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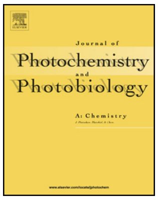

Steering photochemical reactivity of 2,4,6-triisopropylbenzophenonate anion in a crystalline state

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ABSTRACT

The Norrish–Yang reaction was conducted in crystals of benzylammonium, pyrrolidinium and ammonium 4-(2,4,6-triisopropylbenzoyl)benzoates (1–3). The crystal structures of 1–3, six structures of the partly reacted crystals of these compounds and the structure of the pure product crystal for 1 were determined. The content of the product in the partly reacted crystals allowed to calculate the values of the rate constants and the orders of the reaction for 1 and 3 by the JMAK model. The results indicated that the Norrish–Yang reaction proceeded homogeneously for 3 and according to a hybrid mechanism for 1. The rate constant was much higher for 3 than for 1. The differences in the reactivity were explained by the intramolecular geometrical parameters and intermolecular interactions mapped onto the Hirshfeld surfaces. The results showed that it is possible to largely change reactivity of the one organic species, even several hundred times, by modifying the crystal lattice in which it is embedded.

1. Introduction

The Norrish–Yang reaction is one of the most important photochemical reactions of ketones. It can proceed in solution, a vapour phase and a solid state, also including crystals. The equation of this reaction is shown in Scheme 1 (path a). The reaction consists of two steps [1]. In the first step, known as the Norrish type II reaction, a γ-hydrogen atom is abstracted and transferred to a carbonyl group, as a result of which a 1,4-diradical is formed. In the second stage, the Yang photocyclization, a new single bond and a cyclobutane ring are created. If a molecule contains a δ-hydrogen atom, then a 1,5-diradical and a five-membered ring can be formed (path b) [2]. 1,4- and 1,5-diradicals can also give rise to the formation of hydrol (path c). However, it is possible that the diradicals will not create rings and go back to the starting ketone.

In general, the fact whether a reaction proceeds in a crystalline state depends not only on the kind of molecules and substituents in them, but also on geometrical parameters of molecules and crystals and additionally experimental conditions. The set of molecular geometrical factors describing possibilities of a chemical reaction depends on the kind of reaction, for instance, it is different for the Norrish–Yang reaction [3–5] and for the [2 + 2] cycloaddition [6,7]. The formation of four and five-membered rings in the reactions shown in Scheme 1 is influenced by parameters d, D, ω, Δ and Θ depicted in Scheme 2. Molecular reactivity in a crystal is also influenced by surroundings, namely, free space near a reaction centre [8–11] and intermolecular interactions [2,8,12–14].

In the light of the above, it should be possible to largely modify reactivity of the one chemical species by modifying its surroundings in crystals. Different surroundings, in which it is embedded, can influence not only the size and shape of voids near a reaction centre and change intermolecular interactions, but also modify some intramolecular geometrical parameters of the species.

In this paper we will analyse the possibilities of steering reactivity of the one organic chemical species, 4-(2,4,6-triisopropylbenzoyl)benzoate, positioned in different crystals in ambient conditions. *o*-Isopropylbenzophenones and their derivatives are known for their photoreactivity [15,16]. Different forms of crystals containing the same chemical species were obtained by introducing different counterions. The bottom part of Scheme 1 presents the chemical formulas of the studied compounds, *i.e.* benzylammonium 4-(2,4,6-triisopropylbenzoyl)benzoate (compound **1**), pyrrolidinium 4-(2,4,6-triisopropylbenzoyl)benzoate (compound **2**) and ammonium 4-(2,4,6-triisopropylbenzoyl)benzoate (compound **3**). The work will also contain the results of monitoring changes proceeding in the crystal structures as the result of the reaction. As an experimental method, X-ray structure analysis was applied. This technique provides valuable information about atomic coordinates and displacement parameters.

2. Material and methods

2.1. Synthesis

The starting 4-(2,4,6-triisopropylbenzoyl)benzoic acid was prepared according to the procedures reported by Ito et al. [17].

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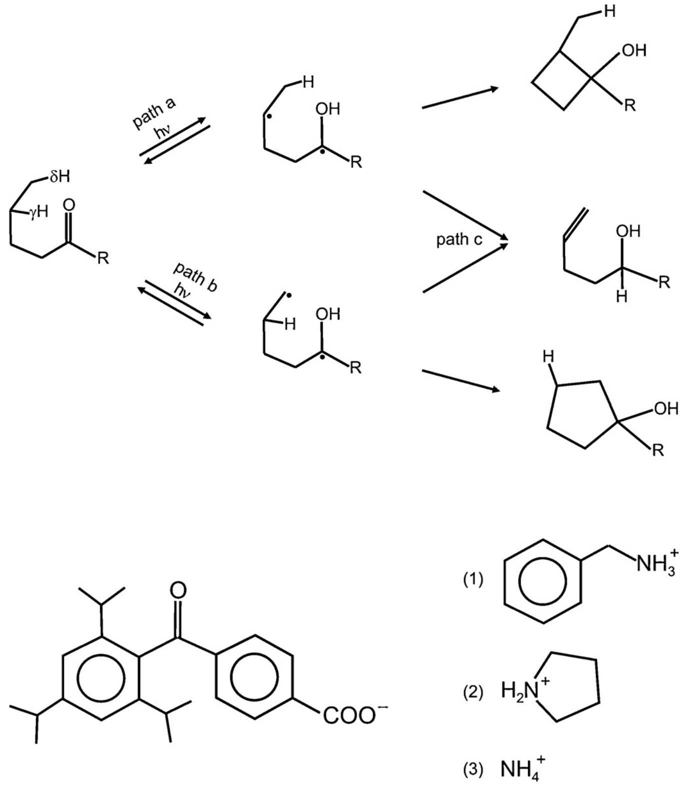
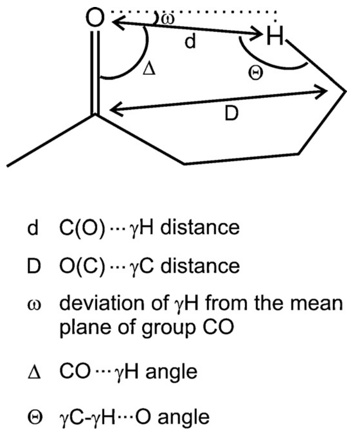


