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Structural Transformations in Crystals Induced by Radiation and Pressure. Part 7. Molecular and Crystal Geometries as Factors Deciding about Photochemical Reactivity under Ambient and High Pressures

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Abstract: We studied the photochemical reactivity of salts of 4-(2,4,6-triisopropylbenzoyl)benzoic acid with propane-1,2-diamine (**1**), methanamine (**2**), cyclohexanamine (**3**), and morpholine (**4**), for compounds (**1**), (**3**), and (**4**) at 0.1 MPa and for compounds (**1**) and (**2**) at 1.3 GPa and 1.0 GPa, respectively. The changes in the values of the unit cell parameters after UV irradiation and the values of the intramolecular geometrical parameters indicated the possibility of the occurrence of the Norrish–Yang reaction in the case of all the compounds. The analysis of the intramolecular geometry and free spaces revealed which *o*-isopropyl group takes part in the reaction. For (**1**), the same *o*-isopropyl group should be reactive at ambient and high pressures. In the case of (**2**), high pressure caused the phase transition from the space group I2/a with one molecule in the asymmetric unit cell to the space group $P\bar{1}$ with two asymmetric molecules. The analysis of voids indicated that the Norrish–Yang reaction is less probable for one of the two molecules. For the other molecule, the intramolecular geometrical parameters showed that except for the Norrish–Yang reaction, the concurrent reaction leading to the formation of a five-membered ring can also proceed. In (**3**), both *o*-isopropyl groups are able to react; however, the bigger volume of a void near 2-isopropyl may be the factor determining the reactivity. For (**4**), only one *o*-isopropyl should be reactive.

Keywords: solid-state chemistry; Norrish–Yang reaction; high-pressure crystallography; single-crystal X-ray structure analysis

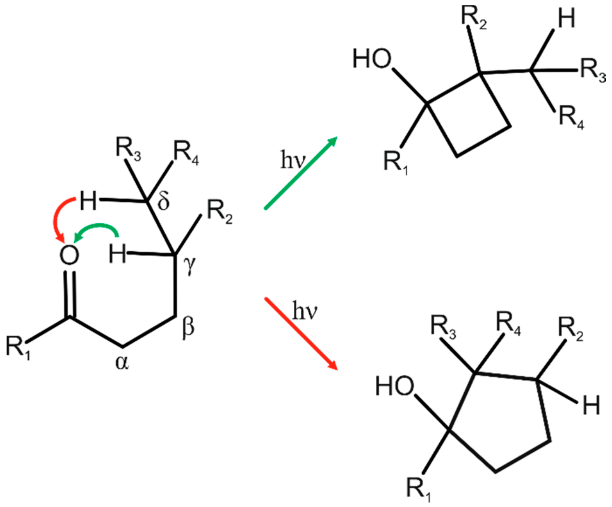
1. Introduction

The Norrish–Yang reaction is the photochemical reaction proceeding in compounds with a carbonyl group and a γ-hydrogen atom and leading to the formation of a four-membered ring (Scheme 1). The reaction is induced by UV radiation, which causes the transfer of the γ-hydrogen to the carbonyl oxygen atom and the formation of a 1,4-diradical. In the next step of the reaction, a four-membered ring is created.

The factor necessary for the Norrish–Yang reaction to take place in crystals is the relevant geometry of the reaction center. Five parameters were introduced to describe this geometry, owing to which it is possible to predict the reaction occurrence [1,2]. These parameters are as follows:

- the distance between the γ-hydrogen atom and the carbonyl oxygen atom (d), with the ideal value less than 2.7 Å;

- the distance between the reacting carbon atoms (*D*), with the ideal value less than 3.2 Å;
- the C=O···H angle between the carbonyl group and the γ-hydrogen atom (*Δ*), with the ideal values in the range 90°–120°;
- the C–H···O angle formed by the γ-carbon, γ-hydrogen, and carbonyl oxygen (*θ*), with the ideal value 180°;
- the torsion angle describing the deviation of the γ-hydrogen from the plane of the carbonyl group (*ω*), with the ideal value 0°.



Scheme 1. The Norrish–Yang reaction leading to a four-membered ring and the Yang cyclization leading to a five-membered ring.

In some cases, the formation of a five-membered ring can occur with the participation of a δ-hydrogen atom (Scheme 1) [3,4]. The ideal values of the geometrical parameters are the same as for the Norrish–Yang reaction, except for *D* which should be less than 3.4 Å [5]. Occasionally, both reactions can proceed concurrently [3].

In general, photochemical reactions in crystals occur when there is the possibility of atomic shifts required for breaking old chemical bonds and forming new ones. When the atomic shifts are small and voids are present in close proximity of a reaction center, the reaction will be easier. Sufficient elasticity of voids can also be beneficial [6–8]. The occurrence of a photochemical reaction was explained in some cases by the analysis of size and shape of voids: a big void promoted the reaction [9–11], whereas one that is too small hindered it [12].

The volume of voids in crystals and the geometry of intermolecular interactions are factors dependent on each other; for instance, smaller voids suggest that many shorter intermolecular contacts will be present. Nevertheless, a detailed analysis of single contacts can provide valuable information on the direction of a reaction [13].

