



Structural transformations in crystals induced by radiation and pressure. Part 3. The pressure-induced structural changes *versus* the rate of the Norrish–Yang reaction in crystals



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ABSTRACT

The X-ray diffraction studies of the salt of 6,6-diethyl-5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid with (1S)-1-(4-methylphenyl)ethylamine were carried out at high pressure. The compound underwent the Norrish–Yang reaction in crystals brought about by UV–vis radiation. In order to understand the photoreactivity of the compound at high pressure, the structures of pure reactant crystals at 0.1 MPa and 1.8 GPa were compared in terms of the intramolecular geometrical parameters, the intermolecular interactions, the free space, the size of the reaction cavity and the cell parameters, which all changed with pressure. The course of the photochemical reaction was monitored at 1.0 GPa and 1.8 GPa. The changes in the unit cell parameters indicated that the reaction proceeded faster at 1.0 GPa than at 1.8 GPa, which was connected with the decrease of the volume of the reaction cavity and the increase of the intermolecular interactions at high pressure.

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1. Introduction

The Norrish–Yang reaction is widely examined with the use of X-ray diffraction and spectroscopic methods [1–12]. Nevertheless, mainly powder samples have been examined, spectroscopic methods have been used and ambient conditions have been applied. The studies of the Norrish–Yang reaction conducted for single crystals at high pressure with the use of X-ray diffraction methods are extremely rare [13–15], although such research is helpful in understanding a path which crystals follow during photochemical reactions.

A crystal lattice has a big impact on photochemical reactivity of molecules [1–3,5,16]. High pressure modifies structures of crystals, and in this way influences reactivity of molecules. For instance, it decreases volume and elasticity of a reaction cavity and in consequence lowers reactivity in crystals [17–19]. The detailed comparison of structure deformations brought about by high pressure with structure changes induced by a chemical reaction (including a photochemical reaction) in ambient conditions can rationalize molecular reactivity at high pressure [20,21].

In the previous work concerning the salt of 6,6-diethyl-5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid with (1S)-1-(4-

methylphenyl)ethylamine, compound **1**, the unit cell parameters at 0.6, 0.7, 1.3 and 1.8 GPa were presented for the compound before the photochemical reaction and at 0.6 GPa for a crystal irradiated during 60 and 240 min, however, no high-pressure crystal structure was given [13]. In the present paper, we analyze the high-pressure structure of a pure reactant crystal at 1.8 GPa and discuss the rate of the Norrish–Yang reaction at 1.0 and 1.8 GPa on the grounds of the determined structure and the changes in the cell parameters.

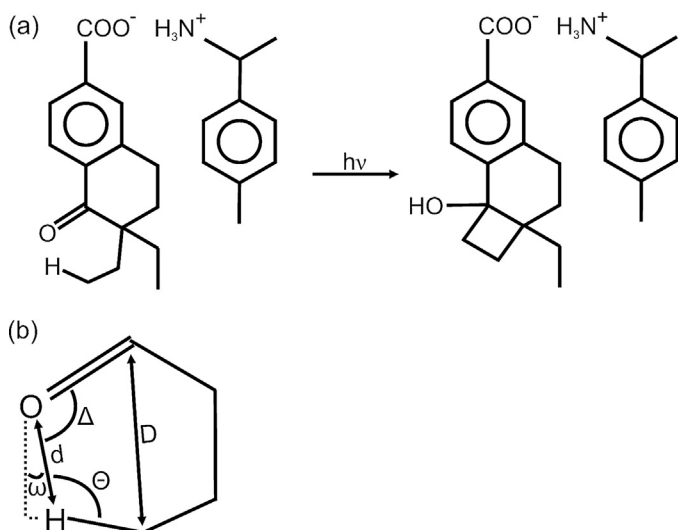
The Norrish–Yang reaction proceeds in two stages. In the first step a biradical is formed by γ -hydrogen transfer to an oxygen atom of a carbonyl group and in the second step a single covalent bond is formed between a γ -carbon atom and a carbon atom of a carbonyl group (Scheme 1a).

2. Materials and methods

The photochemical reaction was conducted at high pressure and in darkness. The high pressure in crystals was generated by closing them in a high-pressure Boehler-Almax diamond anvil cell (DAC) [22]. As a hydrostatic medium, a glycerine: water mixture (vol. 3:2) was used. The values of high pressure were determined using quartz as a pressure sensor. The relationship between the cell parameters of quartz and the values of high pressure was taken from Angel et al. [23]. The determined values of the high pressure

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Scheme 1. (a) The Norrish-Yang reaction for compound **1**. (b) The geometrical parameters describing the possibility of the Norrish-Yang reaction in crystals.

Table 1
Crystallographic data for the pure reactant crystal at 1.8 GPa.

