ФЕДЕРАЛЬНЫЙ ИССЛЕДОВАТЕЛЬСКИЙ ЦЕНТР ПРОБЛЕМ ХИМИЧЕСКОЙ ФИЗИКИ И МЕДИЦИНСКОЙ ХИМИИ РАН

**FEDERAL RESEARCH CENTER
OF PROBLEMS OF CHEMICAL PHYSICS AND MEDICINAL CHEMISTRY RAS**

QUANTUM-CHEMICAL STUDY OF HIGH-ENERGY DERIVATIVES OF TRIS(1,2,4-TRIAZOLO)-1,3,5-TRIAZINES

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Russian Supercomputing Days 2025

Development of high-energy components of rocket fuels in FRC PCP MC RAS

- FRC PCP MC RAS in collaboration with other RAS institutes 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.

High-energy density materials (HEDM)

- military affairs
- mineral exploration
- rocket and space technology
- construction
- metallurgy
- mining

Enthalpy of Formation (ΔH_f): Why and How

- Key thermodynamic parameter for evaluating **energy content** and **stability** of compounds
- Determines **potential performance** of high-energy materials
- Can be obtained via:
  - **Experiment** (e.g. calorimetry)
  - **Quantum-chemical calculations**
- We focus on **theoretical prediction** of ΔH_f for new, unsynthesized compounds

Enthalpy of formation
$\Delta_f H^0_{298}$

Prediction before synthesis!

Computational Tools: Gaussian and NWChem

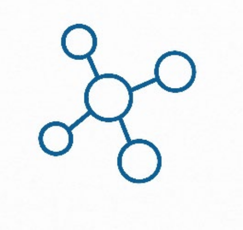
Gaussian
- Widely used commercial quantum chemistry software
- Broad selection of methods and basis sets
- User-friendly interface, extensive documentation

NWChem
- Open-source and scalable for large systems
- Optimized for high-performance computing
- Flexible and script-based — ideal for automation

Both are used to compute **optimized geometries**, **electronic energies**, and **thermodynamic properties** including ΔH_f

What Quantum Chemistry Software Actually Does

Molecular structure → Solve Schrödinger equation → Get electron distribution, energy → Add vibrations and thermal effects



Ψ E_{total}

Thermodynamic properties: ΔH_f, S, C_p

Stationary Schrödinger Equation

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

Hamiltonian of a polyatomic molecule

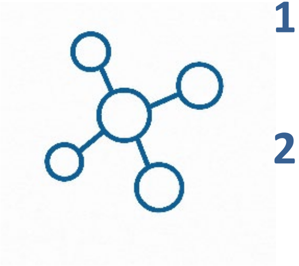
$$\hat{H} = \underbrace{\sum_{i}\hat{T}_i + \sum_{\alpha}\hat{T}_\alpha}_{} + \underbrace{\sum_{i>k}V_{ik} + \sum_{i,\alpha}V_{i\alpha} + \sum_{\alpha>\beta}V_{\alpha\beta}}_{} + V_{so}$$

Electronic and nuclear kinetic energies

Electronic and nuclear Coulomb interaction energies

Spin-orbital interaction

General Workflow for Quantum-Chemical Investigations



1. **Geometry optimization**
   – Find the most stable 3D structure (lowest energy configuration)
2. **Frequency analysis**
   – Confirm the structure is a true minimum (no imaginary frequencies)
   – Compute zero-point energy and thermal corrections
3. **Single-point energy calculations**
   – Use higher-level methods on the optimized structure
4. **Reference reactions or atomization scheme**
   – Compute ΔH_f using a thermodynamic cycle or isodesmic reaction

Calculating the enthalpy of formation

Atomization approach

- Calculate total energies of the molecule and its constituent atoms
- Use the atomization energy to derive ΔH_f
- Pros: conceptually simple, directly related to total energies
- Cons: sensitive to calculation accuracy for open-shell atoms

