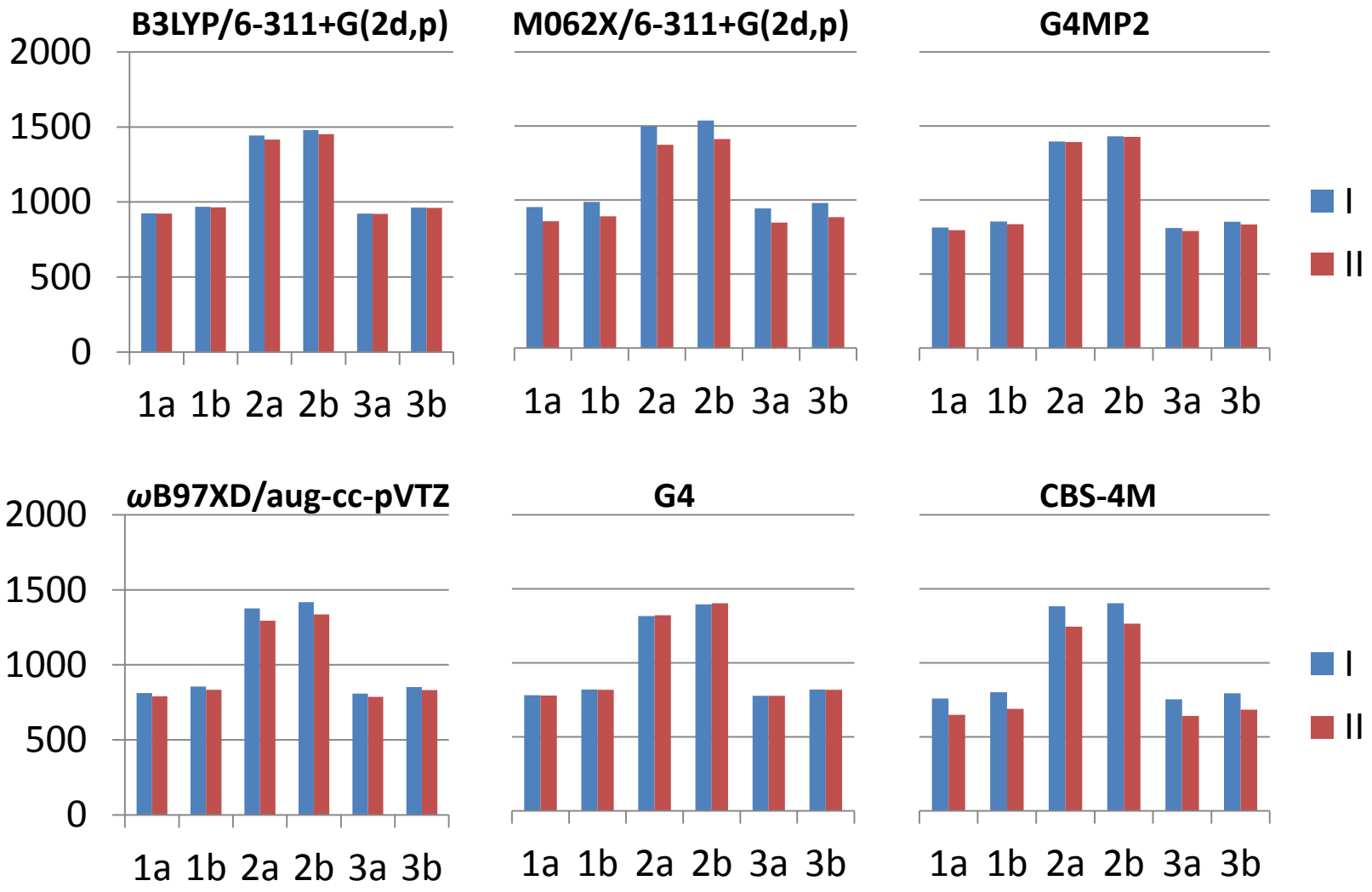
The atomization reaction

$$\Delta H_f(I): xC(g) + yN(g) + zO(g) = C_xN_yO_z(g)$$