In this paper, we have described the photochemical behavior of molecules in the salts of 4-(2,4,6-triisopropylbenzoyl)benzoic acid with propane-1,2-diamine (**1**) and methanamine (**2**) at ambient and high pressures and with cyclohexanamine (**3**) and morpholine (**4**) at ambient pressure on the grounds of the analysis of the crystal and molecular structures. Different amines served as factors modifying the geometry of the crystal lattices together with the volumes of the voids near *o*-isopropyl groups, and influencing the geometry of the 4-(2,4,6-triisopropylbenzoyl)benzoate anions. These changes should have an impact on the photochemical reactivity. The next factor influencing the crystal and molecular structures was high pressure. It decreased the volume of free space in the crystals (also in close proximity to the reaction center) and modified soft intramolecular geometrical parameters.

2. Materials and Methods

In order to synthesize compounds (**1**)–(**4**), the stoichiometric amounts of propane-1,2-diamine, methanamine, cyclohexanamine, and morpholine, respectively were added to a solution of 4-(2,4,6-triisopropylbenzoyl)benzoic acid in ethanol. The studied crystals of (**2**) were obtained from the reaction mixture and those of (**1**), (**3**), and (**4**) after recrystallization from ethanol, ethanol/toluene (vol. 5:1), and acetone, respectively.

Compounds (**1**) and (**3**) were examined at 0.1 MPa (ambient pressure) before and after UV irradiation. The results of the studies for (**2**) at 0.1 MPa were published previously [14]. The crystal of (**4**) was also irradiated at 0.1 MPa, but due to photo-damage, only the X-ray data before UV irradiation were obtained. Compound (**2**) was studied at 1.0 GPa before and after UV irradiation and compound (**1**) at 1.3 GPa before UV irradiation. Unfortunately, the crystal quality of (**1**) at high pressure under the influence of UV irradiation and that of (**3**) and (**4**) under the influence of high pressure (even without UV irradiation) decreased significantly, which precluded structural studies in such conditions.

The high-pressure studies were carried out in a Boehler-Almax diamond anvil cell (DAC) with diamonds of type IIa [15]. A mixture of glycerine and water (vol. 3:2) was used as hydrostatic fluid and a quartz crystal as a pressure sensor. The values of high pressure were determined on the basis of the changes in the unit cell parameters of quartz [16]. The samples were irradiated using a mercury lamp equipped with water and BG-39 glass filters. The water filter blocked infrared radiation. Transmittance for the glass filter was 0% for $320 > \lambda > 680$ nm, ca. 55% for $\lambda \approx 350$ nm, and 95% for $\lambda \approx 460$ nm. The glass filter passed the wavelengths corresponding to the low-energy absorption tails of the studied compounds, which helped to maintain the homogeneity of the reaction [17,18]. The times of irradiation were as follows: 0, 5, 15, 25, 35, 50 min at 0.1 MPa for (**1**); 0 min at 1.3 GPa for (**1**); 0, 5 min at 1.0 GPa for (**2**); 0, 35 min at 0.1 MPa for (**3**); and 0 min at 0.1 MPa for (**4**).

Before and after each UV irradiation, X-ray data were collected: for (**1**), (**2**), and (**4**), this was done by means of a KM4CCD diffractometer [19] and for (**3**), by Bruker APEX-II CCD diffractometer [20]. The quality of the measured X-ray data allowed for the determination of pure reactant structures of (**1**)–(**4**), i.e., for the crystals before the UV irradiation. The structures were determined by SHELXS and SHELXL [21–23]. The X-ray data for the irradiated crystals of (**1**), (**2**), and (**3**) only provided the values of the cell constants.

In the case of (**1**), (**3**), and (**4**) at 0.1 MPa, all non-hydrogen atoms were refined anisotropically, except for the carbon atoms of the minor component in (**4**) which were treated isotropically. For the high-pressure structures of (**1**) and (**2**), the oxygen, nitrogen, and terminal carbon atoms of *o*-isopropyl groups were refined anisotropically and the remaining atoms were treated isotropically. The atoms in the C1→C6 and C8→C13 benzene rings of (**1**) and (**2**) were considered to be rigid rotating groups and their atomic displacement parameters were refined using one common parameter for each ring. In the refinements of other atoms of (**1**) and (**2**), weak restraints DFIX, DANG, SIMU, and ISOR were applied. Due to the disorder in the crystal of (**4**), the cation, the C8→C13 benzene ring, and the atoms in the carboxylate group were refined over two positions with the final site occupation factors 63.6(10) and 36.4(10)% and the 2-isopropyl group with 72(4) and 28(4)%. In the asymmetric unit cell of (**4**), there was also one water molecule.

During the structure determination it was checked how many hydrogen atoms at nitrogen were seen in difference Fourier maps. The protonation state was identified clearly in the case of all compounds. The hydrogen atoms at N2 of (**1**) at 0.1 MPa and 1.3 GPa which were localized in difference Fourier maps were refined without constraints. The hydrogen atoms at N1 of (**1**) at 0.1 MPa and 1.3 GPa and in the methyl group of the cation of (**1**) at 0.1 MPa were located on the grounds of difference densities and were afterwards considered as rigid rotating groups; the rest of the hydrogen atoms were positioned geometrically with Uiso(H) = 1.5Ueq(C) for the methyl groups and Uiso(H) = 1.2Ueq(C,N) for the remaining carbon atoms and nitrogen.