$$\Delta H_f: wC(g) + xH(g) + yN(g) + zO(g) = C_wH_xN_yO_z(g)$$

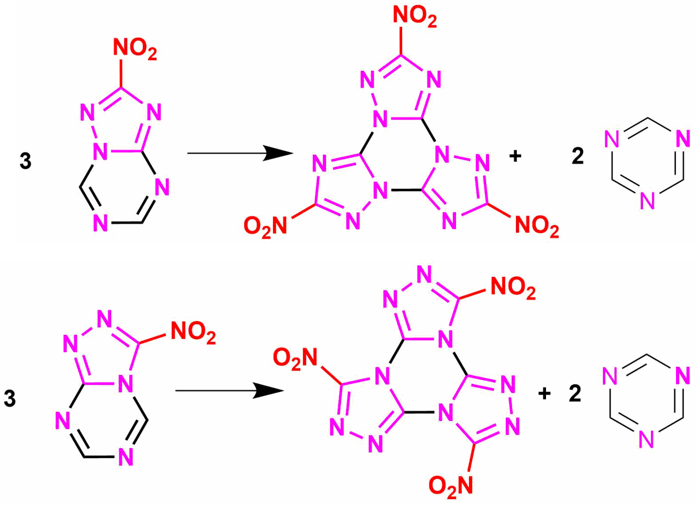
Isodesmic / reaction scheme

– Design a balanced reaction with similar types of bonds

– Compute ΔH_r and combine with known or computed ΔH_f of reference molecules

– Pros: cancels out systematic errors, often more accurate

– Cons: Requires careful selection of reference compounds



Quantum-chemical calculation methods

Gaussian:

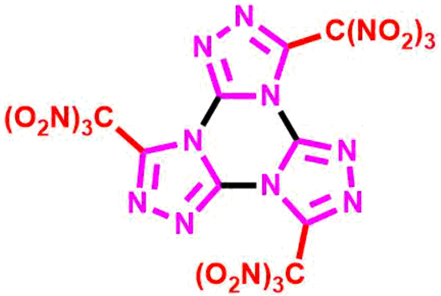
- **Density Functional Theory (DFT)**
  - **B3LYP/6-311+G(2d,p)**
    - Fast and widely used for geometry optimization
    - Good balance between speed and reasonable accuracy (~5 kcal/mol)
    - Often used as the first step before high-level methods
  - **B3LYP/cc-pVTZ**
    - DFT with correlation-consistent triple-ζ basis set
    - More reliable for optimized geometries and vibrational frequencies
    - Improves accuracy compared to split-valence basis sets
  - **ωB97XD/cc-pVTZ**
    - Long-range corrected hybrid functional with empirical dispersion (D)
    - Well-suited for noncovalent interactions and delocalized systems
    - Provides improved description of relative energies
- **G4MP2**
  - Composite method based on MP2 with corrections
  - Faster than full G4, but still quite accurate (~1–2 kcal/mol)
  - Suitable for series of compounds and energetic materials

NWChem: custom implementation of the G4MP2 protocol using available methods.

Molecules Under Study

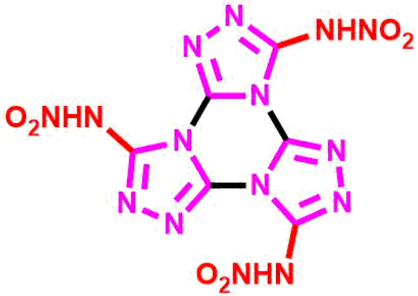
1a

1b



2

3



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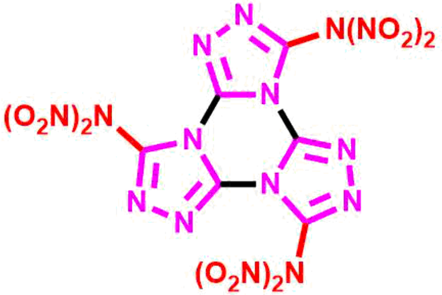

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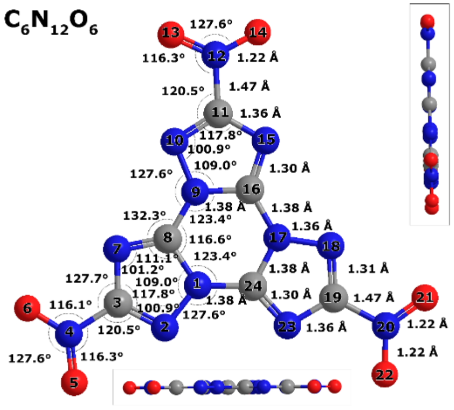
Hypothetical **tris(1,2,4-triazolo)-1,3,5-triazines** with explosophoric oxidizing groups: nitro (–NO_2) (**1a** and **1b**), trinitromethyl (–$C(NO_2)_3$) (**2**) nitroxy (–ONO_2) (**3**), nitramino (–$NHNO_2$) (**4**), or dinitramino (–$N(NO_2)_2$) (**5**) groups.