Scheme 1. The equation of the Norrish–Yang reaction and the formulas of the studied compounds.

Benzylamine and pyrrolidine were added to the acid dissolved in chloroform (1.1:1 and 1:1, respectively). After several days colourless crystalline products of compounds **1** and **2** were collected and recrystallized from ethanol and mixture of ethanol and chloroform (4:1), respectively. Aqueous ammonia was added to the acid (1:1) dissolved in methanol. The mixture was left for evaporation at room temperature, after which colourless crystals of compound **3** were collected.

2.2. Photoirradiation

All irradiations and X-ray diffraction experiments were conducted in darkness and in ambient conditions. The crystals were irradiated in steps using an Hg 100 W lamp equipped with BG-39 glass and water filters. Transmittance for the glass filter was: 0% for 320 > λ > 680 nm, about 55% for λ ≈ 350 nm and 95% for λ ≈ 460 nm. A water filter protected the crystals from over-heating. The crystals were situated in the same region of the UV beam and were rotated during irradiations. The direction of the beam was almost perpendicular to the longest crystal edges. The low energy of the beam (at the absorption tail) [18,19], the perpendicular direction, the rotation of the crystals during irradiations and additionally the thinness of the crystals ensured good penetration of the studied objects by UV radiation. It was noticed in the past, but also by other researchers [20] that very small crystals react in a much more homogeneous manner than macro crystals. The lengths of time of the irradiations of the crystals were in total: 0, 20, 60, 120, 240, 480 and 720 min for compound **1**, 0 and 5 min for compound **2** and 0 (crystal 1), 0.5, 1.0, 1.5 and 2.5 (crystal 2) min for compound **3**.



Scheme 2. The definition of the intramolecular geometrical parameters describing the possibility of the Norrish–Yang reaction.

2.3. X-ray crystallography

After each step of the irradiations, the X-ray data were collected [21]. The reflections were collected by means of a CCD diffractometer. For each data set the cell constants were determined. We observed that the values of the unit cell parameters were changing along with the time of irradiation (see Section 3). It should be said that changes in cell parameters could be a result of not only a photochemical reaction, but also a decrease of a translational order in a crystal owing to UV or X-ray irradiation. Such a decrease of translational order manifests in an increase of a unit cell volume and a decrease of intensities of reflections [22]. The crystals of the studied compounds **1**–**3** were not sensitive to X-rays; however, they showed a decrease of intensities of reflections owing to UV irradiation. This means that the observed changes in the unit cell parameters for compounds **1**–**3** were a result of two effects: the photochemical reaction in the crystals and a slow decrease of translational order in them. Additionally, we also checked that the reaction did not go back without irradiation.

The crystal structures were solved by means of SHELXS97 and refined using SHELXL97 [23]. For compound **1** the structure determination was completed for 0, 60, 120, 240 and 720-min of the crystal irradiation, *i.e.* for 0%, 7.0(5)%, 17.2(6)%, 41.4(8)% and 100% of the product in the crystal, for compound **2** for 0 and 5-min of the crystal irradiation, *i.e.* for 0% and 27.7(9)% of the product in the crystal and for compound **3** for 0, 0.5 and 1-min of crystal irradiation, *i.e.* for 0%, 47.2(11)% and 68.1(12)% of the product in the crystal. The values of the content of the product were obtained during the crystal structure determination by refinement of the site occupation factor (SOF). For other lengths of the irradiation time, quality of the structures was not satisfactory. In the case of the crystals of compounds **2** and **3** it was not possible to determine the crystal structures of pure products owing to a decrease of diffraction power of the examined crystals. For compound **3** the intensities of reflections after irradiations were low: for 2θ more than 42°, these intensities were at the level of the background and were not taken into crystallographic calculations.

In the case of the pure reactant and pure product crystals for compounds **1**–**3**, all non-hydrogen atoms were refined anisotropically. For the partly reacted crystals, atoms in the reaction centre were separated in refinements and the remaining atoms of the reactant and product molecules were treated as overlapping. For compounds **1** and **2** the non-hydrogen atoms in the reaction centre were refined isotropically for the minor component and anisotropically for the major component and the remaining atoms were treated anisotropically. For compound **3** the non-hydrogen atoms in the reaction centre were refined isotropically and the remaining ones anisotropically. The pyrrolidinium cation in compound **2** was described as disordered with site occupancy factors 0.40 and 0.60.

In general, hydrogen atoms were positioned geometrically and treated as riding. However, in the case of crystal structures of