Chemical formula	C ₃₀ H ₃₇ O ₃ N
Formula weight M _r	381.50
Crystal dimensions/mm	0.21 × 0.13 × 0.10
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.4744 (5)
b/Å	11.1855 (10)
c/Å	25.50 (2)
V/Å ³	1846.7 (15)
Z	4
D _x /Mg m ⁻³	1.372
μ/mm ⁻¹	0.089
T/K	299
Reflections collected	7921
Reflections independent	1085
Reflections observed	669
Completeness/%	36.84
R _{int}	0.1627
R, wR (F ² > 2σ(F ²)), S	0.077, 0.168, 1.05
Δρ _{max} , Δρ _{min} /eÅ ⁻³	0.16, -0.14

were 1.0 GPa and 1.8 GPa for crystals 1 and 2, respectively. In order to induce the Norrish-Yang reaction, both crystals were irradiated by a 100 W mercury lamp equipped with a water filter and a WG320 glass filter. The glass filter absorbed wavelengths shorter than 300 nm and transmitted longer ones with 50% transmittance

for 320 nm and ca 100% transmittance for longer than 365 nm. For this region both the applied diamonds and the hydrostatic medium transmitted all wavelengths. The filter ensured the energy of the beam from the end of the absorption tail of compound **1**, which helped to conduct the reaction homogeneously [24,25]. The time of irradiation was 5 min for crystal 1 at 1.0 GPa and 10 min for crystal 2 at 1.8 GPa. Both crystals were of the same size.

The data collections were carried out before and after irradiation of crystal 1 at 1.0 GPa and crystal 2 at 1.8 GPa using a CCD diffractometer and the CrysAlisPro software [26], which allowed the determination of the cell parameters. The quality of the data collected at 1.8 GPa before irradiation enabled us to determine the crystal structure. The structure was solved with SHELXS-2013/1 and refined with SHELXL-2014/7 [27,28]. All carbon atoms and a nitrogen atom were refined isotropically and all oxygen atoms anisotropically. Hydrogen atoms bonded to C24 were treated as a riding rotating group and the remaining ones as riding groups. In order to improve the model, FLAT restraints were applied on C5 → C10 (the benzene ring in the anion). The selected crystallographic data are given in Table 1. The full data can be found in the cif file (Supplementary data).

3. Results and discussion

The high-pressure structure of the pure reactant crystal of compound **1**, i.e. before UV-vis irradiation of the crystal, is presented in Fig. 1.

The sensitivity of compounds to the Norrish-Yang reaction in crystals is often assessed by five intramolecular geometrical parameters (Scheme 1b) [30–32]. Parameter *d* describes the distance between an oxygen atom of a carbonyl group and a γ-hydrogen atom, *D* is the distance between two carbon atoms that create the single covalent bond during the reaction. Parameters Δ, Θ and ω stands for the C=O...γH angle, the γC—γH...O angle and the angular displacement of γH from the plane of the carbonyl group. The values of the above parameters calculated for the crystal structure at 1.8 GPa are better than the respective values for 0.1 MPa (the ambient pressure) taken from reference [8] in terms of the proceeding of the reaction. They are closer to the ideal data (Table 2). The pressure-induced geometrical changes in the reaction center and in the molecule have also been shown in Fig. 2.

The characteristic feature of crystal structures of achiral carboxylic acids with primary chiral amines are columns of hydrogen bonds having the 2₁ symmetry [33]. In the case of the studied compound, such columns are created along the *a* axis (Fig. 3). With the increase of pressure from 0.1 MPa to 1.8 GPa, the geometry of the hydrogen bonds linkage changed. The donor-acceptor distances became shorter, which was expected, however, some angles also altered (Table 3). The biggest change in the D...A distance is ca -0.1 Å and in the D—H...A angle is 10°. Moreover, at

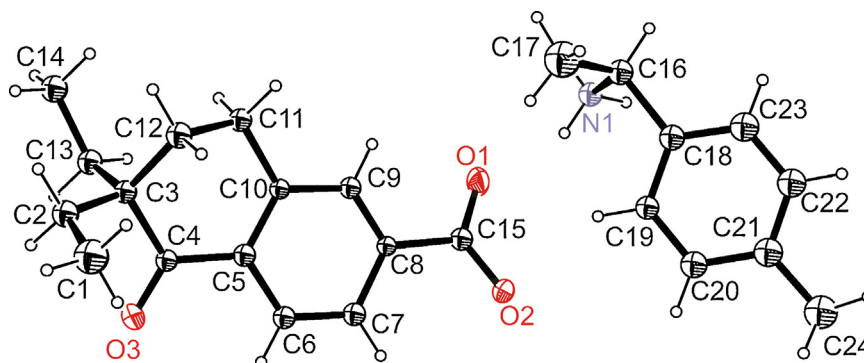


Fig. 1. The chemical species of compound **1** at 1.8 GPa drawn by means of the ORTEP software [29]. The displacements ellipsoids are drawn at the 20% probability level.

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