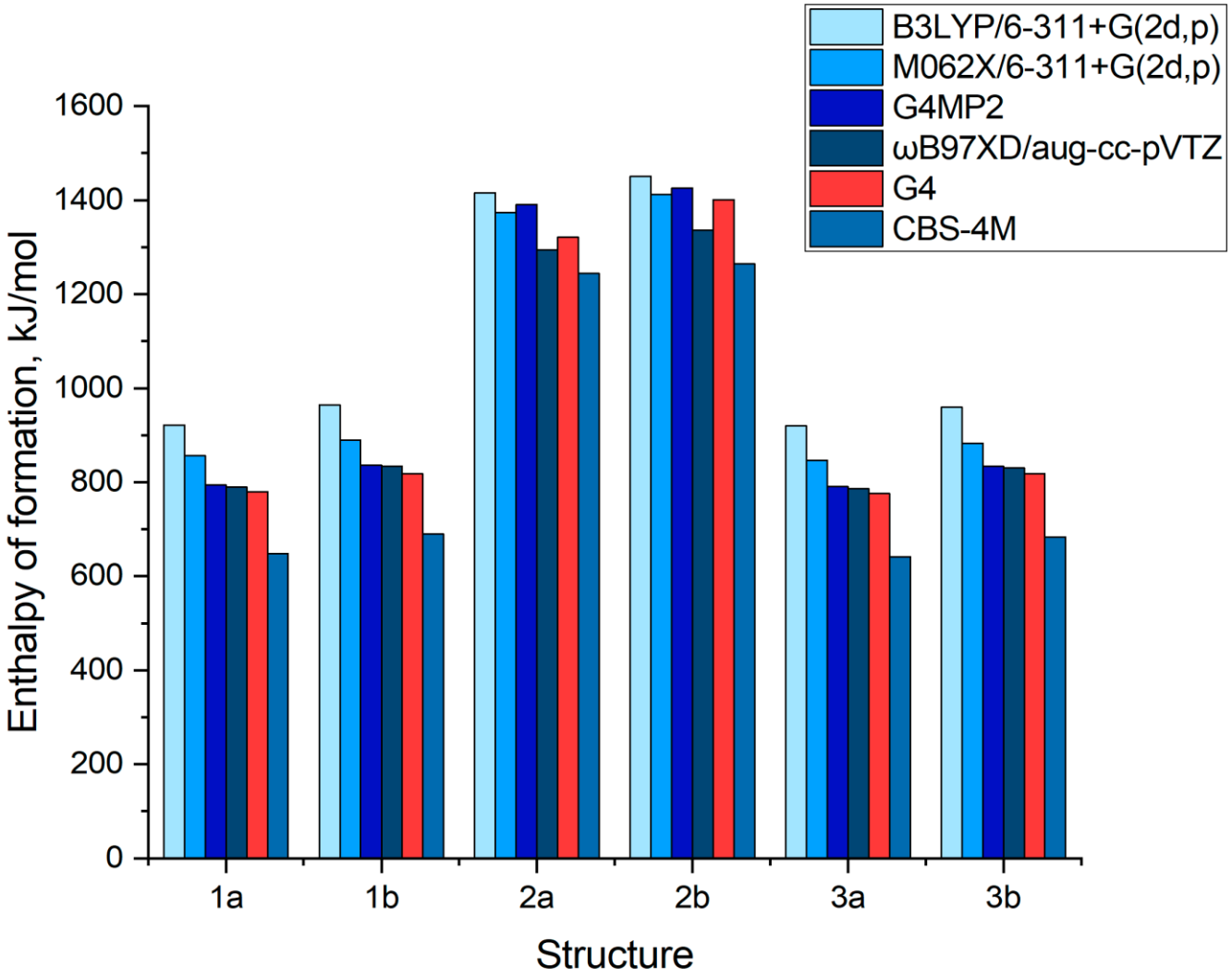
The reaction of formation of the compound from simple substances