The hydrogen atoms in (**2**)–(**4**) were positioned geometrically, except for the atoms at nitrogen for (**2**) and (**3**), in the methyl fragments for (**2**) and in the methyl fragments of the *p*-isopropyl group for (**4**), which were located on the grounds of difference densities and afterwards treated as rigid rotating groups. The hydrogen atoms in the methyl groups and in the water molecule were refined with Uiso = 1.5Ueq (C,O) and the remaining hydrogen atoms with Uiso(H) = 1.2Ueq(C,N).

The selected crystallographic and experimental data for the determined structures of (**1**)–(**4**) are gathered in Table 1. CCDC 1848871 - 1848875 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1. The crystallographic and experimental data for (**1**)–(**4**).

Compound	**(1)**		**(2)**	**(3)**	**(4)**
Pressure	0.1 MPa	1.3 GPa	1.0 GPa	0.1 MPa	0.1 MPa
Chemical formula	$C_{26}H_{38}N_2O_3$	$C_{26}H_{38}N_2O_3$	$C_{24}H_{33}NO_3$	$C_{29}H_{41}NO_3$	$C_{27}H_{39}NO_5$
Formula weight	426.58	426.58	383.51	451.63	457.59
Crystal dimensions/mm	0.26 × 0.22 × 0.04	0.25 × 0.18 × 0.04	0.19 × 0.16 × 0.11	0.40 × 0.10 × 0.03	0.30 × 0.20 × 0.06
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\overline{1}$	$P2_1/c$	$P2_1/c$
a/Å	25.4217(11)	25.34(3)	6.1205(7)	24.434(3)	25.9788(19)
b/Å	8.5125(4)	8.2143(11)	16.6401(17)	6.3455(8)	8.4472(9)
c/Å	11.8343(5)	11.4907(13)	21.596(4)	17.538(2)	12.2065(11)
α/°			101.627(15)		
β/°	95.110(3)	94.67(3)	96.245(15)	91.774(4)	99.931(7)
γ/°			91.507(9)		
V/Å^3	2550.8(2)	2384(3)	2138.9(5)	2718.0(6)	2638.6(4)
Z	4	4	4	4	4
D_x/Mgm^{-3}	1.111	1.189	1.191	1.104	1.152
μ/mm^{-1}	0.07	0.08	0.08	0.07	0.08
T/K	299	299	299	130	299
Reflections collected	9335	11,637	10,631	28,358	9294
Reflections independent	4483	1363	2286	4790	4644
Reflections observed	2059	594	1083	2962	2062
R_{int}	0.061	0.207	0.119	0.104	0.049
R ($F^2 > 2\sigma(F^2)$), wR, S	0.077, 0.176, 1.01	0.075, 0.220, 0.98	0.109, 0.353, 1.05	0.075, 0.171, 1.09	0.098, 0.289, 1.03
$\Delta\varrho_{max}$, $\Delta\varrho_{min}$ /eÅ^{-3}	0.17, −0.16	0.12, −0.13	0.21, −0.21	0.25, −0.20	0.30, −0.37

3. Results and Discussion

The molecular structures of salts of 4-(2,4,6-triisopropylbenzoyl)benzoic acid with propane-1,2-diamine (**1**), methanamine (**2**), cyclohexanamine (**3**), and morpholine (**4**), are presented in Figure 1. There are two nitrogen atoms in (**1**) but only one of them, i.e., that bound with the terminal carbon atom, undergoes protonation (Figure 1).

As the result of UV irradiation, the unit cell parameters of (**1**) change, which shows that the Norrish–Yang reaction occurs in the crystal (Figure 2 and Table 2). These changes are gradual and monotonic, indicating that the photochemical reaction also proceeds in such a manner. During the UV irradiation, the crystal gradually lost its diffracting power, which disabled the structure determination for partly reacted crystals with satisfactory quality. Nevertheless, while determining the crystal structure after 50 min of UV irradiation at 0.1 MPa, the maxima of difference electron density were observed evidencing the occurrence of the Norrish–Yang reaction with the participation of *o*-isopropyl at C2, i.e., 2-isopropyl.

