The structural changes in crystals brought about by the Norrish-Yang reaction in conditions of high pressure

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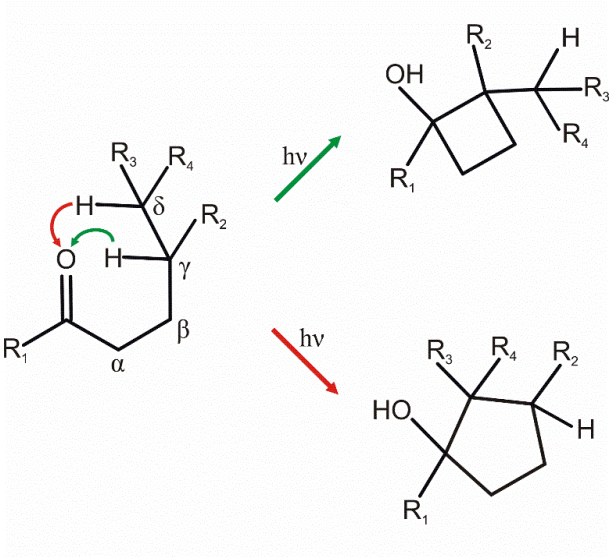
ABSTRACT

The aim of this research was the monitoring of structural changes brought about in crystals by high pressure, a photochemical reaction and both of these factors acting simultaneously. Owing to this, it was possible to learn of the influence of high pressure on the course of the photochemical reaction. The research method was X-ray structure analysis.

The studies were carried out for crystals of 8 compounds in conditions of various pressures. The first 7 compounds were the salts of 4-(2,4,6-triisopropylbenzoyl)benzoic acid with the following amines: (*S*)-(–)-1-phenylethanamine, 1-phenylmethanamine, 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane, methanamine, propan-1-amine, propane-1,2,-diamine and with sodium hydroxide. Compound 8 was the salt of 6,6-diethyl-5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid with (1*S*)-1-(4-methylphenyl)ethanamine.

Apart from the salt 4-(2,4,6-triisopropylbenzoyl)benzoic acid with sodium hydroxide, which is photostable in the solid state, in crystals of all remaining compounds the Norrish-Yang reaction occurs. In crystals of the salt of 4-(2,4,6-triisopropylbenzoyl)benzoic acid with (*S*)-(–)-1-phenylethylamine, besides the Norrish-Yang reaction, the Yang cyclization leading to the formation of a 5-member ring also takes place.



The Norrish-Yang reaction (green) and the Yang cyclization leading to formation of a 5-member ring (red).

The influence of the photochemical reaction and high pressure on the crystal structure was analyzed by means of:

- changes in the unit cell parameters and volume
- changes in molecular geometry in the crystal lattice, especially in the reaction centre
- changes in intermolecular interactions, including hydrogen bonds
- changes in the size and shape of a reaction cavity

Also, the content of reactant and product molecules along with the reaction progress was monitored.

On the grounds of the conducted research, it was shown that:

- Pressure significantly influences the kinetic of the examined photochemical reactions.
- The main reason for the reaction rate slowdown is the reduction of reaction cavity volume.
- High pressure can change the direction of structural changes brought about by the photochemical reactions.
- The reaction center geometry, free space volume and intermolecular interactions are the factors determining the direction of the studied photochemical reactions.
- The molecular geometry of the reactant and product/products in the crystal lattice changes along with the changing proportions between these components.
- Although compounds 1-7 belong to the same group (they are the salts of 4-(2,4,6-triisopropylbenzoyl)benzoic acid), the course of the photochemical reaction in crystals of each of them differs. The organic anion studied in crystals may undergo different types of reactions and in more than one manner, or it can be photostable.

The research presented provides evidence of a huge impact of the crystal lattice on the course of the photochemical reactions. It primarily shows the efficiency of high pressure as a factor modifying the properties of crystalline materials.