Optimized geometry

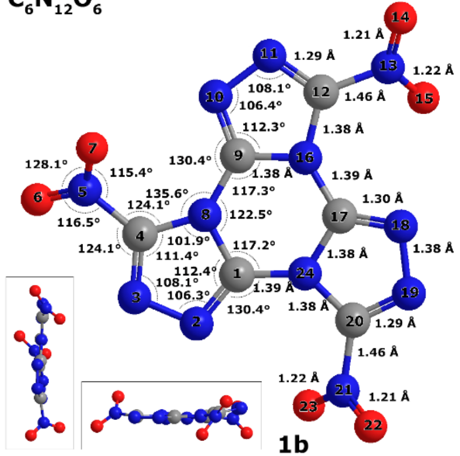
Calculation level: **B3LYP/6-311+G(2d,p)**

$C_6N_{12}O_6$



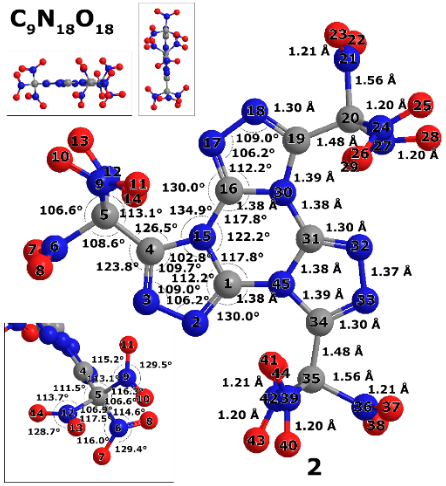
1a

$C_6N_{12}O_6$



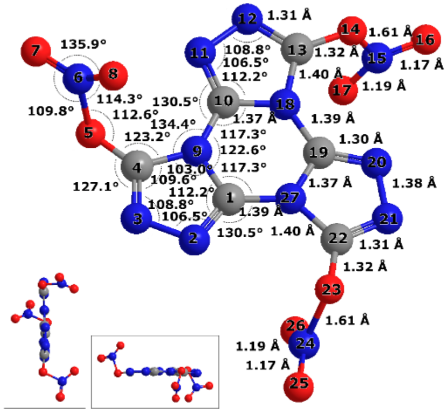
1b

$C_9N_{18}O_{18}$



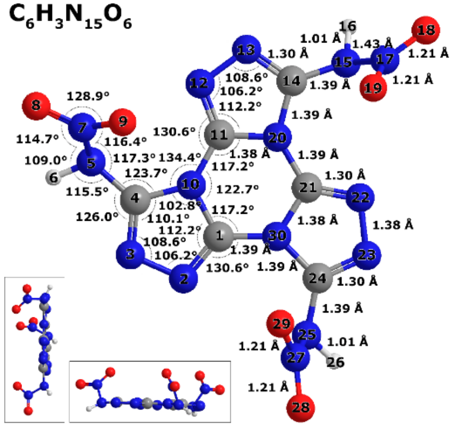
2