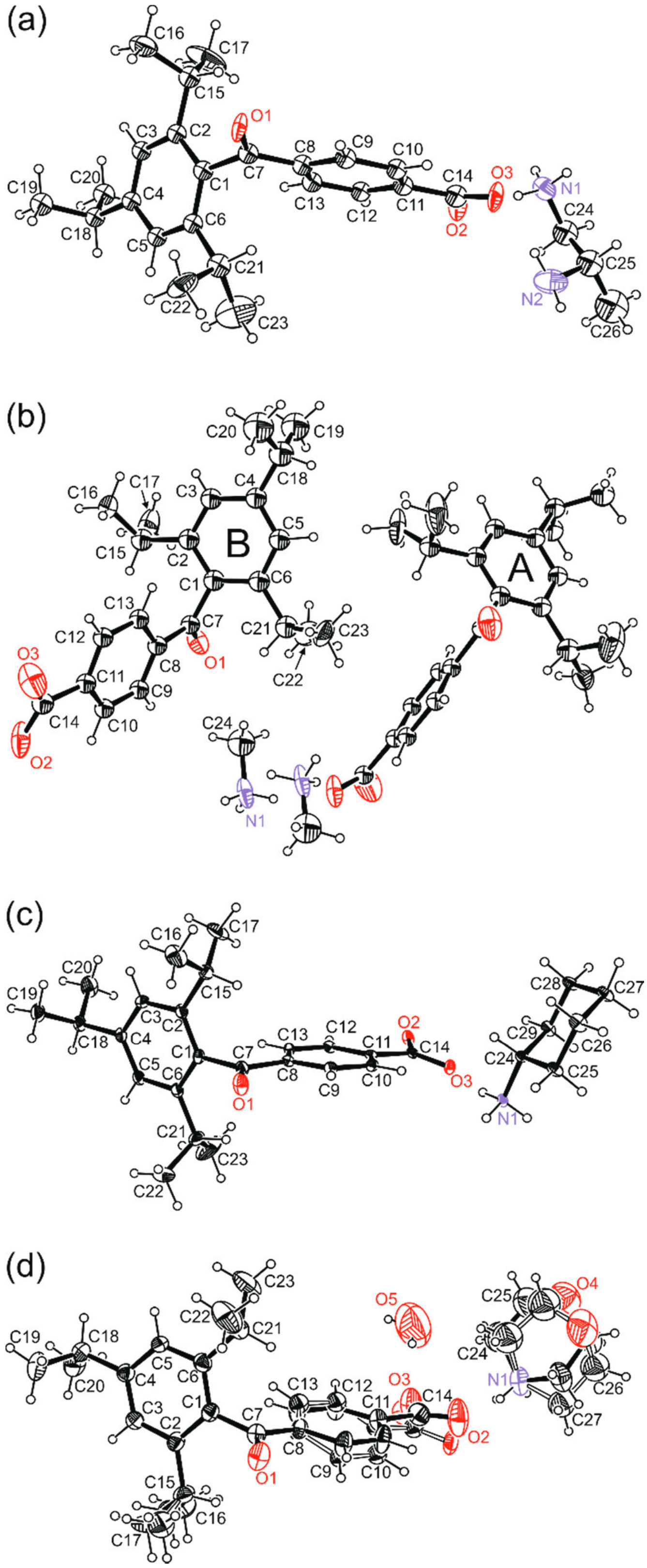


Figure 1. The Ortep view [24] for compounds (**a**) (**1**) at 1.3 GPa; (**b**) (**2**) at 1.0 GPa; (**c**) (**3**) at 0.1 MPa; and (**d**) (**4**) at 0.1 MPa. The displacement parameters of non-hydrogen atoms were drawn at a 30% probability level. The atoms of the minor component of (**4**) were connected by empty bonds.

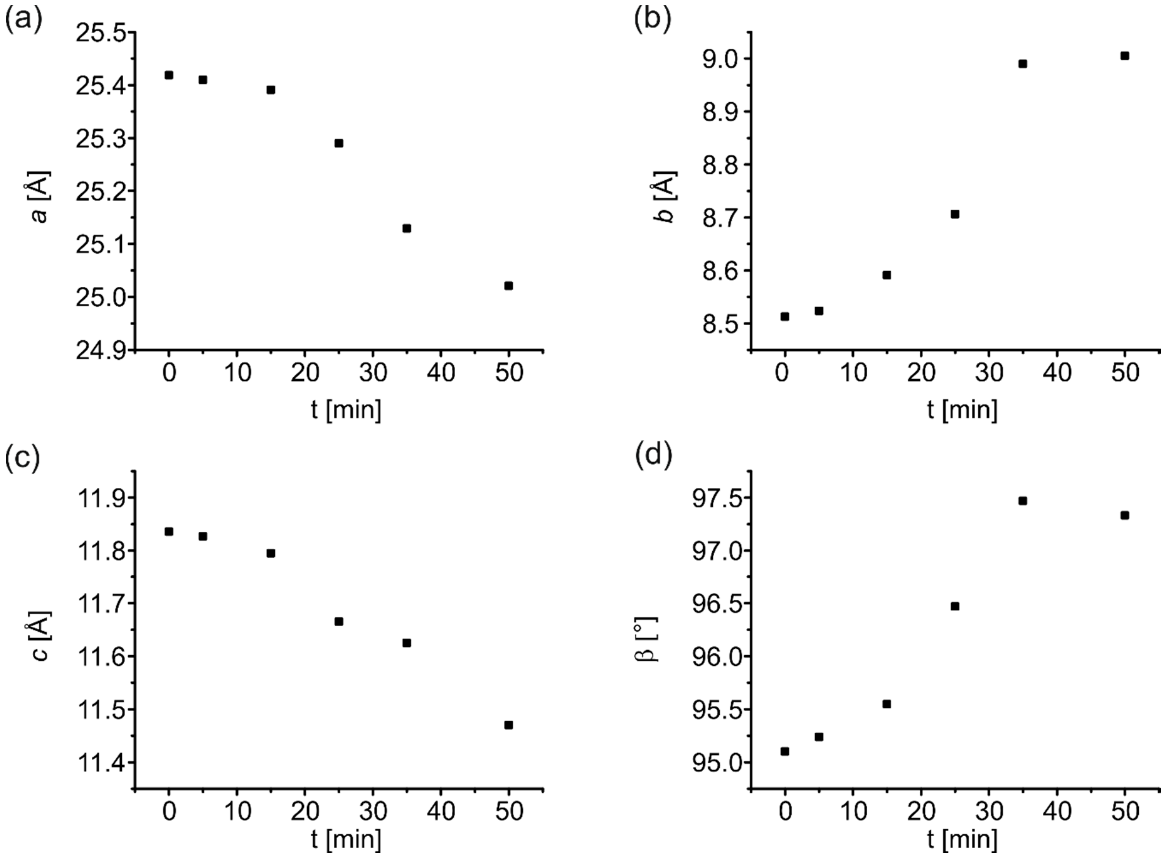


Figure 2. The variations in (**a**) a; (**b**) b; (**c**) c; and (**d**) β for compound (**1**) at 0.1 MPa along with the time of UV irradiation. For a better comparison, the range of the y axis was set the same for plots (**a**)–(**c**).

