

## Short note

## Photo-induced structural transformations in crystals at high pressure. Part 1. The crystallographic studies of the photochemical reaction at high pressure

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## ABSTRACT

The preliminary results of high-pressure X-ray diffraction studies of the intramolecular photochemical Norrish–Yang reaction in single crystals of the salt of 6,6-diethyl-5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid and (1*S*)-1-(4-methylphenyl)ethylamine are presented. The photo-induced changes in the cell parameters at high pressure along with the time of UV irradiation and the changes in the cell parameters along with pressure are discussed. The percentage change in the cell parameters brought about by the photochemical reaction at high pressure is similar to that at normal pressure. The cell volume decreases non-linearly with increasing pressure. The crystals lose their crystallinity above 2 GPa. This is the first paper in scientific literature on monitoring photochemical reactions in crystals at high pressure by X-ray diffraction.

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### 1. Introduction

The structural transformations proceeding in crystals and brought about by intra- and intermolecular photochemical reactions are the main subject of our research. In particular, we study geometrical changes in a reaction center and movements of molecules and molecular fragments in crystals [1–9]. For approximately ten years we have carried out crystallographic studies on monitoring photo-induced structural changes in crystals of organic compounds at normal pressure. Recently, we have undertaken studies at high pressure.

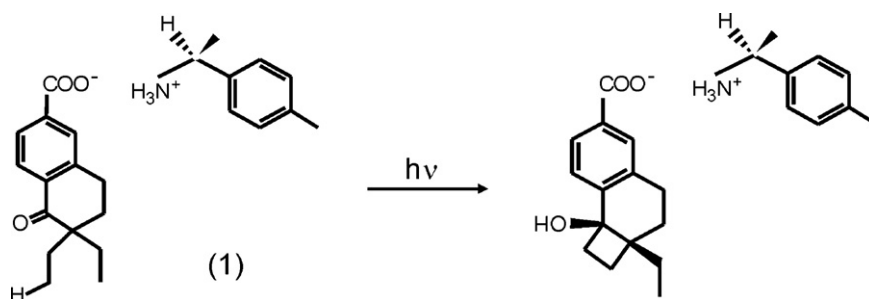
In scientific literature, we can find papers showing results of studies of pressure-induced chemical reactions. Until now, chemical reactions in crystals at high pressure have been reported for small molecular systems [10] like nitrogen, carbon dioxide, carbon monoxide and nitrous oxide, for simple unsaturated compounds, in particular, for hydrocarbons [10–16] such as acetylene, ethylene, propylene or butadiene, and aromatic compounds [10,11,17–23] like benzene, styrene, furane and thiophene. Most of them undergo polymerization, addition and amorphization. Some of the reported transformations were induced not only by high pressure itself, but simultaneously by electromagnetic (laser) radiation. In many cases,

the use of radiation made it possible to obtain a different compound with different properties. Such a situation was observed for polymerization of butadiene [10,11,24–26]. Most chemical reactions at high pressure were studied by means of spectroscopic methods, mainly IR and Raman, and only sometimes final products and their structures were characterized by X-ray diffraction methods, mainly powder diffraction. In scientific literature there are no papers on monitoring photochemical reactions in crystals at high pressure by X-ray diffraction.

High-pressure techniques are important and useful tools in material science. High pressure can induce various changes in crystal and molecular structures, for instance: shortening distances between neighboring atoms and molecules; changes in molecular orientation; a decrease in cell volume and volume of a reaction cavity and also a decrease in values of atomic displacement parameters [27,28]. It can bring about phase transitions and chemical reactions and influence their rate and direction.

In this paper, we present the preliminary results of the high-pressure X-ray diffraction studies of crystals of the salt of 6,6-diethyl-5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid and (1*S*)-1-(4-methylphenyl)ethylamine (**1**) undergoing the Norrish–Yang reaction (Scheme 1). The Norrish–Yang reaction was studied by us in the past for several compounds at normal pressure [4,6,7,9] and compound **1** was one of them [7]. The reaction consists of two steps. In the first step, a  $\gamma$ -hydrogen atom is abstracted and transferred to an oxygen atom of a carbonyl group and, as a result,

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**Scheme 1.** The equation of the Norrish–Yang reaction for compound **1**.

a 1,4-hydroksybiradical is formed. In the second step, named the Yang photocyclization, a cyclobutane ring may be formed from the biradical [29–31] (Scheme 1).

## 2. Experimental details

The experiments were carried out at high pressure and in darkness. The crystal of compound **1** was closed in a high-pressure Boehler–Almax diamond anvil cell (DAC) [32]. The values of the pressure in the DAC were determined on the grounds of the cell volume of quartz inserted into the DAC together with the crystal of compound **1**. The relationship between the pressure and the cell volume of quartz was taken from Angel et al. [33]. In the case of our experiments it was inadvisable to use a ruby crystal and a laser-induced fluorescence phenomenon as the measure of pressure (which is commonly done in high-pressure experiments [34,35]) owing to the photosensitivity of compound **1**. The set of collected reflections contained data coming from two diamonds, quartz and compound **1**. Nevertheless, it was possible to remove reflections coming from the diamonds and to group the remaining set into two separate parts: those coming from quartz and those from compound **1**, and to determine the cell parameters for both of them. The values of the pressure calculated from the above-mentioned relationship [33] were as follows: 0.66, 1.30 and 1.82 GPa. The X-ray data were collected using a CCD diffractometer and the cell constants were determined on the basis of 500 strongest reflections [36].