$$\Delta H_f(II): xC(g) + (y/2)N_2(g) + (z/2)O_2(g) = C_xN_yO_z(g)$$

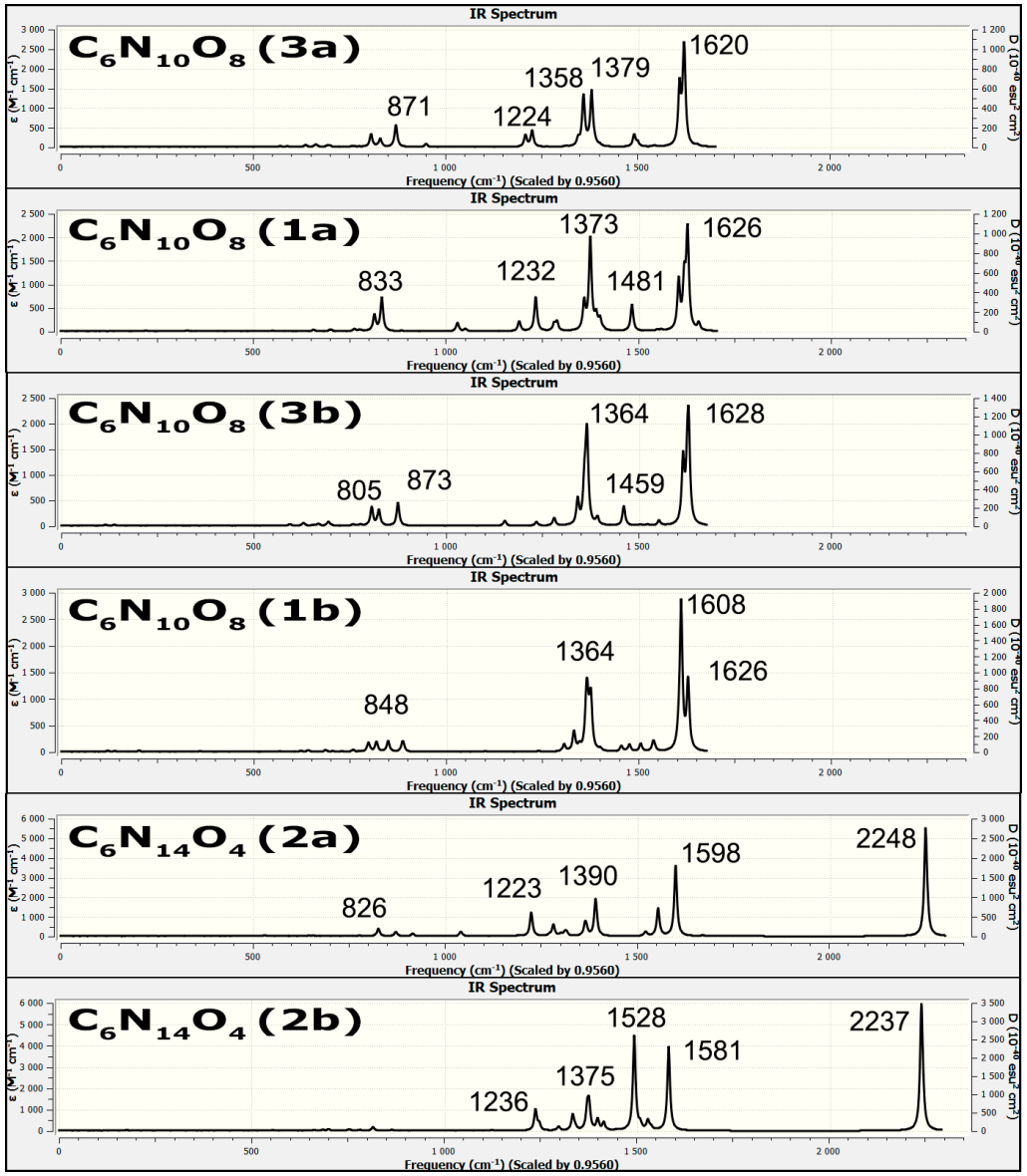
Comparing two approaches to calculating the enthalpy of formation