Table 2. The unit cell parameters for the irradiated crystals of (**1**)–(**3**).

t/min	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/Å^3
			(**1**) at 0.1 MPa				
0	25.4217(11)	8.5125(4)	11.8343(5)		95.110(3)		2550.8(2)
5	25.410(2)	8.5235(8)	11.8269(9)		95.237(7)		2550.8(4)
15	25.391(4)	8.591(2)	11.795(2)		95.548(17)		2561(1)
25	25.29(2)	8.706(9)	11.665(12)		96.47(7)		2552(4)
35	25.130(3)	8.969(11)	11.625(14)		97.47(1)		2598(5)
50	25.021(5)	9.0053(18)	11.470(3)		97.332(17)		2563.3(9)
			(**2**) at 1.0 GPa				
5	6.102(3)	16.123(8)	22.295(19)	100.55(6)	97.68(10)	90.37(5)	2136(2)
			(**3**) at 0.1 MPa				
35	24.202(9)	6.3227(18)	18.035(5)		90.766(12)		2759.6(15)

The values of the geometrical parameters describing the susceptibility of (**1**) to the Norrish–Yang reaction in crystals indicate that the *o*-isopropyl group at C2 and not at C6 should take part in this reaction (Table 3). The values of d, Δ, θ, and ω are better for 2-isopropyl than for 6-isopropyl and D is similar for both of them. Moreover, the difference between the geometries of the potential reaction centers slightly increases at high pressure in 2-isopropyl's favor. The intramolecular geometry also shows that the formation of a five-membered ring is excluded.

Table 3. The values of the intramolecular geometrical parameters describing susceptibility to the Norrish–Yang reaction.

			d [Å]	D [Å]	Δ [°]	θ [°]	ω [°]
Ideal value			<2.7		90–120	180	0
Literature range [a]			2.39–3.07	2.82–3.12	52.0–88.0	104.3–131.6	50.8–85.5
				(1)			
2-isopropyl, γ-H		0.1 MPa	2.63	2.948(6)	67.0	122.5	72.9
6-isopropyl, γ-H			3.10	2.943(6)	47.0	116.0	88.4
2-isopropyl, δ-H			3.39	3.935(6)	95.6	110.9	39.3
6-isopropyl, δ-H			3.49	3.782(6)	79.2	120.1	58.9
2-isopropyl, γ-H		1.3 GPa	2.5	2.94(2)	72	126	69
6-isopropyl, γ-H			3.2	2.93(1)	43	115	91
2-isopropyl, δ-H			3.4	3.96(2)	97	108	34
6-isopropyl, δ-H			3.5	3.76(1)	76	123	63
				(2)			
2-isopropyl, γ-H		0.1 MPa [d]	3.07	2.920(4)	53.4	104.3	83.4
6-isopropyl, γ-H			2.89	2.931(4)	54.6	115.0	83.4
2-isopropyl, δ-H			3.09	3.694(4)	90.7	125.2	56.8
6-isopropyl, δ-H			3.33	3.815(5)	88.8	119.6	54.3
2-isopropyl, γ-H	A	1.0 GPa	2.9 [b]	2.917(15)	53	115 [b]	84
	B		3.0 [b]	2.88(3)	49	113 [b]	86
6-isopropyl, γ-H	A		3.0 [c]	2.90(3)	53	108 [c]	83
	B		2.8 [b]	2.906(14)	61 [b]	108 [c]	78
2-isopropyl, δ-H	A		3.3	3.786(16)	89	121	57
	B		3.2	3.62(3)	83	122	53
6-isopropyl, δ-H	A		2.8 [b]	3.57(4) [b]	92	130 [b]	56
	B		2.7 [b]	3.505(18) [b]	103	118	58
				(3)			
2-isopropyl, γ-H		0.1 MPa	2.88	2.907(5)	53.9	118.7	84.6
6-isopropyl, γ-H			2.81	2.936(5)	57.6	122.2	79.9
2-isopropyl, δ-H			3.40	3.817(6)	86.1	117.6	54.7
6-isopropyl, δ-H			3.54	3.928(7)	87.6	113.4	50.3
				(4)			
2-isopropyl, γ-H [e]		0.1 MPa	2.65	2.931(6)	65.2	123.4	74.5
			2.82		260.2	2110.8	277.1
6-isopropyl, γ-H			3.12	2.938(7)	47.1	111.7	88.0
2-isopropyl, δ-H [e]			3.47	3.967(15)	93.9	110.7	42.4
			22.80	23.62(3)	298.8	2127.7	247.1
6-isopropyl, δ-H			3.26	3.688(8)	82.2	125.0	59.6

[a] taken from reference 13. [b,c] significantly improved at 1.0 GPa or worsened at 1.0 GPa, respectively. [d] taken from reference 14. [e] the upper and lower lines are for the major and minor components, respectively.