During the experiments we noticed a gradual decrease in the intensities of the reflections along with increasing pressure. Pressure higher than 2 GPa caused the total loss of crystal diffracting power. However, during this process the crystal did not change its external appearance.

In the next experiment for the second crystal of compound **1** (closed in the DAC together with quartz) at 0.61 GPa, we successfully induced the photochemical reaction using UV radiation. The crystal was irradiated in steps by means of a mercury lamp. The beam was filtered by a WG-320 glass filter. The filter blocked shorter and transmitted longer wavelengths: 0% transmittance for  $\lambda < 300$  nm, ca. 95% transmittance for  $\lambda = 350$  nm and 100% transmittance for  $\lambda > 365$  nm. Such wavelengths enabled us to carry out the reaction homogeneously [37,38]. The length of the time of irradiation was: 0, 60 and 240 min in total. After each irradiation we carried out high pressure data collection using the CCD diffractometer and determined the cell constants. Owing to the small size of the crystal of compound **1** (the last owned crystal) the cell constants were determined on the basis of 100 reflections, but with the same indices for all data collections.

## 3. Results and discussion

The photochemical reaction of compound **1** at normal pressure can be carried out in a single-crystal to single-crystal mode [7]. The

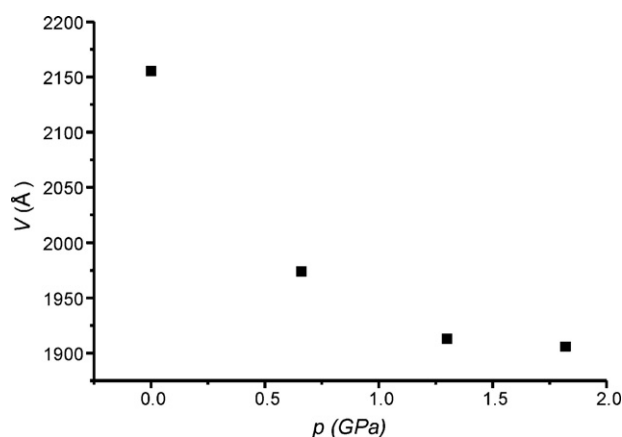
**Table 1**

The changes in the cell parameters of the crystal of compound **1** with the time of UV irradiation at 0.61 GPa.

	0 min	60 min	240 min
<i>a</i> (Å)	6.681(14)	6.820(15)	6.818(16)
<i>b</i> (Å)	11.68(4)	11.85(4)	11.86(4)
<i>c</i> (Å)	25.48(8)	24.65(9)	24.64(9)

same is possible in the case of the irradiation of compound **1** at high pressure. Owing to this, the crystal structure can be monitored by X-ray diffraction as the photochemical reaction proceeds at normal and high pressures. In this work, we monitored the cell constants. In the case of normal pressure, the parameters *a* and *b* increased slightly, but *c* decreased with the time of irradiation, namely by 2.0, 1.8 and –3.9%, respectively. The relevant data for the crystal of compound **1** studied at ca. 0.61 GPa are presented in Table 1. As can be noticed, the percentage change in the cell parameters brought about by the photochemical reaction at high pressure is very similar to that observed at normal pressure, namely 2.0, 1.5 and –3.3% for *a*, *b* and *c*, respectively. The values of the cell parameters change only slightly after 60 min of UV irradiation, which indicates that the photochemical reaction was almost completed after that time. In the case of normal pressure, but for a bigger crystal of compound **1**, the reaction reached 73% progression after 60 min [7]. These data indicate that the rate of the studied reaction in the high-pressure diamond anvil cell is quite similar to the rate observed at normal pressure (without the DAC). However, we cannot exclude the possibility of some change in orientation of the reacting ethyl group under high pressure. This means that, contrary to normal pressure, we cannot rule out the formation of two enantiomorphs of the product in crystals.

We also monitored the changes in the cell parameters of compound **1** along with the increase of pressure inside the DAC without



**Fig. 1.** The variations in the cell volume of the crystal of compound **1**, *V*, with the increase of pressure, *p*.

photoinduction. Fig. 1 presents the relevant data. As can be seen, the cell volume decreases by 3.4% with the increase of pressure, which is typical for molecular compounds [39,40]. The dependence is not linear. At the beginning the changes are bigger. This is understandable, because close intermolecular contacts in the crystal are then longer and it is easier to shorten them.

#### 4. Conclusions

For the first time, the results of monitoring of the structural changes (by the cell parameters) brought about by the photochemical reaction in crystals at high pressure are presented. We plan to extend the high-pressure studies of photochemical reactions to X-ray structure analysis.

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