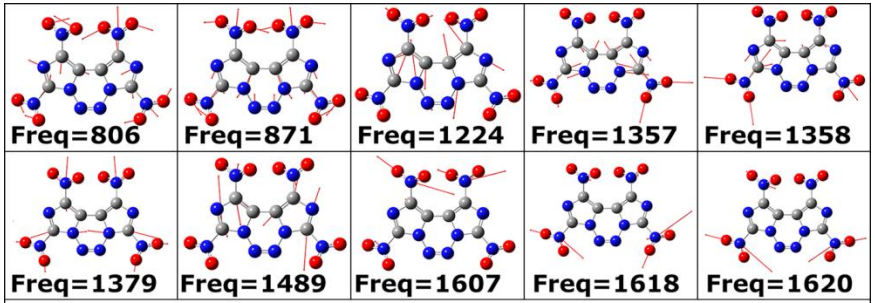
Calculated values of the enthalpy of formation



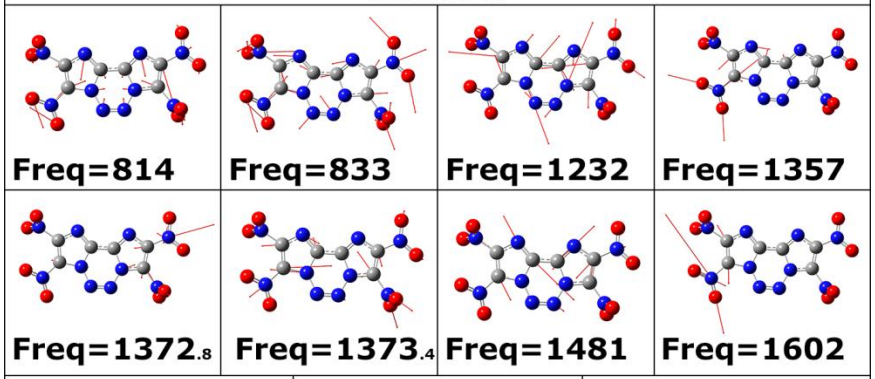
The IR absorption spectra

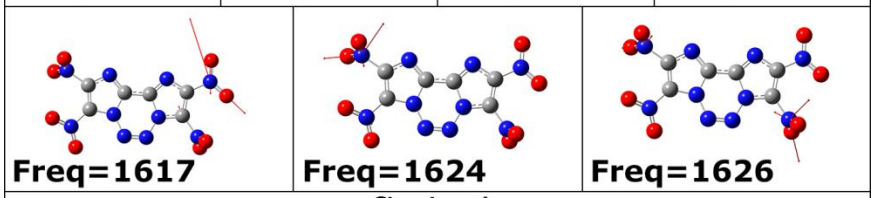


Atom displacements for the most intense vibrations

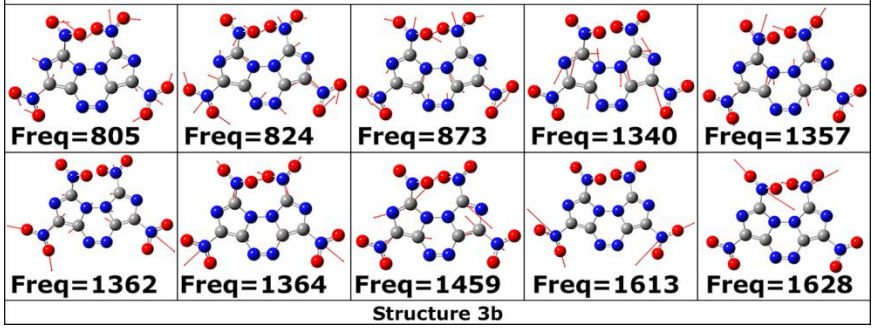


Structure 3a

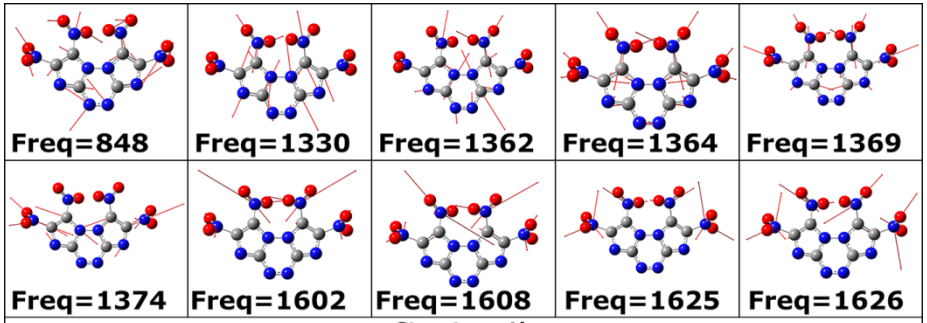




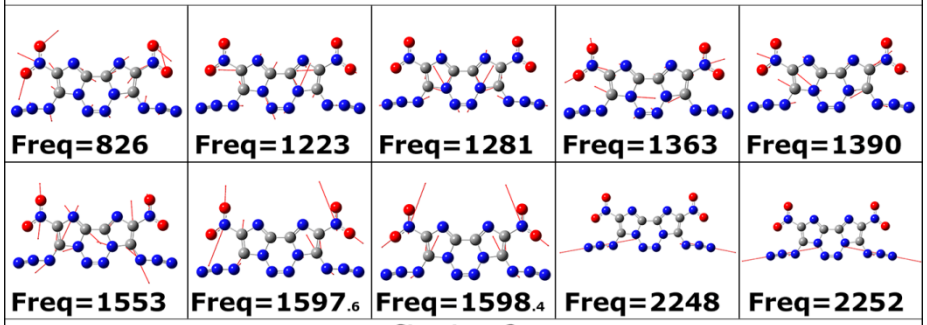
Structure 1a



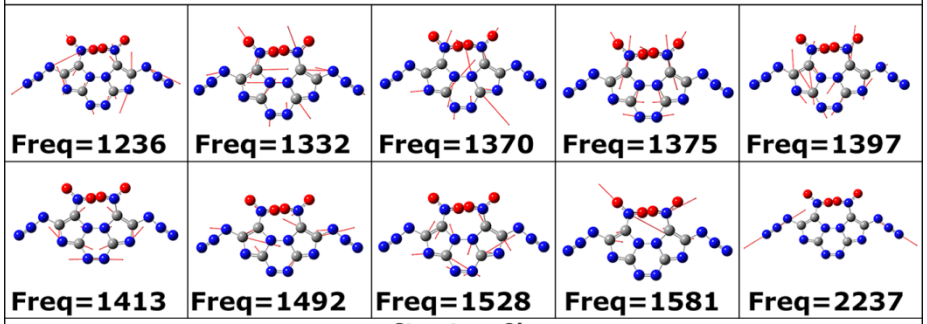
Structure 3b



Structure 1b

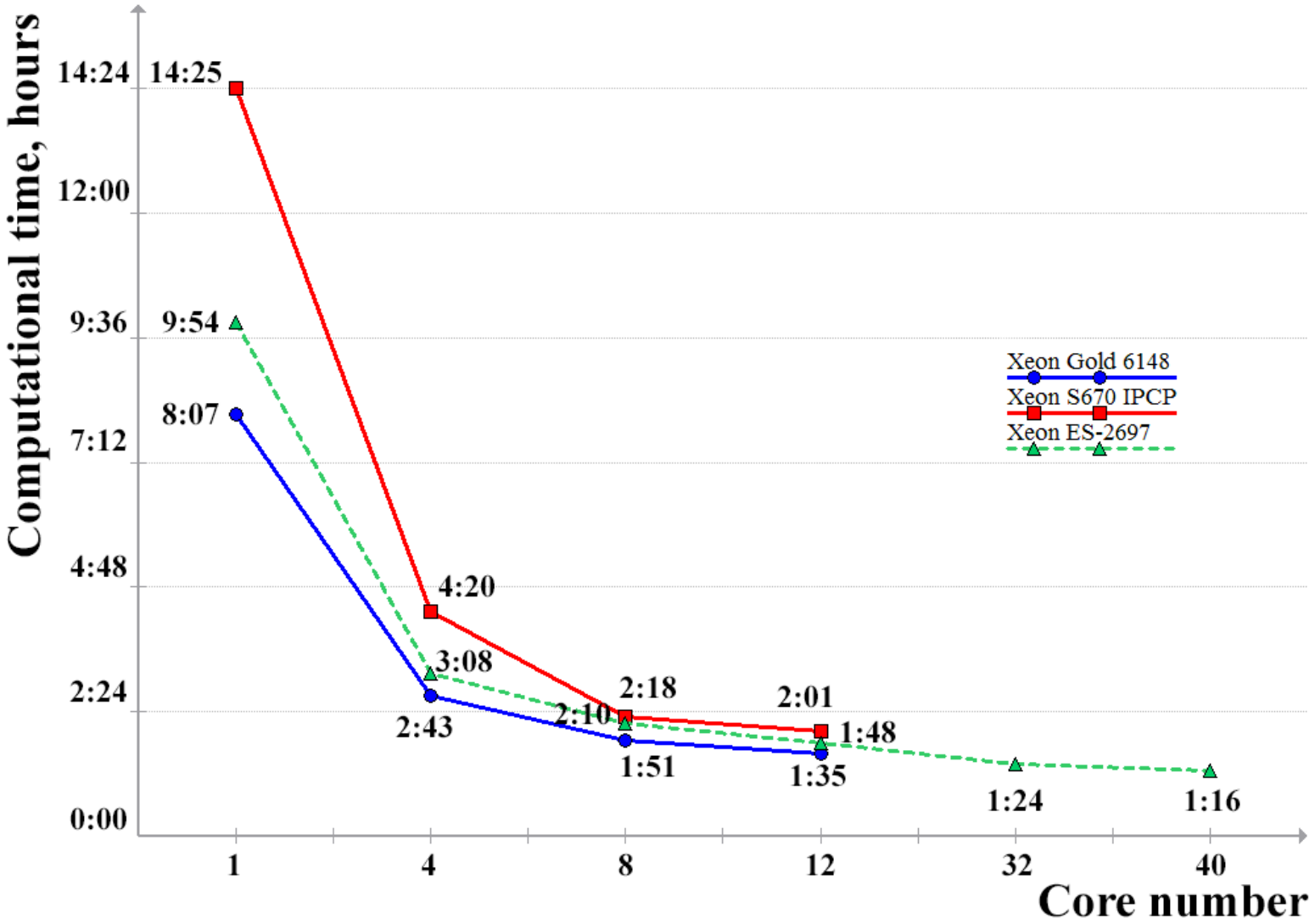


Structure 2a



Structure 2b

Computational details



Conclusions

- Geometric and thermochemical parameters of imidazole derivatives of 1,2,3,4- and 1,2,4,5-tetrazines in the gas phase have been obtained by ab initio quantum-chemical methods (Gaussian 09).
- Calculations by methods of varying complexity and by two different approaches for determining the enthalpy of formation have been compared.
- The values of the enthalpy of formation of the considered molecules in the gas phase lie within the range of 776–1402 kJ/mol (G4). The replacement of the NO_2 group by the N_3 group in the structures under consideration leads to a noticeable increase (more than 500 kJ/mol) of the enthalpy of formation.
- Structures based on 1,2,4,5-tetrazine are characterized by higher enthalpy of formation than those based on 1,2,3,4-tetrazine.

The work was performed using the equipment of the Center for Collective Use of Super High-Performance Computing Resources of the Lomonosov Moscow State University.

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THANK YOU FOR THE ATTENTION!