The analysis of free space in the crystals of (**1**) at 0.1 MPa and 1.3 GPa reveals that there is a void suitable for the Norrish–Yang reaction near 2-isopropyl only (Figure 3). This is the next indication that the photochemical reaction will proceed with the participation of 2-isopropyl and not 6-isopropyl. The volumes of these voids are 15.0(3) and 5.0(1) Å^3 at 0.1 MPa and 1.3 GPa, respectively. This shrinking can make the photochemical reaction more difficult at high pressure.

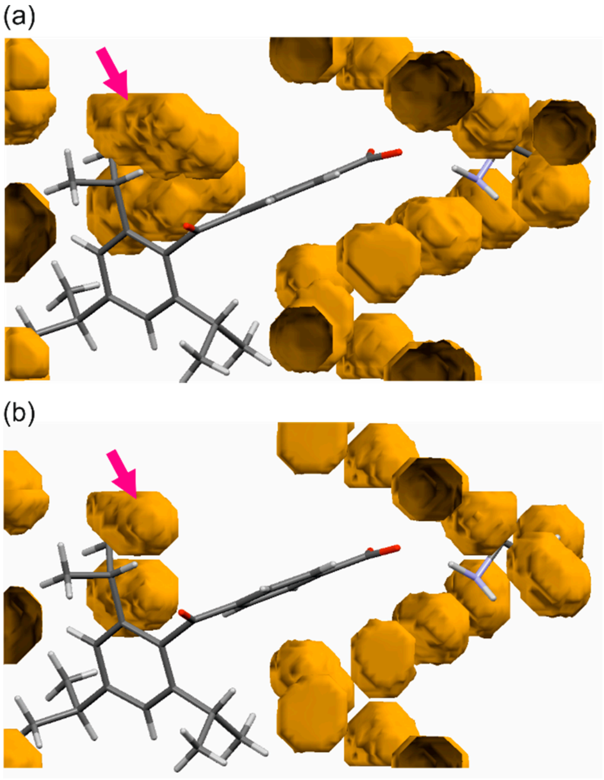


Figure 3. The free space for compound (**1**) at (**a**) 0.1 MPa and (**b**) 1.3 GPa. The arrow indicates the void suitable for the Norrish–Yang reaction with 2-isopropyl. The radius of a ball was 0.9 Å and the grid was 0.2 Å [25].

In the case of (**2**), the results of monitoring structural changes brought about by the Norrish–Yang reaction at 0.1 MPa were already published [14]. Here, we present the results for the high-pressure studies. The application of high pressure causes the phase transition of (**2**) from monoclinic I2/a with 8 molecules in the unit cell to triclinic $P\bar{1}$ with 4 molecules in the unit cell (Table 4). This means that after the phase transition there are two molecules, named A and B, in the asymmetric unit in comparison with only one molecule in ambient conditions. The existence of two symmetrically independent molecules is also revealed by the fingerprint plots (Figure 4). Both plots look different which indicates that both molecules are not related by symmetry. The differences between both plots are mainly the result of the C–H$\cdots\pi$ interactions of the C8→C13 benzene ring and the interactions in which the carbonyl oxygen is involved. Molecules A and B differ not only in the interactions with the environment, but also in the intramolecular geometry. The difference in the shape of both molecules is distinct (Figure 5) and can be expressed, for instance, by the values of the dihedral angle between the aromatic rings: 88.4(3)° and 111.1(3)° for A and B, respectively.

Table 4. The unit cell parameters for (**2**) before and after the phase transition.

a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/Å^3
			(**2**) at 0.1 MPa, I2/a			
17.1387(10)	6.3047(4)	44.649(3)		98.744(6)		4768.4(5)
			(**2**) at 1.0 GPa, $P\bar{1}$			
6.1205(7)	16.6401(17)	21.596(4)	101.627(15)	96.245(15)	91.507(9)	2138.9(5)

