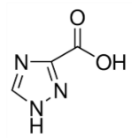
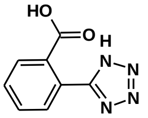
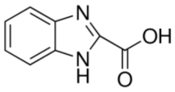
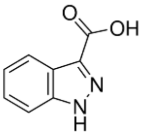
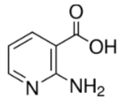
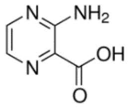
Summary

The aim of this study was to learn about conformational/tautomeric preferences and to analyze the photochemical activity of a selected group of N-heterocyclic compounds with a carboxylic group. The subjects of this study were six compounds showing structural differentiation:

 **1,2,4-triazole-3-carboxylic acid** **(TC)**	 **2-(tetrazol-5-yl) benzoic acid** **(TB)**
 **benzimidazole-2-carboxylic acid** **(BC)**	 **indazole-3-carboxylic acid** **(IC)**
 **2-aminopyridine-3-carboxylic acid** **(ANA)**	 **3-aminopyrazine-2-carboxylic acid** **(APA)**

The research methods used were the technique of isolation in low-temperature matrices coupled with infrared spectroscopy (FTIR) and quantum-mechanical calculations carried out using the DFT density functional method. The B3LYP and the B3LYPD3 functionals were applied for the calculations and the 6-311++G(2d, 2p) basis set was used.

As part of theoretical research, analyzes of conformational and tautomeric equilibria were conducted for all systems by determining the geometry of possible isomers of a given compound, estimating their energy and population. These calculations allowed the determination of the most stable forms of the studied molecules. Based on the analysis of infrared spectra of isolated compounds and theoretical spectra of optimized isomers, the composition of deposited low-temperature matrices was determined. The height of the energy barriers in the ground electronic state S_0 between the selected minima was also estimated, which allowed for the characterization of possible conformational and tautomeric transformations.

In the second part of the study, an analysis of photochemical processes under the influence of UV and NIR radiation was carried out for four acids: 2-(tetrazol-5-yl) benzoic, indazole-3-carboxylic, 2-aminopyridine-3-carboxylic acid and 3-aminopyrazine-2-carboxylic)

isolated in low-temperature matrices. Based on the analysis of the infrared spectra obtained in the experiment and their comparison with the theoretical spectra of isomers and possible photoproducts, paths of photochemical reactions of isolated compounds were proposed. These were various conformational transformations, amine-imine tautomerizations, and annular tautomerization. The table presents a summary of the photoisomerization reactions under the influence of UV and NIR radiation. The ✓ sign means the observation of phototransformation, while the ✗ sign means no such transformation.

Compound / type of phototransformation	**Conformational isomerization *cis*/*trans* COOH**	**Conformational isomerization rotamerization COOH**	**Annular tautomerization**	**Amine-imine tautomerization**
2-(tetrazol-5-yl) benzoic acid (TB)	✓	✗	✗	✗
Indazole-3-carboxylic acid (IC)	✓	✗	✓	✗
2-aminopyridine-3-carboxylic acid (ANA)	✗	✓	✗	✓
3-aminopyrazine-2-carboxylic acid (APA)	✓	✓	✗	✓

It was also observed that irradiating the matrices of isolated compounds with UV radiation induces, simultaneously with the photoisomerization processes, also the photolysis reactions of the studied systems. The analysis of the spectra recorded after irradiation and the theoretical results allowed detection a number of photoproducts and it was possible to suggest pathways of the photodecomposition reactions. It has been shown that the main products of photolysis are formed by decarboxylation and/or opening of heterocyclic rings.

In the course of experimental studies, it turned out that in the case of two compounds (1,2,4-triazole-3-carboxylic acid, benzimidazole-2-carboxylic acid), thermal decomposition processes occurring as a result of deposition were observed. However, the spectra obtained for these systems provided interesting information about these processes. It was shown that molecular complexes were formed from the products of thermal decomposition of the two compounds. Theoretical analysis of decarboxylation mechanisms was carried out.

The results presented in this paper demonstrate that matrix isolation in combination with quantum-mechanical calculations at the DFT level is an excellent tool for studying the molecular structure of isolated compounds, analysis of photochemical processes and investigation of molecular complexes. Both research methods significantly contributed to the knowledge of the properties of a selected group of N–heterocyclic compounds and allowed for a better understanding of the photoisomerization processes and photolysis of isolated molecules under the influence of UV and NIR radiation.