$C_6N_{12}O_9$



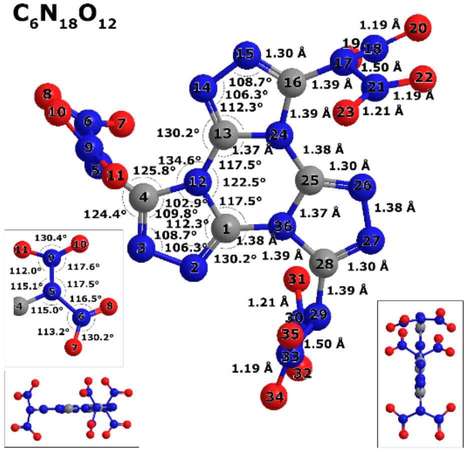
3

$C_6H_3N_{15}O_6$



4

$C_6N_{18}O_{12}$



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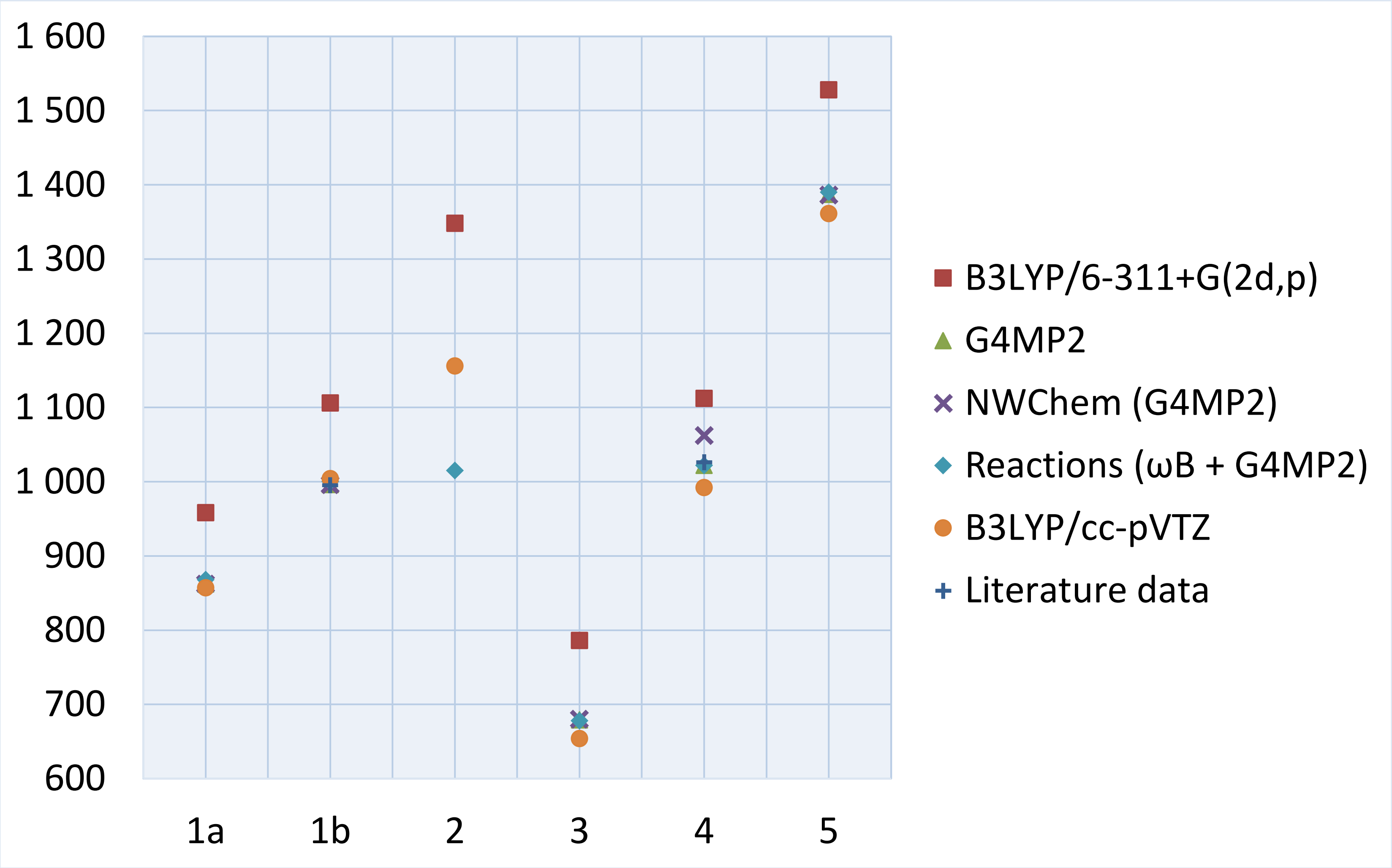
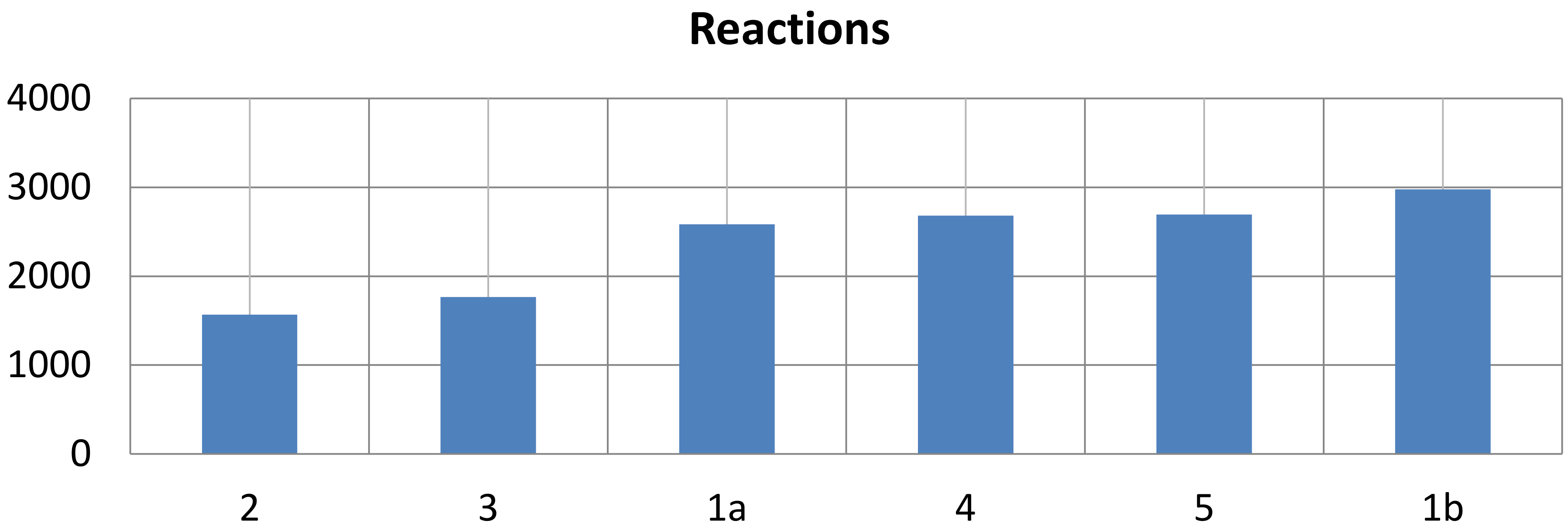
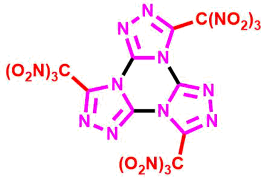
Enthalpy of formation, kJ/mol