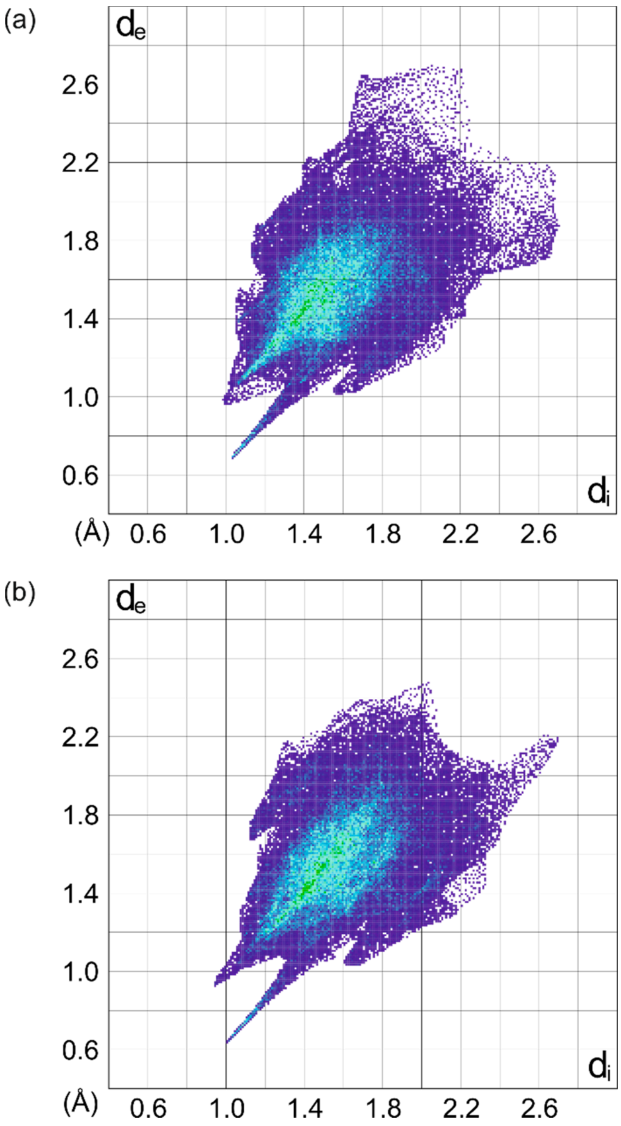


Figure 4. The fingerprints for anions (**a**) A and (**b**) B of compound (**2**) at 1.0 GPa [26,27].

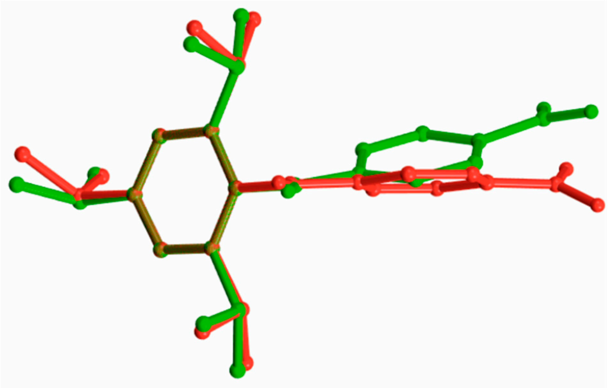


Figure 5. The A (red) and B (green) anions of compound (**2**) at 1.0 GPa superimposed in the C1→C6 plane.

The crystal of (**2**) was exposed to UV radiation at 1.0 GPa in order to induce the Norrish–Yang reaction. After 5 min of irradiation, the changes in the values of the unit cell parameters, analogous to the changes accompanying the reaction at ambient pressure, were observed (Table 2). The *a* parameter (corresponding to *b* at 0.1 MPa) decreased by only 0.019 Å, the *b* parameter (corresponding to *a* at 0.1 MPa) decreased by 0.517 Å, and the *c* parameter increased by 0.70 Å. This fact is a sign that the photochemical reaction occurs in the crystal of (**2**) at 1.0 GPa.

Owing to the phase transition of (**2**) and the presence of two symmetrically independent molecules, the analysis of the high-pressure structure is interesting since both molecules can react in a different way and their reactivity can vary from that at 0.1 MPa. In Table 3, the values of the geometrical parameters are gathered for 2-isopropyl and 6-isopropyl in molecules A and B and also in the molecule at 0.1 MPa. One of the important differences between the structures at 0.1 MPa and 1.0 GPa is the considerable improvement of the geometry stimulating the formation of a five-membered ring by 6-isopropyl. This product was not formed at 0.1 MPa due to unsuitable values of *d* (above 3.3 Å) and *D* (above 3.8 Å) [14]. Moreover, it can also be concluded that molecules A and B should still undergo the Norrish–Yang reaction with the participation of the 2- and 6-isopropyl groups, as was the case at 0.1 MPa. In ambient conditions the key factor determining the direction of the reaction of (**2**) was the free space [14]. At 1.0 GPa the void near 2-isopropyl in molecule A, similar to that at 0.1 MPa, also exists (Figure 6a). The volume of this void is 7.0(1) Å^3, i.e., only 2.0(2) Å^3 less than at 0.1 MPa. There is not a void of comparable size near 6-isopropyl of molecule A and both *o*-isopropyl groups of molecule B. It is intriguing as to why pressure does not reduce the void at 2-isopropyl of A to a stronger degree, although the total volume of free space decreases to 1.2% of the volume of the unit cell. The reason for this fact must be the stronger compression of the free space in close proximity to molecule B. The above analysis demonstrates that the Norrish–Yang reaction at high pressure should be easiest in the case of 2-isopropyl of molecule A.

Molecules of (**3**) also undergo the Norrish–Yang reaction in crystals. This is clearly shown by changes in the values of the unit cell parameters after UV irradiation at 0.1 MPa (Table 2). Namely, *a*, *b*, *c*, *β*, and *V* alter by −0.232 Å, −0.0228 Å, 0.497 Å, −1.008°, and 41.6 Å^3, respectively. The intramolecular geometrical parameters of both *o*-isopropyl groups do not univocally indicate which of these groups should take part in the Norrish–Yang reaction (Table 3). Nevertheless, their values are within the literature ranges characteristic for compounds undergoing this reaction. The formation of a five-membered ring is excluded, since *d* for the closest δ-hydrogen atom exceeds 3.4 Å. In close proximity, both *o*-isopropyl groups have a large void; however, it is about twice greater at 2-isopropyl than at 6-isopropyl: 18.0(3) and 8.0(1) Å^3, respectively (Figure 6b). This difference can increase the photochemical reactivity of 2-isopropyl.

