ABSTRACT

The influence of pressure on structural transformations induced by the [2+2] photodimerization in crystals

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The aim of the studies carried out within the doctoral thesis was the monitoring of structural transformations in crystal lattices induced by: the [2+2] photodimerization, high pressure and both these factors acting simultaneously. The comparison of the results of these studies for only one factor with the results for both factors made it possible to know and understand the modifications of the reaction path by pressure.

The research method was the X-ray structure analysis of single crystals.

In conditions of various pressures, crystals of the following compounds were studied:

- (2*E*)-3-(2,6-difluorophenyl)prop-2-enoic acid (**1**)
- (2*E*)-3-(2,5-difluorophenyl)prop-2-enoic acid (**2**)
- (2*E*)-3-(3,5-difluorophenyl)prop-2-enoic acid (**3**)
- (2*E*)-3-(4-chlorophenyl)prop-2-enoic acid (**4**)
- (2*E*)-3-(4-chlorophenyl)prop-2-enamide (**5**)
- (2*E*)-3-(2H^5)phenyl(2H^2)prop-2-enoic acid (**6**)
- 1,3-dihydroxy-4-chlorobenzene and *trans*-1,2-*bis*(4-piridyl)ethylene (**7a,b**).

In crystals of compounds **1**-**7** the [2+2] photodimerization proceeded.

The parameters, which underwent changes owing to the photochemical reaction and owing to the increase of pressure, and which were monitored read:

- unit cell parameters
- volume of free spaces between molecules
- intermolecular interactions and their geometry
- changes in the position of molecules
- geometry/shape of molecules

The content of reactant and product molecules in crystals along with the reaction progress was also monitored.

The influence of pressure on the magnitude and character of the changes of the above-mentioned factors was analyzed. High pressure decreased the magnitude of geometrical changes caused by the reaction in the crystals. It also brought about an increase in the reaction rate. The factors responsible for the increase of the reaction rate were changes in intermolecular geometry induced by high pressure.

Along with the reaction progress, both in atmospheric and high pressure conditions, the decrease of crystal quality for compounds **1** - **4**, **6** and **7** was observed. The differences in geometry of reactant and product molecules, as well as in the size and position of free spaces in a unit cell, had a significant impact on this phenomenon. In the case of compounds **1** - **3**, which are derivatives of cinnamic acid, the differences in reactivity in crystals were discussed.

The comparison of all the studied compounds determine the influence of packing (and free space volume) on the magnitude and speed of structural changes caused by the [2+2] photodimerization.

The studies carried out within this doctoral thesis show how far pressure and radiation can influence crystal structures, and how far pressure can modify the path of the [2+2] photodimerization.