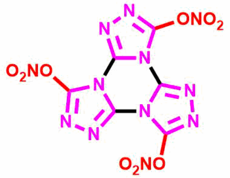


Specific enthalpy of formation, kJ/kg

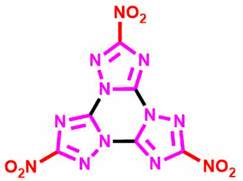




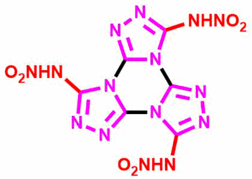
trinitromethyl
($–C(NO_2)_3$)



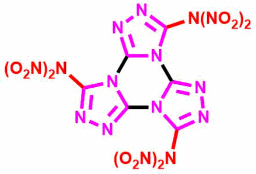
nitroxy
($–ONO_2$)



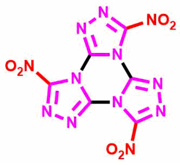
nitro
($–NO_2$)



nitramino
($–NHNO_2$)

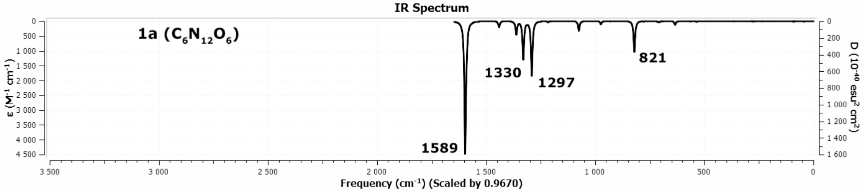


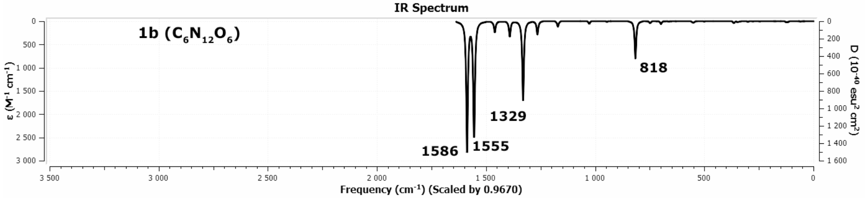
dinitramino
($–N(NO_2)_2$)