The values of the intramolecular geometrical parameters in (**4**) are closer to ideal for 2-isopropyl, which indicates this group is preferred in the Norrish–Yang reaction (Table 3). The values for 6-isopropyl are at the border of the literature ranges and do not guarantee the occurrence of this reaction. Moreover, the values of the intramolecular geometrical parameters for one δ-hydrogen atom of the 2-isopropyl group in the minor component with occupancy 28% indicate that the formation of a five-membered ring cannot be excluded (see Table 3). The analysis of voids near both *o*-isopropyl groups also supports the above statements (Figure 6c). The volume of the void near the 2-isopropyl group is 16.0(5) Å^3. There is not such a void close to 6-isopropyl.

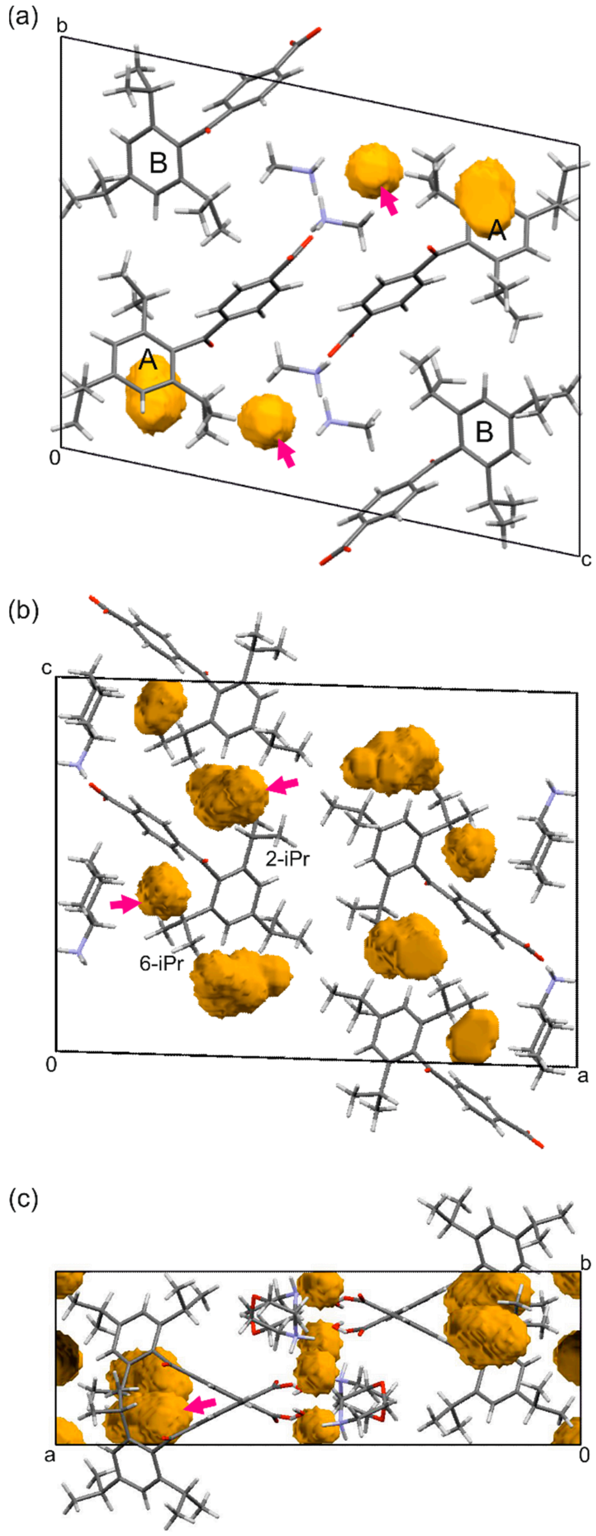


Figure 6. The free space in the crystals of compounds (**a**) (**2**) at 1.0 GPa; (**b**) (**3**) at 0.1 MPa; and (**c**) (**4**) at 0.1 MPa. The arrows show the voids in close proximity to *o*-isopropyl groups. The radius of a ball was 1.0 Å and the grid was 0.2 Å [25].

4. Conclusions

We presented the comparative studies concerning the photochemical behavior of 4-(2,4,6-triisopropylbenzoyl)benzoate anion in the crystal lattices of geometry modified by different counter-ions. The changes in the unit cell parameters under UV irradiation, the values of the intramolecular geometrical parameters describing the positions of both *o*-isopropyl groups with respect to the carbonyl group, and also the size of the voids between the carbonyl group and each *o*-isopropyl group show that the Norrish–Yang reaction proceeds in crystals of (**1**)–(**4**) and which *o*-isopropyl takes part in the reaction. The intramolecular geometry excluded the formation of a five-membered ring for (**1**) and (**3**). For (**2**), the phase transition from monoclinic I2/a with one molecule in the asymmetric unit to triclinic $P\bar{1}$ with two independent molecules was observed under high pressure. The geometry of the molecules at high pressure was suitable for the formation of both four- and five-membered rings. High pressure decreased the volume of free spaces, which could make the photochemical reaction more difficult.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/8/7/299/s1, Figure S1: The Ortep view for compound (**1**) at 0.1 MPa after 50 min of UV irradiation. The fragment of the product molecule was shown by empty bonds. The maxima O1P and C7P for the product were found in a difference Fourier map. Figure S2: The 4-(2,4,6-triisopropylbenzoyl)benzoate anions from the crystals of compounds (**1**)–(**4**) in ambient conditions, superimposed on each other. Molecules (**1**), (**2**), (**3**), and (**4**) are marked in red, green, blue, and yellow, respectively. The data for (**2**) at ambient pressure were taken from reference 14.

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