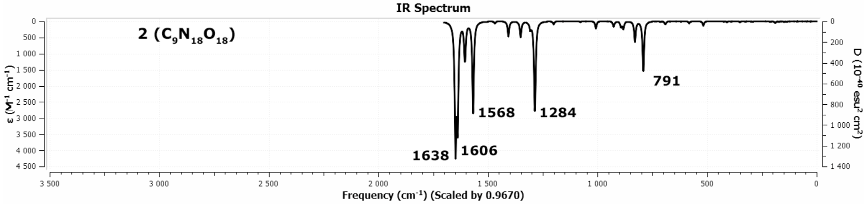


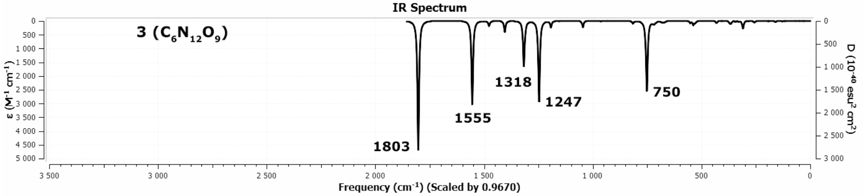
nitro
($–NO_2$)

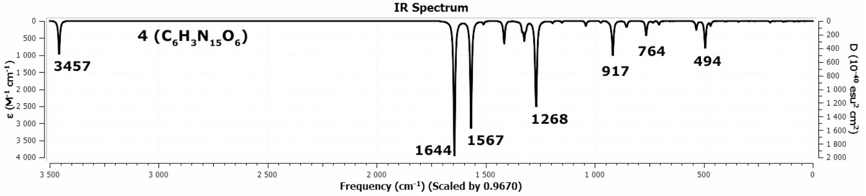
The IR absorption spectra

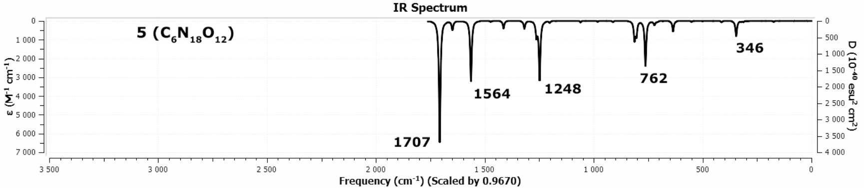












B3LYP/cc-pVTZ 0.967

1570–1555 cm^{-1}:
C–N bonds in the triazine - *stretching*

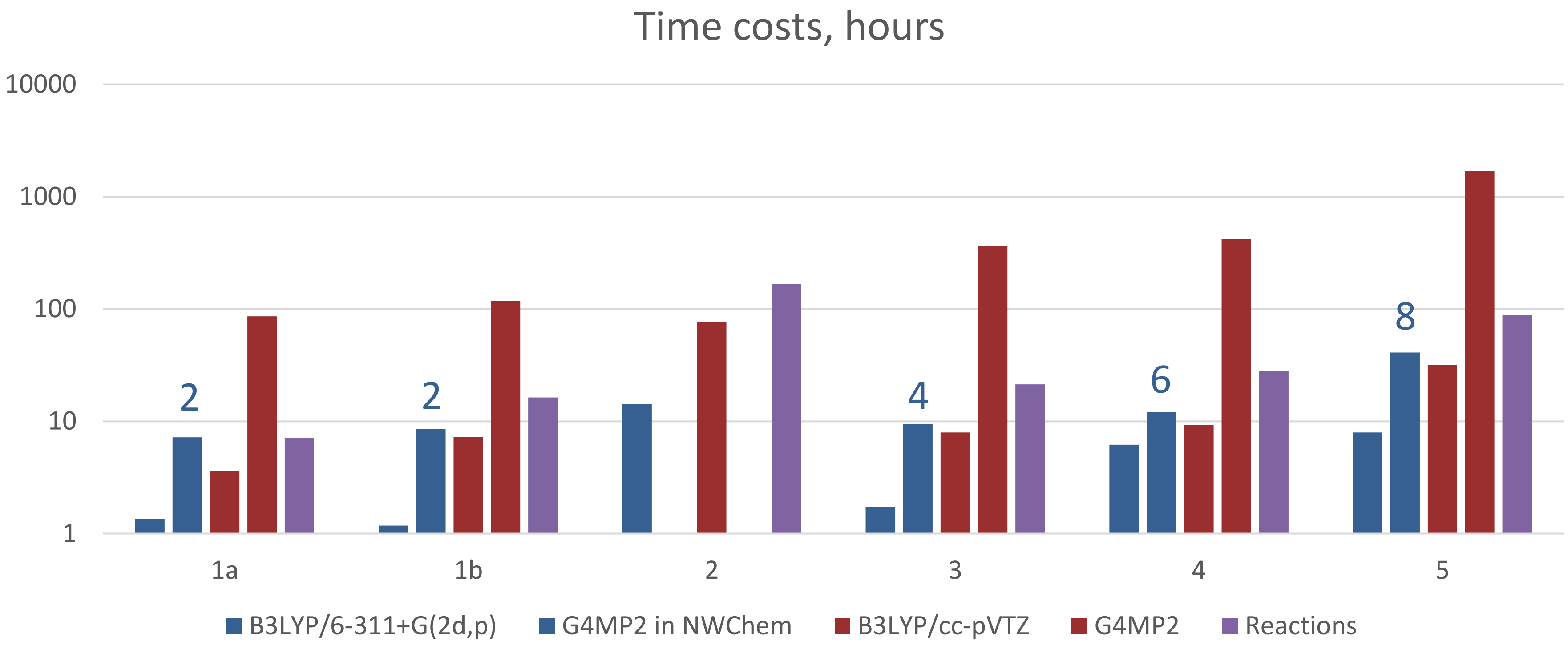
1644–1638 cm^{-1} in **2** and **4**:
N–O bonds in nitro groups - *asymmetric stretching*
~1586 cm^{-1} for **1b**
~1589 cm^{-1} for **1a**
~1800 cm^{-1} for **3**
~1700 cm^{-1} for **5**

820–750 cm^{-1} :
N–O bonds in nitro groups - *scissoring bending*

1290–1247 cm^{-1}:
C–N bonds in the triazoles – *stretching*

~3457 cm^{-1} and ~494 cm^{-1} in **4**:
N–H bonds - *stretching and bending*

Computational details



Volta2 (Lomonosov-2)

Intel Xeon Gold 6240 processors (18 cores, 2.60GHz - 1497.6 GFlop/s)
Nvidia Tesla V100 graphics accelerators (900-2G500-0010-000, 1246 MHz, 7 TFlop/s)
Time limit 48 hours

FRC PCP MC RAS

Intel Xeon Gold 6140 CPU (2.30 GHz, RAM 259 Gb, 20Tb disk space)

Conclusions

- Geometric and thermochemical parameters of high-energy tetracyclic compounds based on tris(1,2,4-triazolo)-1,3,5-triazines have been obtained by ab initio quantum-chemical methods (Gaussian 09 and NWChem).
- The enthalpy of formation was calculated using various methods and software packages. The atomization approach at the B3LYP/6-311+G(2d,p) level tends to overestimate ΔHf°, whereas B3LYP/cc-pVTZ, G4MP2, and the use of isodesmic reaction schemes yield more consistent results.
- The relationship between enthalpy of formation and structural features of the molecules was analyzed. The lowest specific enthalpy of formation (by mass) was observed for the compound containing trinitromethyl groups ($–C(NO_2)_3$), while the highest value was found for an asymmetric compound with nitro groups ($–NO_2$).
- Calculated IR spectra confirmed the presence of characteristic vibrations associated with key functional groups.
- The use of isodesmic reaction schemes significantly reduced computation time without compromising accuracy, making this approach efficient for the discovery of promising high-energy compounds.
- Thermodynamic analysis indicated that all proposed structures are theoretically stable, though some require experimental validation.

The work was performed using the equipment of the Moscow State University Supercomputer Complex (project 2312).

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THANK YOU FOR THE ATTENTION!